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PACIFIC BASIN CONFERENCE ON HAZARDOUS WASTE

PROCEEDINGS

November 4-8, 1996
Kuala Lumpur, Malaysia

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Technology, and the Environment, Malaysia

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FOREWORD

These proceedings of the seventh Pacific Basin Conference on Hazardous Waste demonstrate a clear picture of the extent of the hazardous waste problem in the region. While there has been progress in the control of hazardous wastes throughout Asia and the Pacific, there is still much room for improvement.

At the first conference held in 1988, many countries reported that they did not have hazardous waste control regulations in place. There were few waste treatment facilities, even fewer cleaner production technologies being implemented, and little insight into the health impacts of improper handling of hazardous materials. The papers presented at this conference demonstrate that significant strides have been made in all these areas.

Nevertheless, the quantity of hazardous waste continues to grow throughout the region. While control regulations are now implemented in most of the countries, implementation and enforcement lags behind. Severe health impacts from improper hazardous waste handling continue, particularly among the elderly, children, and other susceptible groups. Much still needs to be done to bring the problem under control.

The papers in these proceedings cover the full range of issues dealing with hazardous waste control. They cover pollution prevention, waste treatment technology, health and ecosystem effects research, analysis and assessment, and regulatory management techniques. The experiences of many countries in the region are included. It is our hope that this body of information will contribute to a better understanding of the hazardous waste problem and the identification of efficient, cost-effective solutions.

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PLENARY SESSION: CONFERENCE OPENING

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OPENING ADDRESS

Honorable Dato' Abu Bakar Daud, Deputy Minister
Ministry of Science, Technology and
the Environment, Malaysia

Mr. Chairman; Dr. William Suk, Chairman of the Technical Program; Dr. David Barnes, Chairman of the Pacific Consortium on Hazardous Waste Research and Management; Ir. Tan Meng Leng, Director-General of the Department of Environment, Malaysia; conference directors; distinguished guests; and ladies and gentlemen. It is indeed my pleasure to be with you on this auspicious day to officially open the Seventh Pacific Basin Conference on Hazardous Waste, better known as the *PBC Conference.*

Let me first and foremost extend a very warm welcome, with our traditional bid of *Selamat Datang* to all of you, especially to our overseas participants.

I understand that the venue of the PBC Conference alternates between the Asia-Pacific region and North America. Malaysia is therefore very honored to host the three-day Seventh PBC Conference. The timing, location, and the subject matter of the PBC Conference are most appropriate and meaningful recognition of Malaysia's local and international level of effort in hazardous waste management.

Over the last two decades, Malaysia has developed progressively environmentally sound management practices, not only in the area of air and water pollution, but also in the management of hazardous wastes. Since May 1989, we began to enforce the Malaysian Environmental Quality Act of 1974. In view of rapid development in our industrial sector, new waste streams have been created. As such, Malaysia, through the Department of Environment, is reviewing these regulations, which are expected to be completed at the end of the year. The review also examines provisions to cater to emerging problems associated with the management of hazardous wastes in this country.

The strategy to manage hazardous wastes in Malaysia is based on a cradle-to-grave concept. This concept includes waste reduction at the source, tracking and monitoring of waste movement, recycling and recovery, treatment, and safe disposal.

The Department of Environment has recently launched a program called MAWAR (Malaysian Agenda for Waste Reduction) aimed at encouraging industries to reduce waste generation within a period to be determined by the industries themselves. Several options can be used by industries, such as waste minimization programs and use of cleaner technology. For now, the program is on a voluntary basis. We hope that this program will receive good response from industries, as this sector continues to reap real benefits from it.

The movement of waste from the point of its generation to its final disposal site is tracked by means of a manifest system. The system has now been computerized to assist in fast monitoring and retrieval of information to facilitate enforcement activities.

Malaysia is fully committed for the safe treatment and disposal of hazardous waste. Our first integrated facility for the treatment and disposal of such waste is expected to be fully operational by mid-1998. However, in line with the policy of encouraging industries to implement recovery, recycle, and reuse (or the 3R concept), Malaysia will continue to allow industries to recover or treat their own waste within their premises.

Before becoming a party to the Basel Convention, Malaysia observed the strict requirements of the Basel Convention on a prior-informed-consent (PIC) basis. In addition, it is our policy not to allow the importation of waste into the country or its exportation when the transaction does not meet the requirement of the Basel Convention. Industries are expected to manage as much as possible their wastes locally. We are very much concerned that there are attempts to export waste under the disguise of waste recovery.

Malaysia has been consistently enforcing the law against illegal transport or dumping of waste. For instance, in a recent incident on illegal dumping of potassium cyanide in northern Malaysia, the violator was fined the maximum penalty of RM10,000 and sentenced to one day in jail. In this regard, I wish to inform that we have recently amended the Environmental Quality Act of 1974 to include specific provisions on the control of import, export, and transit of wastes. The amendment also includes stricter penalties for offenses pertaining to illegal handling of hazardous waste — up to RM500,000 fine and a jail term of up to 5 years. In addition, vehicles or ships used in illegal transport of or disposal of scheduled waste are liable to be seized and subsequently forfeited. This indeed reflects Malaysia's consistent stand made at various international fora. We may be critical, but we are sincere in our efforts toward contributing to global environmental protection.

I understand that the PBC has brought together researchers, policymakers, industrialists, and other professionals from 18 countries. With this wide spectrum of delegates, I sincerely hope that this conference will give the participants an opportunity to review progress and seek ways to accelerate research and the application of research results in the Pacific Basin countries, to discuss issues of hazardous wastes and environmental trade, such as tracking and monitoring of hazardous waste, and to discuss other issues related to hazardous waste management. It is in fora such as this, where constructive dialogue and exchanges of opinions could disseminate current information in the critical area of hazardous waste management among participants from various countries.

I wish all of you the most productive and memorable conference. With these thoughts and words, it is now my pleasure and privilege to officially open the *Seventh Pacific Basin Conference on Hazardous Waste* and its associated poster exhibition. Thank you.

PLENARY SESSION: CURRENT DIRECTIONS IN HAZARDOUS WASTE CONTROL

Chair: Hajah Rosnani Ibarahim, Department of Environment, Malaysia

1996 HAZARDOUS WASTE MANAGEMENT SURVEY IN SELECTED ASIAN COUNTRIES

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This report documents the results of a 42-question survey submitted to countries in Asia concerning their hazardous waste management programs and other issues. The same survey questions were distributed in 1992. This report compares the 1992 and 1996 responses. The respondents were Australia, New Zealand, Malaysia, Philippines, Hong Kong, People's Republic of China, Taiwan, Japan, Korea, Singapore, Thailand, and Indonesia.

1 HAZARDOUS WASTE TRANSPORTATION

In 1992, 70% of countries surveyed had regulatory requirements in place for transporting hazardous waste. These requirements covered the licensing of transporters and use of manifests. By 1996, 90% of the countries surveyed had regulatory requirements in place. The one exception is the PRC, which responded in the negative to the survey questions about regulatory requirements in both 1992 and 1996. Most notably, private-sector transport of hazardous waste has increased dramatically; 90% of the respondents in 1996 stated that private-sector services now exist. There were no affirmative responses in the 1992 survey. Government transportation services doubled from one affirmative response to two in 1996 (Hong Kong and Korea).

2 TSD FACILITIES

There has been a clear trend toward increased regulatory requirements for TSD facilities from 1992 to 1996. The requirements cover siting criteria, design requirements, facility operation rules, and on-site storage regulations. Centralized TSD facilities now operate in 40% of the surveyed countries (compared with 30% in 1992). Construction of new or expanded facilities is underway in 50% of the countries. There has been no change, however, in the number or names of specific countries that had proposed centralized TSD facilities in 1992. New Zealand and Singapore do not have centralized TSD facilities. (Malaysia did not answer this question on the survey.) In 1996, 40% of the countries co-dispose of some hazardous wastes with municipal wastes. This is an increase of 33% from 1992. Conspicuously, the PRC has not followed the regional trends toward increased regulatory requirements (with the exception of landfill design).

Private hazardous waste incinerators operate in 80% of the countries, while public incinerators operate in 40%. Both percentages are increases from 1992, with the number of countries operating public incinerators doubling during the last 4 years (from two to four). Interestingly, the percentage of countries proposing the construction of hazardous waste incinerators has dropped from 70% to 60%, perhaps reflecting an increased capacity (i.e., diminished need) or an increase in public opposition to these facilities. Australia is no longer proposing a hazardous waste incinerator. The percentage of countries requiring air emission controls for hazardous waste incinerators increased from 60% to 90% during the same 4-year period. The PRC is the notable exception.

3 PERMITTING/LICENSING

There has been a conspicuous trend toward increased requirements for licensing and/or permitting in most of the countries surveyed. Notification to government agencies by hazardous waste generators is now required by 80% of the countries. In 1992, there were no affirmative responses to this question. Waste characterization is now required in 100% of the countries surveyed. Except for the Philippines, respondents feel that analytical testing capabilities are adequate. A clear trend toward increased licensing/permitting requirements has been evident for both on-site and off-site disposal facilities.

4 INVESTIGATION/REMEDIATION

The investigation of dumps or disposal areas has not changed significantly since the 1992 survey. Only one additional country reported "proposed" investigation of contaminated dump sites in the 1996 survey. Cleanup of actual contaminated sites, on the other hand, was reported by twice as many countries in 1996 as in 1992 (three in 1992 versus six in 1996). Furthermore, the percentage of the countries reporting legal requirements for the cleanup of contaminated sites increased from 0% in 1992 to 40% in 1996. Likewise, groundwater protection regulations increased from 30% to 70% of the countries surveyed.

5 LIABILITY

Cradle-to-grave regulations increased from 70% of the countries surveyed in 1992 to 100% in 1996. Criminal liability has also been established in 90% of the surveyed countries (28% more than in 1992). Taiwan is the only country that did not report criminal liability for improper waste handling and disposal.

6 PUBLIC AWARENESS/ACTIVISM/HEALTH EFFECTS

Public concern over hazardous waste issues has remained at a high level (90% of the surveyed countries). Only Singapore responded in the negative to this question. Nongovernment organization (NGO) activity was reported by two additional countries in the 1996 survey (PRC and Japan), for a total of 90% of the countries surveyed. Again, Singapore did not report NGO activities. Documented health effects from exposure to hazardous waste were reported by 50% of the countries surveyed in 1996. This represents a decrease of one country from 1992. Both Taiwan and Japan responded in the negative to this question in 1996, while their response in 1992 was affirmative. The opposite situation was true for Singapore. One additional country (Singapore) reported the legal allowance for public input in the siting of a hazardous waste treatment facility. The countries that did not report a legal allowance for public input in the 1996 survey were the Philippines, Hong Kong, and the PRC.

7 TRANSBOUNDARY HAZARDOUS WASTE DISPOSAL POLICY

In 1996, 40% of the countries surveyed reported allowing the legal import of hazardous waste to the host country for treatment/disposal. This percentage is the same as it was for the 1992 survey; however, the countries allowing the import are not the same. Australia no longer allows the legal import of hazardous waste, but Taiwan now does. Japan, Singapore, and the Philippines continue to allow the import of hazardous waste. Only 20% of the countries surveyed (Australia and the Philippines) reported the import of hazardous waste to be illegal in the 1996 survey. All others reported no such activity, similar to the 1992 survey.

In 1992, 30% of the countries surveyed (Philippines, Japan, Korea) allowed ocean dumping as a disposal option for hazardous wastes. None of the respondents answered in the affirmative in the 1996 survey. Only the Philippines answered affirmatively when asked if ocean dumping was practiced, albeit illegally.

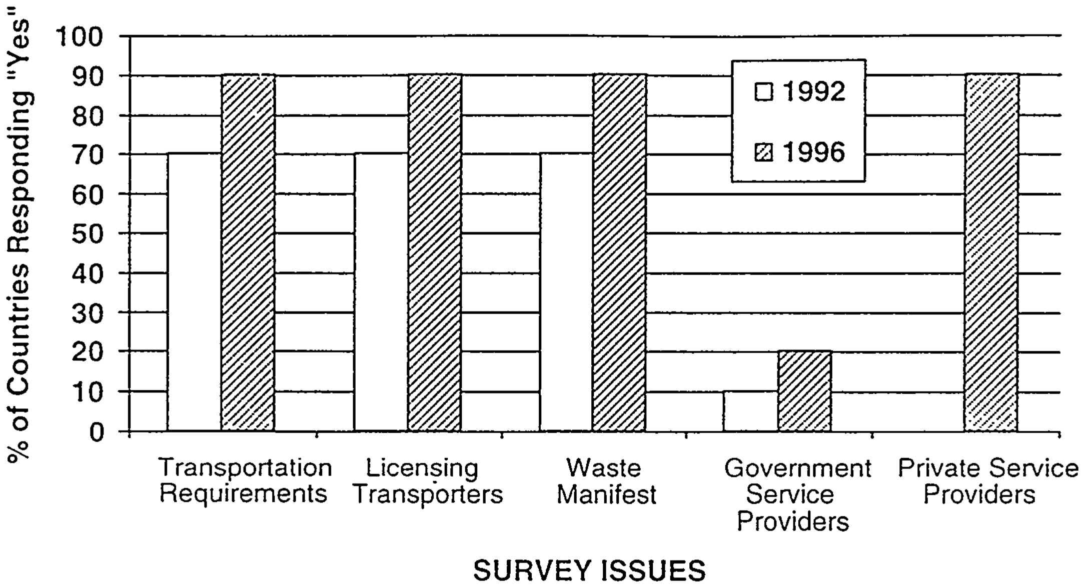

Fig. 1 Responses Regarding Hazardous Waste Transportation

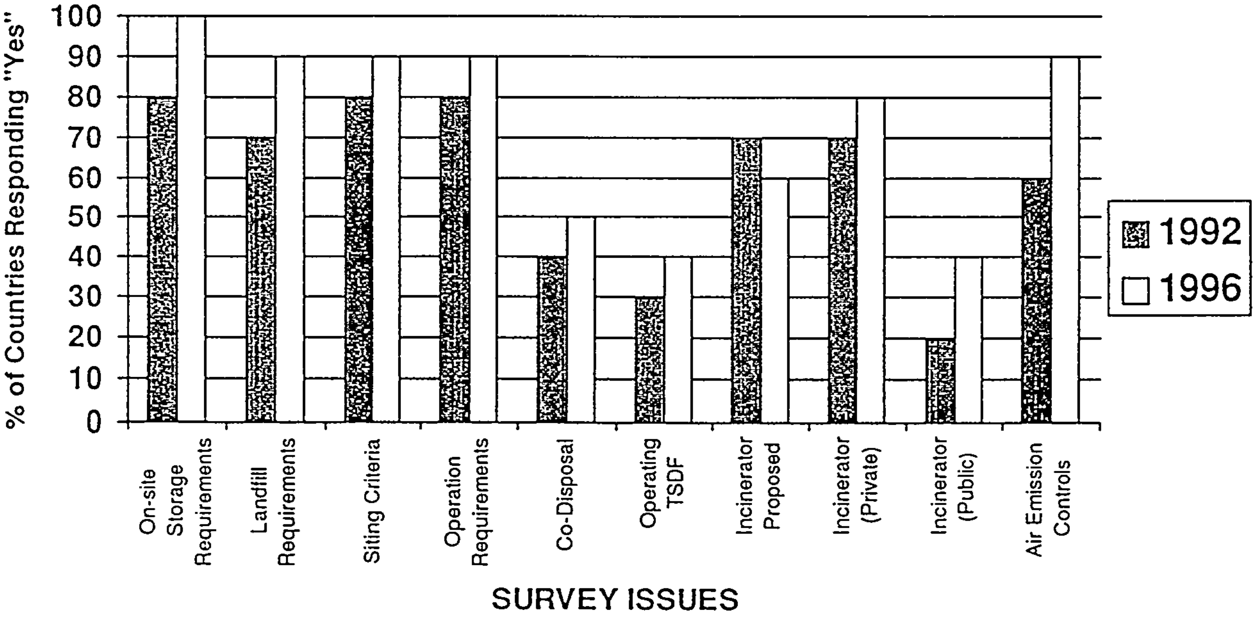

Fig. 2 Responses Regarding Treatment, Storage, and Disposal Facilities

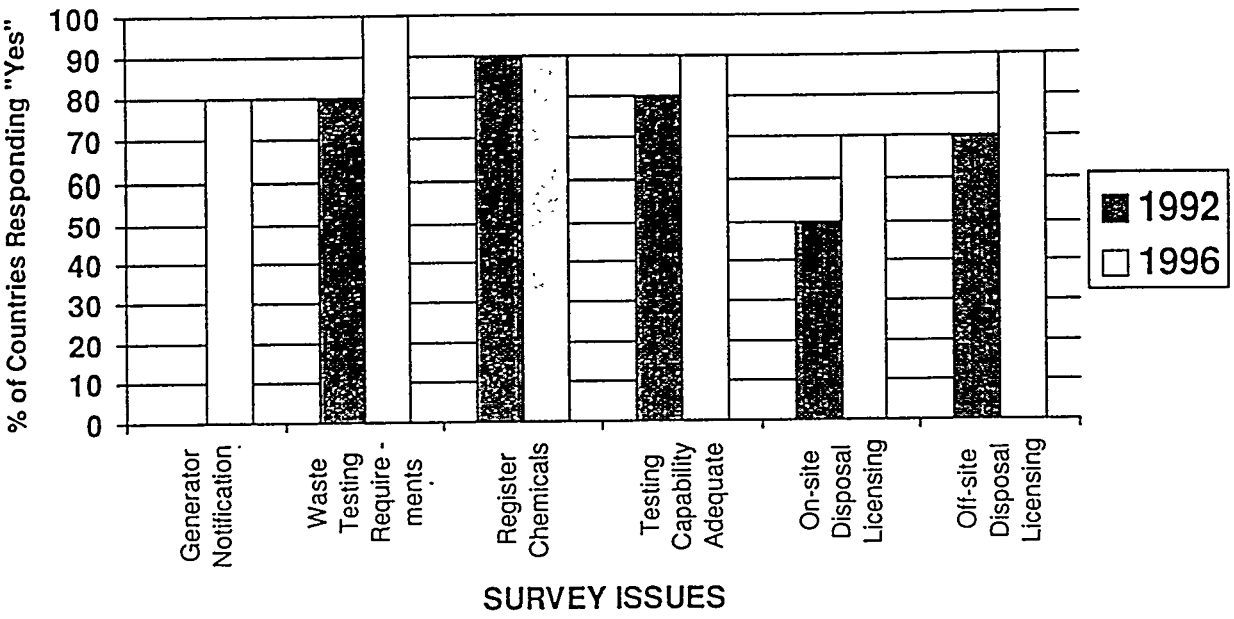

Fig. 3 Responses Regarding Permitting and Licensing

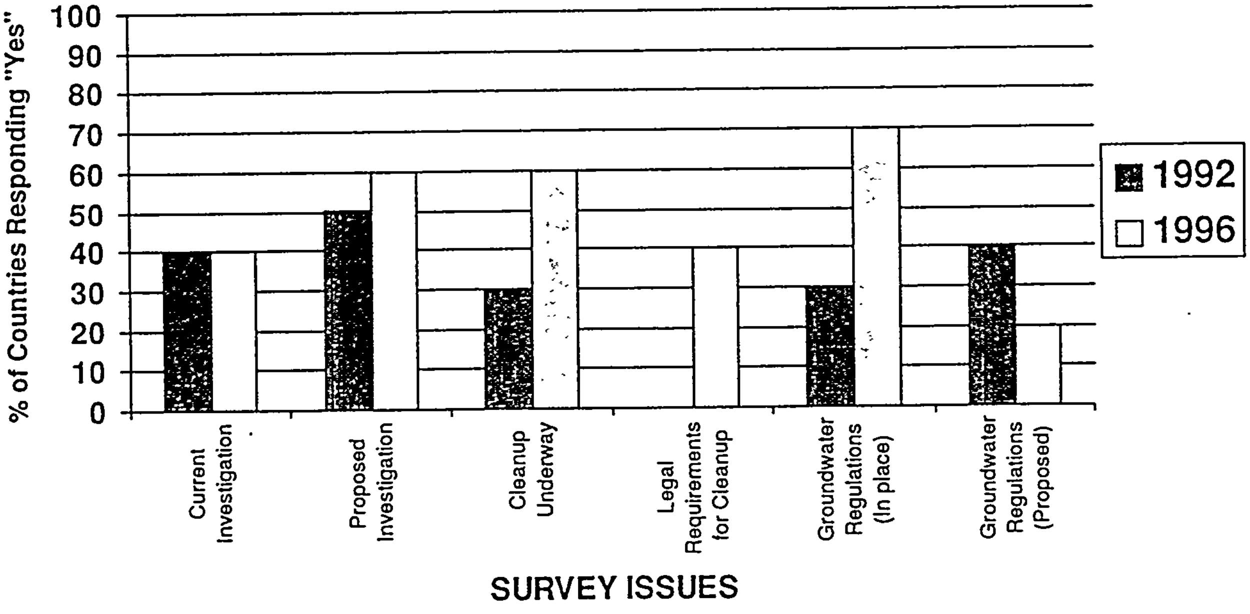

Fig. 4 Responses Regarding Investigation/Remediation

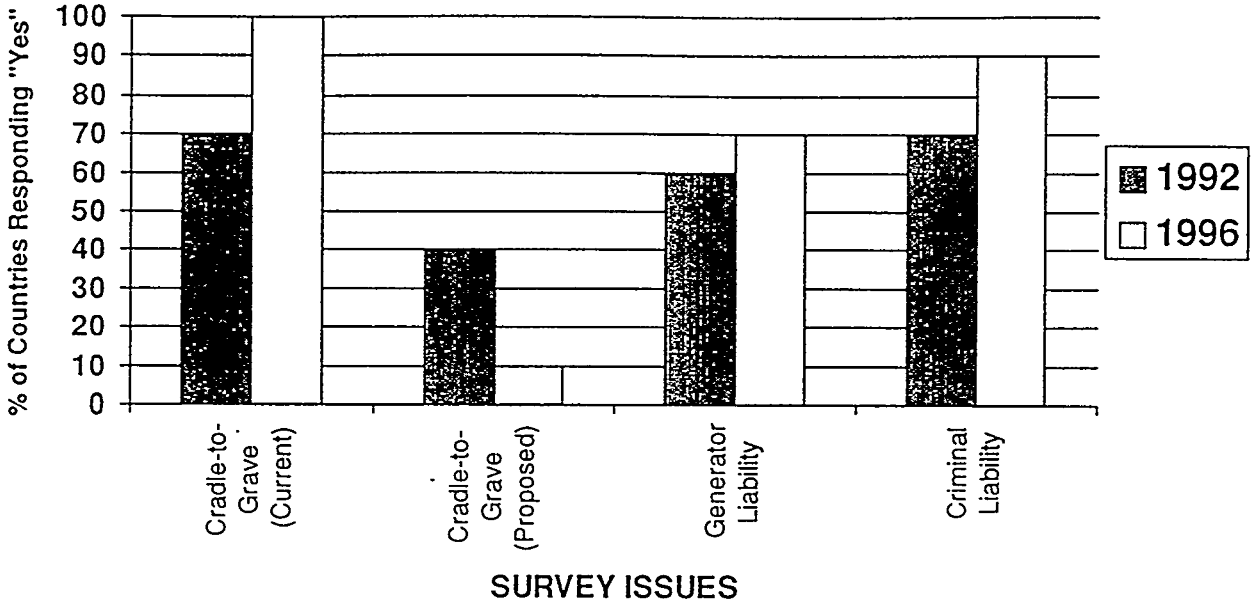

Fig. 5 Responses Regarding Liability

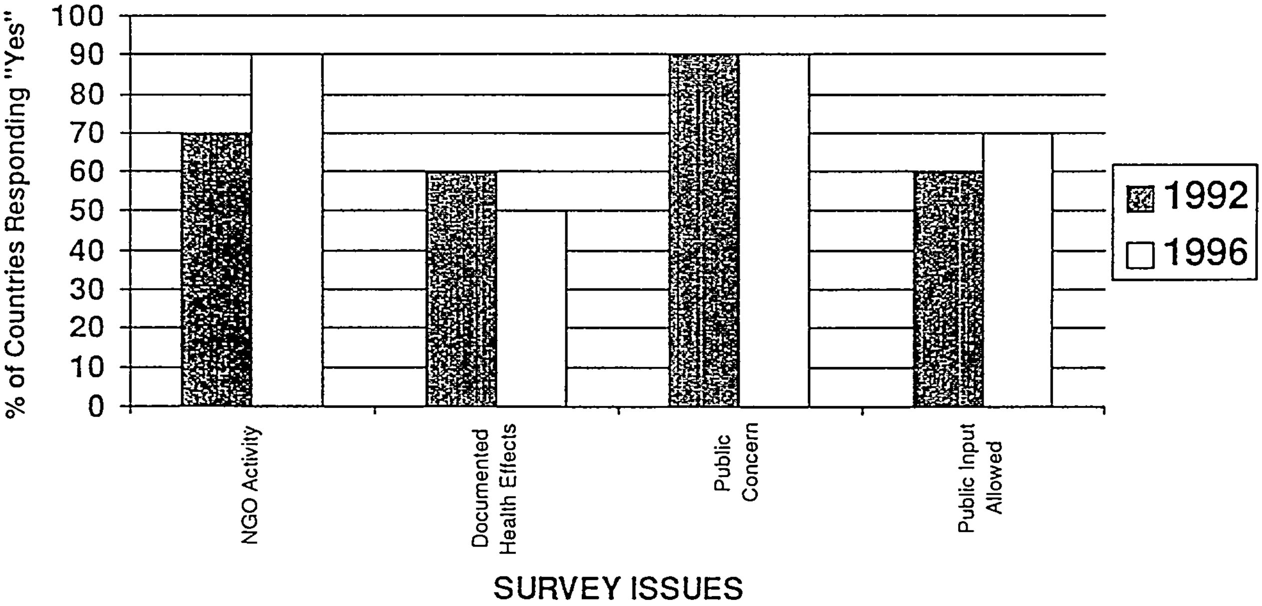

Fig. 6 Responses Regarding Public Awareness and Activism

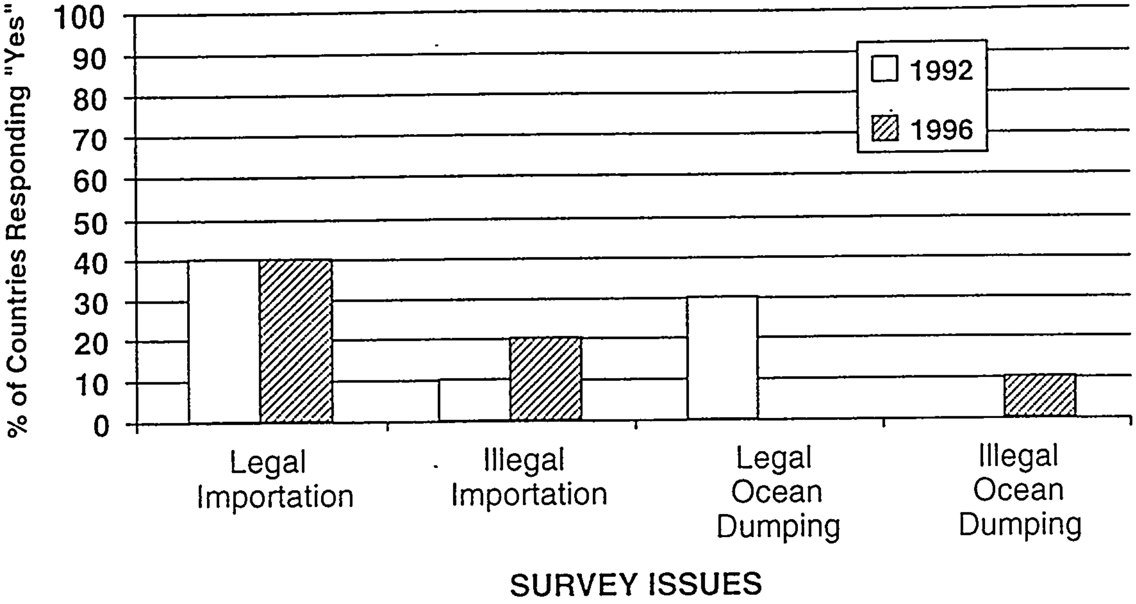

Fig. 7 Responses Regarding Transboundary Hazardous Waste Disposal Policy

MATCHING THE NEEDS OF A NATION: THE STRATEGIC ROLES OF INDICATORS FOR DECISIONMAKING

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ABSTRACT

Indicators are important tools for communicating and making accessible scientific and technical information to policymakers and the general public. They therefore play an important role in transforming information into action. Worldwide, many initiatives are underway to construct indicators for a variety of purposes, including those for reporting on sustainable development. This paper briefly describes the attempts made so far, but stresses that the users of the indicators should play a greater role in indicator construction. In developing countries, a substantial lack of data has meant that specific policy formulation may develop without adequate technical input. In developed countries also, data gaps may hinder policy formulation, implementation, and evaluation. However, the development of indicators as tools to assist in the management of hazardous wastes and toxic chemicals is still in the early stages of formulation. A more imaginative program of indicators and indices is required, where targets are well defined and the users clearly identified to assist in decisionmaking, especially at the local and national levels. A broader range of pressure indicators, beyond hazardous wastes, is proposed to integrate toxic chemicals, emissions, and environmental and human health impacts.

1 INTRODUCTION

Much technical discussion and public debate have occurred in recent years on the positive and negative impacts of industrialization. Yet, industrialization has provided the momentum for economic and sociocultural development worldwide. Serious impacts of poorly controlled industrialization on the environment, human health, and on the quality of life, especially in some countries, are recognized, although often not adequately addressed through lack of knowledge and understanding of the environment-economic-social linkages.

The concept of "sustainable development," which links environment with economic and social concepts, has become a central issue internationally since the release of the Brundtland Report (WCED 1987). Sustainable development is defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." It is a compelling expression of concern for future implications of present practices. The problems associated with development are not just ones of industrial pollution as was well recognized in Agenda '21 — a Programme of Action for Sustainable Development Worldwide (UN 1993). They are accumulative consequences of development that include population growth and associated poverty in the developing world, lifestyles in the industrialized world and their excessive demands on nonrenewable resources, and a lack of concern globally for natural life-support systems. The need to change production and consumption patterns is now on the international political agenda (UN 1996).

This paper addresses one element of sustainable development, namely, the concern with the need for substantial and continuous improvement in environmental protection. Emphasis is placed on hazardous wastes and associated issues, while recognizing that environmental degradation and impacts of development are interrelated with social and economic concerns.

2 REPORTING OF INFORMATION

Sustainable development is impossible to achieve without adequate and accessible data and information. This implies not only reporting by governments and industry but access to data by nongovernmental organizations (NGOs) and the public. The construction of local and national databases and information systems is a basic requirement needed to assess human activities and environmental pressures. National state-of-the-environment (SOE) reports, national reports to the United Nations Commission on Environment and Development (UNCED), regional and international SOE reports, and annual reports by government agencies along with reports from the U.N. agencies, contribute to data and information provisions necessary for decision making. Publication of annual reports and/or topical reports by national and international NGOs provides an independent view of the SOE and of contentious issues.

Recent trends in increased environmental reporting by transnational corporations and industrial companies and their annual reports provide further information on environmental policies and impacts (Deloitte 1993; Gray 1993; Gray et al. 1995), although the information may not be comparable, quantitative, or verifiable (Gibson and Guthrie 1995). Such reports will no doubt improve through best practice and benchmarking.

However, many countries lack the data necessary to measure and manage the environment and to evaluate the effectiveness of that management. In some countries, especially developing countries, the local lack of experience in problem identification and problem solving further reduces their ability to evaluate whether present and future development will be sustainable. Institutional arrangements, such as a protection of traditional compartmentalized departmental approaches, can also hinder progress in developing coherent analyses. Integrated environmental management as a concept has, therefore, to be introduced and adopted as a useful and essential part of policy development in these countries.

Strategic environmental audits, although often not readily accessible provide further information of "best practice reporting." The recent draft international ISO 14000 standards on environmental management provide a further catalyst for the industrial sector to adopt positive procedures to improve overall environmental performance and consequential release of such information to satisfy accountability relationships. The ISO 14000 standards, in fact, represent only the beginnings of such actions.

3 THE ROLES OF INDICATORS AND INDICES

Available, accurate, and accessible information and data are required for all stages of environmental management. In the past, the emphasis has been on the data providers, i.e., those who generate the data whether by monitoring or modeling, rather than by determining the needs of the data users and their requirements for decision making. Policymakers seek only the relevant data to satisfy their obligations in the broadest sense. Indicators and indices have been developed to meet these needs.

Two defining characteristics of indicators have been put forward by SCOPE (1995), namely,

- Indicators quantify information, so its significance is more readily apparent.
- Indicators simplify information about complex phenomena to improve communication.

Indicators are distinct from statistical and primary data, even though they are often presented in statistical or graphical forms.

Indicators are components of the "information pyramid" whose wide base contains primary data and whose apex comprises condensed data, such as indices. Indicators lie within the middle of the pyramid, providing aggregated data as a tool for decision makers. Data and information should then be accessible and in the appropriate form for *the target audience* so as to avoid "information overload."

Indicators can be of various types. "Descriptive" indicators, as the term implies, describe and summarize relatively simple data on environmental conditions and trends. Most indicators are of this type. "Performance" indicators can be used to measure how much progress has been made in moving toward a target or goal. In their construction, performance indicators usually include descriptive information and a specific policy target.

One of the widely used approaches to indicator development and matrixes is the Pressure-State-Response (PSR) model proposed by the Organization of Economic Cooperation and Development (OECD 1994). Human activities or driving forces affect the environment and exert pressures on the environment. Pressures include, for example, production of hazardous waste and emissions of toxic chemicals. These pressures can modify the SOE by affecting ecosystems and human health. Measures on how society responds to such changes can be financial, institutional, legal, etc.

The PSR model has also been refined by some authors to include the concept of *effects* or *impacts* to provide a greater degree of certainty about what is happening. Similarly, the concept of pressure has been replaced by some authors with the term *driving force* to indicate more clearly the pressures from human activities (Peterson 1996).

The PSR approach provides a simplistic but useful model illustrating causal relationships. Of the three types of indicators, scientists seem to be more concerned with an examination of state indicators. However, pressure indicators provide the key for policy development, for they link environmental damage caused by human activities with the need to address the efficiency of environmental policies.

3.1 Indicator Criteria

Criteria for useful and reliable indicators have been detailed by many organizations (e.g., OECD 1994; U.S. Environmental Protection Agency [USEPA] 1995), although it is rare for all of the criteria to be met in a "single indicator" (HMSO 1996a). Arguably, the most important criteria include analytical soundness (i.e., validity) and measurability (i.e., data are available) (OECD 1994). Indicator selection criteria have been further expanded and detailed by the USEPA (1995) to include feasibility and cost-effectiveness. Such indicator attributes are no doubt important for accurate comparisons to be made between nations. But in developing countries, such criteria may have limited usefulness should the data be sparse in quantity and of variable quality. The luxury of monitoring for timely, reliable, accurate, and complete data sets is unrealistic in developing countries. In this situation, environmental policy making should present measures as a societal response to emerging environmental degradation, i.e., the adoption of the "precautionary principle" (principle 151) of the Declaration of Rio de Janeiro on Environment and Development in 1992 (UN 1993).

From a policymaker's point of view, the essential criteria are not absolute but depend on the purpose for which indicators are required. For policy planning, the criteria will center on strategic information, especially the adoption of the precautionary principle. For the general public, it should "strike a chord" with the intended audience — they must want to understand it and act upon it. If indicators are required for SOE reporting to the nation as the client, indicator criteria will center on representative information and reflect environmental trends with time.

3.2 Indicator Frameworks

To conceptualize and develop indicators that inform the community about progress toward sustainable development, a coherent analytical framework, or classification scheme, is required to integrate relevant information. Much has been written on such frameworks. They try to provide a clear model, usually describing interactions between human activity and the environment. Recently, the SCOPE (1996) Scientific Workshop on Indicators of Sustainable Development concluded that "no significant consensus exists as to the appropriate framework for indicators of sustainable development in the long term."

Up to six different frameworks have been proposed by various national and international organizations to help in the groupings or associations of environmental and human health issues. Some overlap of concepts is evident within and between the groups. The frameworks are as follows:

- Reporting a national SOE (e.g., Environment Canada [1991]);
- Assessing renewable or nonrenewable resources nationally (HMSO [1996a]);
- Evaluating countrywide performance in addressing key national issues (e.g., Danish Ministry of the Environment [1992, 1995]);
- Implementing national management policies (e.g., Adriaanse [1993]);
- Reporting regional- or international-scale status and trends (OECD [1994]); and
- Monitoring progress toward sustainable development internationally (DPCSD [1995]).

However, for a number of reasons, too much emphasis has been placed on indicator frameworks and indicators in a theoretical sense rather than on what is required for decision making. The U.N. Department for Policy Coordination and Sustainable Development (DPCSD 1995) initiative is aimed at establishing an international set of sustainable development indicators and a common body of knowledge, but such indicators alone will not measure sustainable development in a critical sense. Similar comments can be applied to the OECD (1994), World Bank (1995), and UNDP (1996) indicator initiatives. Indicators are only one tool for measuring and reporting sustainable development

With regard to hazardous wastes, the topic is dealt with differently in each of the six framework models. In the SOE approach, whatever data are available are included under a separate topic on hazardous waste. In the second framework model, hazardous wastes are viewed within a category of "damage to the carrying capacity of the environment and the risk to human health and biodiversity from the effects of human activity" (HMSO 1996a). Also included within this category are those issues related to toxic chemicals, such as air pollution, freshwater quality, soil contamination, and so on. Recycling and minerals extraction also fall within this concept of waste management, thus providing a wider view of these issues.

With the third approach, hazardous wastes are again considered as one of many separate issues, usually within the urban context. Recycling is a separate issue, as is groundwater quality. The approach is a pragmatic one based on many indicators. The data are presented in a simple format that is totally different from the fourth approach. With the fourth approach (Adriaanse 1993), the concept of an integral approach to key environmental issues is adopted for the implementation of national management policies. Wastes are included as a thematic issue, but the policy target group includes the main economic sectors contributing to the waste, i.e., industry, refineries, the energy sector, etc. The main intention is to integrate environment and economy by presenting a measure for the economic activity of the sector together with a measure for environmental pollution caused by the sector. Only one performance indicator per theme is produced with a sustainable development target being proposed.

The fifth approach especially includes the OECD (1994), which considers wastes, hazardous wastes, and toxic contamination separately. Comparable approaches for issues of concern are also adopted by the Economic and Social Commission for Asia and the Pacific (ESCAP 1996) and the European Environment Agency (1995). In the sixth framework approach, the DPCSD (1995) has adopted indicators for the respective chapters of Agenda '21; i.e., chapter 20 deals with management of hazardous wastes, and chapter 19 deals with management of toxic chemicals. Indicators have been proposed using the PSR model of the OECD to report each issue.

3.3 Indicator Scales

The challenge is to develop indicators for decision making, which by their very nature imply differences of scale, i.e., local, national, and international decision making. The tendency has been to develop international indicators as though these are all that are required for nations.

In this paper, indicators are viewed at all three levels of scale and with the target audience to the stakeholders' community groups, NGOs, and industry forefront. The audience may encompass stakeholders' community groups, NGOs, industry managers, management accountants, government agencies, and so on. The approach proposed here involves replacing attempts at the systematic classification of indicators to certain predetermined categories for international reporting, with a pragmatic subjective provision of information for constructing indicators for specific decision making (Peterson 1996).

4 THE TARGET AUDIENCE

As environmental issues have gained prominence in recent years, much public debate has focused on environmental impacts, with toxic chemicals and hazardous wastes being seen as especially important issues. The major thrust internationally has been to produce "standard" indicators for all nations to adopt, irrespective of level of development and applicability. Comparisons between nations and regions can then be readily assessed.

In general, indicator developers have failed to recognize one basic assumption. Different users usually need different indicators, whether based on different levels of scale, degrees of aggregation, differing prevailing public interests nationally and regionally, and different societal values and goals. This failure is unfortunate given the critical importance of communicating with policymakers and decision makers at all societal and developmental levels.

The need for greater flexibility of indicator construction can be illustrated with reference to communicating waste and hazardous waste information to different users or recipients of information by reference to Fig. 1.

SOCIETAL INTERESTS indices/aggregated data	Public interests	pollution wastes
	Societal responses	hazardous wastes, household wastes recycling
	Policy-making	pollution prevention waste minimization cleaner production
SCIENTIFIC INTERESTS indicators and basic data	Expert assessments	hazardous waste classes waste toxicity emissions inventories
POLITICAL INTERESTS international agreements	Chemical legislation	Basel Convention

Fig. 1 Representation of Different User Interests and Indicator Requirements for Wastes and Hazardous Wastes (modified from Jesinghaus [1995])

At the public interest end of the spectrum, indicators are needed to promote local actions and inspire public participation. They are also needed to communicate environmental information to the public, so they can appreciate and understand the effectiveness of policies. At the expert assessment end of the spectrum, scientists need indicators to establish benchmarks, establish linkages between issues, and track sustainable development.

5 INDUSTRIALIZING NATIONS

In industrializing nations, the environmental pressures change in type and extent as the nation is transformed from an agrarian society to an industrialized and increasingly urban society (Fig. 2).

In an agrarian society, especially in tropical climates; disease vectors; contaminated water; indoor air pollution from biomass combustion; uncontrolled waste disposal; and lack of medical, social, and economic resources, have been implicated in the prevalence of environmental and health risks. In an industrial urbanized society, pressures include air pollution, noise, soil contamination, industrial emissions, hazardous waste dumping, toxic chemical releases, along with human population pressures, resource depletion, and so forth.

Since the pressures are different in the two illustrative trends in Fig. 2, national environmental policies have to change to reflect realities. Consequently, a series of indicator options need to be developed to enable policymakers to address "new" and "old" issues. Accuracy and timeliness of indicators, while important, are no substitute for the establishment of relevant indicators, especially for the not-so-global decision making. The policymaking cycle of problem identification, formulation, implementation, and evaluation therefore has to be repeated frequently as industrialization proceeds and problems emerge.

A worldwide awareness of hazardous waste issues has arisen from industrialization; from its links to other issues, such as toxic chemicals, air emissions, and water pollution; and from the need to adopt a broader integral approach. Although progress has been made on both implementing hazardous waste management schemes and developing cleaner production and pollution prevention strategies, there is a need for a greater shift from awareness to action by public and private sectors (UNEP 1994). Much of the concern is focused on toxic substances that can accumulate in environmental media, in living organisms, and in the food chain, thus endangering human and ecosystem health. Most of the discussion in this paper centers on hazardous wastes within the context of the terrestrial and freshwater environment, although contamination of the marine environment by dumping is also a serious issue.

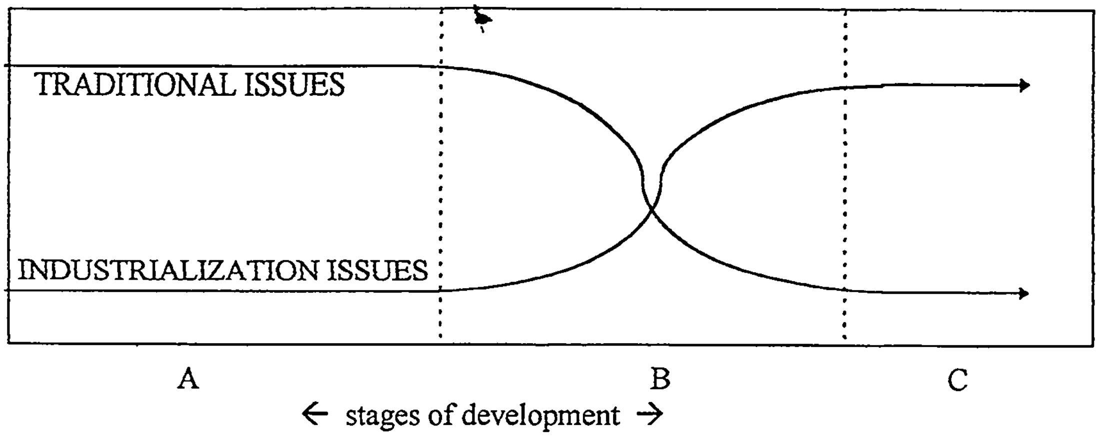

Fig. 2 Changes in Environmental and Environmental Health Issues as Nations Industrialize
Source: UN (1995)

6 SEARCH FOR HAZARDOUS WASTE INDICATORS

Most attention has focused on hazardous waste from industrial processes. However, the problem of hazardous residues from agriculture, hospital, and domestic wastes that can contain hazardous substances, has not been sufficiently addressed. Discussion in this paper considers only wastes from industrial concerns to keep the paper to an acceptable length.

Indicators for hazardous wastes have been proposed by many organizations. Indicators that reflect wider environmental management issues, such as cleaner production, waste minimization, life-cycle assessment, emissions inventories, and environmental impact assessments (EIAs), are relatively less well developed and are discussed in the following section.

The DPCSD (1995) has considered four indicators of sustainable development proposed by the Secretariat of the Basel Convention (SBC) as providing a basis for hazardous waste indicators, namely:

- Generation of hazardous wastes (tonne/yr), a pressure indicator;
- Imports and exports of hazardous wastes subject to transboundary movements (tonne/yr), a pressure indicator;
- Area of land contaminated by hazardous wastes (km^2), a state indicator; and
- Expenditure on hazardous waste treatment ($/yr), a response indicator.

All four indicators provide basic national, regional, and worldwide trends using data that nations collect at least in part and report to the SBC.

These four indicators address the overall hazardous waste objectives and program areas identified in Agenda '21 (UNEP 1994). But they do not address many of the difficulties in their implementation at a national level. Countries undergoing rapid industrialization often lack the regulatory framework and the subsequent enforcement systems necessary to compel industry to use cleaner production. In many countries, industry and, in particular, small and medium-sized enterprises lack awareness, access to information, and expertise to implement cleaner production.

Additional indicators could be developed to add detail data on hazardous wastes, although differences in national definitions of hazardous wastes complicate even basic data gathering. Possible indicators include the following:

- Percentage of imported/exported hazardous waste going to recovery or reuse operations, a response indicator; and
- Percentage of imported/exported hazardous waste going to disposal a pressure/state indicator, depending on the disposal option.

The OECD (1994) proposed several indicators:

- Generation of hazardous wastes (tonne/yr);
- Generation of hazardous wastes per unit of GDP (kg/$), as production is largely driven by patterns of production;
- Imports/exports of hazardous wastes (tonne/yr); and
- Imports/exports of hazardous wastes as a percentage of production.

ESCAP (1996) has proposed the adoption of the first three of the DPCSD indicators. The U.K., along with several other countries, reports generation of hazardous wastes. The U.K. also includes out-of-date or "spent" chemicals from the business sector in the hazardous waste category.

The key to strategic indicator development, however, lies beyond the gathering of such basic data, interesting though it may be. Trends in data on production of hazardous wastes, for example, do not reveal the causes of indicator trends in hazardous wastes, such as a decline in traditional heavy manufacturing industries in some nations, nor does it reflect the expansion of the electronics sector. To understand such trends, data on waste classification have to be considered.

Many hazardous waste dump sites, which resulted from past improper waste disposal, are now threatening human health and the environment with soil contamination and related groundwater contamination. The latter is beginning to appear as a new environmental issue. The extent of contamination of land by hazardous wastes is difficult to estimate even in developed countries because of the different definitions often described by Acts and different hazards and risks associated with the potentially wide range of chemical and physical contaminants. Even estimating the area of land contaminated by the most significant groups of heavy metals, nonvolatile hydrocarbons, other persistent organic compounds, and the mineral fiber asbestos, is difficult. The Confederation of British Industry has estimated that there are around 200,000 ha of contaminated land in the U.K., with a total remediation cost of around US$20-40 billion (HMSO 1996b). Although statutory definitions of contaminated land may define the area, estimation of the risk to human health associated with the different types of contaminated sites is difficult without detailed study.

Indicators are also required that readily reflect the toxicity of the wastes and their real impact on the environment. But there is a general lack of health surveys and epidemiological studies of the health impacts of hazardous waste mismanagement and a lack of health impact assessment of hazardous waste treatment or disposal facilities. To be able to use these studies, hazardous waste indicators need to be developed, but the link between pollutant sources and health effects is complex and incompletely understood. Assessments of human exposure to chemicals from the Superfund sites in the United States and the development of generic models, do provide the basic information needed to examine how chemicals behave when they come into contact with humans (Kamrin et al. 1994). Despite the complex array of information that must be gathered, including environmental transformations, indicators or indices could be developed using biomarkers to measure exposure at least to some chemicals (Smith and Suk 1994).

In addition to the human studies that require much information, wildlife as sentinels of exposure, at least to those chemicals they are sensitive to, could be a useful indicator approach. Avian species especially fit many of the necessary criteria, although population variability and seasonal changes complicate data interpretations (Kendall et al. 1990). In developing countries in the absence of detailed hazard and risk assessments and human exposure studies, the wildlife indicator approach can provide a first approximation as to which sites should be targeted first.

Perhaps concentrations of metals and organic compounds in environmental media and living species using the biomarker concept (Ernst and Peterson 1994) will have to be developed as state indicators to reveal the extent of contamination, unless emissions of major metals and organics can be carefully assessed as pressure indicators based on toxicological and ecotoxicological risk assessments. Cadmium in moss is one such state indicator proposed as a component of Nordic Environmental Indicators (Statistics Norway 1995). Another indicator is the concentration of persistent organochlorine compounds in eggs of fish-eating birds in Canada (Environment Canada 1993). In some senses, the information is a state indicator, but it also clearly shows the environmental pressures society has placed on the aquatic ecosystem. The requirement for detail and the linking of chemicals and effects is only applicable in some countries where such relationships have been established through years of environmental toxicological research.

Nevertheless, a greater emphasis has to be placed on the concept of pressure indicators, for this is where policy action and human activities meet to assess options for different actions. Such indicators have to satisfy the decision-makers' need for a tool that enables evaluation of environmental performance. Human activities that cause irreversible damage to the environment and its components have to be addressed within an efficient environment policy.

In a slightly different approach, the World Bank (1995) has addressed the issue of resource consumption especially as applied to metals and minerals, which is relevant to the decline in heavy industries referred to earlier. They showed that although consumption of metals and minerals in OECD countries fell over several decades, it increased in middle- and low-income countries. On a per capita basis, low-income countries showed the largest increases. In both OECD and middle-income countries, consumption of metals and minerals per unit of GNP has decreased, suggesting increased efficiency and/or a shift toward higher value materials. In low-income countries, it is still increasing. Calculation of a Kuznets-type curve of GNP per capita versus consumption (in tonnes) revealed that the peak GNP per capita is around $1,700, showing that metals and minerals manufacturing industries are especially important in developing countries.

7 HAZARDOUS-WASTE-RELATED INDICATORS

There is a growing need for industrial concerns to consider and evaluate whether they are operating in a sustainable manner within the context of national environmental strategies. The sustainable development debate has now widened to encompass sustainable production and consumption patterns, as called for in Agenda '21. Indicators for sustainable production and consumption need to take into account different socioeconomic, environmental, and cultural contexts. This is where indicators for the promotion of waste minimization, cleaner production, adoption of pollution prevention procedures, life-cycle assessment, and EIAs in an earlier phase become relevant.

In the case of EIAs, an international response indicator could be based on whether all countries have *mandated EIA requirements*. The purpose is to ensure that environmental considerations are taken into account in the development, planning, and decision-making process.

Waste minimization can be applied to a reduction in physical wastes from manufacture of the product and equally to a reduction in emissions, energy, and water per unit of product produced. In the mining and smelting industry, waste minimization indicators could well apply to smelter tailing, refining residues, and also to increased efficiency in the production process, including industrial energy used per metal produced (MJ/tonne), or industrial water used per mineral processed (kL/tonne). Such indicators are now being reported (WMC 1995).

Life-cycle assessment, on the other hand, is a tool for assessing overall environmental impacts of industrial products and services, especially within the framework of the International Standards Organization. It includes the so-called "cradle-to-grave" approach, i.e., from extraction of raw materials and production, manufacturing, use, and waste disposal to life-cycle inventory. Aggregation of environmental variables is carried out through classification, characterization, and valuation, as illustrated in Fig. 3.

As environmental policy aims both at reducing emissions and increasing the sustainable use of resources, leading simultaneously to diminishing waste, integrated life-cycle management indicators need special attention. An indicator could be developed for each of the stages within the life cycle of the product, as proposed by Adriaanse (1995):

- Resource production and processing,
- Primary raw material production and intermediate products,
- Production of end products,
- Consumption or use of products, and
- Waste management.

An index could be constructed of weighted indicators for the entire cycle to link together source and sink functions so that improvements at any one stage in the complex cycle can be shown.

Environmental accounting is also placed in the same Fig. 3 in a form integrating environment and economics related to initial human impacts. Damage valuation, for example, includes both monetary valuation as well as weighting of environmental issues or themes within the context of the Adriaanse approach. Hence, emissions can be calculated by sector throughout the lifecycle and related to detailed costs.

Indicators for cleaner production to some extent depend on its definition. Does cleaner production apply in a narrow sense or does it encompass on-site hazardous waste treatment and off-site recycling? The establishment of toxic release inventories or pollutant release and transfer registers for manufacturing industries, where data are reported on releases of designated toxic chemicals into the air, water, and land, provides a series of indicators. Data on off-site transfers, including reporting of data on disposal, treatment, recycling, or energy recovery, provide further opportunities for indicator development as well as pollution prevention policies. Trends in environmental releases of toxic chemicals and chemical waste management, especially for release reduction, provide the public with information that manufacturers are adopting cleaner and safer processes. Publication of such

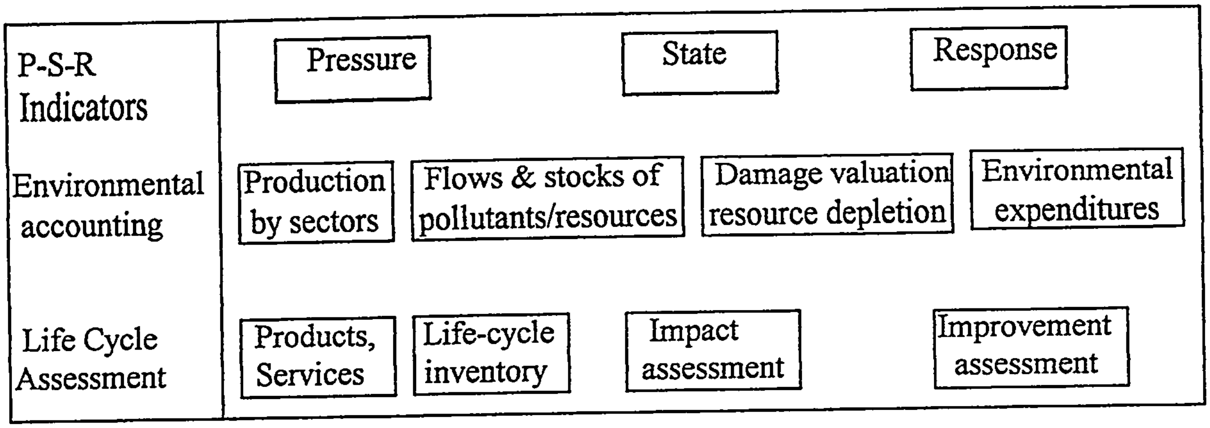

Fig. 3 Comparison of Frameworks of Environmental Indicators, Environmental Accounting, and Life-Cycle Assessment (from Moriguchi 1995).

data generates pressures on companies to improve performance and move toward cleaner production approaches. The change-over from organic solvent-based paints to water-based paints is a well-known example.

While all of the above approaches to environmental management represent exciting technical initiatives, there are growing reservations in some developing countries on the extent to which they are able to incorporate complex sets of sustainable development indicators into national planning. Some may lack the political will to implement the policy conclusions, while others lack the administrative capacity that can lead to action. In the final analysis, priority must be given to indicators of local relevance.

8 AGGREGATIONS OF INDICATORS

The aggregation of several hazardous waste indicators to form an index has not been widely considered. Probably the best known example is the Composite Pollution Index proposed by Adriaanse (1993) for the Netherlands, which was calculated on the basis of six composite indicators. Each was measured in terms of environmental pressure equivalents so that data could be interpreted in an additive way. The indicators were those described earlier, i.e., toxics, waste, acidification, etc. Trends in the index provided a useful, comprehensive measure for policymakers on whether the national situation was getting better or worse. The index can be recalculated on a per capita basis or per GNP so that the effectiveness of national or regional actions can be compared.

In developing countries where data are sparse, a simpler procedure is required, especially for evaluating hazards and risks following inspection of contaminated sites. The approaches cannot have the same policy-level relevance because they will be qualitative in nature. The hazard index could comprise relative values between 1 and 3; i.e., 1 is weak, 2 is moderate, and 3 is high, for each of several issues:

- *Hazardous waste sites.* The values depend on the substantial presence of priority hazardous substances in the wastes (or on the hazard ranking of the industry concerned), their environmental distribution (hazard properties), and risk potential.

- *Environmental degradation around the site.* The values would be based on noted environmental effects or estimated risks to the surrounding biota.

- *Human exposure around the sites.* Values are based especially on possible water and food contamination and dust fall.

- *Health risks near the site.* Values of morbidity and/or mortality are assigned over expected norms.

Each of the hazardous waste sites is stepwise profiled, and the most hazardous areas identified for immediate cleanup operations. The approach provides a rapid qualitative resolution of difficult issues and has been applied in an expanded form in Poland to establish priorities among the hazardous areas (Dutkiewicz 1993).

The third index is a pressure index, which can be seen as midway between the two examples mentioned above. It is designed to aggregate local and national indicators into a single descriptive index of human pressures but does not consider environmental or human health effects; rather, it considers the implications for health. Again, four indicator aggregates are considered for hazardous wastes, toxics, and air and water pollution. Each of the four aggregate indicators comprises current indicators weighted according to a consensus of the relative importance of the topic. For wastes, the issues would be as follows:

- Hazardous wastes, amount, classification, and relative toxicity;

- Disposal, incineration, extent of emissions, and landfill of residues;

- Disposal, landfill, areal extent, and containment characteristics; and

- Storage.

The other three aggregate indicators could be dealt with similarly. Aggregating the indicators into numerical values, although simplistic, draws attention to the need for pollution prevention approaches, i.e. a reduction in the numerical value of each aggregate and the total. Again the concept is "do-able" in nations where industrialization is rapid and emissions and hazardous wastes poorly controlled.

This latter approach could also be used to rank the environmental performance of operations producing hazardous wastes. On the basis of site inspections, self-reporting, and some independent calculations, facilities could be "ranked" into one of several wide categories and color coded for effect. Compliance with standards, a reduction of emissions, and adoption of "clean technologies" would enable the facility to move to the next category. The approach is one to drive to improved performance. A comparable concept has been adopted by the National Environmental Agency of Indonesia for ranking industries for their control (or lack of it) of water pollution.

9 MALAYSIAN CONTEXT

The Department of the Environment within the Ministry of Science, Technology, and Environment, is empowered under the Environmental Quality Act of 1974 to control and prevent pollution, as well as to protect and enhance the quality of the environment. In terms of hazardous waste, this Act was followed by the Environment Quality (scheduled wastes) Regulation of 1989, which prescribed a listing of 107 categories of toxic and hazardous wastes defined as "scheduled wastes." Further Orders related to EIAs and to waste treatment and disposal facilities have been described. The most recent Environment Quality Act (Amendment) of 1996 further details environmental auditing, environmental management systems, and a range of provisions related to hazardous waste and toxic chemicals.

In terms of hazardous waste generation, around 380,000 m^3 of hazardous industrial waste was reportedly generated in 1987 and around 500,000 m^3 in 1994 (CAP-SAM 1996). In 1992 this represented around 337,000 tonnes (MP7 1996). The major contributing industries are metal finishing and electroplating, chemicals, electronics and electrical, printing and packaging. To treat scheduled wastes in the country, Malaysia is constructing a facility at Bukit Nanas. This facility, Negri Sembilan, is a high-temperature incineration plant, secure land fill, a stabilization facility, and a physicochemical treatment facility; the first phase has just been commissioned.

Malaysia is both an exporter and importer of hazardous wastes. It ratified the Basel Convention on October 8, 1993, which necessitated further Orders under various customs acts. Malaysian experts are active members of technical working groups. Malaysia also supports the voluntary application of the prior informed consent procedure for certain hazardous chemicals and pesticides in international trade, possible further measures beyond prior informed consent, and possible action on persistent organic pollutants. Malaysia also has an active participation in the Climate Change Program, including implementation of measures to reduce chlorofluorohydrocarbons and halons.

To date, Malaysia has not adopted a widespread program of indicators/indices, nor of indicators for hazardous wastes and toxic chemicals, although discussions are ongoing.

10 CONCLUSIONS

Indicators provide a useful tool for decision makers, for they convert data into information of direct use. They are therefore a crucial link in the decision-making chain. In this context, if decision-makers are to take the actions needed to prevent environmental and/or health damage, they need reliable and relevant information. In some situations, the adoption of the indicator as a tool for decision making is more of a sociopolitical challenge than a technical problem.

Data and information on hazardous wastes, toxic chemicals, and associated environmental management issues, including cleaner production, life-cycle analysis, etc., are relatively poor even in some industrialized countries. But it is crucial that indicators are property conceived and understood even if the information is not yet available. Of particular relevance are pressure indicators that reflect measures to be taken locally, nationally, and regionally to reduce the burden that human actions place on the environment. Some progress has been made, but more remains to be achieved.

In many developing countries where data can be sparse and where financial and skilled human resources are limited, the development of environmental statistical departments is not always seen as a necessity. In these situations, essential data may have to be calculated by scientists (from emissions data rather than from environmental monitoring data, for example) or by the use of proxies or from rapid assessment techniques. Perhaps the construction of what O'Connor (1994) calls "optimally inaccurate indicators," which will support correct policy decisions, will be a useful way forward. Data can only be collected in a cost-effective way when linked to a policy need or to a user-driven need in such countries.

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PLENARY SESSION: HAZARDOUS WASTE RESEARCH PROGRESS

Chair: Patrick Tan Hock Chuan, Department of Environment, Malaysia

NEW DIMENSIONS IN OUR UNDERSTANDING OF THE HUMAN HEALTH EFFECTS OF ENVIRONMENTAL POLLUTANTS

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ABSTRACT

The term "hazardous" waste is used primarily in reference to potential hazards to human health and, to a lesser degree, hazards to wildlife and the ecosystem. Many of the chemicals associated with hazardous waste sites are also widely distributed throughout the environment; therefore, the health hazards associated with hazardous waste sites are not different from those associated with general environmental contamination. Until recently, it was generally assumed that cancer was the human disease of greatest concern associated with toxic chemicals. In fact, most governmental regulations related to exposure are designed on the basis of presumed cancer risks. Since the evidence that hazardous chemicals can cause cancer is strong, it is appropriate to be concerned about cancer risk. Recent evidence, however, has triggered a reevaluation of the assumption that only cancer is of concern. New evidence suggests that noncancer endpoints may occur more frequently than cancer, may affect a greater number of individuals, and may occur at lower concentrations. Of particular concern is evidence of irreversible effects on the embryo and very young children, which influence intelligence, attention span, sexual development, and immune function. Although these effects are often subtle and difficult to quantify, the combined evidence is sufficiently compelling to necessitate a reevaluation of those outcomes of primary concern to human health.

1 INTRODUCTION

The primary reasons for concern about hazardous wastes relate to the possibility of effects on human health. Exposure to hazardous substances may occur directly at hazardous waste sites in workers or other individuals like children who have access to the site, or from migration of toxic substances from the site into air, drinking water, sediments, and soils. Such substances may also be hazardous to wildlife.

Typically, hazardous wastes contain a variety of toxic substances, each with its own toxicity in biological systems. In addition, many toxic substances interact such that two or more substances together may be much greater than the sum of individual effects (Arnold et al. 1996). Hazardous wastes are usually considered to fall into categories of solvents, metals, persistent organics, and radioactive wastes. This paper considers only the first three categories of contaminants. Each of these categories consists of many different substances with varied and sometimes interactive toxicities.

The purpose of this paper is to review human health effects known to occur upon exposure to environmental contaminants commonly found in hazardous wastes and recent advances that have led to a new understanding of the variety of effects seen in animals and humans. In addition to cancer, emphasis will be placed on effects resulting from prenatal or early postnatal exposures to substances that result in the permanent alteration of the individual, since subtle effects on physical growth, reproductive capacity, and mental and cognitive capacity resulting from exposure to toxic chemicals have only recently been delineated. Since the solvents, metals, and persistent organics found at hazardous waste sites are also widely distributed in the environment, the hazards to human health are also general problems of environmental contamination.

2 CANCER

Animal toxicology studies have long demonstrated that exposure to a variety of metals and organic substances can increase the risk of various cancers. A number of epidemiological studies, primarily those dealing with occupational exposures, confirm the conclusion that humans are equally vulnerable to chemically induced carcinogenesis (Buffler et al. 1985). As knowledge about the causes of cancer increases, environmental exposures of various sorts have apparently become proportionately more important causes of cancer.

Types of cancer and causes are, of course, different in different countries and cultures. Table 1 lists data on the changing incidence of various cancers in the United States. What is particularly dramatic is that almost all of the cancers that are increasing in incidence show evidence of at least some involvement of an environmental factor. The greatest increase is in malignant melanoma, a skin cancer known to result from exposure to sunlight. The increase in incidence is likely secondary to the depletion of the protective ozone layer that has resulted from the release of ozone-reactive chlorofluoro-hydrocarbons into the atmosphere. Lung cancer continues to increase as a result of smoking, primarily because of the polyaromatic hydrocarbons (PAHs) as well as cadmium and benzene metabolites present in tobacco smoke. PAHs are also major contaminants at hazardous waste sites in the form of coal tars and are known to be carcinogens for a variety of forms of cancer, including skin, lung, and bladder cancer (Mastrangelo et al. 1996; White 1986). Some hormonally dependent cancers (breast, testis, prostate) are also increasing, and a considerable body of evidence suggests that the widespread contamination of the environment with xenoestrogens, which are a variety of different chemical substances that have estrogenic activity, at least contribute to the increased incidence of these cancers. The variety of the effects from these substances is discussed in detail below.

Lymphoma is a cancer that has been shown to be, at least in part, a result of exposure to both organic and arsenate pesticides (Woods et al. 1987). The increase in cancer of the kidney and bladder is likely secondary to exposure of these organs to carcinogenic substances that are ingested and excreted in the urine (Koivusalo et al. 1994). Brain cancer has been demonstrated to be related to exposure to a variety of hydrocarbons (Johnson et al. 1987). Glioma incidence has been shown to be elevated in individuals working in the rubber and plastics industries (Preston-Martin et al. 1990). In general, cancers of the digestive tract are decreasing, presumably secondary to improved diets with more fiber and less fat.

It is not only organic substances that may contribute to cancer, since some metals are also carcinogens (see Buffler et al. 1985). Arsenic, for example, is well documented to cause skin, bone, gastrointestinal, liver, lung, kidney, and bladder cancer (Enterline et al. 1995; Hsueh et al. 1995; Smith et al. 1992). Meningiomas are elevated in individuals exposed to metal dusts and fumes (Preston-Martin et al. 1990). A variety of metals are found in hazardous waste sites, but the major source of exposure is usually via air transport or drinking water, which may be contaminated by local mining or smelting operations or via transport from a hazardous waste site into drinking water. Although it is impossible to know, at present, the exact degree to which environmental contaminants contribute to cancer incidence, it is clear that such exposure is an important contributing factor.

Table 1 Changing Incidences of Cancer in the United States

Cancers Increasing (1973-1987)	Increase (%)	Cancers Decreasing (1973-1987)	Decrease (%)
Melanoma	83.3	Cervix	-36.4
Non-Hodgkins lymphoma	50.9	Uterus	-26.1
Prostate	45.9	Stomach	-20.5
Testes	39.0	Hodgkin's disease	-15.9
Lung	31.5		
Kidney	27.0		
Breast	24.2		
Brain/central nervous system	23.0		

From Henderson et al. (1991).

3 BIRTH DEFECTS

Definitive evidence that living near a hazardous waste site results in an increase in the incidence of birth defects has been provided by a study in which the birth defects registry in New York state was used to plot the residences of babies born with birth defects relative to the locations of documented hazardous waste sites in New York (Geschwind et al. 1992). Table 2 shows some of the results obtained from that study. The results show that there is a distance-dependent increase in the frequency of birth defects in those individuals living close to hazardous waste sites. This observation is important because proximity to any identified hazardous waste site, alone, would be expected to be a very inexact indicator of exposure. This categorization of exposure does not take into consideration whether toxics migrate from the site, what the contaminants are, or any other factor related to the lifestyles of the individuals. In spite of these factors, the relationship is clearly statistically significant. Other previous studies have demonstrated that newborns living very near hazardous waste sites tend to have lower birth weights (Vianna and Polan 1984).

Another serious environmental cause of birth defects comes from exposure to pesticides. This factor is potentially very important in developing countries, where potent pesticides are used extensively without adequate protection of both the persons applying these chemicals and the general population. Garry et al. (1996) have shown that there is a significantly elevated incidence of birth defects in children born to pesticide appliers, and that the rate of birth defects is greatest among children conceived in the spring, when most pesticides were applied. An alteration in the male/female birth ratio was also detected in children born to pesticide appliers.

Table 2 Birth Defects and Proximity to Hazardous Waste Sites in New York

Exposure	All Defects	CNS	Musculoskeletal	Integument
None	1.00	1.00	1.00	1.00
Low	1.09 (1.04-1.15)**	1.27 (1.03-1.57)*	1.09 (1.00-1.18)	1.22 (1.08-1.38)**
High	1.63 (1.34-1.99)**	1.48 (0.69-3.16)	1.75 (1.31-2.34)**	2.63 (1.90-3.67)**

From Geschwind et al. (1992).

*$p < 0.05$

**$p < 0.01$

4 COGNITIVE AND BEHAVIORAL ABNORMALITIES AS A RESULT OF EXPOSURE TO HAZARDOUS WASTES

It has been known for several centuries that exposure to toxic metals such as lead can lead to severe nervous system dysfunction and even to death at extreme exposures. There is speculation that the decline of the Roman Empire may have been in part triggered by lead poisoning secondary to the use of lead goblets for drinking wine, which, by virtue of being acidic, promotes solubility. However, it is only relatively recently that we have learned that much lower concentrations of lead can cause irreversible reduction in the cognitive functioning of children, and that the period at which this effect occurs is prenatal and in the very early postnatal years. Needleman et al. (1979) first demonstrated this effect by documenting concentrations of lead in deciduous teeth and blood of young children and relating the concentrations of lead to school performance. Children with elevated lead levels showed reduced performance on several cognitive function tests, poorer school performance, and a shortened attention span. Numerous studies have confirmed the general conclusions of Needleman et al. (1979) over the intervening years (ATSDR 1988; Feldman and White 1992; Fergusson and Horwood 1993), and this confirmation has led to a progressive lowering in the level of blood lead considered to be "safe." In 1985, the U.S. Centers for Disease Control considered 25 µg/dL to be a safe background level, but its recommendation fell to 20 in 1986 and 10 in 1990. The shift in IQ of the highly exposed children may be as much as 6 IQ points and is reflected in a shift in the IQ-frequency curve to the left. Thus, lead-exposed children still show a range of IQ values, but the average is less. This has a disproportionate effect at the extreme ends of the curve, with many fewer very bright and many more very poorly performing children. A recent review of the status of children studied first in 1979 reports that the effect is permanent (Needleman et al. 1990). Others, however, have performed a meta-analysis of multiple studies of IQ and lead exposure and calculate that a doubling of serum lead from 10 to 20 µg/dL leads only to a decrement of 1-2 IQ points (Pocock et al. 1994). Lead-exposed children also show a variety of behavioral problems, although it is not clear whether the cognitive or the behavioral problems are primary (Bellinger et al. 1994).

Other metals are known to interfere with nervous system function and may cause mental retardation. Children born to mothers accidentally exposed to methyl mercury in incidents in Japan and Iraq were found to have profound retardation if the exposure levels were greater than about 50 parts per million (ppm) (see WHO 1990). Methylmercury is thought to interfere with the normal migration of nerve cells during development, presumably as a result of the fact that this organometal binds to sulfhydryl groups. Other organo metals, especially tin and lead, may also have similar effects (see Carpenter 1994). Inorganic mercury exposure has also been reported to be detrimental to memory and cognitive ability (Piikivi et al. 1984; Smith et al. 1983).

Recent studies have shown that some persistent chlorinated hydrocarbons, particularly polychlorinated biphenyls (PCBs), may exhibit very similar effects to those of lead. This problem was first seen in children born to mothers who were exposed to PCBs through consumption of rice oil highly contaminated with PCBs and dibenzofurans, a heat degradation product, in Japan and Taiwan (Chen et al. 1992). As occurred with lead exposure, the IQ curves of these children were shifted to the left by about 5 IQ points. Since many of the children were born years after the exposure of the mother, the effects appear to be mediated via exposure of the fetus from the PCB stores in the mother's body fat. PCBs and furans are persistent in that they are fat soluble and poorly degraded by the human body. Therefore, they accumulate in body fat but remain in equilibrium with lipids circulating the blood, which provide the source of exposure to the fetus. In addition to prenatal exposure, the child may be exposed to PCBs via breast feeding, which is the only way the human body has for excreting fats.

Two groups have studied U.S. populations for effects of PCB exposure from ambient sources. Rogan and colleagues have compared cognitive and behavioral indicators with concentrations of PCBs in blood and cord blood. Gladen et al. (1988) and Rogan and Gladden (1992) found that transplacental exposure to PCBs and DDE resulted in low psychomotor scores in infants at 6 and 12 months of age. Children with the greatest prenatal exposure showed hypotonia and hyporeflexia at birth, slower motor development through age two, a defect in visual memory processing at 7 months, and defects in short-term memory at 4 years. Jacobson et al. (1990) and Jacobson and Jacobson (1990) studied children of individuals who fish and consume fish from the Great Lakes, where there is significant contamination. They found reduced physical weight, neonatal behavioral anomalies, and poorer recognition memory in women who had consumed contaminated Lake Michigan fish. In a recent report, Jacobson and Jacobson (1996) revisited the children reported in an earlier study and found that those with the highest exposure have, on average, a 6.2 IQ point deficit when studied at 11 years of age, and that the magnitude of the deficit correlates best with prenatal exposure. Thus, it appears that PCBs, like lead, cause a permanent reduction of IQ and that the most significant time of exposure is before birth, when the brain is in the process of development. Also as occurs with lead, these investigators noted that exposed children were characterized by a shortened attention span and an increase in the reports of behavioral disturbances. It is possible, indeed likely, that the shortened attention span has much to do with the reduced IQ; it is difficult to learn if you cannot pay attention.

Recent studies in animal model systems have demonstrated that for both lead and PCBs, direct effects on the brain may explain the reduction of IQ (Carpenter et al. 1997; Hori et al. 1993). The exact mechanisms responsible for these actions are still unclear, and it remains uncertain whether lead and PCBs are acting in a similar fashion. However, the ultimate pollution is one that causes a permanent reduction in the intelligence of the next generation; therefore, this effect from at least two categories of hazardous waste must receive priority attention from all countries.

5 IMMUNE SYSTEM ALTERATIONS AS A RESULT OF EXPOSURE TO ENVIRONMENTAL POLLUTANTS

The immune system is the body's first line of defense against infectious diseases and cancer. The healthy person is characterized by an immune system that can identify and remove foreign organisms and abnormal cells and substances while, at the same time, does not overreact and thereby cause excessive responses to external agents and allergic responses to one's own body and tissues. A healthy immune system is in balance, but this balance can be shifted in either direction by a variety of environmental contaminants. Many metals and solvents cause an increased immune reactivity, and these substances frequently result in skin rashes, systemic allergic reactions, and even autoimmunity, a variety of conditions in which the body becomes allergic to and rejects its own cells. Another concern is the role of environmental agents in asthma, especially in children. Childhood asthma, particularly, appears to correlate with indoor air pollution, including tobacco smoke, allergens from insect and rodent pests, and other environmental factors (Dekker et al. 1991). It is not clear, however, whether these factors cause asthma or only contribute to symptoms in patients with preexisting disease. On the other hand, many persistent organics, pesticides, and herbicides are known to cause an immune suppression (see Brooks and Sullivan 1992). This suppression results in an increased susceptibility to infections of various kinds. The immune suppression may also be reflected in an increased incidence of cancer, since the immune system normally kills cells that become malignant (Herberman 1980). Obviously, it is difficult to quantify the magnitude of influence of environmental contaminants on infections and cancer incidence, because both are the result of a variety of causes.

6 ENDOCRINE DISRUPTION VIA INTERFERENCE WITH THYROID FUNCTION

Recently, it has become clear that some environmental contaminants can cause health effects by interacting with hormonal systems. As shown in Fig. 1, there is some structural similarity between thyroid hormone and PCBs and dioxin. In animals, it has been documented that exposure to these substances can induce hypothyroidism (Gray et al. 1993; McKinney et al. 1985; Rickenbacher et al. 1986). This effect on thyroid function is particularly important both because the thyroid hormone regulates physical growth and development and also because it has an important role in regulating the nervous system (Pasquini and Adamo 1994; Porterfield 1994).

Thyroid hormone is critical to normal intelligence. There is a large body of information on the effects of hypothyroidism on human functioning, both during development and in adults. The thyroid gland is the master gland for regulating metabolism and therefore controls growth and development, including development of the brain. Infants born without functional thyroids become cretins, characterized by short stature and profound mental retardation. Many countries now screen all newborns for hypothyroidism, and when infants without adequate thyroid function are identified, they are given thyroid supplements to restore metabolic function to normality. While it is usually

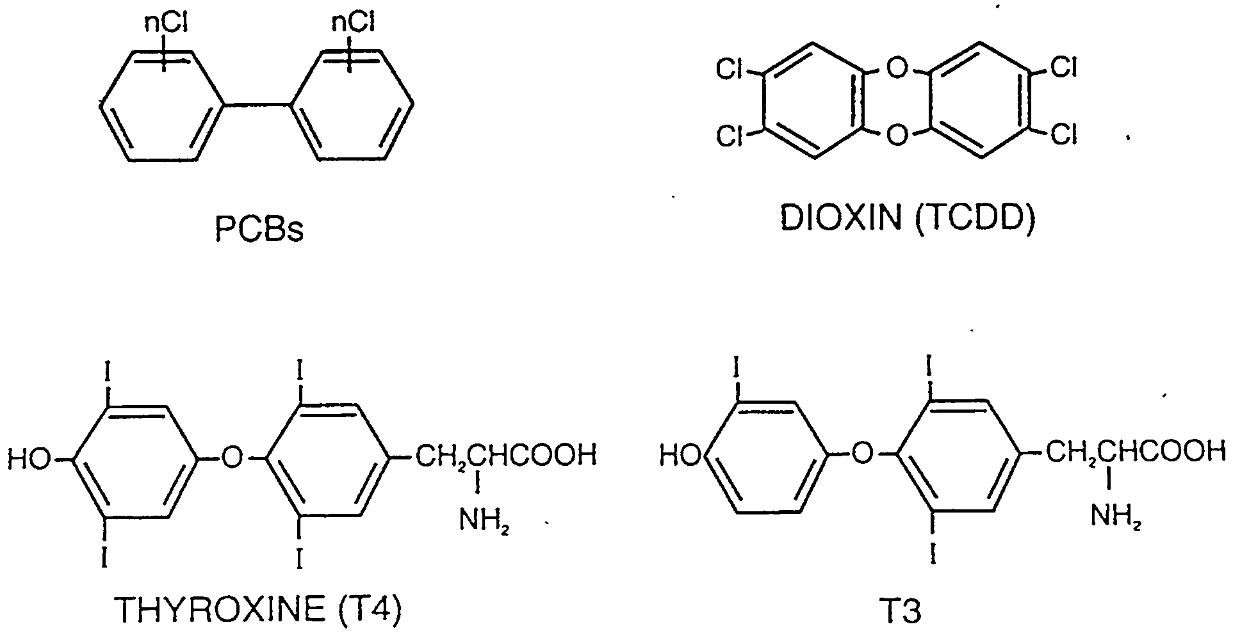

Fig. 1 Structure of Thyroid Hormone PCBs and Dioxins

assumed that this practice results in totally normal development, a recent study of such individuals has shown that development is not quite normal. Most such individuals are characterized as having a syndrome of minimal brain dysfunction, with a somewhat lower IQ, difficulty in learning and remembering, and difficulty in concentration (Kooistra et al. 1994). Individuals with resistance to thyroid hormone show a variety of psychiatric symptoms, including hyperactivity, attention deficit disorder, antisocial personality, and depression (Hauser et al. 1993). Therefore, it is possible that loss of cognitive ability after exposure to environmental contaminants that induce hypothyroidism may be secondary to the effect on thyroid function.

There is a debate at present over exactly how PCBs interfere with thyroid function. Some actions may be at the level of direct damage of the thyroid tissue (Byrne et al. 1987), but clearly some are also at the level of the serum proteins that normally bind circulating thyroid hormone and protect it from degradation and/or excretion (Darnerud et al. 1996; McKinney and Waller 1994).

7 ENDOCRINE DISRUPTION VIA SEX STEROID HORMONES

Humans and animals come in two varieties — male and female — and the characteristics of each are determined during development, primarily on the basis of the balance and ratios of the two major sex hormones: the female estrogens (especially beta-estradiol) and the male androgens (primarily testosterone). While both sexes have some of both kinds of hormones, females have more estrogen and males more testosterone.

A massive experiment involving the administration of extra estrogen during human development was conducted for a quarter century following World War II, when many physicians throughout the world gave pregnant women the synthetic estrogen, diethylstilbestrol (DES), ostensively to reduce the incidence of spontaneous abortion. This practice was abruptly stopped when, in 1971, it was found that girls exposed in utero to DES were developing an unusual vaginal cancer that was almost never seen otherwise. When studied later in life, girls who were so exposed were found to demonstrate a greater incidence of birth defect abnormalities of the female reproductive tract, infertility, emotional disturbances, and abnormal sexual preferences. Males were also affected. This effect was first demonstrated in mice, where males exposed in utero were found to have a variety of genital defects, including undescended testes, abnormal sperm, infertility, and genital tumors (McLaughlin et al. 1975). Later, Gill (1988) reported that human males exposed to DES in utero had a greater incidence of small or undescended testes, small penises, and a greater percentage of abnormal sperm. Newbold (1995) has recently reviewed the extensive variety of genital defects seen both in humans and mice exposed to DES.

Recent studies have found that a variety of chemicals may exhibit estrogenic or antiestrogenic activities. Some of these substances are shown in Table 3. What is surprising is that this list includes a variety of substances that do not appear to have particular structural similarity to the structure of estrogen. Most of the substances shown in Table 3 are significantly less potent than the parent compound, but this does not necessarily mean that they have no biologic effect. Particularly those substances that are persistent may indeed influence development and behavior.

Table 3 Estrogenic Chemicals

DDT/DDE
Some other pesticides and herbicides
Some PCB congeners
Bisphenol A
Alkyl phenols
Some phthalates
Phytoestrogens in plants
Some mycotoxins

The strongest evidence that xenoestrogens, as they are now referred to, alter sexual development and behavior comes from wildlife studies. In 1994, Guillette and colleagues reported that American alligators in Lake Apopka in Florida showed profound abnormalities of sexual development and were infertile. On inspection, the males had very small penises, abnormal testes, and elevated levels of estrogen. This effect was shown to be secondary to the extensive contamination of Lake Apopka with dicofol, an estrogenic pesticide, and possibly DDE, an estrogenic metabolite of DDT. Thus, the genital development of the male alligators was altered by exposure to a xenoestrogen.

Further evidence that xenoestrogens can alter reproductive capacity and structure of the reproductive organs has been found in studies of birds of prey, gulls, mink, and fish in natural settings and in laboratory animals (see reviews by Colburn et al. 1993, 1996). The toxicities were manifested in a variety of ways, from thinning of the shell of eagle eggs secondary to contamination with DDT and dieldrin, to reduced fertility in fish, panthers, turtles, and otters, to tumors of reproductive organs in whales.

In human populations, there are a number of reports that the sperm count of men in developed countries has decreased by about 50% over the past quarter century or so (Auger et al. 1995; Sharpe and Skakkebark 1993; Toppari et al. 1996). In addition, there has been a marked increase in incidence of undescended testis, hypospadias, and small penises over the same period, and these defects in reproductive structure have been suggested to be secondary to increased exposure of male infants to xenoestrogens during development.

Marked increases in the incidence of cancer in organs that are influenced by sex hormones is mentioned above. Evidence is accumulating that these cancers may be secondary to some combination of prenatal and adult exposure to xenoestrogens. It has long been known that undescended testes was a strong risk factor for the development of testicular cancer, one of the cancers that has been increasing in incidence. Many of the young men who develop testicular cancer did not have undescended testes; therefore, it is possible that xenoestrogen exposure during development has contributed to the increased incidence of this disease.

Breast cancer is one of the most frequent cancers of women in developing countries, and it has been increasing in incidence. The cause of breast cancer is imperfectly understood, but the greatest risk factor appears to be the number of menstrual cycles that a woman experiences in life. Thus, incidence of breast cancer increases when menses are earlier and menopause is later. Breast cancer decreases with the number of children, possibly because during pregnancy, there is no longer the normal cycling of hormone levels. In a recent study, Wolff et al. (1993) found that the levels of DDE and PCBs in serum of women with breast cancer were significantly larger than in women with nonmalignant breast nodules, suggesting the possibility that xenoestrogens may contribute to the cause of breast cancer (also see Davis et al. 1993).

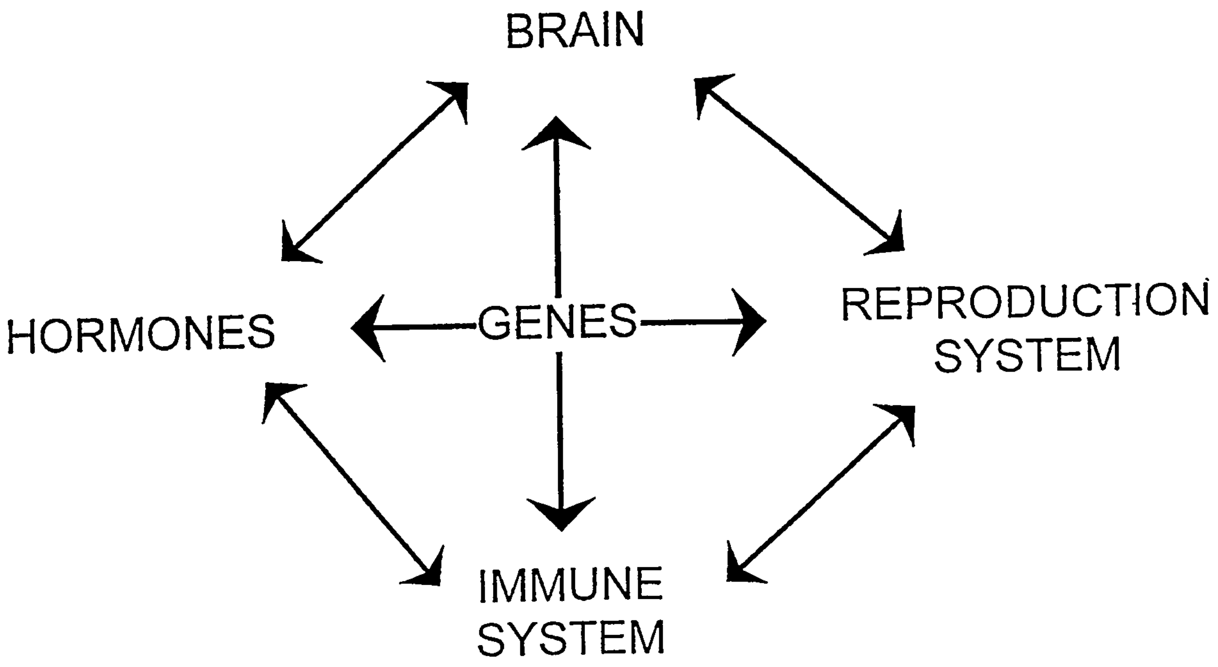

Fig. 2 Interactions among the Genetic System and Various Organ Systems Involved in Environmental Diseases

In conclusion, hazardous wastes may affect human health in a wide variety of ways. Although many substances may directly damage chromosomes and, in so doing, cause cancer and birth defects, many other effects that are more difficult to monitor and document may be even more serious from a societal point of view. Furthermore, the understanding of the degree to which the various organ systems interact has recently been much greater, as shown in Fig. 2. The nervous, immune, hormonal, and reproductive systems all interact and are under genetic control. When an environmental agent alters the activity of one of these organ systems, there is often a secondary change in another.

The developing human embryo appears to be at particular risk for harm from environmental contaminants, which may result in birth defects and congenital abnormalities. Among the most important harmful effects are decrements of intelligence and altered behavior that may be permanent, as well as altered hormonal, immunologic, and reproductive functions. Recent evidence strongly suggests that prenatal environmental contaminants may cause a permanent and irreversible alteration in these various organ system functions, whether it is reflected in IQ, immune function, fertility, or sexual preference. Although the full magnitude of harmful effects to humans of exposure to such substances is not yet known, it is clear that protection of humans, especially children and women of reproductive age, should be an international priority.

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PLENARY SESSION: LOOKING TOWARD THE FUTURE

Chair: Richard R. Cirillo, Argonne National Laboratory
Executive Secretary, Pacific Basin Consortium

WHO COLLABORATION IN HAZARDOUS WASTE MANAGEMENT IN THE WESTERN PACIFIC REGION

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ABSTRACT

Since April 1989 when the World Health Organization's (WHO's) activities in hazardous waste management in the Western Pacific Region were presented at the Pacific Basin Conference in Singapore, WHO and its Member States have carried out a number of collaborative activities in hazardous waste management. These activities focused on three main areas: national capacity building in the management of toxic chemicals and hazardous wastes in rapidly industrializing countries, management of clinical or medical waste, and hazardous waste management in Pacific Island countries. This paper summarizes these collaborative activities, identifies the main problems and issues encountered, and discusses future prospects of WHO collaboration with its Member States in the area of hazardous waste management.

1 INTRODUCTION

At the 1989 Pacific Basin Conference on Hazardous Waste Management in Singapore, the World Health Organization's (WHO's) collaborative activities in hazardous waste management were presented. The number of collaborative activities in hazardous waste management at that time was small, partly because many developing countries in the Western Pacific Region had limited interest in the subject and partly because the WHO staff responsible for this field had just been recruited and did not have time to develop many collaborative activities.

Since the 1989 conference, industrialization has continued in several rapidly developing countries, and "open market" policies of some socialist countries have accelerated the pace of economic development in their countries and international trades with other countries in the region. Such industrialization and economic policies have increased the awareness and interest for safe disposal of hazardous waste among professionals and the general public. At the same time, small island countries in the Pacific region became concerned about the transboundary movement of hazardous waste. The protection of their fragile ecosystems from hazardous waste, both imported and generated locally, has become a major environmental issue.

In response to these problems, the WHO Regional Office for the Western Pacific has enhanced its collaboration with developing Member States in the region (see Fig. 1 for WHO Member States in the Western Pacific Region) and implemented a number of activities related to hazardous waste management. This paper describes these activities, discusses problems and issues encountered, and presents future prospects of WHO's hazardous waste management program in the region.

2 WHO'S COLLABORATIVE ACTIVITIES IN HAZARDOUS WASTE MANAGEMENT

Table 1 summarizes the WHO collaborative activities with Member States carried out since April 1989. During this period, 46 activities in 20 countries and areas were carried out. Except for a few activities in response to ad-hoc government requests, three areas dominated:

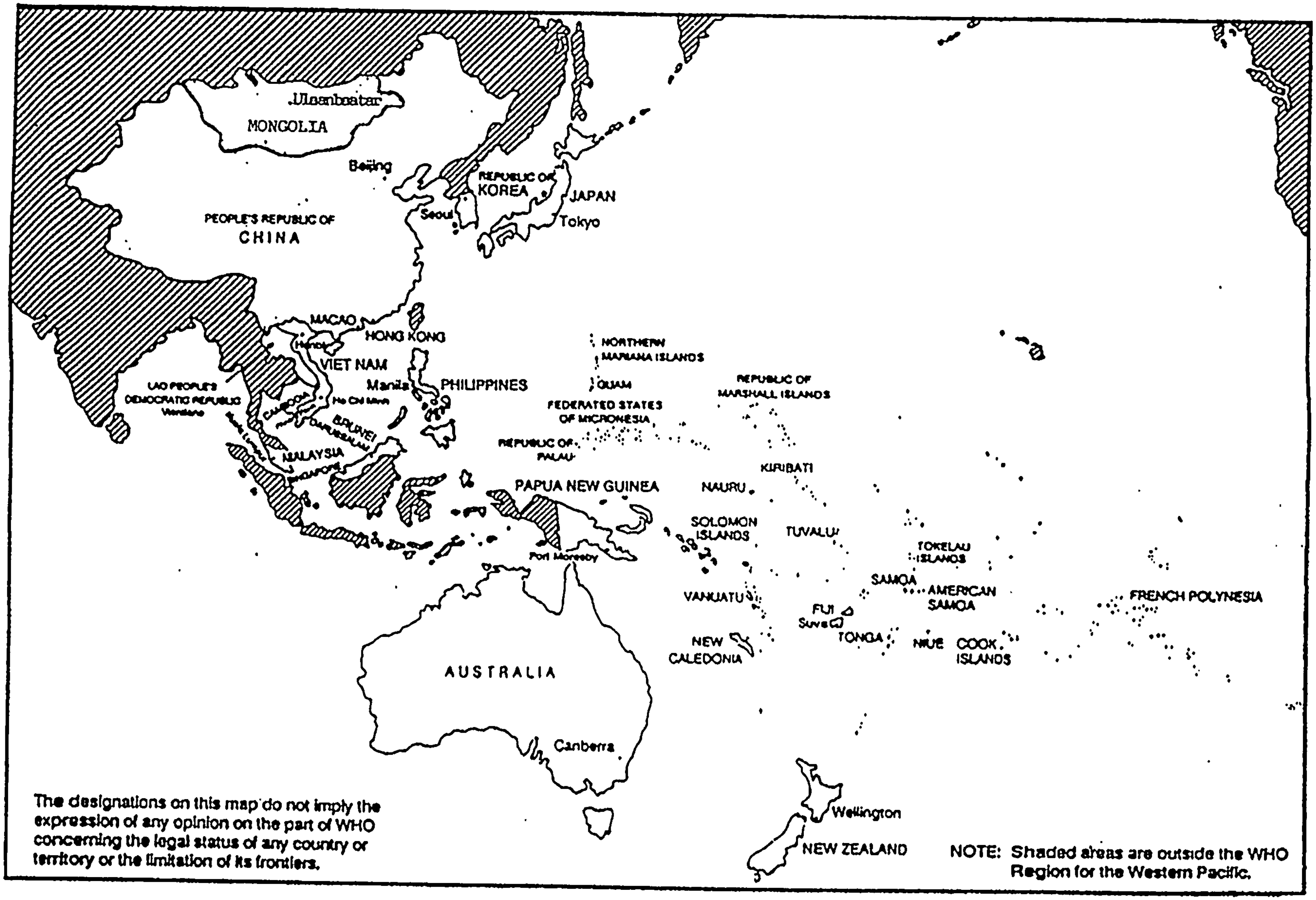
- United Nations Development Program (UNDP)/WHO project on safety and control of toxic chemicals and hazardous wastes,
- Hazardous waste inventory and disposal in Pacific Island countries, and
- Hospital and clinical waste management.

2.1 UNDP/WHO Project

The UNDP/WHO project on safety and control of toxic chemicals and hazardous wastes was jointly funded by UNDP and WHO, with WHO implementing the project activities. This two-year project covered all aspects of chemical safety, including the production, use, storage, transport, and disposal of hazardous chemical substances, and focused on national capacity building in chemical safety. It involved five countries, namely, China, Malaysia, Republic of Korea (South Korea), the Philippines, and Singapore, and several agencies in each country that implemented various activities. The national organizations in the project were mainly environmental agencies, except for China where the Ministry of Chemical Industry served as the national focal point.

The main activities carried out in the project included:

- Preparation of country profiles in all countries;
- National workshops on the control of toxic chemicals and hazardous wastes, involving relevant government agencies and professional associations in all countries;



The designations on this map do not imply the expression of any opinion on the part of WHO concerning the legal status of any country or territory or the limitation of its frontiers.

NOTE: Shaded areas are outside the WHO Region for the Western Pacific.

Fig. 1 WHO Member States in the Western Pacific Region

Table 1 WHO Collaborative Activities in Hazardous Waste Management in the Western Pacific Region

Country or Area	Year							
	1989	1990	1991	1992	1993	1994	1995	1996
America Samoa							1	
Brunei					1			
China		1	2^a	2^a				
Cook Islands				1^b				
Fiji				1^b				
Lao PDR							1^c	
Malaysia	$2(1^c)$		$3(2^a)$		2^c			
Marshall Islands				1^b				
F. S. of Micronesia				1^b	1	1		
Northern Mariana Is.				1^b				
Palau				1^b				
Papua New Guinea				1^b	1^c			
Philippines	1		1^a		2^a			
Republic of Korea			1^a	1^a				
Western Samoa				1^b			1	1
Singapore			1^a					
Solomon Islands				1^b				1
Tonga				1^b				
Vanuatu				1^b	1			
Viet Nam			1					1^c
Regional			1		1^c	1^c	1	
Total	3	1	10	14	9	2	4	3

[a] UNDP/WHO project on safety and control of toxic chemicals and hazardous wastes.
[b] Hazardous waste inventory and disposal in Pacific Island countries.
[c] Hospital and clinical waste management.

- Development of national priorities and proposals to improve national capabilities in the management of toxic chemicals and hazardous wastes in all countries;
- Review and drafting of relevant legislation in selected countries;
- Regional workshop on chemical safety legislation held in Kuala Lumpur;

- Development of educational and training materials for industrial chemical safety and translation of materials into local languages (e.g., Malay and Chinese);
- Provision of consultants on specific activities (e.g., design of a hazardous waste incinerator, risk assessment of a contaminated site, etc.) in selected countries;
- In-country training courses in selected countries; and
- Overseas study tours.

Overall, the implementation of the UNDP/WHO project was timely for all the participating countries, as they were developing national programs for the management of toxic chemicals and hazardous wastes. Especially, China, Malaysia, and the Philippines benefited most from the project, as their national programs were in the early stages of development. They now have hazardous waste management legislation in place, key government officials trained in chemical safety and hazardous waste management, and clear national policies or plans available.

2.2 Hazardous Waste Management in Pacific Island Countries

In the late 1980s, several Pacific Island countries received proposals to dispose of hazardous wastes generated in some industrialized countries. These countries consulted WHO for advice and became aware of potential dangers associated with the transboundary movement of hazardous waste to these countries with such fragile ecosystems. Releasing its policy statement against such hazardous waste movement, WHO also committed to support strengthening hazardous waste management activities in these small countries. The issue was discussed at the WHO Regional Workshop on Chemical Safety Legislation held in Kuala Lumpur in 1991. Participants in this workshop identified the following problems and needs:

- No effective legislation is in place to prevent the transboundary movement of hazardous waste, and border control agencies are powerless to stop it.
- The financial incentives offered in the proposals to small countries are difficult to turn down.
- Many island countries do not have the technical expertise to fully assess the hazards presented by the proposals to ensure that facilities are operated properly even if the proposals are approved.

- Effective and comprehensive legislation is needed in each country based on the Basel Convention and the provisions of the London Dumping Convention.

- A required mechanism needs to be developed, whereby countries can access technical expertise to collaborate with the assessment of waste disposal activities and proposals.

- A requirement is needed for ongoing auditing and evaluation of existing waste disposal facilities to monitor progress and control systems.

- The establishment of acceptable methods of hazardous waste disposal for waste generated in each country is required.

- A provision needs to be made for training and upgrading knowledge on the correct development and operation of waste disposal facilities, particularly in developing countries.

Guided by these conclusions, WHO initiated a project on hazardous waste management in Pacific Island countries. The first activity was carried out in 1992 to develop a hazardous waste inventory and action plan in these countries. As shown in Table 1, the activity was implemented in 11 Pacific Island countries and areas, namely, Cook Islands, Fiji, Marshall Islands, Federated States of Micronesia, Northern Mariana Islands, Palau, Papua New Guinea, Western Samoa, Solomon Islands, Tonga, and Vanuatu. Visits by WHO staff and consultants were made to assess the types, sources, and quantities, where possible, of hazardous wastes generated in these countries; to evaluate existing waste management practices; and to identify potential hazardous waste management options.

The hazardous wastes commonly found in these countries include:

- Pesticide, herbicide, and insecticide wastes,

- Lubricant motor oil waste,

- Used lead-acid batteries,

- Hospital infectious waste,

- Waste oil from power plants,

- Spent photographic chemicals,

- Discarded transformer oil/PCB waste, and
- Timber treatment chemical waste.

In some countries, dry cleaning solvent sludge, asbestos, and paint waste were found. Because these countries do not have a large industrial/commercial facility, only small quantities of these wastes are generated. However, the lack of suitable waste management and disposal facilities and technical expertise in the small island countries threatens underground drinking water sources and reef waters with contamination from hazardous substances.

To follow up on these findings, WHO extended its collaboration to selected countries where the personnel involved in handling hazardous waste were trained and national guidelines and plans for the management of specific hazardous wastes were developed. In 1993, Vanuatu and the Pohnpei State of the Federated States of Micronesia made provisions for appropriate storage containers to replace old and leaking pesticide waste containers. In these countries, WHO staff demonstrated how to repack pesticide waste and then provided hands-on training of local officials who handled such waste. A similar activity was carried out in Chuuk and Yap States of the Federated States of Micronesia in 1994 and in the Solomon Islands in September 1996. In 1993, WHO collaborated with Papua New Guinea in assessing of, and preparing national guidelines for, hospital waste management.

WHO convened a Regional Workshop on Hazardous Waste Management in Pacific Island Countries in 1995 in Fiji. The workshop participants reviewed and discussed appropriate and affordable technologies and assessed alternative approaches to hazardous waste management in small Pacific Island countries. The discussion on the disposal of hazardous waste focused on incineration and landfills, particularly on existing facilities. The participants acknowledged the existence of appropriate and affordable technologies for most of the wastes generated in Pacific Island countries. However, these technologies were not being used because of the lack of sufficient, practical know-how and information on any secondary pollution or hazard created. The participants recommended the following actions:

- Compile a hazardous waste management source book for detailed technology, techniques, information, equipment, service contractors, and contracts for managing each of the main types of hazardous waste generated by Pacific Island countries.
- Prepare and distribute booklets listing and explaining affordable and appropriate technologies for the types of hazardous waste generated by Pacific Island countries.

- Prepare booklets, pamphlets, and posters for educating workers and farmers about the hazards, safe use, and proper disposal of hazardous waste, preferably translated into local languages.

- Provide background and support information for educating urban communities about the need for and the strategy by which to achieve better hazardous waste management.

- Provide expert consultation for preparing environmental standards and legislation that take into account both local conditions and prevailing cultural sensitivities.

- Promote regional recycling efforts.

- Avoid duplication and maximize benefits to Pacific Island countries by coordinating key interests and responsibilities for improving hazardous waste management.

2.3 Hospital and Clinical Waste Management

Hospital and clinical waste management became a common concern among Member States, initially in more developed countries and later in developing nations. In 1989, WHO collaborated with the Malaysian Ministry of Health in conducting a preliminary study on the generation of hospital waste and problems of its disposal in the country. Following this WHO initiative, the Ministry of Health, Malaysia, employed a consultant from the United Kingdom to carry out an in-depth study and prepare a plan of action and guidelines for clinical waste management in the country. Although this activity was not carried out as a WHO collaborative activity, WHO was consulted from time to time during the implementation. At the completion of this activity in 1993, WHO was asked to collaborate with the Ministry in conducting training courses to disseminate the clinical waste management guidelines to those officers responsible for implementation. The plan of action includes the construction and operation of centralized high-temperature incinerators in six regions in Peninsula Malaysia and of small hospital incinerators for main hospitals in East Malaysia.

In 1992 and 1993, the Philippine Department of Health was developing a manual for dealing with hospital waste management for environmental health officers at the local government level, with the support of WHO. They were also developing training materials on the subject. Recognizing the efforts of the governments of Malaysia, the Philippines and Papua New Guinea (Section 2) and the potential needs of other developing countries in the region, WHO embarked on the preparation of a draft regional guidelines for health care waste management in 1993. These were completed in 1994.

WHO conducted a Regional Workshop on Clinical Waste Management in 1994 that was attended by 18 participants from 15 countries in the Western Pacific Region and Indonesia. The workshop discussed policies, approaches, and problems of managing clinical waste in these countries; reviewed guidelines, procedures, and techniques of clinical waste management for some developing countries; and examined their transferability and usefulness to other developing countries. After the discussions, the participants came to the following conclusions:

- Many developing countries in the Western Pacific Region do not have specific national policies and guidelines for clinical waste management.

- Guidelines are not applicable to all Member States in the region; guidelines provided at the workshop need to be modified and adapted by each country.

- Funds to develop and implement clinical waste management programs and associated human resources are limited in most countries in the region.

- Gradual and sustainable improvement in clinical waste management is necessary in countries that do not have a program in place. Such improvements would ensure the affordability and practicability of the waste management system introduced and the provision for adequate health and environmental protection.

- Consideration should be given to the immediate improvement of current disposal practices that can be easily carried out to minimize health risks without incurring excessive costs.

- Clinical waste management has received relatively low priority in most countries in the region but should be given due consideration by policymakers.

- Awareness of risks associated with clinical waste is limited to personnel involved in waste management, and steps should be taken to raise awareness of risks among all personnel in health care institutions, as well as decision makers and the general public.

- There is lack of experienced and trained personnel in most countries, and training programs should be provided to personnel handling clinical waste.

- Considering that there is insufficient epidemiological information on infections related to improper handling of clinical waste and a lack of data on the quantity of clinical waste generated and current practices in clinical waste management, a mechanism should be established for the collection, analysis, and dissemination of such information.

Following this regional workshop, WHO received a request for consultancy on hospital waste management from the Government of Lao People's Democratic Republic and implemented it in 1995. The activity involved a review of their hospital waste management practices and the conduct of local workshops. A draft national guideline for hospital waste management was also prepared. A similar activity was carried out in Viet Nam in 1996.

2.4 Other Activities

In addition to the above-mentioned projects, WHO implemented several activities in response to requests from Member States. National workshops on hazardous waste management were conducted in China in 1990 and in Viet Nam in 1991. The purpose of these workshops was to introduce the subject to professionals potentially involved in hazardous waste management in these countries. The consultancy to assess the situation of hazardous waste management was provided to Brunei in 1993 and to American and Western Samoa in 1995. As a result of these activities, various recommendations were made to the authorities in these countries responsible for hazardous waste management. As a follow-up activity, a national workshop on practical methods of hazardous waste management was conducted in Western Samoa in 1996 with the support of WHO.

3 MAIN PROBLEMS AND ISSUES

Section 2 described the WHO collaborative activities with Member States in hazardous waste management in the past several years. Some problems and constraints faced by developing countries in the region in the management of hazardous waste were presented. This section discusses in some detail, the main problems and issues associated with hazardous waste management in developing countries of the region. They include:

- Availability of financial and technical human resources,
- Know-how and information on practical and appropriate technologies, and
- Availability of effective legislation.

3.1 Lack of Financial and Human Resources

In general, most developing countries do not generate much hazardous waste, as the levels of industrial activities in these countries are low. However, they import agrochemicals (e.g., pesticides and fertilizers) for agricultural production and have small industry and shops using chemicals. As a result, some hazardous wastes are produced, and proper management is required. However, these countries do not usually have sufficient funds and technical expertise to develop and implement effective hazardous waste management program.

Many of these countries receive foreign aid for purchasing equipment and facilities. However, priority is often low for waste management, and such funds are rarely allocated for hazardous waste management. Even if funds are allocated, equipment and facilities purchased are often inappropriate, because of the lack of technical expertise to assess the local situation and select the most appropriate technology for the situation.

The lack of technically qualified human resources in waste management is a common problem in all developing countries. This problem is particularly acute in Pacific Island countries where the number of scientists and engineers is small, and only few are engaged in environmental management. In most of these countries, public health inspectors are responsible for pollution control. In Cambodia, Lao People's Democratic Republic, Mongolia, and Viet Nam, few professionals have been trained in pollution control and waste management. Scientists in biology, chemistry, and hydrology and medical doctors specializing in hygiene are in charge of waste management; few engineers are involved in this field in these countries.

WHO has been collaborating with the Fiji School of Medicine in developing its Environmental Health Department and providing courses on pollution control. WHO has also collaborated with Viet Nam in preparing a plan for human resource development in environmental health, including waste management. Human resource development in other priority countries will be considered in the future.

3.2 Lack of Information on Appropriate Technologies

One of the conclusions from the past WHO collaborative activities is that practical, affordable, and appropriate technologies for hazardous waste management are available and can be applied in developing countries. It is the information on these technologies that is not available to the users.

For instance, simple incinerators can be used for nonchlorinated combustible hazardous wastes or practical codisposal for various hazardous wastes at municipal solid waste landfills with proper site selection and operational procedure. However, the information on appropriate location, design, materials, and operation is not available to those personnel involved in the management of hazardous waste. What is often available is a catalogue of expensive high-technology equipment and facilities brought by manufacturers or dealers from industrialized countries. The waste management personnel in developing countries do not normally have the expertise or guidelines readily available to evaluate the usefulness of such technologies.

Another type of information useful for developing countries is the technology that has proven useful in other developing countries. The implementation of a demonstration project in a developing country could produce information necessary for those involved in hazardous waste management in other developing countries (e.g., possible secondary pollution, operation know-how).

3.3 Lack of Effective Legislation

In most developing countries in the Western Pacific Region, comprehensive legislation for waste management, whether hazardous or nonhazardous, is not available. Moreover, international conventions (e.g., the Basel Convention and the London Ocean Dumping Convention) have not been ratified in most developing countries.

These countries usually have general environmental or health legislation that prohibits improper management of waste. However, detailed implementation rules and regulations are not available to effectively control hazardous waste from its generation to disposal. For instance, these countries do not have in place a legal definition of hazardous waste, an inventory and registration of hazardous waste sources and quantities, monitoring and surveillance of hazardous waste sources and management systems, standards for transport and storage of hazardous waste, a manifest and consignment system, standards and licensing of hazardous waste treatment and disposal facilities, etc., which are required for effective management of hazardous waste.

4 FUTURE PROSPECTS

The discussion in Section 3 indicates that, by no means, have problems with hazardous waste management in the region been resolved. WHO, with its technical expertise, could provide useful services to its Member States. It will work with other international and regional agencies, where possible, to provide more effective services with tangible impacts.

WHO's future collaboration in hazardous waste management will focus on countries in the Indo-China Peninsula (i.e., Cambodia, Lao People's Democratic Republic, and Viet Nam), which are expected to undergo rapid development, Pacific Island countries, and Mongolia. These are considered to be priority countries for WHO programs on environmental health in general and on hazardous waste management in particular. Those countries involved in the UNDP/WHO project mentioned earlier (i.e., China, Malaysia, South Korea, the Philippines, and Singapore) have hazardous waste management programs in place, and WHO's intensive collaboration is no longer required. These countries can in turn contribute to WHO's effort by providing consultants, information, and training to priority countries.

Areas of focus of WHO future collaboration include the development of national action plans, preparation of technical guidelines, implementation of demonstration projects, and drafting of legislation and regulations on hazardous waste management. These activities will be carried out mainly in those priority countries mentioned above.

Specific activities planned at this time include:

- *Hospital waste management in Viet Nam.* WHO will collaborate with the Ministry of Health, Viet Nam, to upgrade facilities, develop waste management systems in hospitals, train personnel, and implement awareness programs in 1997-1999. Experiences in Malaysia and the Philippines will be transferred to Viet Nam through the provision of short-term consultants from Malaysia and the Philippines and a study tour and training of Vietnamese personnel in those countries.

- *Demonstration project on hospital waste management in Fiji.* WHO will collaborate with the Ministry of Health, Fiji, in implementing a "healthy hospital" project, and waste management will be included as a component. The project will be implemented as a demonstration project for other Pacific Island countries.

- *Preparation of practitioners' guides for the management of various specific hazardous wastes.* Practical guides for managing hazardous wastes (e.g., pesticide waste, waste oil, lead-acid batteries, hospital infectious waste, timber treatment chemical waste, etc.) will be prepared for use by Pacific Island countries. These guides can be adapted later for use in the other priority countries.

- *Development of legislation and regulations and enforcement structure.* WHO will collaborate with Viet Nam and some Pacific Island countries in drafting hazardous waste legislation, particularly implementation rules and regulations, and in developing control mechanisms. In most of the priority countries, basic environmental protection legislation is in place. Therefore, the focus of WHO collaboration in this area will be the preparation of subsidiary rules and regulations on hazardous waste management.

- *Preparation and implementation of human resource development plans.* WHO will collaborate with Cambodia and Lao People's Democratic Republic in formulating and implementing human resource development plans for environmental health, similar to that prepared for Viet Nam. Hazardous waste management will be a component of such a plan. WHO support will conduct short courses for personnel involved in waste management and their trainers and develop curricula for university courses on waste management.

5 DISCLAIMERS

The views expressed in this paper are solely those of the author and do not necessarily represent the opinion of WHO. For the WHO collaborative activities mentioned in this paper, WHO mission reports are prepared and are available from WHO Western Pacific Regional Environmental Health Centre.

REVIEW OF THE 1996 PACIFIC BASIN CONFERENCE AND FUTURE OUTLOOK

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The Pacific Basin Consortium for Hazardous Waste Research and Management fills a unique role in addressing hazardous waste issues for a very dynamic, flourishing part of the world, the Pacific Rim. Hazardous waste problems of concern to Pacific Rim countries are being assessed and evaluated by this organization on many different levels. An exceedingly vital component of the Pacific Basin Consortium's activities includes sponsoring the "Pacific Basin Conference on Hazardous Waste," such as the meeting held in November 1996 in Kuala Lumpur, Malaysia. This seventh meeting of the Pacific Basin Conference on Hazardous Waste could prove to be a pivotal meeting for this consortium, as it deals forthrightly with integrating human health and reducing risk with the broader context of hazardous waste management. Here, an intimate group of scientists, engineers, and policymakers met to exchange ideas, research findings, and experiences.

The stage was set by the Honorable Dato 'abu Bakar Daud, Deputy Minister of Science Technology and Environment of Malaysia, when he conveyed to meeting attendees that Malaysia is committed to enforcing sound environmental practices and is getting tough on offenders. This is important for Malaysia, and we can only hope that this will become the standard for all Pacific Rim countries.

The meeting then proceeded to combine new technologies, case studies and health effects research into a forum for addressing human risk. The plenary speaker, Dr. Peter Peterson, Senior Fellow and Visiting Professor, Universiti Kebangsaan Malaysia, Institute for Environment and Development, Malaysia, stressed that remediation and hazardous waste management must be put in the context of human health and that the reason for remediation is for reducing risk.

In addressing hazardous waste issues from a public health perspective, four components need to be included in any strategy for reducing risk: assessment, identification, remediation, and prevention. All of these were topics of this meeting. While these components occur simultaneously, they may be thought of in a time line, beginning with assessment and, ultimately, resulting in effective preventive measures. To make sound hazardous waste management decisions, an understanding of the problem and an assessment of its impact are needed.

Assessing risk of exposure to hazardous waste must be done on a broad spectrum of endpoints. This issue was discussed by Dr. David Carpenter, Dean of the School of Public Health, University of Albany, USA, in his plenary and technical presentations. He brought to the forefront that while, traditionally, cancer has been the endpoint of concern, we now know that other endpoints, such as immunosuppression, neurotoxicity, and neurobehavioral, developmental, and reproductive dysfunctions must also be incorporated in any assessment of human risk of exposure to hazardous substances. Assessment is a complex issue and includes other approaches besides human health. Assessments must also incorporate hazardous waste practices. Dr. David Nelson, President, EnviroSearch International, USA, presented the results of a recent survey that demonstrated that, to a great extent, awareness of and proactive practices toward hazardous waste are on the rise in Pacific Rim countries. It is noteworthy that these issues are being addressed during a period of growth and development in Southeast Asia; however, he stated that it must be kept in mind that the Western world does not have all the answers. While sometimes it may be perceived that assessments may be more advanced in developed countries, for many issues the West has only been ahead of the curve in posing the question, whereas the solutions have not necessarily been resolved. Therefore, assessing and reducing risk must be done on a state-by-state basis or, at the very least, a region-by-region basis.

A major focus of the technical sessions of this conference was on the second component of the reducing risk equation, identification. Identification was covered on at least two levels. On a macro level, country case studies identified issues of chemical mixtures and sources of exposure in Papua New Guinea, China, Kazakastan, and other regions. Identifying the sources of pollution, the industries responsible, the levels of contaminants and exposure, and the impact on the environment is all necessary to a hazardous waste management strategy on a local, regional, and global scale. Communicating and networking in these areas have always been a strength of this conference, and again this meeting promoted the timely interchange of very real-life issues and experiences. On a micro level, identification of exposures to specific chemicals with disease outcomes was also discussed. For example, papers were presented on pesticide exposure and childhood leukemia; PCBs and the induction of neurotoxicity; and arsenic-induced processes in the induction of arteriosclerosis and cancer. From another perspective, other papers focused on ecological exposures and their effects on wildlife to identify the presence of contaminants. Identification on the micro level was a very successful element for this conference and promises to become an integral part of future conferences.

The other two components, remediation and prevention, are very closely linked. The reason to remediate is to prevent human and environmental exposure. Though from another perspective, prevention, as in pollution prevention, minimizes the need to remediate. Important insights on in situ remediation approaches were the focus of the plenary presentation by Mr. Tim Oppelt, Director, National Risk Management Research Laboratory, EPA, USA. He clearly addressed the need for using the appropriate technology for a particular site. He stressed that no singular approach is appropriate for all circumstances. Remediation decisions must be made based on the situation, future uses of the site, and information gained during the assessment and identification phases of the process.

Most of the presentations at this conference dealt in some way with remediation and pollution prevention practices. Novel remediation approaches for contaminated waste, metals, and PCBs were presented. Other sessions focused on cleaner production technologies and waste minimization. As countries of the Pacific Rim experience rapid growth in industry and manufacturing, it is imperative that information and experiences be exchanged in open forums, such as at this meeting. Furthermore, it is important to be certain to place these activities in the context of protecting public health. This theme was repeated throughout the 1996 Pacific Basin Conference on Hazardous Waste.

Furthermore, the meeting demonstrated that no one individual or no one country lives in isolation and that hazardous waste knows no boundaries. Issues of hazardous waste must be dealt with on a multicultural and multinational level (Carpenter et al. 1996; Carter et al. 1996). One country's problems and solutions can impact a neighboring, or even distant, country. In the same manner, health investigators, policymakers, and remediation professionals must develop a common language and deal with issues from a multidisciplinary perspective. By expanding interdisciplinary research opportunities, such as those developed throughout this conference, more effective hazardous waste management approaches will be implemented.

In looking to the future, the focus of the field of hazardous waste research should be on prevention and its vast implications. Specific areas in critical need of attention include the development of better risk assessment models for child exposures and effects, and for endpoints other than cancer. This is important to effectively address the health and risk reduction issues surrounding hazardous waste exposures, and similarly, to be able to use the best available cleanup technologies in a cost-effective manner. These areas require diligent study to be able to base health and cleanup decisions on sound, scientific information. There must be better translation of research results and management practices. To date scientists have done a poor job in communicating with the communities and decision makers on the importance of their work and its potential impact on reducing risk. Therefore, scientists must work to improve their credibility and establish trust so that sound environmental decisions can be made based on the most current understanding of the science. Along the same lines, information transfer must be accelerated. With the advent of the electronic information network, the capability exists for the timely transfer of information (Anderson et al. 1996). Members of this organization must effectively utilize this technology for advancing their fields of study. Ultimately, the audience for these resources is the entire world; however, the professionals in this area must effectively use these resources and present their data in a clear and accessible manner.

As has been described and discussed at this conference, hazardous waste is not static. Substances are capable of moving through the environment from one stratum to another, interacting with microbes, plants, animals, and humans. Many scientific disciplines must be integrated, thereby crossing over traditional scientific boundaries. In doing so, the procedures of characterizing and evaluating the risks of hazardous waste need to be scrutinized and revised as directed by new research findings. Furthermore, advanced environmental technologies will be developed and validated to better clean up hazardous waste, and by extension, improve human health. Integration of these multifaceted approaches will set the stage for the future of hazardous waste research. Therefore, to address this issue fully, more and better multidisciplinary research is essential (Suk and Olden 1996).

The crossing of traditional scientific disciplines experienced at this conference and previous ones will remain in the forefront as a theme of the Consortium. But as we move forward, emerging environmental scientists must be trained in this multidisciplinary approach to hazardous waste research and management. These training needs must be integrated into academic programs and reinforced by government, industry, and academia at every opportunity.

Finally, it must be considered that the ultimate goal in hazardous waste research and management is prevention — prevention because it is important to human health and the environment and because through prevention risk is reduced and exposures are minimized. All work presented at this meeting in some fashion revolved around the overall theme of prevention, whether it was through remediation, technology development and application, or understanding health effects from exposure to contaminants, or in policy. When considering the consequences of not addressing issues of prevention, it is important to remember that reducing risk and protecting human health is cost-effective compared to the expense and burden to society when it is not done.

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POLLUTION PREVENTION

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FROM WASTE MINIMIZATION TO ISO 14000: TAIWAN'S EXPERIENCE AND PROSPECTS

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ABSTRACT

Taiwan has completed a very successful five-year industrial waste minimization (IWM) demonstration and promotion project sponsored by the government. From 1990 to 1995, the project successfully disseminated the IWM concept of pollution prevention (P2) to industries. It effectively reduced industrial waste while significantly benefitting the economy by assisting industries in implementing in-plant IWM programs. In July 1995, the second stage of the five-year IWM and ISO 14000 promotion project was initiated for further promoting the IWM, P2, and cleaner production and, in particular, coping with the upcoming international environmental management standards (ISO 14000). To assist industries in establishing an environmental management system (EMS) and accumulating related experience, an EMS pilot demonstration project of five model industries and an ISO 14001 EMS demonstration and promotion project for 22 factories in 13 industries were initiated in October 1995 and August 1996, respectively. These projects can assist Taiwan's industries in changing the constitution of their enterprises, enhancing competition in the international market, and helping our nation achieve the forerunner's profits in sustainable development.

1 BACKGROUND

Taiwan is a small island with high densities of population and factories. In the past four decades, Taiwan's economic and social changes have been drastic, as shown in Fig. 1.

Industry played a major role in Taiwan's significant economic growth. However, industrial wastes inevitably cause serious environmental problems. Industrial pollution not only adversely affects the public health and the environment but also wastes valuable resources and increases production costs that will gradually slow industrial growth.

Traditionally, industrial pollution in Taiwan has been abated by conventional "end-of-pipe" (EOP) waste treatment methods. However, those methods are generally economically infeasible in terms of investment and operation and still might not satisfy environmental protection requirements.

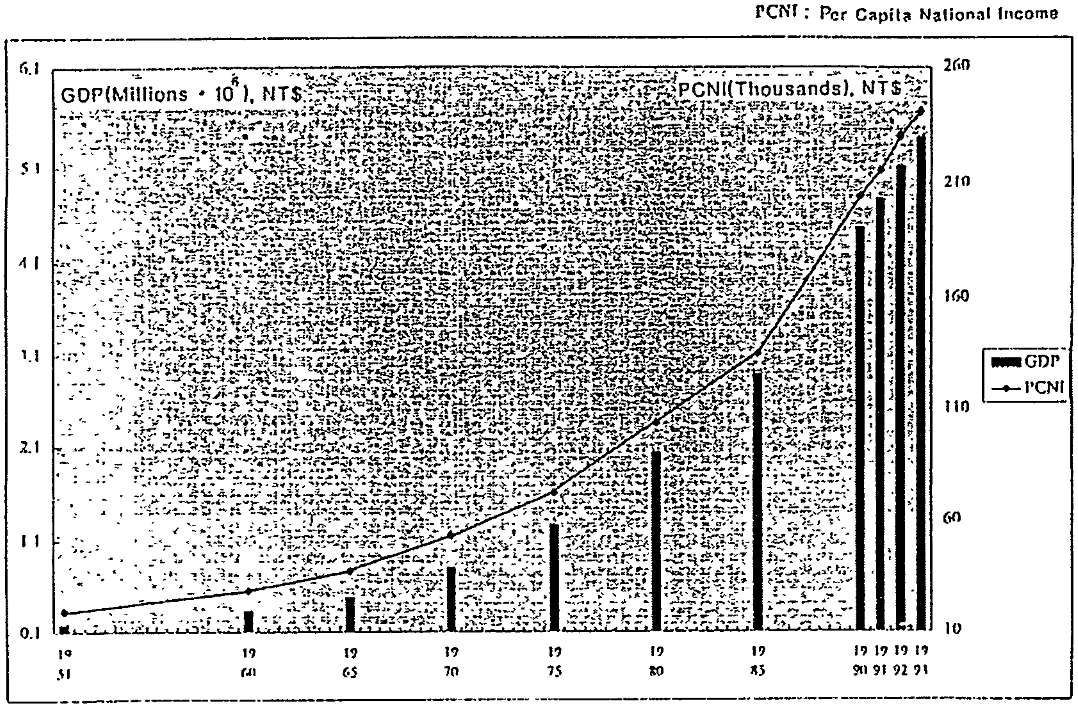

Fig. 1 Economic Indicators of Taiwan, 1951-1993 (PCNI denotes per capita national income.)

Meanwhile, such traditional methods just transfer wastes among different media and do not really solve the intrinsic pollution problems.

Our government and industries have realized that instead of passively resolving pollution prevention (P2) problems by EOP treatment, we should develop "cleaner technology" and take P2 measures to increase the efficiency of resource utilization and minimize or eliminate the generation of wastes and costs for further disposal.

Recognizing the potential benefits of industrial waste minimization (IWM), the Ministry of Economic Affairs (MOEA) and the Environmental Protection Administration (EPA), under an Executive Order of the Executive Yuan, jointly initiated programs in April 1989 to promote IWM. This effort established the Waste Reduction Task Force (WRTF) and provided the ability to formulate strategic practices in Taiwan. A national IWM master plan, approved in July 1990, called for an aggressive program to demonstrate IWM technologies and provide technical assistance and consultation to industry.

From 1990 to 1995, the five-year IWM demonstration and promotion project was successfully completed. For extending the achievement and coping with the international environmental trend, some projects were continued, for example, the second-stage, five-year IWM and ISO 14000 demonstration and promotion project, the environmental management system (EMS) pilot demonstration project of five model industries, and the ISO 14001 EMS demonstration and promotion project for 22 factories in 13 industries.

2 ACCOMPLISHMENTS OF IWM IN TAIWAN

Since 1990, more than six years of promoting IWM in numerous industrial sectors has produced significant results that not only greatly reduced waste generation during processes, but also helped manufacturers achieve substantial economic gains. During this period, the WRTF progressively combined resources from the government, industry, academia, and research organizations to promote the implementation of IWM by industry. Significant reductions of industrial waste have been achieved along with substantial economic benefits. About US$10 million were invested by the government, and more than US$150 million of estimated annual benefit were obtained.

At present, the IWM program in Taiwan includes seven key elements: government regulations and policies; technical assistance; technology research, development, and demonstration; information exchange; financial incentives; industry and public awareness and training; and international cooperation. These achievements are briefly described in the following sections.

2.1 Government Regulations and Policies

The establishment of zero- or low-waste industries is a key principle in the government's industrial development strategy. Increasingly restrictive laws have been enacted to regulate industrial development.

Since its institution in 1987, Taiwan's EPA has systematically introduced environmental protection regulations. More new draft environmental regulations, pending at the Legislative Yuan, include the concept and spirit of environmental conservation and P2 as well as the definition of such terms as reuse, recycling, reduction, etc.

2.2 Technical Assistance

Understanding the concept and technology of IWM is greatly needed in Taiwan's predominantly small- to mid-sized manufacturing plants. The WRTF commissioned some nonprofit organizations to assist industries in implementing IWM. After the IWM plans have been successfully implemented, accumulated experiences, methods, technologies, and practical expertise are shared with other plants throughout the industry.

From 1989 through mid-1996, the WRTF consulted with more than 22 industries, which include electroplating, printed circuit board manufacturing, textile and dyeing, paper manufacturing, leather, food processing, and IC manufacturing industries, etc. More than 100 plants received assistance in the first and second five-year projects.

In 1989, the WRTF started to allocate funding to assist industries in implementing IWM and promoting the reuse of wastes as resources. Concurrent with the government's developing IWM initiatives, private and government-owned industries became aware of the importance of waste minimization and, in effect, initiated independent movement. After many years of development, significant results have been achieved.

Since June 1996, the technical assistance has included promoting ISO 14000 in industries and helping to establish in-plant EMS.

Since 1988, to effectively and economically resolve the problems of industrial waste, the government has helped to establish 10 combined industrial waste treatment systems, including food processing, leather, printed circuit board, metal finishing, printing, plastic, etc. Six are running and have a total treating capacity of 47,160 tons/yr. Four are now being established.

2.3 Technology Research, Development, and Demonstration

Technology research and development (R&D) is critical for transforming a labor-intensive basic industry to a high value-added precision industry. R&D allows an industry to move from contract manufacturing to specialized production using focused technologies.

The developmental waste minimization technologies are applicable to more than 24 industries. More than 76 plants received technical assistance and/or technology transfer, with an annual benefit exceeding US$38 million (in 1994 dollars).

2.4 Information Exchange

The development of databases for available technical information and workforce resources is a vital component in implementing IWM plans.

2.4.1 Technology Information Database

The Technology Information Database contains information regarding IWM-related publications, including books, journals, conference proceedings, reports, and technical manuals. A computer program sorts the information on the basis of broad categories of data, including policy and strategy, management, regulation, technology, and applicable processes for specific industries. Users can look up information directly or ask the computer to search for the needed information. By mid-1996, more than 1,600 entries had been collected in the database.

2.4.2 Manpower Resources Information Database

The Manpower Resources Information Database collects and sorts information regarding manpower with IWM expertise, technical capability, and field experience. The computerized database can be used by industries to locate sources of technical consultation. By mid-1996, more than 500 entries had been collected in the database.

Information of the above databases is now available on computer disks, which are free of charge to industries, research facilities, and academic organizations. Moreover, these databases will be available on the Internet beginning in mid-1997.

2.4.3 Waste Exchange Information Center (WEIC)

The WEIC was established in 1987. Its objective is to promote pollution reduction and resource reuse by facilitating linkages between waste generators and prospective utilizers of the waste.

The supply and demand information is posted in the bimonthly magazine *Waste Minimization Information* (changed to *Cleaner Production Information* in August 1995). The demanding party contacts the suppliers and the WEIC. The Center follows up the exchange and updates the information in the magazine.

Between 1987 and 1995, the Center has overseen nearly 200 exchanges of waste resources, i.e., more than 180,000 tons. It is estimated that the benefit has surpassed US$54 million. The types of waste resources that have been exchanged include organics, inorganics, organic solvents, grease, wax, acids, alkalis, etc.

2.5 Financial Incentives

The implementation of an IWM plan not only requires a substantial workforce and time but also substantial financial investment to upgrade process equipment. To encourage industries to actively participate in IWM, the government offers some tax benefits and financial incentives:

- Tax deduction for investment,
- Accelerated depreciation,

- Tariff exemption for imported pollution control equipment, and
- Low interest loans.

In 1994 and 1995, the applications for tariff exemption for imported pollution control equipment numbered 652 and 646, respectively. The approved loans were more than US$77 and US$80 million.

In 1994 and 1995, the applications for tax deduction for investment on imported pollution control equipment and low-interest loans for purchasing pollution control equipment numbered 1,479 and 1,374, respectively. The approved loans were about US$206 million and US$216 million.

2.6 Industry Awareness and Training

2.6.1 Training Seminars

To implement P2 and IWM technologies, the government sponsors a variety of training courses in the form of seminars and workshops. In 1996, the WRTF began to collaborate with the U.S.-Asia Environmental Partnership (USAEP) and Asian Productivity Organization (APO) to hold workshops and seminars for disseminating and exchanging IWM and ISO 14000 technology and experience with other countries and areas.

2.6.2 Annual Large-Scale Conferences

The annual conference on IWM, started in 1991, has drawn many people from industries, academia, and consulting firms to jointly discuss and share experiences with waste minimization. More than 300 people attend the conference every year. In 1992 and 1995, the conferences were expanded to international scale, with representatives from 17 and 23 countries and areas, respectively. The 1995 annual conference, held in November 1995, was organized jointly with the U.S. Water Environment Federation (WEF).

2.6.3 Publications

The publications produced by the WRTF include video tapes, pamphlets, posters/slogans, proceedings, technical manuals, newsletters, and journals. Most of the publications are free.

2.6.4 Recognition of Plants, Individuals, and Organizations for Outstanding Achievements in IWM

To expand the implementation of IWM, a special committee was formed in 1990 to select factories, individuals, and organizations that have accomplished significant waste minimization initiatives. The committee consists of members from the government, academia, consulting firms, and private organizations.

Selected parties are recognized every year during the opening ceremony of the annual conference on IWM. High-level executives of MOEA and EPA present awards to the selected parties. Since late 1995, 50 plants, 47 individuals, and 17 organizations have been honored.

2.7 International Cooperation

The WRTF is willing to widen cooperation and strengthen coordination and communication between other countries and international organizations with respect to the exchange and dissemination of IWM information and experience. Some organizations have already had good mutual cooperation with Taiwan:

- USAEP: holds workshops, technical/information exchange, mutual visits;
- APO: collaborates in demonstration factory and farm projects (FY95: printing industry; FY96: electroplating industry), technical and information exchange, mutual visits;
- WEF: organizes the conference;
- Hong Kong's Centre of Environmental Technology (HKCET): assists the HKCET in establishing the waste exchange information system, collaborating and exchanging information on waste exchange and recovery; and
- Asian-Pacific Economic Cooperation (APEC): participates in the Cleaner Production Promotion Program.

3 ADVANTAGE OF IMPLEMENTING IWM AND ESTABLISHING EMS

In July 1995, the second-stage five-year IWM and ISO 14000 demonstration and promotion project was initiated to further promote the IWM and, in particular, to cope with the upcoming ISO 14000. For focally assisting the industries establishing EMS and accumulating related experience, an EMS pilot demonstration project of five model industries and an ISO 14001 EMS demonstration and promotion project for 22 factories in 13 industries were initiated in October 1995 and August 1996, respectively.

As in the approach used by Taiwan for promoting IWM, additional effort is now provided to assist industries in introducing and establishing EMS in factories. Those approaches include extending cooperation and strengthening coordination and communication among industry, government, and academic institutions

However, as the EMS was established among factories, we received an unexpected advantage as a result of previous efforts in promoting IWM in industries. The advantage is that those factories that conducted in-plant IWM programs can easily introduce EMS into their existing management systems and quickly establish and apply the EMS requirements.

The reason can be learned by comparing the structure of the EMS principles (Fig. 2) with the major elements of the IWM program (Fig. 3). The similarity between the two systems is obvious. Therefore, if the factories with the experience of implementing IWM transfer their terminology of IWM into EMS, the requirements of ISO 14001 (EMS) are mostly fulfilled. Moreover, the IWM programs are usually quite concrete. Thus, despite the documentation procedure corresponding to programs, the core parts of the requirements of ISO 14001 are actually the EMS.

By now, more than 24 factories have received the EMS certificate, and the number will predictably increase very fast because of the previous effort devoted to promoting IWM in Taiwan.

4 CONCLUSION AND PROSPECTS

IWM has proved to be a key strategy that facilitates economic development and environmental protection. Accomplishment of Taiwan's devotion to IWM has been achieved through a sound methodological approach and continuous efforts.

Through these experiences from promoting IWM and EMS, we have been aware of the following:

- A facility's capabilities of protecting the environment have become the key tools of production.
- Only products that cater to protecting the earth's environment can satisfy consumers' needs.
- In addition to traditional values, products' environmental values should be considered too. The latter constitutes the products' environmental cost.

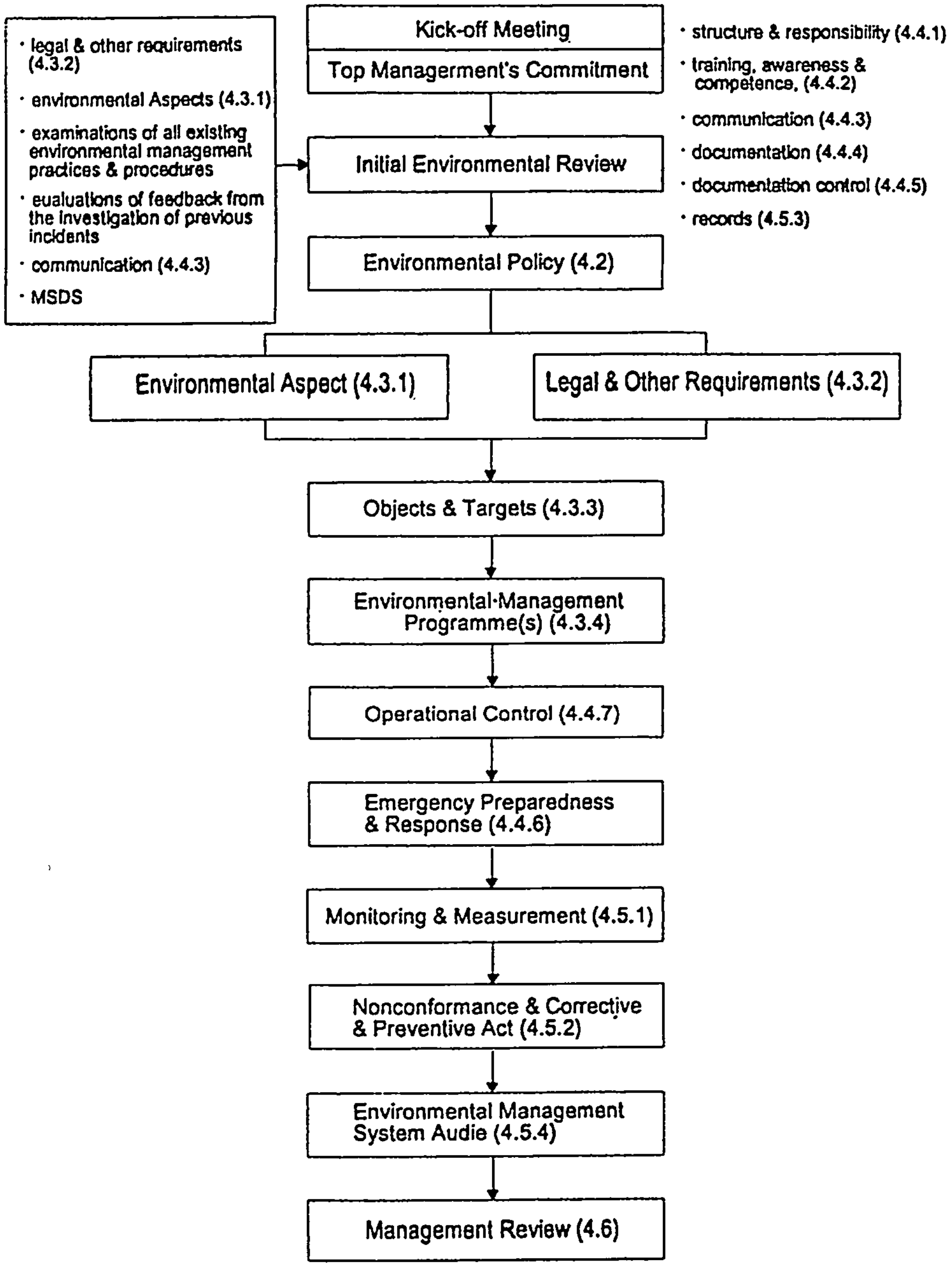

Fig. 2 Structure of ISO 14001 (EMS)

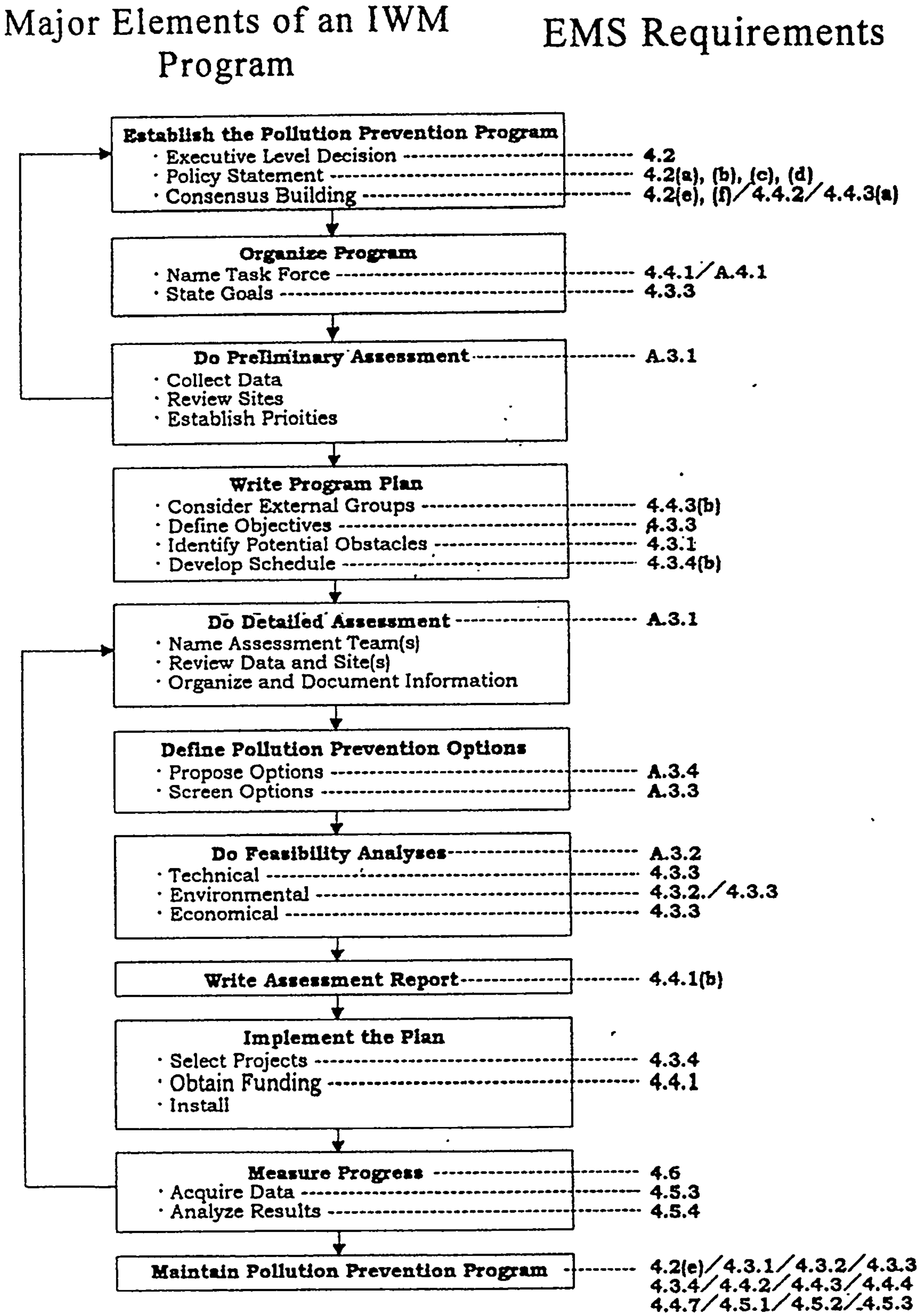

Fig. 3 IWM vs. ISO 14001

- Environmental protection and production can be in harmony.
- Anyone initiating the concept of green products can raise the products' objective and subjective prices, create market segregation, and achieve the forerunner's profits.

Because of rising environmental awareness in the world, many environmental protection issues have extended from regional to international concerns. Environmental protection has shifted from a traditional focus on pollution control to a wider focus on efficient use of global resources.

At present, our government is planning more IWM- and ISO-14000-related projects. On the basis of an already solid foundation, our government will aggressively continue to make its best effort to promote IWM, P2, and cleaner production and to exchange its experiences with other countries and areas. In summary, we will dedicate ourselves to be active participants, cooperators, and contributors in the global pursuit of sustainable development.

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CLEANER PRODUCTION: MINIMIZING HAZARDOUS WASTE IN INDONESIA

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1 INTRODUCTION

In the second long-term development plan, industry plays a significant role in economic growth. In Indonesia, industries grow very fast; such fast growth can adversely effect the environment. Exploitation of assets can mean depletion of natural resources and energy, which, if incorrectly managed, can endanger human life and the environment. The inefficient use of natural resources will accelerate their exhaustion and generate pollution, resulting in environmental damage and threats to economic development and human well being.

In recent years, changes in the approach used to control pollution have been necessary because of the increasing seriousness of the problems. Initial environmental management strategies were based on a carrying capacity approach; the natural assimilative capacity accommodated the pollution load that was applied. The environmental management strategies adopted later included technologies applied to the end of the discharge point (so-called "end-of-pipe" treatments).

Until now, environmental management strategies focused on end-of-pipe approaches that control pollutants after they are generated. These approaches concentrate on waste treatment and disposal to control pollution and environmental degradation. However, as industry develops, waste volumes continue to increase, thereby creating further environmental problems. In addition, the wastes produced tend to have more complex characteristics and are potentially more difficult to treat for a reasonable cost. There are often technical and financial obstacles to regulatory compliance if waste treatment is relied on as the only means of achieving environmental objectives. Consequently, the reactive end-of-pipe treatment approach has been changed to a proactive cleaner production approach. This approach is based on the concept of sustainable development and is designed to prevent pollution as well as to protect natural resources and the quality of the environment.

Cleaner production is defined as a preventive and integrated environmental management strategy that needs to be implemented continuously in the production process and product life cycles to reduce risks to humans and the environment. For the production process, cleaner production means increasing efficiency and effectiveness in the use of raw materials, energy, and other resources and reducing the use of hazardous and toxic materials. The aim is to reduce the volume and toxicity of wastes generated. For products, cleaner production means reducing the impacts throughout their life cycles, starting from extraction of raw materials to final disposal after the product is no longer used. The use of the cleaner production strategy requires some changes in thinking and behavior as well as the implementation of newer, cleaner technology. Cleaner production was included as an important tool to promote sustainable development in Agenda '21 (chapters 20, 30, and 34), in an agreement at the Earth Summit held in Rio de Janeiro in June 1992.

2 ENVIRONMENTAL MANAGEMENT IN INDONESIA

To overcome the traditional challenge associated with the twin aims of industrial development and environmental management, the principles underlying economic development in Indonesia have embodied the concept of sustainable development. Sustainable development in Indonesia was established in the 1973 General Guidelines for Development, which stated that "national development should be carried out in a rational way so that it will not damage the environment and should be carried out within a comprehensive policy considering the needs of the next generation."

A similar concept was later constructed by the Brundtland Commission in 1987. It defined sustainable development as development that meets the needs of the present without compromising the ability of the future generations to meet their own needs. Since this definition was adopted by the United Nations, and especially after UNCED 1992 in Rio de Janeiro, it has been widely used.

Responsibility for environmental management lies within each of the two levels of government in Indonesia: national and regional. The national level has overall responsibility for setting goals, coordinating integrated environmental management, and providing the legal framework and technical guidance for control. The regional or provincial governors are responsible for implementation of pollution control and natural resource management within the policy and guidance provided by the national framework.

Several sectoral agencies have responsibility for various aspects of environmental control. At the national level, the two major national institutions are the Ministry of Environment and the Environmental Impact Management Agency (BAPEDAL). BAPEDAL was created in June 1990 and is primarily responsible for the implementation of programs relating to environmental pollution, environmental degradation, hazardous waste management, environmental impact assessment, and institutional enhancement and capability strengthening.

Act 4 of 1982 was established as the basis for developing environmental management and also as an umbrella for all environmental regulations in Indonesia. Entitled the Basic Provision for the Management of the Living Environment, this act reflects a policy of "managing" the environment to support development rather than focusing only on environmental conservation efforts. In all the development plans, emphasis has been on enhancing the environment and ecology to ensure sustainable development in Indonesia. Act 24 of 1992 on spatial planning was established 10 years after Act 4.

In 1986, Government Regulation 29 on environmental impact assessments (EIAs) was promulgated. The main objective of the EIA policy is to ensure that potential environmental problems are foreseen and addressed at an early stage in a project's planning and design phase. The EIA studies should help identify the best options available for the development proposed. By definition, these will involve cleaner production, more efficient production technologies, and appropriate abatement and mitigating measures that use cleaner and end-of-pipe technologies. The environmental costs of the project and benefits to the community are also to be considered.

This regulation was amended by Government Regulation 51 of 1993, which was intended to simplify and expedite the procedures for both government and private sector proponents. At the same time, it strengthened the regulatory regime by requiring that the process be carried out effectively and efficiently.

Subsequently, some regulations that consisted of discharge or emission-based standards aimed at pollution abatement were established. These include:

- Government Regulation 20 of 1990 on water pollution control,
- Government Regulations 19 of 1994 and 12 of 1995 on hazardous waste management, and
- Several ministerial decrees on the environment via Kepmen 51 of 1995 on the effluent quality standard for existing operations and Kepmen 13 of 1995 on the emission standard for stationary sources.

In response to Government Regulation 20 of 1990, some larger industries installed wastewater treatment units to control pollutants from their discharge effluent. This equipment may have satisfactorily removed the pollutants from the effluent, but in the process, it changed the nature of the problem. Although liquids may have achieved compliance with the required discharge parameters, there was inadequate control of the resultant sludges, which could still be illegally discharged into a river or inappropriately deposited on land. In these cases, the pollution problem was not solved but merely changed in nature from a liquid to a solid phase. Moreover, if the disposal of the sludges was not managed correctly, there was a potential for the pollutants to be remobilized.

Other industries, particularly small and medium-sized enterprises, are not fully aware of environmental issues. When confronted with government regulations, they tend to respond in one of two ways. Either they make investments in end-of-pipe technology, or they install this end-of-pipe technology in such a way that compliance with the environmental regulations is superficially demonstrated without really eliminating the pollutant. The problem caused by this approach can be further compounded if necessary operational and maintenance activities that would actually ensure a real reduction in pollutants are not carried out. Operational costs that accompany end-of-pipe technologies has been increasing over the years, and these costs could prevent industries from being competitive in the future, particularly if discharge standards are progressively tightened.

It is clear that some significant issues are emerging as challenges to effective environmental management. These include the following:

- The amount of waste generated is increasing continuously.
- The characteristics of the waste are getting more and more complex.
- The cost of waste treatment and disposal is steadily increasing.
- Effective treatment is proving to be more expensive than preventing the generation of waste in the first place.
- Waste treatment involves mass transfer from one medium into another medium but does not address the problem of waste generation.
- The rate of environmental pollution is getting faster and faster.
- Existing environmental management regulations still focus on waste treatment and disposal and do not yet emphasize pollution prevention.
- There are now significant global market influences on product competitiveness, particularly with respect to environmental issues.

Therefore, the logical solution to enable environmental protection and sustainable economic development is to introduce state-of-the-art technologies that prevent pollution and minimize waste generation; in other words, cleaner production. In acknowledgment of this need, strategic environmental management in Indonesia has changed from reactive to proactive programs that include prevention, control, and remediation activities.

3 CLEANER PRODUCTION PROGRAM IN INDONESIA

BAPEDAL recognized the importance of prevention initiatives and developed its cleaner production program in 1993. The overall goal of the BAPEDAL Cleaner Production Program is to promote the achievement of sustainable development by encouraging the reduction and/or elimination of pollutants at the source. Specific objectives are listed below.

- Increase the awareness of the government, industry, and the public about cleaner production concepts and the economic and environmental benefits to be derived from their use;
- Encourage, promote, and assist industry in the adoption of cleaner production technologies; and
- Assist in the collection, dissemination, and transfer of information about cleaner production options.

The program requires all stakeholders to integrate and implement cleaner production approaches into the policies and activities of each sector and local institutions through the following programs:

- Apply the concepts of preventing waste at the source or preventing waste generation as early as possible at every stage of production;
- Reduce the use of hazardous materials or gradually replace them with nonhazardous materials; and
- Recycle within the process to prevent pollution and conserve natural resources.

In implementing cleaner production, all stakeholders should cooperate, whether they are government or nongovernmental institutions, industries, or societies. Each group has its own role and should work in partnership. All stakeholders must agree to make cleaner production the main priority in implementing environment management policies in Indonesia, and they should create situations and conditions in which the use of cleaner production strategy can grow. It is also important to develop a culture that encourages the adoption of cleaner production strategies through pollution prevention.

To clarify these fundamental principles of cleaner production in Indonesia, a "national commitment" was launched in 1995. The government expressed its commitment to adopt cleaner production as the guiding principle when deciding on national policies and to include these concepts when implementing national programs. On Environment Day, 5 June 1995, the Indonesian President stated, "Industries, forest industry entrepreneurs and investors must continue to improve efficiency and productivity, and at the same time reduce waste generation from their facilities. All stakeholders must use cleaner production as the basis for developing policies and strategies to improve national productivity." Guidelines have been developed to assist with the implementation of cleaner production in various industry sectors.

Furthermore, Indonesian Cleaner Production Action Plans were established in early 1996 to help cleaner production be incorporated into policy formulation, decision making, legislation, and development programs in all sectoral and regional activities.

Recently BAPEDAL's Cleaner Production Program has achieved significant results. Work in the program is funded by the Indonesian government and also supported by international donors. Although many of the projects are in their infancy, the program has already made significant progress in many key areas, including training and awareness, technical assistance to industry, and information and incentives development.

3.1 Training and Awareness

Education of all stakeholders is necessary to foster awareness of cleaner production concepts. It has been used to inform personnel about the best available technologies and help them develop capabilities for the identification and application of appropriate manufacturing options. Activities related to training and awareness include:

- Conduct/coordinate training programs, seminars, and workshops for industry, government, public, and nongovernment organizations;
- Support in-house training on cleaner production for several multinational companies; and
- Publish general information and awareness-raising materials such as a Cleaner Production Newsletter and other booklets.

3.2 Technical Assistance

Stakeholders require technical assistance to properly understand cleaner production concepts, technologies, and techniques. The first priority has been industry, but other sectors such as mining, energy, agriculture, and forestry also require assistance to understand and implement cleaner production programs. Activities that have been undertaken include these:

- Develop technical guidelines on cleaner production for specific industrial sectors, such as textile, electroplating, tapioca, leather tanning, pulp and paper, palm oil, and gold-mining;
- Develop standard operating procedures for cleaner production audits for certain industries;

- Facilitate industry's access to appropriately experienced technical consultants;

- Conduct cleaner production demonstration projects within industries, such as leather tanning, pulp and paper, and textiles;

- Facilitate the establishment of environmental counseling for specific industrial sectors in several major cities to allow exchange of information and research on cleaner production practices, methods, and techniques;

- Help nine major industrial companies develop and voluntarily implement environmental management systems that focus on preventing pollution at its source and address other opportunities to improve their environmental performance; and

- Initiate a voluntary partnership program with industry designed to encourage and assist industry to establish its own goals, targets, and programs on cleaner production and voluntarily report results to BAPEDAL.

3.3 Information System Development

Centralized compilation and dissemination of information are essential in promoting national cleaner production efforts. As the first step, access has been provided to worldwide information databases on cleaner production. Efforts are being made to expand this access and build a BAPEDAL database of cleaner production case studies and best available techniques.

3.4 Incentives Development

Economic instruments are being increasingly recognized as viable supplements to the traditional "command and control" approach. Such activities include:

- Develop an ecolabeling system to encourage private sectors to move toward implementing cleaner production;

- Develop concepts to support a system of effluent discharge fees and evaluate the possibility of developing an environmental fund scheme;

- Expand existing projects for soft loans and tax exemptions for installation of wastewater treatment plants to place a greater focus on cleaner production equipment; and

- Develop an award program for cleaner production implementation.

To maintain momentum, BAPEDAL's cleaner production programs are reviewed and developed continuously for all target groups. The objective is to support initiatives and practices of the Indonesian government in protecting the environment.

In developing and implementing the cleaner production programs, there has been a positive response from industries and the private sector. Even though there is no obligation to implement them, some have tried to integrate cleaner production programs in their daily activities to improve their efficiency and effectiveness, realizing that through this approach, numerous benefits can be achieved.

4 CLEANER PRODUCTION RESEARCH AND DEVELOPMENT

The cleaner production program in BAPEDAL has been recognized by all stakeholders in Indonesia. In the area of research and development, the Ministry for Research and Technology and the National Research Council have included cleaner production, with a subcomponent of waste minimization, as a priority initiative in national strategic research topics. BAPEDAL has been appointed by the State Minister for Research and Technology and National Research Council to coordinate the National Strategy for Priority Research (i.e., Riset Unggulan Strategis NASIONAL or RUSNAS) for waste minimization activities in Indonesia. The main aim of RUSNAS is to establish and coordinate efforts and activities among government, private agencies, and industrial associations.

Waste minimization plays an important part in contributing to the success of the cleaner production program. In economic and trade terms, implementing waste minimization programs can benefit producers and manufacturers because it presents a means of containing the cost of production. This benefit is especially important with regard to export-oriented products because of the increased competitiveness in domestic and international markets. Today, consumers in developed countries look for more environmentally friendly products and services, and waste minimization can assist in marketing strategies.

Cleaner production programs need to be implemented in all sectors in Indonesia. The priorities for research are reduction at the source; reuse, recycle, and recovery (3R); and remediation of polluted media (water, air, and soil). There are several obstacles to implementing waste minimization; they include the availability of cleaner technologies with suitable efficiencies, substitution of hazardous materials with less toxic materials, and the need to conduct research and development activities aimed at overcoming technical obstacles and implementing waste minimization in a practical manner.

These research programs will focus on three aspects of cleaner production:

- Reduction of waste at its source
  - Implementation of good housekeeping,
  - Waste segregation,
  - Selection of more environmentally friendly raw materials,
  - Reduction and substitution of hazardous materials used in the production process,
  - Optimization of production processes,
  - Process of modification, and
  - Process and technology change.

- 3R (reuse, recycle, and recovery)
  - Efficient water and energy utilization,
  - Optimization of raw materials use, and
  - Waste utilization.

- Waste treatment and remediation
  Although the focus of these activities is on waste prevention, there is still a need to treat wastes that are generated to reduce their toxicity. Such activities include:
  - Utilization of microorganisms to treat wastes produced in manufacturing processes,
  - Development of physical/chemical waste treatment technologies,
  - Waste toxicity analysis,
  - Modification and development of the existing waste treatment.

To promote these programs, the need for networking data has been recognized. Therefore, BAPEDAL will develop an Information System for Waste Minimization. This effort will involve:

- Collecting data from waste audits and related waste minimization research,

- Compiling these data into a networked database,

- Developing networking between BAPEDAL and other institutions with similar objectives, and

- Disseminating information on the results of waste minimization research.

This research will be conducted over 15 years. The results of this research will be used to promote the implementation of cleaner production in every sector, such as the domestic sector, industry, and mining.

5 CLEANER PRODUCTION DEMONSTRATION PROJECT: A CASE STUDY

To provide examples of cleaner production options that can be developed and implemented, BAPEDAL has initiated a number of demonstration projects. Their purpose is to provide a model for all stakeholders, including planners and designers, in controlling and eliminating environmental impacts through applications of cleaner production technology and waste minimization. A case study is presented below as an illustration of the approach taken in the leather tanning industry.

The project was initiated in 1994 to 1995 with funding and assistance from the Canadian International Development Agency (CIDA) through the Environmental Management Development in Indonesia (EMDI) project. A medium-sized company in the city of Yogyakarta, Java, was selected for the project. Work was conducted in partnership with the Institute for Research and Development of Leather and Allied Industries.

The selected facility uses approximately 150,000 salted goat and sheep skins as a raw material each month. Besides tanned goat and sheep skins, the facility also produces small quantities of upper leather from cow hides. During conversion of hide into leather, there are many steps involving chemical and physical processes that produce either liquid or solid wastes and gases. Some of them still contain hazardous material.

The selection of demonstration project facility was based on these criteria:

- Financial stability and demonstrated commitment to development and use of cleaner production,
- Willingness to release information about the project for dissemination,
- Existing environmental condition of the facility,
- Capability to monitor effects of the cleaner production processes that were implemented, and
- Commitment to provide sufficient management and staff time to complete the cleaner production project.

To facilitate the implementation of cleaner production options and understand the process activities in the selected leather tanning facility, data on subjects such as raw material use, chemical use, storage systems, process and equipment, and waste produced and its characteristics were collected through an audit activity. A waste audit is an essential starting point for identifying where waste reduction can be incorporated in an existing production process and equipment. Moreover, an evaluation of all project activities is needed to identify options available to the facility and to monitor their implementation.

During the project, some recommended options for cleaner production were implemented by the facility as they were identified. Because of time and budget limitations, the focus has been on the "housekeeping" mechanism. The following text describes the way in which the project was approached at the facility.

5.1 Improved Housekeeping

To preserve quality and avoid putrefaction of raw stock (hide and skin), some improvements in the stockroom were implemented:

- Construction of additional doors and installation of blowers to optimize air circulation and
- Use of pallets for storing stock, so direct contact with the floors can be avoided.

Construction of a barrier wall with screens along the waste channel can reduce total solid waste in the sedimentation tank by 50%.

5.2 Reduced Water Consumption and Waste Volumes

Realizing that water will become scarce and expensive in the future, the facility has tried to implement some recommendations related to decreasing its consumption. The efforts include:

- Changing washing systems from continuous to batch to reduce water consumption by nearly 50% (saving US$260 per month) and
- Recycling washing liquors from the deliming, bating, and degreasing process to the prewashing stage (saving US$270 per month).

The facility has also examined the option of recycling pickling and chrome liquors in the laboratory and during full-scale production. Advantages of this practice are:

- Reduced salt consumption,
- Reduced chrome consumption,
- Improved wastewater quality, and
- Potential cost savings of approximately US$3,700 per month, with a return on investment of less than four months.

6 CONCLUSIONS

It is obvious that cleaner production is a suitable conceptual and operational tool that can be incorporated in the production process. It can provide a valuable framework to support product life-cycle initiatives as a means of reducing the risks to human health and the environment. Such an approach, which emphasizes preventative strategies and programs, will help preserve our natural resources and promote environmental quality.

Cleaner production is a strategy that should be given high priority and include, wherever possible, efforts to reuse, recycle, and recover waste. Cleaner production through reduced waste or emissions at the source can be achieved by relatively simple changes to operational processes, investment in cleaner production technologies, and the better use of raw materials.

The initiative of Indonesia's Cleaner Production Program is a major step forward in its approach to environmental management. It has already shown its value by raising the level of interest in cleaner production shown by all stakeholders. However, this effort must be maintained to ensure the success of this initiative in the long term.

OVERVIEW OF CLEANER PRODUCTION AS A RESULT OF CLEAN TECHNOLOGY RESEARCH IN VIETNAM

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ABSTRACT

Vietnam is beginning its industrialization process, and it currently lacks the capital necessary for expensive pollution control and treatment systems. Pollution strategies are critical for the country. This study evaluates the present status of industry and the pollution problems associated with industrial development in Vietnam. The purpose of the study is to identify sectors that may have potential for promoting cleaner production practices.

1 INTRODUCTION

With rapid economic growth and accelerated industrialization in recent years, environmental pollution in Vietnam has become a serious problem. Urban and industrial areas are more polluted as a result of expansion of existing industrial areas, creation of new factories and industrial parks, and continued use of old factories. The urbanization program aims to establish three large urban-industrial sites in Hanoi — Hai Phong-Quang Ninh in the north, Quang Nam-Da Nang in the center, and Ho Chi Minh City-Bien Hoa Vung Tau in the south. Establishing these sites will probably have a strong impact on the environmental conditions of very large areas. A number of important questions concerning pollution control in these areas have not been considered, such as sewage treatment, dumping and burning of solid waste, and hazardous and toxic waste management, etc. In fact, Vietnam is just beginning its industrialization process and currently lacks capital to invest in expensive pollution control and treatment systems. Therefore, pollution prevention strategies are critical for the country.

A project on industrial waste recovery and treatment and appropriate "cleaner production technology" for Vietnam has been developed in the framework of the National Research Program on environmental protection in the period from 1992 to 1995. One objective of the project is to evaluate ongoing industrial development and provide information to assist the Vietnamese government in identifying and promoting cleaner industrial development patterns for some sectors. Some preliminary results are reported in this paper.

2 INDUSTRIAL SITUATION AND POLLUTION ISSUES

At the beginning of 1993, Vietnam had 377,000 industrial establishments and small-scale enterprises that employed 2,051,000 people and turned over VND 30,000 billion. Most of the heavy industrial facilities are in northern Vietnam, while small and medium facilities are scattered throughout the country. During 1991–1993, industrial growth occurred at an average of 13.2% per year. As a result, the share of industry in the country's gross domestic product (GDP) increased from 19% in 1990 to 23% in 1993. This trend will continue for the foreseeable future.

Overall, industrial outputs from Vietnam are low in comparison with the size of the population. The public sector dominates most of the power industry; mineral (including oil and gas) exploitation; metallurgy; cement, chemical fertilizer, and pesticide production; and industries for the national defense.

Industries are concentrated in three zones: Ho Ci Minh City and neighboring provinces, which occupy 48% of total industrial output; Me Kong River Delta, 14.1%; and Red River Delta, 13.5%. The Central Highlands contributes only 1.3% of the total output, but this area is experiencing the fastest industrial growth rate (22% a year during 1989–1993).

Industries in Vietnam are characterized by:

- Outdated and inefficient equipment and facilities, resulting in inefficient use of raw materials and severe pollution. In comparison with neighboring countries, a unit of industrial capacity (e.g., in terms of horsepower or rated capacity) in Vietnam consumes more materials and produces more pollutants.

- Most industries do not have effective pollution control facilities, expect for some rudimentary means such as high stacks to disperse air pollutants to higher levels. Only a few industries in joint ventures with foreign companies were forced by city authorities. These cases are the exceptions rather than the rule.

- Old industrial zones were not planned with environmental considerations. The Lam Thao-Viet Tri industrial zones, which have heavily polluting industries, are located at a major confluence of the Red River, and pollutants are discharged into this major water system. Other industrial zones are in similar situations: Ha Bac (fertilizer industry), Thai Nguyen (metallurgical industry), and Hai Phong (cement industry). Zoning of industries in the south before 1975 was rational in terms of separation from built-up settlements, but urbanization has put them closer to residential areas.

- Improper zoning means that industries are scattered in the middle of densely populated urban areas.

3 ENVIRONMENTAL PROBLEMS AS A RESULT OF INDUSTRIALIZATION IN VIETNAM

3.1 Wastewater Discharge

The wastewater discharged from industrial establishments in Vietnam, about 50% from heavy industry, is improperly treated. Industrial contamination is visibly apparent where streams and canals receive highly concentrated wastewater. Monitoring of industrial facilities is almost nonexistent. Unlike human wastes, industrial discharges are likely to cause long-term environmental problems, because they often contain toxic substances. In addition to posing a potentially serious threat to human health, industrial wastewater can be highly acidic and can contain corroding and toxic chemicals that could severely damage piping and pumping systems of proposed biological treatment systems.

3.2 Air Emissions

Industrial air emissions and coal are the main causes of degradation in air quality in urban and industrial areas. Overall exposures to particulates, CO, CO_2, SO_2, and NO_x exceed permissible levels at many urban locations. Because of rapid urbanization, many factories, previously located far from populated areas, are now inside urban zones. Thus, air pollutants, which previously were dispersed over unpopulated areas, now penetrate directly into city houses, posing a serious threat to human health.

3.3 Occupational Health

Occupational health in its various forms is a widespread concern. The rates of occupational disease among the industrial workforce in the construction material industry are high. Of workers employed in the chemical industry, 61% are estimated to suffer from some employment-related illness. In the metallurgical industry, the percentage is 66%.

4 CONCEPTUAL APPROACH

Today, the term "clean technologies," as defined in Europe, refers to technologies designed especially to prevent waste emissions at the source of generation as opposed to the production process. Thus, clean technologies generate less pollution and waste than conventional technologies, while saving raw materials and conserving energy whenever possible. Clean technologies include recycling, process and product reformulation, substitution and use of less hazardous feedstocks, and installation of more efficient equipment.

However, clean technologies are still unfamiliar in Vietnam. When using the term, people easily think of highland expensive technologies, which are not suitable for developing countries such as Vietnam; hence, we need to introduce the term of "cleaner production." The United Nations Environment Program (UNEP) defines this term as "continuous application of an integrated preventive environmental strategy to processes and products to reduce risks to humans and the environment."

Cleaner production has the potential to facilitate the "leap-frog" goal of development, allowing such countries as Vietnam to pass over old technologies and the mistakes made by industrialized countries and move directly to technologies and systems with less environmental impact. Cleaner production methods empower companies and government to analyze systems and choose technological improvements rather than simply replace one environmental hazard with another.

On the basis of a consideration of the above-mentioned status of existing industry, pollution issues, and the technology and equipment renewal process occurring in most industries in Vietnam today, the following activities were completed from 1992 to 1994:

- Three training courses/workshops were conducted on industrial waste auditing and pollution prevention. More than 80 researchers and technical personnel from various institutions and industries participated in this training provided by overseas and local experts.

- Waste minimization audits were conducted in several enterprises in different sectors, such as the chemical fertilizer, textile, and food industries, the output included qualified reports and one P-project.

Priority should be given to industrial sectors according to their hazard potential and the urgency with which environmental problems need to be solved, as follows:

1. Basic chemicals and fertilizers (super phosphate and nitrogen);
2. Consumer goods (textile, paper);
3. Thermoelectric products;
4. Food processing (meat, marine products, beer, alcohol, fruit and vegetable canning); and
5. Metallurgy, mining, and mechanical areas.

In developing cleaner production in the country, attention should be directed first to the chemical fertilizer, textile, paper, and food processing industries that have the potential for water recirculation, recovery and recycling of chemicals, and change of raw material or process modification. A case study on textile and fertilizer industries showed that when wastewater was segregated, from about 20% to 80% of it, respectively, consisted of cooling water, which can be reused. Some chemicals, such as sodium hydroxide in textile mills, or some gases, such as H_2, CO_2, NH_3, etc., in area production can also be recovered.

For Vietnam, it is very important to concentrate on the beginning of the decision-making process of investors. At that stage, cleaner production is easily incorporated. Existing channels consisting of banks, funding agencies, government agencies (licenses and subsidies), and trade organizations should be used to convince investors of the need for cleaner production. Training courses and appropriate information should be available for the investors and the participants in the sensitization process.

Most of the existing industry in Vietnam is old and relies on outdated technology. Some factories still use 1950s technologies. These old systems produce intense pollution. For example, according to the Ministry of Light Industry, 40% of dying chemicals are discharged as liquid effluent. A waste minimization audit is a suitable action for cleaning up pollution from these firms, which lack the capital necessary for cost-treatment systems. This could be the first step toward cleaner production.

5 PRELIMINARY CONCLUSIONS

- Industrial pollution in Vietnam has already become a significant problem in areas of industrial concentration, causing negative impacts on human health and economic costs.

- Simple housekeeping measures and technological improvements are the first step toward cleaner production for Vietnam, which could lead to cost savings and reduced emissions.

- In 10 years, much of Vietnam's current industries should have been replaced by new equipment. Each new investment offers an opportunity to adopt a proper combination of low-waste processes and end-of-pipe controls. This choice would be determined by the most appropriate and economic strategy. Incorporating environmental considerations into industrial development can save the crippling costs of waste treatment and disposal later.

- The chemical and fertilizer, textile, paper, and food processing industries have a greater potential for promoting cleaner production. Therefore, they should be given high priority.

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INTEGRATING HAZARDOUS WASTE MANAGEMENT INTO A MULTIMEDIA POLLUTION PREVENTION PARADIGM: A PROTOTYPE REGULATORY PROGRAM FOR PETROLEUM REFINERIES

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ABSTRACT

An emerging trend in environmental regulatory management promises enhanced environmental protection and more flexibility for regulated entities. This trend reflects three concepts. First, regulations designed to reduce one type of environmental pollution (e.g., air pollution) should not increase other types of pollution (e.g., hazardous waste). Second, pollution prevention is an important alternative to end-of-pipe control requirements. Third, offering polluting entities flexibility in meeting certain performance criteria may produce better environmental results than prescribing specific technologies or approaches. A significant body of literature supports the need to develop regulatory programs that incorporate these concepts. However, little evidence exists that these concepts have been integrated into actual multimedia regulatory programs. Argonne National Laboratory and the U.S. Department of Energy are developing a prototype regulatory program for petroleum refineries that embraces these concepts. The approach in this study is composed of several steps: (1) identifying and evaluating existing regulations that govern petroleum refineries, if any; (2) characterizing expected future operating conditions of refineries; (3) setting goals for the regulatory program; (4) identifying and evaluating options for the program; (5) developing a prototype based on selected options; (6) identifying and addressing implementation issues; and (7) testing the prototype on a pilot basis. The approach being used in this U.S. effort is flexible and can be used in environmental management efforts throughout the Pacific Basin — in both developing and developed countries.

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1 INTRODUCTION

Today, most Pacific Basin countries have laws that limit the release of pollutants into the environment. Some have regulations to implement those laws; others (e.g., Bangladesh or Cambodia) are developing environmental regulations. The success of regulatory implementation varies among Pacific Basin countries. In India, for example, violations of environmental laws are considered criminal acts, but crowded criminal dockets and procedural protections limit enforcement, and fines are typically not high enough to discourage pollution (Chandak 1995). The Philippines has environmental laws and regulations but lacks mechanisms to penalize polluters and reward responsible operators. Thailand has several hazardous waste management laws, but implementing jurisdictions are spread among numerous responsible ministries (Eamsakulrat 1995). Many countries lack the resources to manage, monitor, and enforce environmental laws. Some countries have functioning regulatory enforcement systems in place but suffer from other problems. For example, critics of some programs charge that overly prescriptive regulations force the use of specified technologies and approaches to meet environmental goals, thereby preventing flexibility and discouraging innovative approaches. For example, U.S. hazardous waste regulations forbid wastes that contain even minute quantities of listed hazardous wastes to be disposed of on the land until such wastes have been treated by waste-specific technologies. Such regulations are costly and may not provide commensurate benefits to public health or the environment. Regulators and regulated entities seek reform to address these kinds of problems.

While regulatory development and enforcement vary, Pacific Basin countries often share common environmental management goals. For example, most prefer pollution prevention (P2) over "command and control" or "end-of-pipe" treatment. Thus, a regulatory program should encourage P2 activities. Also, pollution reduction should maximize net environmental benefit; that is, reducing pollutant releases into one medium should not result in greater releases into another medium. Minimizing cross-media transfers can help limit net environmental impact. Another common goal is that environmental protection should be cost-effective. No country has the resources to ensure a pollution-free environment. An environmental regulatory program should be cost-effective, both for regulated entities and for regulating agencies.

No single environmental regulatory program can be designed to meet the needs of all Pacific Basin countries simultaneously. Variabilities in culture, industrial development, geography, population, government, and other factors must be reflected in regulatory programs if those programs are to succeed. A case study of a prototype regulatory program under development for petroleum refineries in the United States may provide ideas for other Pacific Basin countries to consider as they strive to meet environmental goals with limited resources. This paper describes the development of a prototype multimedia P2 program for "next-generation refineries." "Next-generation" refers to refineries that will be operating in the future under conditions that will differ from operating conditions today. This paper also describes how such a program and the approach used to develop the program could be applied by other Pacific Basin countries.

2 IMPETUS FOR THE PROGRAM

In 1993, the U.S. Congress funded the president's Environmental Technology Initiative (ETI) as part of a national strategy to encourage development, commercialization, and use of innovative environmental technology. In administering the program, the U.S. Environmental Protection Agency (USEPA) stressed the need for partnerships with the private sector and federal agencies. The prototype multimedia regulatory program for next-generation refineries is an ETI project that uses the expertise of the U.S. Department of Energy (DOE) and its national laboratories to develop a regulatory program to address the concerns of U.S. refineries operating in a future characterized by the need for new technologies. The project strives to develop a multimedia environmental regulatory program that will encourage the use of innovative technologies.

The focus on petroleum refineries is twofold. First, U.S. petroleum refineries are subject to costly and increasing environmental requirements. In 1990, U.S. petroleum refineries spent $3.7 billion on compliance with air, water, waste, and other environmental regulations; in 1993 they spent $5.7 billion, or about 50% more than in 1990 (API 1995). These expenditures were greater than the entire USEPA budget in those years and do not include reserves for future activities, fines and penalties, or lost business opportunities. Regulations under development will require additional expenditures. Future Clean Air Act Amendments (CAAA) capital costs alone are estimated at $35 to $40 billion (Lichtblau 1992). The USEPA acknowledges that it may be more economical for some refineries to close than to upgrade their facilities to meet the new standards (USEPA 1995). The second reason for the refinery focus is that the industry functions in an increasingly challenging operating environment. The overall quality of crude oil input to the refining process is declining, thereby requiring additional processing to yield an equivalent product. At the same time, the CAAA mandates specific product qualities to reduce environmental impacts of downstream use of the product. Table 1 outlines some CAAA provisions regarding product reformulation and how refineries will likely respond. Many of these requirements entail significant process changes and capital investments. Petroleum refineries need the ability to develop and use new technologies that will both facilitate the refining of heavier crude and meet expanding environmental requirements at the refineries.

3 PETROLEUM REFINING CHALLENGES IN OTHER PACIFIC BASIN COUNTRIES

Other Pacific Basin countries face many of the challenges described above. Several are changing their motor vehicle fuel specifications. For example, Thailand has new clean fuel standards to be implemented by the year 2000. To meet the standards, several refinery modifications must be made. A deep gas oil hydrotreater will be installed to enable the production of 0.05 wt% sulfur diesel oil. A fluid catalytic cracking unit will be added, and modifications will be made to the existing naphtha reformer to produce high-octane, low-aromatic, and low-benzene gasoline. Equipment and facilities will be installed to enhance environmental mitigation systems (World Bank 1996a). Pacific Rim

Table 1 CAAA Requirements for Product Reformulation and Associated Refinery Needs

CAAA Program	Product Reformulation Requirements	Associated Refinery Needs
Oxygenated Fuels Program	Gasoline sold in carbon monoxide nonattainment areas must have a minimum of 2.7 wt% oxygen for at least four winter months. California winter fuel oxygen content is 1.8 to 2.2 wt%.	Increased capacity to produce oxygenates.
Highway Diesel Fuel Program	Sulfur content of all highway diesel fuel must be reduced from 0.5 to 0.05%. Cetane index must be at least 40.	Increased construction of desulfurization units, such as catalytic hydrocracking and hydrotreating units.
Reformulated Gasoline Fuels (RFG) Program	Requires RFG in certain metropolitan areas. RFG must have a minimum oxygen content of 2 wt%, a maximum benzene content of 1% by volume, and no lead or manganese. By 2000, toxic emissions are to be reduced by at least 20%, VOC emissions by at least 25%, and NO_x emissions by at least 5%.	Gasoline formulation to be upgraded. Hydrotreating units needed for meeting lower sulfur specifications.
Leaded Gasoline Removal Program	Sale of leaded gasoline for use in motor vehicles prohibited after 1995.	Clean Air Act of 1970 reduced lead content substantially; provision not expected to require significant changes.

refineries may be subject to increased environmental controls from external pressures as well. For example, on May 18, 1996, the World Bank called for a global phaseout of lead in gasoline, citing health problems caused by leaded gasoline in urban areas of developing countries. Such a phaseout will require refinery modifications (BNA 1996a).

The quality of input crude is also declining in other Pacific Basin countries. As demand for refined products increases, lower-sulfur Asian supplies must be supplemented with higher-sulfur, heavier Middle Eastern crudes. China, for example, had been a net exporter of petroleum; now it is a net importer of crude. Crude oil recoveries from the South China Sea are small relative to the amounts of crude needed to meet local product demand. Outside of Japan, most Asian refineries are simple. Until recently, these refineries could meet local needs, but in the past 10 years, as automobile use has increased, the need for more complex refinery operations has grown. Singapore, Taiwan, and Malaysia are upgrading their refineries to handle heavy, sour crude. New technologies are required for such modifications.

Other pressures on Pacific Basin refineries relate to rapid economic growth and industrialization. In Indonesian urban areas, for example, the number of vehicles is increasing by more than 20% annually (BNA 1996b). Increasing foreign investment magnifies this growth. In Vietnam, foreign investment increased by 50% between 1991 and 1995, and the country hopes to attract $41 billion in new investments by 2000 (BNA 1996c). Petroleum products will be needed to support transportation and industrial growth; extraction and refining can be expected to increase in the area. Table 2 shows existing petroleum refining capacity and capacity under development in Pacific Basin countries.

Accompanying the pressures on refineries to produce more high-quality fuel are increased concerns about the overall environmental effects of growing economies and industrialization. India's rapid economic, population, and industrial growth is causing severe environmental degradation and pollution problems. The Klang Valley in Malaysia suffers from air quality problems related to increased automobile traffic and the burning of fuel oil for electricity. Some developing countries fear that environmental concerns will delay progress in material and social improvement (Anwar 1995). In Singapore, where industrialization and modernization continue to gain momentum, environmental measures and standards are being reviewed and upgraded where possible (Tay 1995). All of these concerns suggest the need for cost-effective environmental programs to help ensure that industrial development and growth continue without unacceptable risk to human health and the environment.

Table 2 Existing and Projected Refining Capacity in Selected Pacific Basin Countries

Country	Capacity (1,000 barrels per calender day)			Country	Capacity (1,000 barrels per calender day)		
	Existing	Projected Additions[a]	Change (%)		Existing	Projected Additions[a]	Change (%)
Australia	732.7	76.4	10	Malaysia	320.7	266.8	83
Canada	1,848.5	29.0	2	Mexico	1,520.0	153.7	10
China	2,867.0	335.0	12	Philippines	323.1	1.5	0
India	1,086.4	1,021.2	94	Singapore	1,170.0	151.3	13
Indonesia	804.7	149.5	19	Taiwan	542.5	0	0
Japan	4,867.0	572.7	12	Thailand	425.8	625.9	147
Korea	1,315.0	551.5	42	USA	15,354.1	461.6	5

[a] Through 2000
Source: PennWell (1995).

4 ADVANTAGES OF A SECTOR-SPECIFIC MULTIMEDIA POLLUTION PREVENTION PROGRAM

Many Pacific Basin countries are making progress in controlling pollution, but more needs to be done. In several Chinese provinces, the amount of pollution generated per unit of output has decreased over the last 10 years as the result of industrial efficiency gains, cleaner technology, and environmental regulation. However, the absolute level of industrial growth has diminished the significance of this relative improvement. As a result, the national government has made improved industrial pollution control its primary environmental target for the 1996-2000 planning period (World Bank 1996b).

4.1 Sector-Specific Approach Allows for Timely, Phased Development

A system developed for individual industrial sectors can focus on the issues specific to each sector and can be developed in phases. While a multisector approach might be more effective in reducing net environmental pollution, such a system may be too difficult to design and implement in a reasonable time frame. By focusing on individual industrial sectors, significant progress can be made, and lessons learned from one sector-specific program can be applied to others. The entire process can continually improve.

An optimal approach for developing sector-specific systems would be to assess the environmental and health impacts of various industrial sectors and then develop regulatory programs starting with sectors with the greatest potential for harm. Indonesia, in its Industrial Environmental Management Project, selected industries to become recipients of pollution management appraisals on the basis of their relative potential risk to health, welfare, and the environment (Jardine et al. 1995). Taiwan has taken a similar approach in selecting industries for demonstrating waste minimization technologies. Industries (1) that cause serious pollution, have a large number of plants and a wide range of pollutants, generate hazardous pollutants, and (2) that meet other criteria are eligible for assistance in developing P2 plans (Chen et al. 1995).

4.2 Multimedia Approach Considers Releases from All Sources

A multimedia P2 program considers releases of pollutants from all sources within a facility as a whole rather than as separate emitting sources. This approach helps ensure that all major sources are considered. Under existing single-medium programs, some important release sources can be missed. For example, in countries with highly prescriptive, source-specific regulations, such as the United States, air pollution regulations restrict air emissions from various types of manufacturing or process equipment, but not necessarily from fugitive emissions. Similarly, federal hazardous waste regulations prescribe technology-based treatment standards for wastes determined to be hazardous, but leave treatment requirements for nonhazardous industrial wastes to states. Because federal laws exclude certain wastes that may contain hazardous constituents (e.g., oil and gas exploration and production wastes, or wastes from publicly owned treatment works) from federal hazardous waste regulation, it is possible that such excluded wastes, even though they may contain the same constituents as a hazardous wastes, may be subject to less stringent requirements at the state level because they are considered nonhazardous.

4.3 Multimedia Program Reduces Cross-Pollutant Transfers

Differences in the costs of controlling releases to individual media can shift pollution releases to the medium with the least expensive control costs. However, the least costly approach may not result in the most acceptable risk to human health or the environment. Bans on land disposal of hazardous wastes under the Resource Conservation and Recovery Act (RCRA) in the United States, for example, have increased toxic releases from incineration of those wastes (USEPA 1991). Emission controls designed to capture these releases may create toxic ash and wastewater, which must then be disposed of. Further, releases to one medium may be transferred to another. Land disposal may generate air emissions or leach toxics to groundwater; contaminants in air emissions may be deposited on land or in surface water. Finally, focusing on the single-medium regulatory approach ignores chemical or physical transformations that may occur once a pollutant is released. Air quality standards written to protect against inhalation health effects do not address transformations that occur when air emissions (e.g., sulfur dioxide) combine with water vapor to form a pollutant (e.g., sulfuric acid) and contaminate soil and water when deposited. In contrast, a multimedia program strives to limit the transfer of pollution from one source to another by viewing the releases to all media holistically and regulating the total emissions of a particular pollutant from a facility. It also reduces the chances for duplication of regulatory requirements and the associated drain on resources. For example, in the United States, certain substances (e.g., benzene) are regulated by several authorities. In countries with fewer prescriptive and potentially conflicting regulations, a multimedia program may help companies meet legislatively established goals, thereby avoiding the need to establish and maintain multiple media-specific enforcement offices.

5 DEVELOPMENT OF A MULTIMEDIA POLLUTION PREVENTION PROGRAM

Developing the prototype program described in this case study consisted of three phases, with two to three steps in each phase. In applying the case study to Pacific Basin countries, however, the distinctions among the phases are not important. Therefore, the development approach is discussed in terms of the steps rather than in phases. The steps in the development process are summarized in Fig. 1.

This approach is extremely flexible and is not intended to be followed exactly. It should reflect a country's goals, culture, and current environmental situation. Some steps may be deleted or

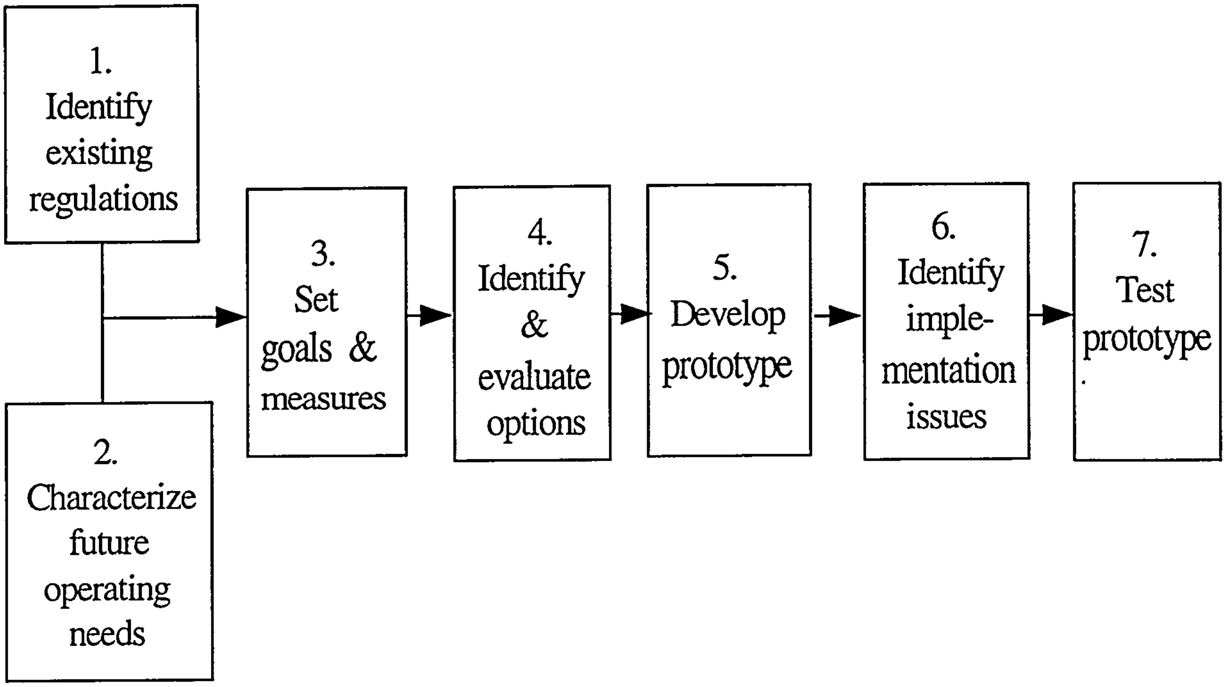

Fig. 1 Steps in Prototype Development Process

modified, and other steps may be added. For example, if no environmental regulatory program exists, step 1 can be eliminated. Similarly, prototype testing (step 7) may not be required. Indeed, in the petroleum refinery case study, consideration is being given to substituting a modeling approach for the pilot test to determine feasibility. Other steps may be added. For example, in the case study, a step was added at the very beginning to establish guidelines and principles for the entire activity. Also, in the case study, provision was made for "stakeholder review." Involving interested parties can be conducted at several stages in the overall approach; it can be conducted simultaneously with the other steps; or, depending on the country or legislative philosophy, it may not be conducted at all. The remainder of this section describes the process used for developing the petroleum refinery regulatory prototype and suggests how individual steps may vary for other countries choosing to use a similar approach. These suggestions are neither exhaustive nor exclusive; the presentation merely offers alternatives to consider when developing regulatory programs.

5.1 Establish Guidelines and Principles

Before developing a regulatory program, it can be useful to establish guidelines and principles to set the bounds for the regulatory approach and provide a reference against which proposed options can be checked. This step is not included in the approach per se; rather, it was added to provide a common understanding and to help reduce potential conflict or misunderstandings among industry, government, and other interested parties as the approaches are actually developed. For this case study, three operating guidelines were set:

- Refineries continue to play an important role in the U.S. economy. Thus, the regulatory program should not restrict the future viability of U.S. refineries.
- Prototype regulatory approaches are limited to refinery activities; extraction of crudes and use of finished products are addressed.
- Prototype regulatory approaches ensure protection of human health and the environment.

Specific principles were also established. Examples of specific principles include, but are not limited to, the following: prototype regulatory approaches should be rooted in the P2 ethic; prototype regulatory approaches should encourage, stimulate, and reward innovation; and prototype regulatory approaches should focus on reducing net environmental impacts associated with refinery operations. Guidelines and principles will vary with the sector for which the regulatory program is being developed and with the culture, economics, and other factors specific to individual countries and regions. In Australia, for example, state governments have developed a set of principles to help guide policy for a national environmental law model. These principles include precaution; intergenerational equity; conservation of biological diversity and ecological integrity; and improved valuation, pricing, and incentive mechanisms. In addition, several concepts have been considered, such as effective integration of economic and environmental considerations in decision-making processes, and maintenance and enhancement of international competitiveness in an environmentally sound manner (Robinson 1995).

5.2 Step 1: Evaluate Existing Regulatory Program

The first step in the case study approach was to establish the regulatory/P2 baseline for petroleum refineries. Evaluating the existing regulatory program helps identify issues to be addressed in the improved program. In the case study, existing laws and regulations governing refining operations in the United States were outlined and reviewed to determine which appeared to be effective and which caused concern. Barriers and incentives for P2 and opportunities for innovation were considered. Once the regulatory system was reviewed, implications of that system for an improved regulatory program were identified.

5.2.1 Case Study Results — Regulatory Environment

Petroleum refining is a resource-intensive industry. It ranks among the top 10 emitting sectors in the United States, according to the USEPA's Toxic Release Inventory, which reports emissions to environmental media from U.S. manufacturing industries. U.S. petroleum refineries must meet regulations promulgated under the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, RCRA, and the Emergency Planning and Community Right to Know Act. The Comprehensive Environmental, Response, Compensation, and Liability Act and the Pollution Prevention Act also affect refineries. Regulations are either category-specific (e.g., effluent guidelines and standards for the petroleum refining point-source category) or are more broadly encompassing (e.g., standards applicable to generators of hazardous waste). In addition, petroleum refineries are subject to permitting processes for air emissions and water discharges under state programs. Also, many refineries must have RCRA permits for hazardous waste incineration units or energy recovery through the combustion of hazardous waste as fuel.

In general, these regulations are media-specific and provide little flexibility. Barriers to P2 are significant. Institutional barriers hinder efforts to implement effective P2 because regulators focus on specific media rather than on multimedia concepts. Technical barriers, which typically affect small- and medium-sized companies more than larger companies, hamper the ability to implement process changes to reduce pollution. Financial barriers constrain facilities, especially smaller ones, from pursuing process changes, and resource limitations affect the ability of regulatory agencies to provide technical assistance. Political barriers can reflect pressure from dischargers. Thus, fearing that mandatory programs could lead a company to relocate its facilities, some state and local governments prefer voluntary programs. Regulatory barriers also impede pollution prevention. For example, even though RCRA mandates that waste generators must have a waste minimization program in place, RCRA's restrictions on acceptable control technologies for hazardous waste land disposal can divert resources from waste reduction. RCRA regulations can result in a preference for disposal over recycling. Permit and storage restrictions impede waste minimization. In most cases, standards are based on best practices, best available technology, or best performers. This approach can keep companies from introducing newer, more efficient control technologies, because they fear that regulators would then require such technologies to be used as best available in applications where they may be less appropriate.

5.2.2 Evaluation of Existing Regulatory Programs in Other Pacific Basin Countries

At the risk of oversimplifying the undertaking of this step in other countries, this section provides examples of potential regulatory findings in other Pacific Basin countries.

In Singapore, current laws promote end-of-pipe treatment. Regulations include penalties for noncompliance but offer few (if any) incentives to "go beyond compliance." A program that lacks incentives (as does the U.S. program) can hinder multimedia P2 and technology development efforts.

India has also borrowed from the U.S. command and control regulatory approach and implements environmental regulations through a disincentive structure. The Central Ministry of Environment and Forests has enunciated a policy for integrating environmental and economic aspects in development planning, which stresses P2 and promotion of technological inputs to reduce industrial pollutants. However, few structured programs exist to implement the policy, and emphasis remains on end-of-pipe controls. Also, some regulatory gaps remain, such as limited focus on past contamination of soil and groundwater, lack of pollution control equipment performance standards addition, and little if any regulation of hazardous air emissions (Chandak 1995).

Indonesia's regulations have also encouraged end-of-pipe waste treatment. This strategy has increased awareness of environmental issues, but because of difficulties in enforcement and compliance, it has produced mixed pollution control results. End-of-pipe controls were found to be expensive and often inadequate in limiting pollution to desired levels. As a result, the Indonesia Environmental Impact Management Agency initiated a results-oriented Cleaner Production Program. The program focuses on a priority industrial sector in each year and provides for technical assistance to industry, information systems, training and awareness, and incentives development (Jardine et al. 1995).

5.3 Step 2: Characterize Expected Future Operating Environment

This step provides information on the industry for which the program is being developed. It is designed to look forward and identify changes that may affect future regulatory programs. Recognizing how current operating environments for individual sectors may change can aid in the design of P2 requirements and performance-based regulatory programs that include the flexibility to react to unanticipated future changes.

5.3.1 Case Study Results — Future Operating Environment

Density and sulfur content are two key characteristics of crude oil. High-density crude feedstocks, which have fewer gasoline and distillate fractions than low-density feedstocks, are less desirable for current and projected U.S. product needs. Sulfur content is important because it may limit potential processing alternatives. High-sulfur crudes are difficult to refine and environmentally dangerous when burned because they lead to smog and acid rain formation. Over the past 10 years, the density and sulfur content of crude oil processed in the United States has increased, and the trend is expected to continue. Lower-quality feedstocks require additional processing. Heavier crudes need "bottoms upgrading capacity," and high-sulfur crudes require desulfurization and other processes to reduce releases of sulfur to the environment. U.S. refineries will need additional equipment and new technologies to meet these needs.

The output side of refinery operations is also changing. Over the past several years, the mix of refinery output has moved toward lighter products. This trend is due to expanded transportation use, which requires lighter fuels; reduced residual fuel oil demand, which results from lower-priced natural gas; growing demand for light petroleum products for plastics and chemicals production; and environmental regulations demanding lighter, higher-quality fuels. The trend is expected to continue as additional but not-yet-determined motor-fuel-specification requirements take effect in the year 2000. Flexibility in product and process development is also needed. Variabilities in testing methods, for example, may require additional changes in product quality. Also, more segregation of products will be required, and products may need to be stored so that they are not commingled with other components. Future profitability will require improved overall plant performance. New technology developments will help refiners meet these types of requirements.

5.3.2 Case Study Results — Implications of Operating Environment for Regulatory Program

The need for new technology to meet the demands of changing input quality and output mix suggests several factors that need to be reflected in a multimedia regulatory program for next-generation refineries:

- The program must be flexible. For example, refiners should be able to plan changes to refinery operations assuming that they need to meet a performance-based standard as opposed to a process-specific, technology-based standard.
- Regulations should focus on refinery-wide releases rather than source-specific releases within the refinery. New processes and changes in existing processes will produce emissions from a variety of sources. Regulating sources separately will be less efficient than regulating emissions from the refinery as a whole.
- The program must allow for the incorporation of new knowledge about health and environmental effects and development of new technologies.
- Because releases have multiple sources and the potential for cross-media pollution is significant, the regulatory program needs to be multimedia.

5.3.3 Characterizing the Operating Environment in Other Pacific Basin Countries

An analysis similar to the one described above could be conducted in other Pacific Basin countries. If done for petroleum refineries, adjustments for fuel-use restrictions, quality of crude, and other factors would be required. Similar analyses could be undertaken for other industries. For example, increased automation presumably would be a factor in textile and tanning industries, and restrictions on logging could be a factor in the pulp and paper industry. Other factors may need to be considered. Many Pacific Basin countries have limited land area for waste disposal, implying that disposal costs can be expected to increase. Many developing countries have limited access to technological information, and the technical information available from abroad often is not relevant, appropriate, or affordable for industries in developing countries. Such factors must be considered as part of characterizing the operating environment.

5.4 Step 3: Establish Goals for Regulatory Program

This step identifies goals for the program that reflect the guidelines and principles established at the outset. The goals reflect the findings and concerns identified in the regulatory review and the characterization of the operating future of the industry. They can also reflect broad national or regional environmental or economic goals.

5.4.1 Case Study Goals and Measures

In this case study, the focus of the proposed regulatory goals is on protection of public health and the environment. Impacts on worker risk and concerns related to cleanups are not addressed. Measures were established to assess how individual options meet each goal. The goals and measures established in the case study are summarized in Table 3.

5.4.2 Goals and Measures for Other Pacific Basin Countries

Regulatory program goals and measures differ among countries and industries. In the Philippines, the goal of the Department of Environment and Natural Resources (DENR) Industrial Environmental Management Project is to encourage sustained economic growth in the industrial sector, while reducing pollution and improving worker health. Although it is not a comprehensive regulatory program, it contains the elements of goal setting and measuring addressed in this step. Thus, the goals of economic growth, increased employment, and reduced health risk are measured by increased savings or profits in target industries resulting from adoption of P2 and control measures, and reduced waste generated by participating facilities (Araza et al. 1995). In some countries, increased public and industrial awareness may be a P2 goal. Some of the measures developed in the case study may be inappropriate for other countries. For example, in developing countries, decreasing capital

Table 3 Prototype Regulatory Program Goals and Performance Measures

Program Goal	Performance Measure
Economic Performance. The program should not weaken economic performance; U.S. refiners should remain competitive in the global market.	• Environmental capital costs decrease. • Environmental O&M costs decrease. • Environmental administrative costs decrease. • Regulatory uncertainty costs decrease.
Environmental Responsibility. The program should allow refineries operating in the future to demonstrate that they are environmentally responsible.	• Quantity of residuals produced decreases. • Quantity of residuals released decreases. • Toxicity of residuals produced decreases. • Toxicity of residual released decreases. • Use of nonfeedstock toxics decreases. • Public participates in development process.
Pollution Prevention Technology Innovation and Use. The program should increase use of technologies that reduce pollution and increase efficiency.	• Promotes penetration of new technologies. • End-of-pipe technology use decreases.

costs for environmental protection may not be a measure of environmental performance. In some countries, public participation in the development process may not be an important measure.

5.5 Step 4: Identify and Evaluate Options

This step identifies and evaluates potential regulatory options for use in the actual prototype. Each option is evaluated according to the measures defined in step 3. Options that do not measure up are eliminated; those that remain can be used to form the prototype.

5.5.1 Case Study Options Development Process

In developing options for the petroleum refinery case study, "a wide net" was cast to avoid missing potentially important options. Analysts identified over 60 options, ranging from broad overall approaches to narrow procedural approaches. Examples included intraplant risk-based trading, industry self-regulation, contaminant-specific (as opposed to media-specific) regulations, P2 revolving loan program, substitution of multimedia permits for single-media permits, enforceable agreements, fee-based incentives, tradable permit systems, consolidation of federal and state permits, and many others. When evaluated against the measures defined in step 3, most of these approaches meet the goals. While none of the approaches could be eliminated from further examination (as had been intended), it became evident, on closer evaluation, that two key approaches emerged and that several individual options could be incorporated into these two. The two approaches — a release-based approach and a risk-based approach — were developed further in the next step.

5.5.2 Options Development Process in Other Pacific Basin Countries

Regulatory prototype options are vast, and the relevance of an option to a country's situation needs careful evaluation. Provided below are some examples of the types of options under consideration in other Pacific Basin countries.

- Indonesia's cleaner production program uses economic incentives. These incentives supplement or substitute for traditional command and control approaches, use markets to influence behavior, and focus on results rather than on methods. Incentives under consideration include ecolabeling, an annual industry award for companies most effectively employing cleaner production, and taxes on wastewaters (Jardine et al. 1995).

- Australia's EPA has introduced a system of accreditation for companies that have approved environmental management systems, improvement plans, and audit systems. Such companies receive simplified licenses, which set environmental outcomes for the sites, allowing the companies to manage their environmental affairs without regular compliance checks and with minimal approvals. License fees are also reduced (Robinson 1995).

- Recognizing the need for sustainable pollution reduction programs while allowing for individual choice in meeting industry objectives, the DENR in the Philippines is investigating market-based incentives that include a fee per unit of pollutant discharged to the environment; markets for the purchase, sale, and transfer of waste products; surcharges on recyclable or reusable products; risk and liability insurance to cover costs of environmental, economic, and health remediation; and user fees on raw materials (Araza et al. 1995).

- Options being considered for implementing industrial P2 policies in India include government dissemination of information on P2 options; revised pricing of natural resources to curb wasteful consumption; mandates to incorporate pollution prevention; government funding of demonstration projects to mitigate the "not me first" syndrome; pollution taxes; international demonstration projects; and information exchanges with developed countries (Chandak 1995).

- To promote pollution prevention, Singapore is considering providing financial incentives for companies that adopt pollution prevention well in excess of legal control requirements. It is also considering tax incentives for investments based on case-specific merits. Evaluation criteria would be the use of cleaner processes or technologies that substantially exceed the basic standards required for the industry, and forming strategic technical alliances with overseas institutions.

5.6 Step 5: Develop Prototype on the Basis of Selected Options

In this step, the options identified in step 4 are further refined and consolidated. Because one of the objectives in the case study was to develop an overall regulatory program, individual options needed to be combined into a comprehensive scheme. The intent was to develop two or three comprehensive approaches to be reviewed by interested parties. On the basis of comments from these parties, refinements would be made and one approach would be selected for pilot testing. However, aggregating options may not be necessary in all situations. In some countries, selecting one or two individual options for implementation may provide measurable results.

5.6.1 Case Study Prototype Development

This section describes two multimedia regulatory prototype program options. Both programs have three key elements reflected in a common format: (1) establishing a baseline, (2) setting limits on releases of pollutants, and (3) assuring compliance. One approach, the "negotiated performance agreement," is release-based, with the objective of reducing releases. The other, the "risk-based bubble," is risk-based, with the objective of ensuring that releases do not pose unacceptable risks to human health and the environment. Table 4 summarizes key components of the two options.

5.6.2 Prototype Development in Other Pacific Basin Countries

Any number of prototypes can be developed. As noted above, it may not be necessary to combine individual options into a comprehensive approach.

5.7 Step 6: Identify and Address Implementation Issues

The draft prototypes raise numerous issues that must be addressed before implementation. For example, parts of the risk-based bubble approach require changing existing laws and regulations. Also, reasonably priced monitoring technologies, which may not be available currently, are needed for full implementation. Table 5 identifies several implementation issues that need to be addressed for the risk-based bubble prototype option and suggests approaches for mitigating those issues.

Potential implementation issues may necessitate modifications to the prototype programs. They will undoubtedly require interested parties to develop mutually acceptable approaches. It is conceivable

Table 4 Key Components of Draft Prototype Regulatory Programs

Component	Negotiated Performance Agreement	Risk-Based Bubble
Premise	Release-based	Risk-based
Baseline purpose	To provide for identifying P2 opportunities and a base for measuring progress	To provide release data and environmental characterization for setting limits
Baseline contents	• Inventory of residuals • Costs of inputs and environmental management	• Inventory of releases • Characterization of environment
How release limits are set	Based on current regulatory requirements and negotiation	Based on risk
Basis for assuring compliance	• Cooperative interaction • Monitoring • Progressive penalty system • High visibility of failure	• Direct measurement of releases through monitoring and modeling • Incentives

that not every aspect of a given approach will be able to be implemented. However, the knowledge gained during the process can be applied to further regulatory development or reform efforts.

5.8 Step 7: Test Prototype on a Pilot Basis

The final step in the development approach is to test the prototype. In the United States, this step would be done at an existing refinery, since no new refineries are being built. In other countries, it may be possible to test the approach on a new refinery. Ideally, the refinery would be selected on the basis of appropriate criteria (e.g., size, location, regulatory climate, local community interest).

All program participants, including regulators and industry, should be involved in the selection process. Test results would be fed back into the overall approach, which would be refined accordingly.

Because of the expense and risk involved, alternatives to pilot testing may be investigated. One alternative would be to use a mass-balance computer model of the refinery inputs, outputs, and environmental controls, and to run that model with different assumptions that embody the concepts of the prototype options. With such "proof-of-concept" testing, an interactive model would allow users to change assumptions and observe the results in real time. The model would help demonstrate the viability of the options and show how costs, product, and environmental releases would change as various assumptions are changed.

Table 5 Implementation Issues for Risk-Based Bubble Approach

Implementation Issue	Example	Possible Mitigating Measure
Statutory changes	Existing statutes are based on single media.	Identify models for statute that would allow for multimedia legislation.
Regulatory changes	Many existing regulations are not risk based. The approach implies that existing regulations may not be met.	Negotiate pilot program with regulators to temporarily lift non-risk-based regulations in lieu of overall environmental improvement. Industry could agree to revert to existing regulation if pilot fails.
Development of risk-based standards	Models and approaches need to be agreed upon by regulated and regulatory community. Development requires significant sources of expertise and can be resource intensive.	Conduct workshop with interested parties to develop standards on a site-specific basis.
Emissions banking and trading	Not all releases are appropriate for banking and trading.	Identify pollutants for which banking or trading is appropriate and feasible. Examine existing trading and banking programs for lessons learned.
Procedural issues	Standards are to be reexamined when conditions (land use, emissions) change or new knowledge becomes available.	Analyze and recommend specific mechanisms for reexaminations, considering responsibilities, time limits, and so on.
Monitoring technologies	Fence-line monitoring is not economically viable today.	Feasibility and costs of fence-line monitoring for various pollutants would be investigated. Models would be identified for those substances that cannot be monitored.
Public acceptance	Many in the public perceive risk-based standards as weakening environmental protection.	Conduct meetings and focus groups with local publics to share information.

6 CONCLUSION

Throughout the Pacific Basin, refineries will be required to produce ever-increasing amounts of lighter products from heavier and higher-sulfur crude. Often, such production occurs at the same time that environmental regulations become more strict. Stricter operating conditions combined with increasing environmental controls should be met with a regulatory program that allows refineries to operate effectively while not subjecting public health and the environment to unacceptable risks.

Generally, environmental regulatory programs in the Pacific Basin have been based on end-of-pipe controls directed at a single medium. Such regulations can be costly and may not provide commensurate environmental benefits. To help improve the regulatory environment for petroleum refineries, DOE and Argonne National Laboratory are developing a prototype multimedia regulatory program. This effort provides a case study that can be used by other countries and industries seeking improved regulatory programs.

The approach for developing the prototype program consists of seven integrated steps. They include assessing the existing environmental regulatory requirements (if any), characterizing the expected future operating environment of the industry for which the regulatory program is being developed (in this case petroleum refineries), setting goals for the regulatory program, identifying and evaluating options, developing prototypes based on selected options, identifying and addressing implementation issues, and testing the prototype on a pilot basis. The program, although not developed as an ISO 14000 environmental management system per se, can be tailored to meet the ISO 14001 standards, which call for policy development, planning, implementation and operations, checking and corrective action, and review. The case study provides an approach for developing environmental regulatory programs that meet goals, can be revised to reflect changing conditions, offer flexibility to the regulated community, and strive to protect human health and the environment.

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ADOPTION OF WASTE MINIMIZATION TECHNOLOGIES TO BENEFIT ELECTROPLATERS

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ABSTRACT

Because of increasingly stringent environmental legislation and enhanced environmental awareness, electroplaters in Hong Kong are paying more heed to protect the environment. To comply with the array of environmental controls, electroplaters can no longer rely solely on the end-of-pipe approach as a means for abating their pollution problems under the particular local industrial environment. The preferred approach is to adopt waste minimization measures that yield both economic and environmental benefits. This paper gives an overview of electroplating activities in Hong Kong, highlights their characteristics, and describes the pollution problems associated with conventional electroplating operations. The constraints of using pollution control measures to achieve regulatory compliance are also discussed. Examples and case studies are given on some low-cost waste minimization techniques readily available to electroplaters, including dragout minimization and water conservation techniques. Recommendations are given as to how electroplaters can adopt and exercise waste minimization techniques in their operations.

1 INTRODUCTION

The electroplating industry is one of Hong Kong's oldest industries. It is important in metal finishing and a vital support industry closely associated with other manufacturing industries. According to published statistics, 455 electroplating factories operate in Hong Kong, with 4,138 employees. This represents an average employment size of 9 persons per establishment. Most establishments are small- to medium-sized enterprises (SMEs). Moreover, most are located in multistory industrial buildings with limited space. Over 90% of local electroplaters perform metal plating, while the remainder perform plastic plating. Both rack and barrel plating are currently practiced in Hong Kong, although rack plating is dominant. Most electroplaters receive workpieces from their clients, generally larger enterprises, and perform electroplating processes in accordance with their client's specifications. With the exception of large establishments, which mostly operate automatic plating lines, many electroplaters employ rather conventional manual operating methods.

Small-sized SMEs have advantages in terms of flexibility and adaptability, which enable them to respond rapidly to changes in production as demanded by the market. They face, however, the difficulty of meeting the increasingly stringent environmental requirements because of a number of constraints. Without knowing available options for dealing with pollution problems cost-effectively, most SMEs become baffled when they are required by law to improve their environmental performance.

Before discussing a cost-effective strategy to tackle their pollution problems, it is important to understand the factors causing the pollution problems and the constraints causing the ineffectiveness of the traditional end-of-pipe pollution control approach in a local context.

2 FACTORS CAUSING POLLUTION PROBLEMS

Electroplating operations generate a significant amount of liquid waste every day. Their effluents often embrace large amounts of toxic compounds, like cyanide, complexing agents, and heavy metals, and vary greatly in pH. A survey conducted by the Hong Kong Productivity Council (HKPC) recognized various major factors that lead to pollution problems in most local electroplating operations. These factors are discussed in Secs. 2.1–2.3.

2.1 Use of Toxic Chemicals

Apart from containing heavy metals, many electroplating bath formulations currently used by local electroplaters contain some extremely toxic chemicals, such as cyanide and hexavalent chromium. For instance, cyanide-based formulations are commonly used for cleaning processes, copper plating, zinc plating, silver plating, gold plating, etc. In addition, all the local platers use hexavalent chromium in their chromium plating process, which contains chromic acid — a known carcinogen.

2.2 Lack of Control on Conservation of Materials

Most electroplaters pay little or no heed to chemical conservation and waste minimization, resulting in an excessive loss of chemicals that usually end up in drainage. Excessive chemical loss is caused by, for example, excessive "carryover" of solution when workpieces are withdrawn from a plating bath, lack of proper control on material usage, poor housekeeping practices, and poor layout of process tank arrangement, which causes too many back-and-forth movements, etc.

2.3 Overconsumption of Water

Rinse water contributes more than 90% of the total liquid waste generation of a typical electroplating factory in Hong Kong. Most local electroplaters are too generous in water usage, and they exercise little or no control measures to conserve water. It is not uncommon in many electroplating firms to see water running continuously, even when no work is being carried out. In many cases, the amount of water used to perform a rinsing function is more than the amount required, due to either the inefficient design of the rinsing system or the indifference of the front-line operators to conserve water.

3 ENVIRONMENTAL REQUIREMENTS AND CONSTRAINTS IN ACHIEVING COMPLIANCE

Two main ordinances now affecting the electroplating industry are the Water Pollution Control Ordinance (WPCO), which stipulates that all effluents must comply with the discharge standards before they can be released into the environment, and the Waste Disposal Ordinance (WDO), which requires all chemical waste producers to be registered and to arrange for proper disposal of their wastes at licensed facilities. In addition to these regulatory requirements, the government has enacted a number of charging schemes, which work under the "polluters pay" principle, to encourage waste minimization. The schemes more related to local electroplaters include the charge for delivering chemical waste to the centralized Chemical Waste Treatment Center for treatment, as well as the sewage charge, which is calculated in proportion to the volume of water consumed.

As a result of government's stringent environmental control and its associated penalties, some electroplaters have realized the importance of improving their environmental performance. Unfortunately, most electroplaters who pioneered to combat their imminent pollution problems resorted to end-of-pipe pollution control methods. However, most did not realize that the pollution control measures implemented were not totally effective for dealing with the varying pattern and quantity of production they experience, and they failed to meet government requirements. Generally, users of the end-of-pipe approach in a local context encounter the limitations. These constraints are discussed in Secs. 3.1–3.3.

3.1 Limitations on Financial Resources

Most SMEs in Hong Kong work on a low-capital basis; that is, they rely on low-capital assets (e.g., primitive machinery, tools, etc.) to reap profits of limited marginal values. Even though the actual cost of installing end-of-pipe treatment facilities may not seem particularly expensive by western standards, the cost incurred usually represents a relatively high additional cost to SMEs.

3.2 Limitations on Premises

Because of the scarcity of industrial land, most SMEs are housed in flatted industrial premises, where physical conditions restrict or make it impossible for them to construct end-of-pipe treatment installations. Examples of restrictions include the following:

- *Free space*: shortage of free space is common in most SMEs.
- *Headroom*: a low headroom of 3-4 m in most flatted premises means components of an end-of-pipe treatment system must be installed horizontally, requiring additional area.
- *Structural considerations*: large installations in flatted premises having a permissible floor loading of 750 kg/m^2 may not be structurally permissible.

3.3 High Variance in Production and Waste Generation

As SMEs usually operate on a varying pattern and loading of work, the production outputs or even the types of products of most SMEs are not constant over time. Their business level experiences significant fluctuations determined by an array of factors beyond their control. As the generation of waste has a direct relationship with the type and volume of production, these SMEs produce highly varying characteristics and volumes of waste. Thus, it is difficult to install an end-of-pipe treatment system having variable capacity, unless it is designed for a considerable degree of overcapacity, thereby incurring further investment.

4 WASTE MINIMIZATION — A STRATEGY TO SOLVE THE DILEMMA

In view of the pressing environmental controls and the inherent constraints of using end-of-pipe measures, a cost-effective solution is urgently needed for local electroplaters. The solution is obvious and readily available to electroplaters if they can be more open to accept new concepts and changes. These changes may involve substituting less or eliminating toxic chemicals, rationalizing the use of resources, and producing less waste through process, procedural, or product modification, etc. Some illustrations are given in Table 1.

Table 1 Possible Options to Tackle Pollution Problems

Pollution Problem Sources	Appropriate Options
Use of toxic chemicals	• Substituting or eliminating toxic chemicals. Examples include substituting noncyanide-based pretreatment chemicals for cyanide-based formulations, substituting noncyanide zinc for alkaline cyanide zinc, substituting trivalent chromium for hexavalent chromium bath, etc.
Lack of control on conservation of materials	• Exercising proper housekeeping practices to ensure that raw materials are used in a rational manner and as required. • Employing auxiliary devices in process baths to minimize materials loss as far as practicable.
Overconsumption of water	• Exercising proper housekeeping practices to ensure that water is used in a rational manner and as required. • Conversion of the existing inefficient rinsing systems to more efficient rinsing systems. An example is converting a single rinse tank to a multistage counter-current rinse tank. • Installing auxiliary facilities in a rinsing system to facilitate water conservation. An example is installing a flow restricter in the water-in pipe to limit the amount of water supplied to that is needed.

In contrast to end-of-pipe pollution control, waste minimization is a priority option because it can help electroplaters to improve environmental performance and gain economic benefits simultaneously. These benefits are attributed to the following factors :

- Reduced raw material cost;
- Reduced material storage and handling costs;
- Revenue from the sale, reuse, or recycle of wastes;
- Increased production efficiency (productivity);
- Reduced waste treatment, transportation, and disposal costs;
- Reduced health risk to workers;

- Improved product quality; and
- Enhanced corporate image and customer trust.

5 ELECTROPLATERS BENEFIT FROM WASTE MINIMIZATION

Recognizing the importance of motivating industries to adopt waste minimization measures, HKPC has undertaken various activities to make industries aware of the possible benefits and options of waste minimization techniques. Recent initiatives include organizing a wide range of waste minimization seminars, workshops, and conferences; establishing a demonstration factory in Hong Kong; providing waste minimization consultancy services; and producing manuals, videos, and directories as technical guides for various industries. In particular, HKPC has recently undertaken a study to develop waste minimization techniques for electroplating applications. As part of this project, HKPC has developed some cost-effective waste minimization techniques and has successfully pilot-tested these techniques at local factories to assess their feasibility and effectiveness. The positive findings and feedback obtained from the factories demonstrate that adopting waste minimization techniques does not necessarily require sophisticated equipment and substantial capital outlay. The continuous savings associated with the application of these techniques could, on the contrary, far outweigh the relatively modest initial investment. Sections 5.1 and 5.2 describe two categories of waste minimization measures — dragout minimization and water conservation — with examples.

5.1 Dragout Minimization Techniques

Dragout is the solution that is lost from a process bath when workpieces are withdrawn from it. Experience shows that dragout is the most significant source of chemical loss in an electroplating firm. By reducing the quantity of dragout, the amount of waste that requires treatment/disposal can be significantly reduced. Therefore, reducing dragout from a process bath not only saves the cost of replenishing chemicals to compensate loss, but also reduces the wastewater treatment and disposal costs. Many of the dragout minimization techniques involve very simple devices; yet, they can effectively prevent waste generation. Depending on various conditions, such as operating procedure, physical characteristics of process solution, shape of workpieces, etc., different situations require different dragout minimization techniques. Some case examples are given in the following sections.

5.1.1 Case Study 1: Drip Bar at the Pretreatment Process of a Manually Operated Plating Line

In pretreating a manually operated plating line of an imitation jewelry plating firm, cylindrical and perforated steel baskets hold thousands of small metal workpieces for mass cleaning. This operation usually causes a significant volume of dragout because a large amount of process solution is trapped inside the steel basket and consequently causes significant dragout loss if adequate draining time is not allowed. Recognizing the problem, the factory installed a drip bar above each of the pretreatment process baths, where a basket can be temporarily hung on the bar after emerging from the bath. Using these drip bars greatly reduces dragout loss and prevents worker fatigue as well. The cost for the installation of a drip bar is HK$1,000. Our findings show that in one of the pretreatment baths, the savings in chemicals through properly using a drip bar can be up to HK$4,700 per year. The payback period is 3 months.

5.1.2 Case Study 2: Drip Holder at the Pretreatment Process of a Plastic Plating

The factory performs plating on plastic workpieces like plastic combs, houseware, etc. In the pretreatment process, dozens of plastic workpieces are held inside a perforated container formed by tying two similar plastic baskets together, and the container is immersed sequentially in each of the baths for pretreatment. Similar to Case 1, this arrangement usually leads to a significant dragout volume because the solution trapped inside the container cannot be easily drained. A drip bar is not suitable in this case because of the limitation of the strength of the container. Alternatively, the factory installed a series of drip holders that work like a shelf, where the whole container can be placed on it until the draining process is completed. Each drip holder is equipped with a "bridge" directing the collected solution in the drip holder back to the bath to avoid loss. The cost of a drip holder is about HK$1,400. A drip holder installed above the electroless nickel plating bath can save the factory about HK$2,700 per year on electroless nickel plating chemicals. The payback period is 7 months.

5.1.3 Case Study 3: Spray Gun at a Manually Operated Barrel Plating Line

The dragout volume in the barrel plating process is usually much greater than that in the rack plating process. In this case study, the factory performs barrel plating. The nickel plating line of this factory involves a nickel bath operating at an elevated temperature of 58°C, a dragout tank to recover solution, and a rinse station. Despite the use of a dragout tank, dragout loss was serious. To reduce dragout loss, the factory installed a manually operated spray gun near the dragout tank. Every time a barrel is emerged from the dragout tank, the inside of the barrel is thoroughly sprayed with a jet of water from the spray gun to rinse off any trapped solution above the dragout tank. The solution thereby collected is periodically replenished to the nickel bath to avoid loss. The use of a spray gun to reduce dragout loss involves very little cost (less than HK$100). However, it can save the factory HK$2,100 per year in chemical costs, and the payback is essentially immediate.

5.2 Water Conservation Techniques

The objective of rinsing is to remove the residual dragout film adhered on the surface of workpieces. Rinse water makes up the largest volume of waste in a typical electroplating shop and accounts for most of the waste treatment cost. Water conservation must therefore be integrated into the overall waste minimization strategy. Reducing water usage can save money through reduced water and sewage costs, reduced wastewater treatment loading, and increased potential for recovery.

The essential step toward water reuse requires minimizing the fresh water inflow into the rinse by predicting rinse water requirements, so that the corresponding outflow of wastewater can be effectively and economically recycled. If the rinse flow rates are reduced sufficiently, it is possible to use rinse water to make up for evaporative losses in the plating tanks, enhancing metal recovery and reducing waste discharge. In some tests conducted by HKPC, it was observed that some simple and cost-effective techniques can easily reduce water consumption by more than 50%. Below are some case examples.

5.2.1 Case Study 4: Reactive Rinse at the Pretreatment Process

The pretreatment session of a watch plater involves three cleaning steps, namely, soak cleaning, electrocleaning, and acid dip. Next to each step, a rinsing tank is installed. Each rinsing tank was continuously fed with fresh water at a rate exceeding the normal rinsing requirement, even in idle periods. The result was overconsumption of water and generation of an excessive volume of effluent. This situation has been corrected since the introduction of the reactive rinse technique, which is the strategic reuse of rinse water from one rinsing step as the source for another. In this case, the acid rinse water is conducted under gravity to the preceding alkaline electrocleaning rinse tank as the rinse water source. This step not only enables the feed water to the electrocleaning rinse tank to be shut off, but also enhances the rinsing efficiency due to self-neutralization between acid and alkali. The stream of rinse water is further conducted under gravity to the soak cleaning process and reused. No mechanical pumps are required in the transfer of water, as flow is directed by gravity due to differences in water level among the rinsing tanks. To allow better rinsing performance, an air agitation system was also installed to provide the necessary mixing of rinse water in each tank. The system is technically feasible and economically attractive, and the factory can save up to 55% of water in the pretreatment process. This system can save the factory about HK$12,000 per year against the initial investment of HK$10,000. The payback period is only 10 months.

5.2.2 Case Study 5: Conductivity Controlled Rinse at a Manually Operated Plating Line

One of the plating lines of a spectacle frame plater has a total of 10 two-stage counterflow rinsing tanks. Each rinsing tank is continuously fed with fresh water, even during idle periods, at a rate exceeding the normal rinsing requirement. This results in overconsumption of water on one hand,

and generation of an excessive volume of effluent on the other hand. The situation has been modified as a result of the installation of 10 sets of conductivity-controlled water addition devices in respective rinsing tanks. Each device is equipped with a controller, a sensor to detect variation of conductivity of rinsing water, a solenoid valve to control water addition, and an air agitation assembly to thoroughly mix water within each rinsing tank. Conductivity control operates on the principle that fresh water has a lower conductivity than water contaminated with plating solutions. The amount of plating solutions accumulated in each rinsing tank determines the adequacy of rinsing water. Therefore, this device takes advantage of this principle to control the amount and period of water feeding. Normally, the water supply is cut off by the solenoid valve. When the conductivity sensor detects that the conductivity of the rinse water in the tank exceeds a certain setpoint, the controller opens the solenoid valve to add fresh water. Water addition is automatically cut off when the conductivity becomes lower than the precalibrated level. The operation avoids wasting water. The system is technically feasible and economically attractive and can reduce water consumption by 60% in that plating line. This system can save the factory about HK$100,000 per year, with an initial investment of HK$45,000. The payback period is only 6 months.

5.2.3 Case Study 6: Pulse Counterflow Spray System at an Automatic Plating Line

The area where the system is installed is the nickel plating area in the factory's automatic plating line. Nickel plating equipment consists of a nickel bath, a static dragout tank, and a two-stage counterflow rinsing tank. This tank is fed with fresh water and discharged wastewater continuously, while the static dragout tank is essentially a tank filled with water. The solution in the static dragout tank, upon accumulation to a certain level of concentration, is manually replenished to the nickel bath periodically to compensate for dragout and evaporation losses.

To reduce the amount of dragout loss and the quantity of water consumption, the factory installed a pulse counterflow spray system. The lip of each tank has an array of strategically spaced nozzles. Water from each succeeding tank is used as spraying water in the preceding spray rinse stage. With the control of a sensor that detects the movement of the plating racks, spraying of water through these nozzles occurs only when workpieces are withdrawn from the baths. The automatic water spraying action minimizes the amount of loss due to solution carryover. Water is fed only when needed, and the amount of water is optimally calibrated. Furthermore, the system eliminates manual replenishment of dragout solution in the dragout tank to the nickel bath. Spraying of workpieces above the nickel bath also minimizes dragout carryover, thereby reducing chemical loss. Our findings show that the system is technically feasible and economically attractive. The factory can reduce the use of water by 85% and the dragout loss by 70%. This system can save the factory about HK$40,000 per year, with an initial investment of about HK$21,000. The payback period is only 7 months.

6 WHAT ELECTROPLATERS NEED TO DO

The above examples demonstrate that waste minimization options are available to electroplaters. Electroplaters urgently need a commitment to making continual improvements through the adoption of waste minimization measures, rather than continuing under existing situations. They are encouraged to use various opportunities to enhance their waste minimization knowledge. Where possible, electroplaters should use possible channels, such as industry association gatherings, demonstration factory visits, seminars, etc., to share experiences and exchange information on waste minimization. Because most SMEs may not have sufficient financial support for the initial consultancy fees for waste minimization, a "consortium-based approach" in which electroplating firms of similar operation are grouped together to seek consultancy services may be adopted.

Before an effective waste minimization program is established, an important first step is to assess the current operating situations and waste generation pattern in your company. The following assessment procedures can help to identify and adopt the appropriate waste minimization measures for your electroplating firm:

Step 1. Understand the production processes in your plant.

Step 2. Determine the process inputs and outputs.

Step 3. Identify likely improvement areas, where significant material loss occurs or considerable wastes are produced.

Step 4. Quantify, by yourself or with the assistance of external consultants, the amount of material loss or waste produced.

Step 5. Identify potentially useful waste minimization techniques with your technical staff or consultant.

Step 6. Implement the clearest and simplest waste minimization techniques immediately.

Step 7. Evaluate with your consultants the viability of other waste minimization opportunities.

Step 8. Implement an action plan to reduce waste and increase production efficiency.

Step 9. Review and make continual improvements.

7 CONCLUDING REMARKS

With the increasingly stringent environmental requirements and escalating production costs, waste minimization is undoubtedly the most appropriate strategy for coping with environmental issues. A number of simple, yet effective, waste minimization measures are available to electroplaters. As evidenced in the many examples given in this paper, adopting waste minimization measures not only reduces the level of pollution in their operations, but also reaps economic benefits for electroplaters. It is envisaged that adopting waste minimization as part of business practices will eventually evolve as a norm.

PHYSICAL/CHEMICAL/BIOLOGICAL TREATMENT

Chairs: G. Yull Rhee, State University of New York at Albany, USA
Kalsom Abdul Ghani, Department of Environment, Malaysia

ABIOTIC SYSTEMS FOR THE CATALYTIC TREATMENT OF SOLVENT-CONTAMINATED WATER

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ABSTRACT

Three abiotic systems are described that catalyze the reductive dehalogenation of heavily halogenated environmental pollutants, including carbon tetrachloride, trichloroethene, and perchloroethene. These systems include (a) an electrolytic reactor in which the potential on the working electrode (cathode) is fixed by using a potentiostat, (b) a light-driven system consisting of a semiconductor and (covalently attached) macrocycle that can accept light transmitted via an optical fiber, and (c) a light-driven, two-solvent (isopropanol/acetone) system that promotes dehalogenation reactions via an unknown mechanism. Each is capable of accelerating reductive dehalogenation reactions to very high rates under laboratory conditions. Typically, millimolar concentrations of aqueous-phase targets can be dehalogenated in minutes to hours. The description of each system includes the elements of reaction mechanism (to the extent known), typical kinetic data, and a discussion of the feasibility of applying this technology for the in situ destruction of hazardous compounds.

1 INTRODUCTION

Heavily halogenated organic solvents, such as trichloroethylene (TCE), perchloroethylene (tetrachloroethylene, PCE), and carbon tetrachloride (CCl_4) are among the most widespread and persistent contaminants in U.S. soils and groundwaters. These compounds have been in widespread use in the latter half of the twentieth century as solvents, pesticides, herbicides, flame retardants, degreasers, and electrical insulators. Many resist biological transformation, leading to persistence in the environment. Because many halogenated compounds have adverse health effects, they contribute heavily to the U.S. Environmental Protection Agency's (USEPA's) list of priority pollutants. In fact, 13 of the 14 regulated volatile organic chemicals found in the 1986 amendments to the Safe Drinking Water Act are halogenated, and 10 of those 13 would be considered moderately to highly halogenated. Because these compounds degrade slowly under aerobic conditions, if at all, and sluggishly under abiotic conditions in the absence of molecular oxygen, reductive dehalogenation is the treatment of choice for their degradation.

Repeated studies have shown that the oxidized nature of CCl_4, TCE, and PCE generally blocks their participation in further oxidative transformations, including those of both abiotic and biochemical origin. Only a handful of known biochemical pathways initiates the aerobic transformation of TCE via oxygen insertion, for example. Each relies on the activity of a novel oxidase — methane monooxygenase in the methanotrophs (11); propane monooxygenase in *Mycobacterium vaccae JOB5*, a propane-oxidizing bacteria (13); ammonia monooxygenase in *Nitrosomonas europa*; and toluene dioxygenase in *Pseudomonas putida F1* and other select toluene degraders (7). None of these organisms produces biochemically useful energy from these conversion, and, in fact, all may suffer to some degree from the toxicity of reaction intermediates and/or unrepaid investment of metabolic energy to drive the conversion process. As a consequence, it is not possible to envision a selective mechanism that favors competent bacteria (aerobic TCE conversion) under natural conditions, and efforts to promote such cometabolic conversions in the field have proved less successful than originally anticipated.

Reductive processes, including those requiring biochemical catalysis, have proved much more adept at transforming PCE and TCE under field conditions. Most commonly, these contaminants are converted to less halogenated homologues, including (unfortunately) vinyl chloride, a known human carcinogen, and ethylene. Details of the responsible mechanism, which produces the sequential replacement of halogens with hydrogen (hydrogenolysis), are not completely known. A variety of bacterial systems and bacterially produced enzymes can catalyze such reactions, and biochemical catalysis of this type of reaction has been linked to cell respiration by a few facultative anaerobes (8). Unlike those species that promote aryl dehalogenation reactions, however, dehalogenation reactions involving alkyl substituents, e.g., hydrogenolysis of PCE and TCE, have not been linked to the generation of metabolic energy (6). Consequently, selective strategies for the promotion of capable species in field settings are again lacking.

In addition to biochemical catalysis of hydrogenolysis reactions, a number of abiotic reactions can promote contaminant dehalogenations. Reactions involving zero-valence metals, namely,

$$\mathrm{Me(0)} + \mathrm{RX} + \mathrm{H}^{+} \rightarrow \mathrm{ME(II)} + \mathrm{RH} + \mathrm{X}^{-} \ , \qquad (1)$$

have been relied on to prevent pollutant dispersal in several engineered funnel-and-gate systems (2). In those instances, contaminated groundwaters are directed through permeable "gates" in otherwise low-permeability cutoff walls. Elemental iron has been the metal of choice for inclusion in such gates because of its low cost and its reactivity with a number of halogenated targets.

The utility of elemental metals as sources of reductant for dehalogenation reactions was recognized by Gillham (2). Criddle and McCarty (1) and Warren (14) subsequently used metals as cathodes for electrolytic reductive dehalogenations. The advantages of an electrolytic system in this context include (a) independence of the set (cathodic) potential from the standard reduction potential of the metal electrode and (b) lack of associated metal corrosion. The latter feature, i.e., lack of Fe(II) liberation when Fe(0) serves as reductant, can prevent iron oxide deposition and associated fouling of the reactive surface.

A second system for the catalytic dehalogenation of chlorinated solvents that has been investigated at the University of Arizona consists of a semiconductor (TiO_2)–macrocycle (cobalt-tetrasulfophthalocyanine; CoTSP) hybrid. When irradiated with light in the range $\lambda<360$ nm, TiO_2 valence-band electrons are elevated to the conduction band, leaving behind a positively charged hole. The CoTSP macrocycle was covalently attached to the TiO_2 surface in order to minimize electron-hole recombination. In its reduced form, Co(I)TSP is a supernucleophile with an extremely high affinity for heavily halogenated aliphatic compounds like TCE, PCE, and CCl_4. Previous experiments in this system have shown that illumination of the TiO_2 surface results in reduction of the attached macrocycle to the Co(I) state and that addition of a suitable halogenated target (CCl_4, $CHBr_3$, PCE, or TCE) results in target attachment with electron transfer from Co(I) to yield Co(II). A halogen ion is released. Although mechanistic details beyond this point are less certain, it has been hypothesized that a second photon/conduction-band electron produces an aqueous-phase carbanion from the original target, namely,

$$CCl_4 + 2e_{CB}^- \rightarrow CCl_3^- + Cl^- \quad . \tag{2}$$

The overall reaction is then completed via acquisition of an aqueous-phase proton. Alternatively, a short-lived radical is produced via transfer of a single conduction-band electron, which is then extinguished via abstraction of a hydrogen atom. Observed kinetics for the photocatalyzed reaction were exceptionally fast.

In this paper, we describe efforts to develop both an electrolytic and a photocatalytic system that can be applied for the in situ dehalogenation of heavily halogenated groundwater contaminants, including PCE, TCE, and CCl_4. Furthermore, we describe a novel system, based on a mixture of common solvents, the halogenated targets, and light energy for dehalogenation reactions. Prospects for field or commercial applications are explored.

2 ZERO-VALENT METALS

A two-compartment reactor of the type described by Criddle and McCarty (1) was developed for electrolytic experiments (Fig. 1). The pH of the cathodic compartment was controlled by using a pH stat (Brinkmann, 665 Dosimat and 614 Impulsomat). The cathode potential was set by using a potentiostat (The Electrosythesis Co., 410 Potentiostatic Controller). In this manner, reaction energetics were uncoupled from the standard reduction potentials of the various cathode materials. The cathodic and anodic compartments were separated by a Nafion (cation permeable) or sintered glass membrane, and the electrolyte consisted of 0.1 M Na_2SO_4. The anode was composed of 2.0 × 2.5 cm platinum foil. Cathodes were constructed to the same dimension (2.0 × 2.5 cm) from a variety of metals.

Independent variables for these experiments included the set potential and the pH of the cathodic compartment. The initial concentration of halogenated targets was in the range 0.5–0.7 mM. Dependent variables were the time-dependent concentrations of the target compound and the expected products. When CCl_4 was the target, for example, analytical methods were selected for the measurement of each of the less chlorinated homologues including methane. Analyses were conducted via GC/ECD following liquid-phase extraction in pentane or GC/FID (headspace samples only). In a subset of the experiments shown, care was taken to ensure that reported rates represent reaction-limited kinetics, as opposed to mass transfer limitations at the cathode interface or the gas-liquid interface that separated the working solution from the headspace.

Under our experimental conditions, chloroform was the primary product of CCl_4 dechlorination processes. Chloroform can be further reduced to dichloromethane (CH_2Cl_2) and methane (CH_4) (Fig. 2). The distribution of products developed during CCl_4 reduction was metal- and potential-dependent (Table 1); a significant fraction of CCl_4 disappearance was accounted for as CH_4 in experiments conducted using Ni and Cu electrodes. The discovery of multi-carbon molecules (i.e., ethane, ethylene, and propane) among the product species implied that a free radical reaction mechanism contributed to CCl_4 reduction. Since CH_2Cl_2 generally proved unreactive when provided as the aqueous-phase target in other experiments, it is hypothesized that successive reductions including reduction of CH_2Cl_2 occur at the electrode interface, prior to loss of reaction products to the bulk aqueous phase, allowing the less chlorinated homologues, CH_4 and CH_3 Cl, to reach measurable concentrations. A conceptual model is provided in Fig. 2.

CCl_4 dechlorination rates were generally first order with respect to CCl_4 (Fig. 2). The first-order rate constant of CCl_4 reduction again depended on cathode materials and cathode potentials (Fig. 3). Under similar conditions (cathode potential equal to -0.8 V vs. SHE), the order of cathode activity for CCl_4 reduction was Ni > Cu > Co > Fe, Pd > Al. From a series of experiments involving Fe, Cu, and Ni cathodes (Fig. 3), it is evident that, up to the mass-transfer limit of our reactor, reaction rate was dependent on the set cathode potential, as expected from the Butler-Volmer representation of electrode kinetics:

$$i = i_0 \exp(-\alpha n f \eta) \quad , \tag{3}$$

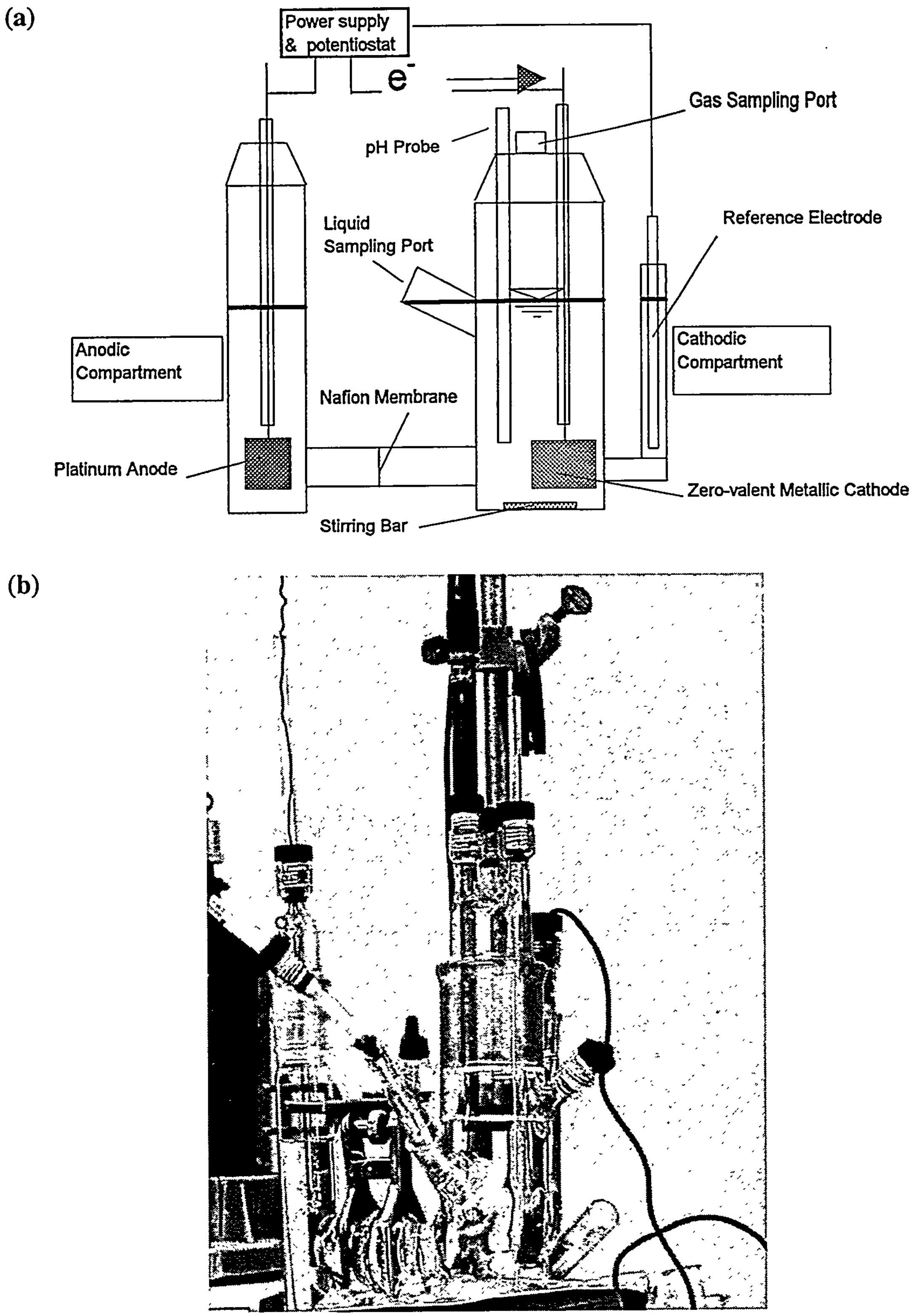

Fig. 1 Two-Compartment Electrolytic Reactor for the Reductive Dehalogenation of Heavily Halogenated Target Pollutants (The cathodic potential is maintained by using a potentiostat and Ag/AgCl reference electrode. The pH of the cathodic compartment is held constant by using a pH stat: (a) reactor schematic; (b) photograph of system components.)

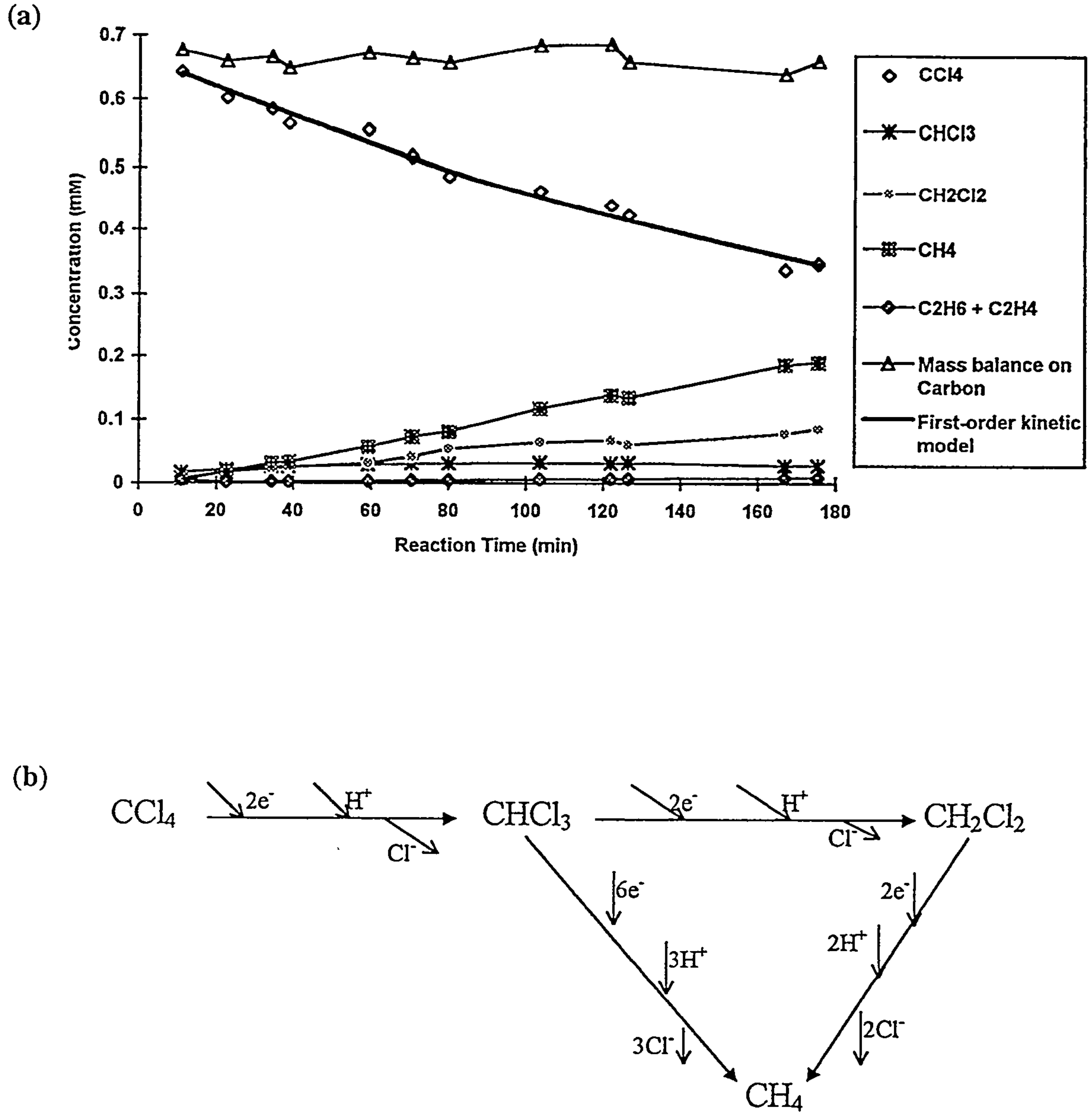

Fig. 2 The Degradation of CCl_4 Using a Nickel Cathode and Fixed Cathode Potential of -1.0 V (vs. SHE); pH 7.0 ((a) Time-dependent concentration of CCl_4 and reaction products. Chloromethane was not detected. The first-order kinetic model was of the form: $d[CCl_4]/dt = -k[CCl_4]$; k was fitted via regression analysis; (b) Conceptual model of primary conversion pathways in zero-valent metal systems, including the nickel cathode used here.)

Table 1 Product Distribution of Carbon Tetrachloride Degradation Processes in the Zero-Valent Metal System

Cathode Electrode	Set Potential vs. SHE (V)	Primary Product	Secondary Products	Experiment Duration (h)	Distribution of products CH_2Cl_2/CH_4
Fe	-0.8	$CHCl_3$	$(CH_2Cl_2)^a$, CH_4	3.5	—
	-1.0	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$	3.5	1/0.58
	-1.2	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8	2.5	1/1.2
Cu	-0.8	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8	3.0	1/0.45
	-1.0	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8,[c]	3.5	1/2.3
	-1.2	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8,[c]	2.2	1/2.1
Ni	-0.8	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8	3.0	1/1.1
	-1.0	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8,[c]	3.5	1/2.6
	-1.2	$CHCl_3$	CH_2Cl_2, CH_4, $C_2H_6/C_2H_4{}^b$, C_3H_8,[c]	2.5	1/2.5
Al	-0.8	$CHCl_3$	$(CH_2Cl_2)^a$, CH_4	5.0	—
	-1.0	$CHCl_3$	$(CH_2Cl_2)^a$, CH_4	4.0	—
Co	-0.8	$CHCl_3$	CH_2Cl_2, CH_4	3.0	1/1.3

[a] Dichloromethane was not detected during the experimental period by GC/FID.

[b] Ethane and ethylene could not be separated by the column (DB-624) used in GC/FID.

[c] More products were detected, but not identified.

where i is current density and is proportional to CCl_4 degradation rate; i_0 is the exchange current density; α is a transfer coefficient; n is the number of electrodes transferred to reactants in the rate determining step; f is a known constant; and η is the overpotential.

The kinetics of these and other electrolysis experiments suggest that electrolytic hydrogenalysis may provide an economical method for promoting the in situ restoration of groundwaters contaminated with CCl_4 (and presumably other heavily halogenated contaminants). Using data for zero-valent iron at a set cathode potential of -1.0 V vs. SHE, and assuming that 1 m^2 is a realistic surface area for a working, field-scale cathode, it should be possible to reduce the concentration of CCl_4 by six orders of magnitude (from parts-per-thousand to parts-per-billion concentrations using reactor detention times on the order of 5 minutes).

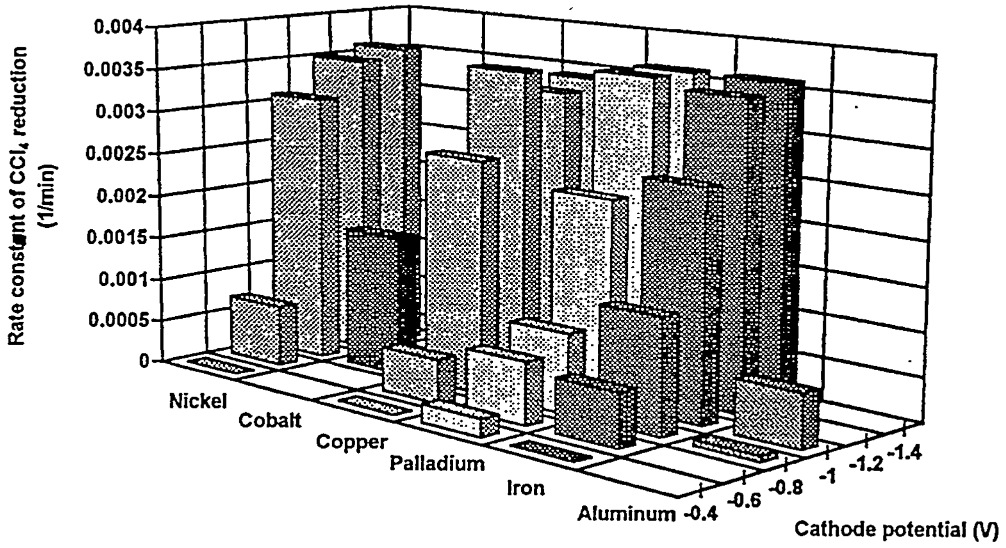

Fig. 3 Summary of First-Order Rate Constants Generated Using a Variety of Cathode Materials and Set (Cathodic) Potentials in the Two-Compartment Electrolytic System (Fig. 1) (Cathode potentials shown are vs. SHE. The highest values shown probably represent mass transport limits of the reactor. The kinetic model used to estimate rate constants was of the form: $d[CCl_4]/dt = -k[CCl_4]$.)

As envisioned, a field of continuous flow, electrolytic reactors would be inserted in well casings at the depth of the contamination. Water would then be withdrawn from the aquifer, treated, and discharged within the overlying vadose zone. Since residuals would not reach the surface, their destruction under aerobic conditions in the vadose zone is a possibility. Otherwise, it is expected that waters containing untreated residuals would return to the unconfined aquifer under the influence of gravity, to be reentrained among waters entering the treatment system. The electrolytic system could then be operated continuously until residuals reach a specified level, or intermittently, acknowledging the roles of contaminant desorption and rebound as limitations to overall mass conversion and aquifer restoration rates. As envisioned, the system is not altogether different than subsurface gas-transfer (stripping) reactors for removal of volatile and semivolatile groundwater contaminants. In both situations, it is not necessary to pump contaminated water to the surface for treatment, and energy savings should be significant.

3 SEMICONDUCTOR-MACROCYCLE HYBRIDS

Since earlier work in our laboratory had already shown the potential of the TiO_2/CoTSP system for rapid dehalogenation of bromoform and a few other heavily halogenated aliphatic compounds, our objective in this work was to illustrate the potential applicability of TiO_2/CoTSP hybrids for in situ remediation of contaminated groundwater. The most obvious problem to be faced is underground delivery of light energy to the semiconductor. To solve this problem, we followed the lead of Peill and Hoffmann (9), who attached TiO_2 particles to the surface of optical fibers to promote the oxidative destruction of chlorophenol using the TiO_2 holes. Light energy was passed with essentially no attenuation to portions of the fiber from which the cladding was removed and replaced with TiO_2 particles. The attached semiconductor can harvest energy via interaction with light as it propagates down the coated portion of the fiber. To date we have shown that light energy, transported and harvested in this fashion, can be used for electron/hole production in attached TiO_2. In essence, we repeated experiments similar to those conducted by Peill and Hoffmann (9) with similar results (Fig. 4). Here we show that attachment of CoTSP to TiO_2 via a silanization/covalent linking procedure (4) leads to reductive dehalogenation of heavily halogenated targets in this (now semiconductor/macrocycle/optical fiber) system. To that end, CCl_4 was added to a reactor containing water, isopropanol (a hole scavenger), and the suitably coated fiber (Fig. 5).

Transmission of light energy in the range $200 < \lambda < 420$ nm produced a noticeable change in the color of the attached CoTSP (blue to white), dehalogenation of CCl_4, and the formation of methane (Fig. 6). We consider this to be proof of concept for the system as a whole. To emphasize this point, we calculated a quantum efficiency for CCl_4 reduction by transmitted light energy defined as

$$\phi = \frac{n \times dCCl_4/dt \times V}{\text{rate of photon transmission}} , \qquad (4)$$

where n is the number of photons required to convert CCl_4 to methane (here assumed to be 4) and V is the reactor volume (50 mL). The rate of photon transmission was determined by actinometry using the ferrioxalate procedure described previously by Rabek (10). Results of the calculation suggest that the overall quantum efficiency for the single-fiber process is on the order of 100. Values in excess of unity indicate a chain-reaction mechanism. It is also evident that dehalogenation of CCl_4, and presumably other heavily halogenated targets, via a light-driven system is a potentially cost-effective methodology.

As envisioned, a similar system for the in situ remediation of contaminated groundwater would consist of bundles of optical fibers, with cladding removed, coated with the TiO_2/macrocycle hybrid at an exposed end that would be extended down a well casing. Contaminated water would be drawn through the bundle and discharged in the overlying vadose zone, per above.

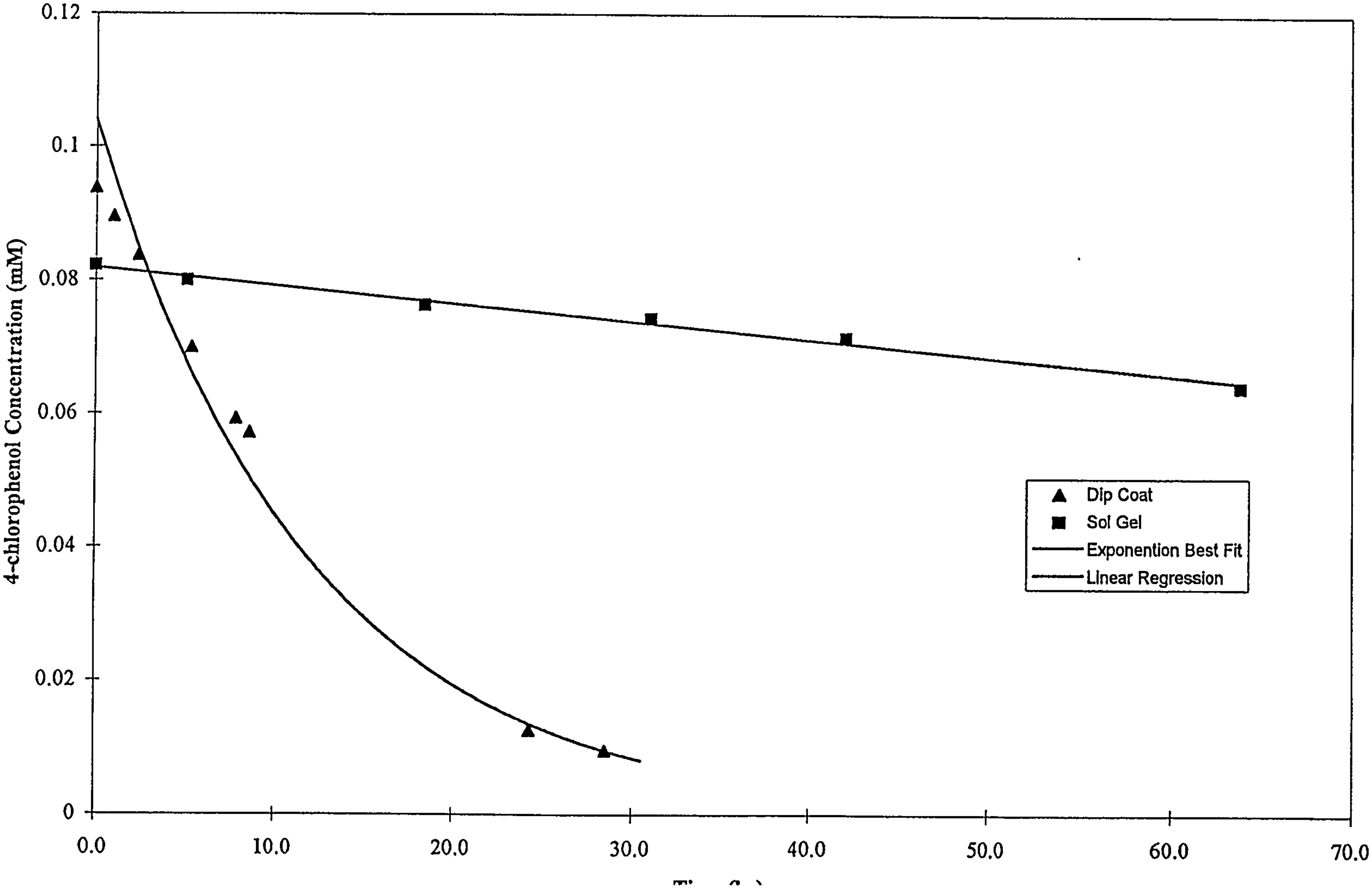

Fig. 4 Oxidative Degradation of 4-Chlorophenol Using an Optical Fiber Coated with TiO_2 (Both a sol gel method (3) and a dip-coating method (9) were used to apply the TiO_2 coating to the naked optical fiber.)

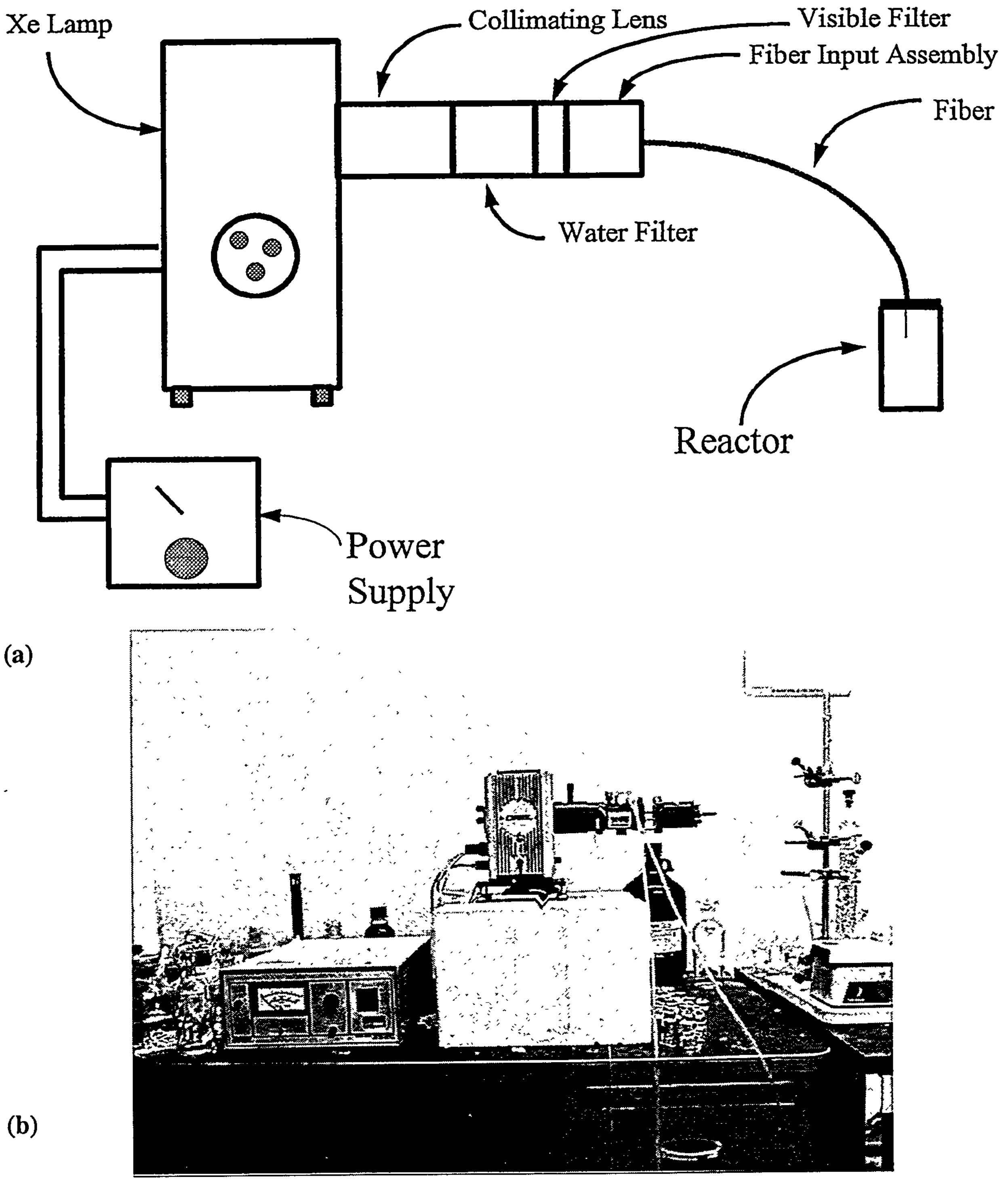

Fig. 5 Components of the Optical Fiber/Semiconductor/Macrocycle System Used in These Experiments (Filters were designed to provide light of wavelengths 200<λ<400 nm. The water filter was jacketed for constant-temperature operation. The length of exposed, coated fiber in the reactor was 10 cm. (a) system schematic; (b) photograph of system components. The system schematic for the two solvent system was identical with the exception of reactor type and exposed fiber length [1 cm].)

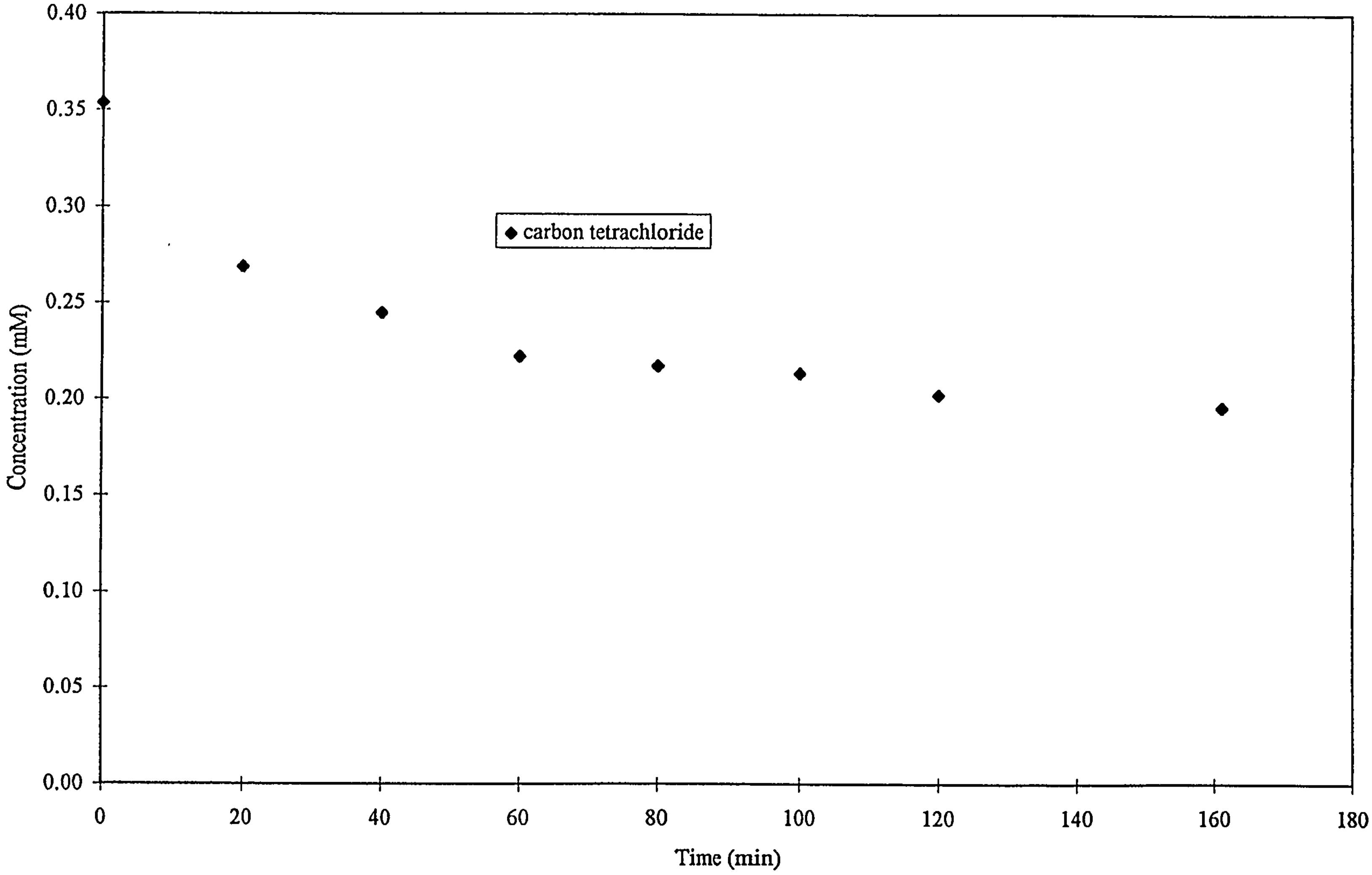

Fig. 6 Reductive Degradation of CCl_4 in the Optical Fiber/TiO_2/CoTSP system (Fig. 5) (Significant quantities of CH_4 were developed over the course of the experiment, although not quantified. No other reaction products were apparent.)

4 TWO-SOLVENT SYSTEM

Finally, related experiments involving alternative dehalogenating systems indicated that CCl_4 can be reduced to $CHCl_3$ and less-chlorinated homologues in a photocatalyzed system consisting of only isopropanol, acetone, and the halogenated target. In general, the system schematic was identical to that shown in Fig. 5, although at times reactor vials were exposed to direct sunlight. Dechlorination reactions were observed in closed glass vials containing CCl_4 in He-purged isopropanol, acetone, and water. When exposed to direct sunlight, the reaction was extremely fast (Fig. 7). In the absence of either isopropanol or acetone (but not water) the reaction was inhibited significantly.

In order to provide better control and a more quantitative understanding of the reaction process, we devised a reactive system that consisted of a xenon light source with band pass and water filters ($200<\lambda<420$ nm), collimating lens and optical fiber, and reactor with reactants (Fig. 5). Subsequent experiments showed that the rate of dechlorination is zero order in the concentration of the target (Fig. 8). Typically, no reaction was observed until residual O_2 was removed from the reactor by extensive purging or (presumably) chemical reduction via a mechanism similar to that of the responsible dehalogenation reaction.

The dependence of reaction rate on the concentrations of acetone and isopropanol is illustrated in Figs. 9 and 10. It is apparent that relatively small amounts of acetone (0.7 mM) can drive the reaction at acceptable (presumably light-source-limited) reaction rates and that there is a power-law relationship between reaction rate and CCl_4 concentration over a broad range of the concentrations tested ($10^{-3.5}$ to $10^{-0.5}$ M). It is also apparent that reaction rate is linearly dependent on the isopropanol concentration over most of the experimental range (0.0 – 9.0 M), although some sort of saturation effect was observed at the top end of the curve.

From these measurements, the acknowledged reactivity of isopropanol with free radicals, and the absorption spectrum of acetone (Fig. 11), the following reaction mechanism is tentatively proposed:

- Initiation reaction

  $$(CH_3)_2\,CO + h\nu \rightarrow (CH_3)_2\,CO^*$$

- Propagation reactions

  $$(CH_3)_2\,CO^* + RX + (CH_3)_2\,CHOH \rightarrow (CH_3)_2\,CO + R^\bullet + (CH_3)_2\,\dot{C}OH + H^+ + X^-$$

  $$(CH_3)_2\,CHOH + R^\bullet \rightarrow RH + (CH_3)_2\,\dot{C}OH$$

- Termination

  $$2(CH_3)_2\,\dot{C}OH \rightarrow (CH_3)_2\,CO + (CH_3)_2\,CHOH$$

$$\text{Overall: } RX + (CH_3)_2\,CHOH \xrightarrow{h\nu,\ \text{acetone}} RH + H^+ + X^- + (CH_3)_2\,CO$$

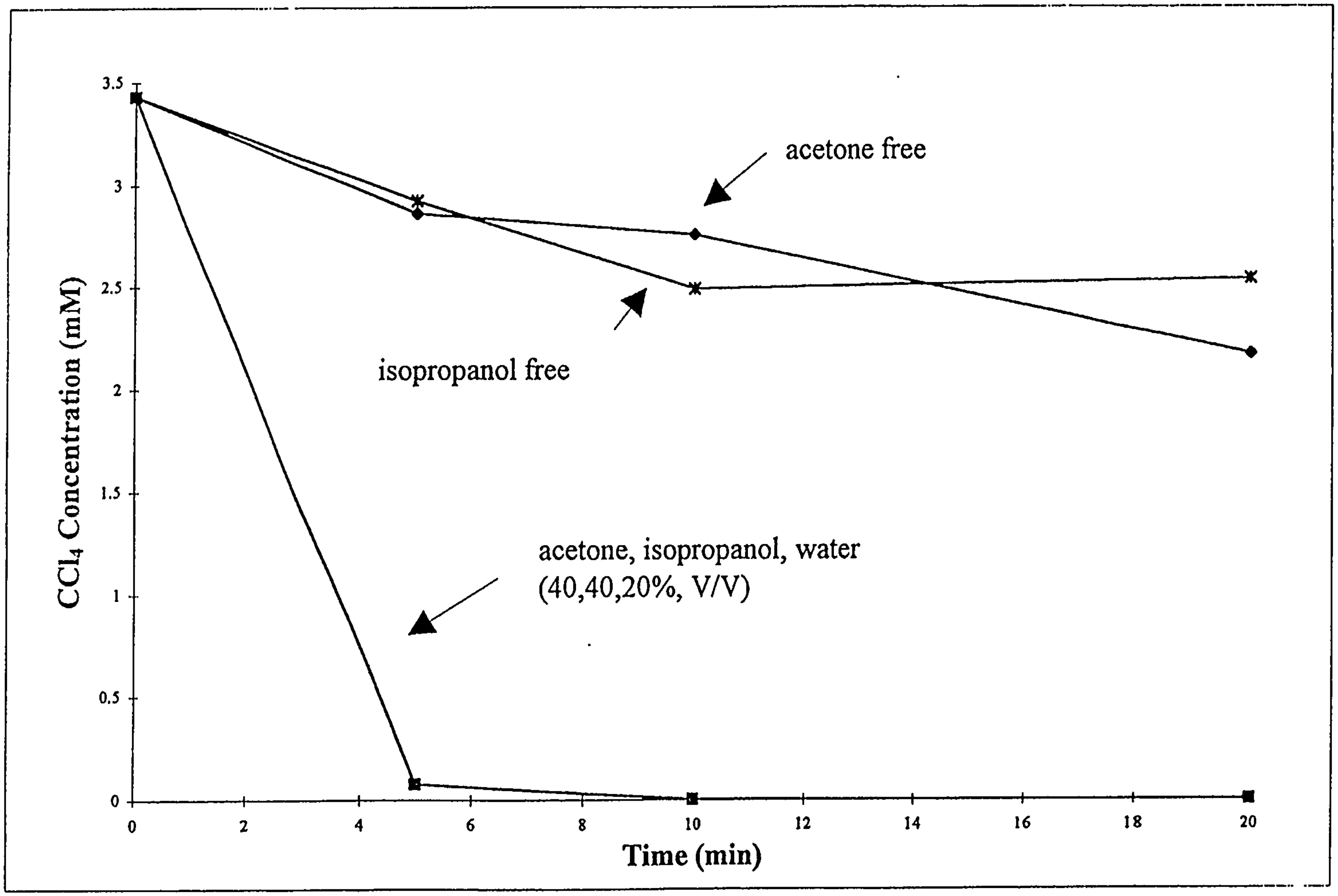

Fig. 7 Degradation of CCl_4 in Reactor Vials Containing Acetone, Isopropanol, and Water in Addition to the Chlorinated Target (The glass vials were exposed to direct sunlight.)

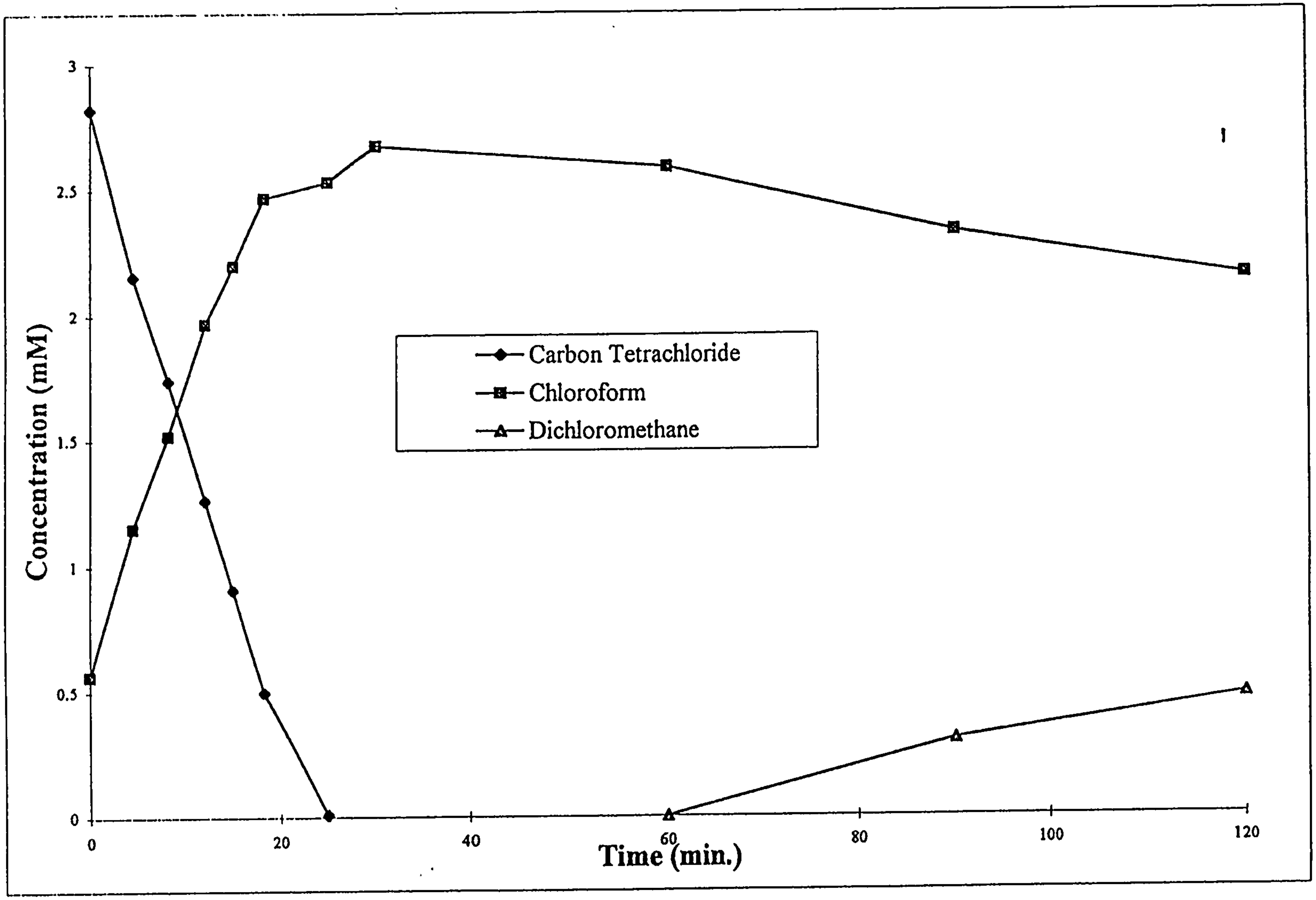

Fig. 8 Time-Dependent Concentrations of CCl_4, $CHCl_3$, and CH_2Cl_2 in a Glass Reactor Containing 3.79 M Isopropanol and 0.691 M Acetone (A xenon lamp was used to initiate the photocatalytic reaction sequence [Fig. 5]. The CCl_4 degradation rate conformed to a zero-order kinetic model.)

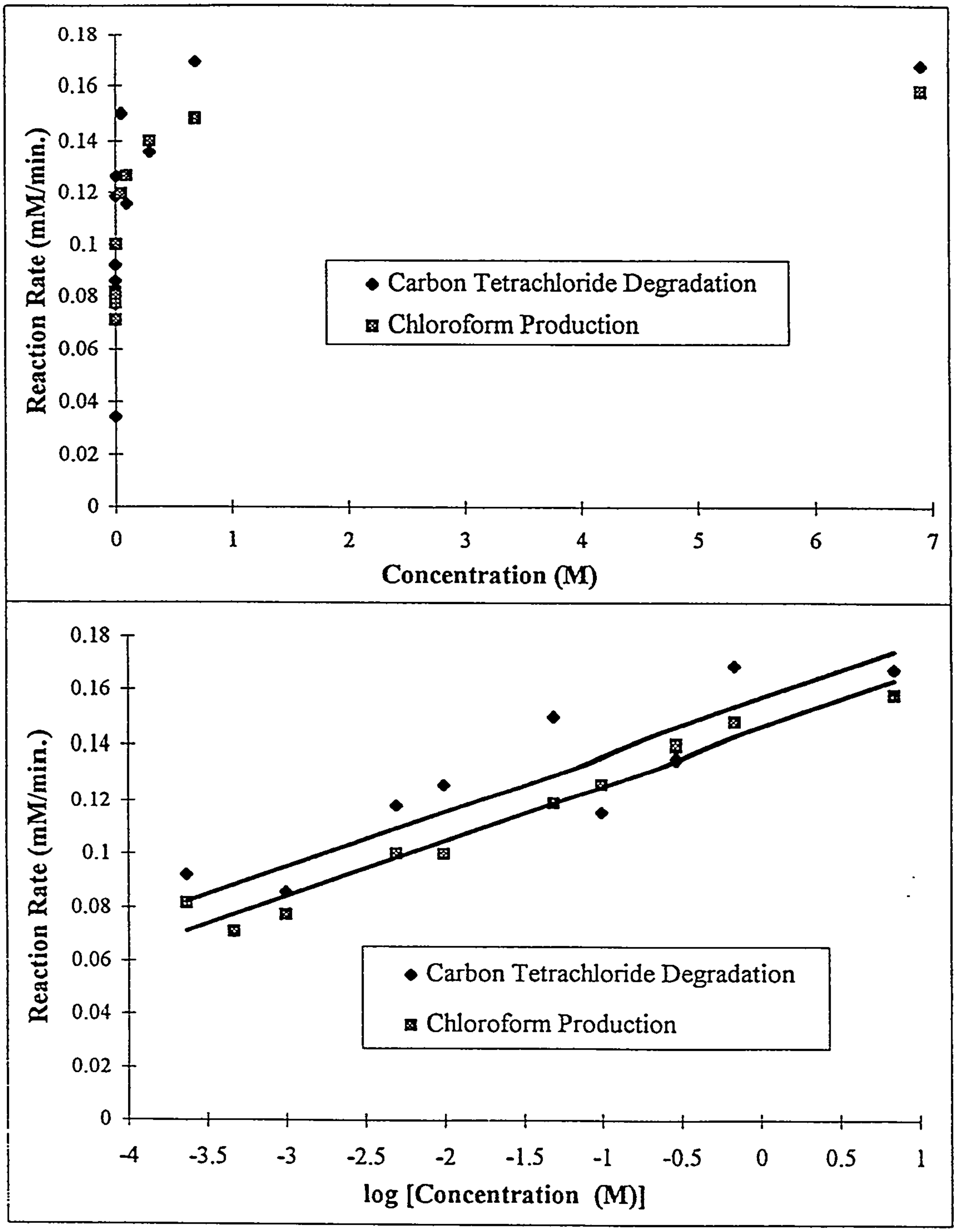

Fig. 9 Dependence of (Zero-Order) Rate of CCl_4 Disappearance on Acetone Concentration in the Range from 0.0 to 6.91 M (Reactor configuration was shown in Fig. 5. Isopropanol concentration was constant at 5.68 M.)

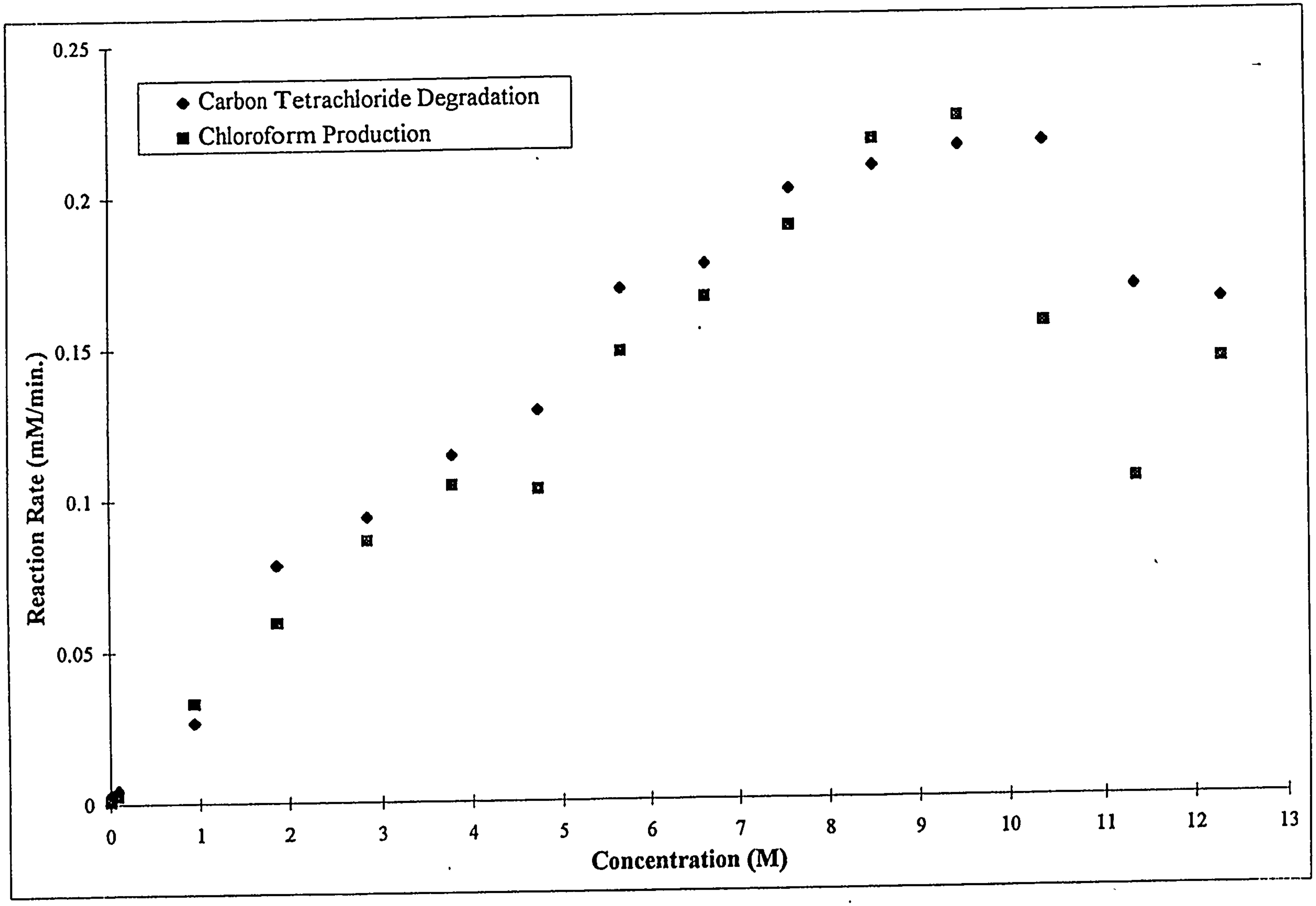

Fig. 10 Dependence of (Zero-Order) Rate of CCl_4 Disappearance on Isopropanol Concentration in the Range from 0.0 to 12.31 M. (Acetone concentration was constant at 0.691 M.)

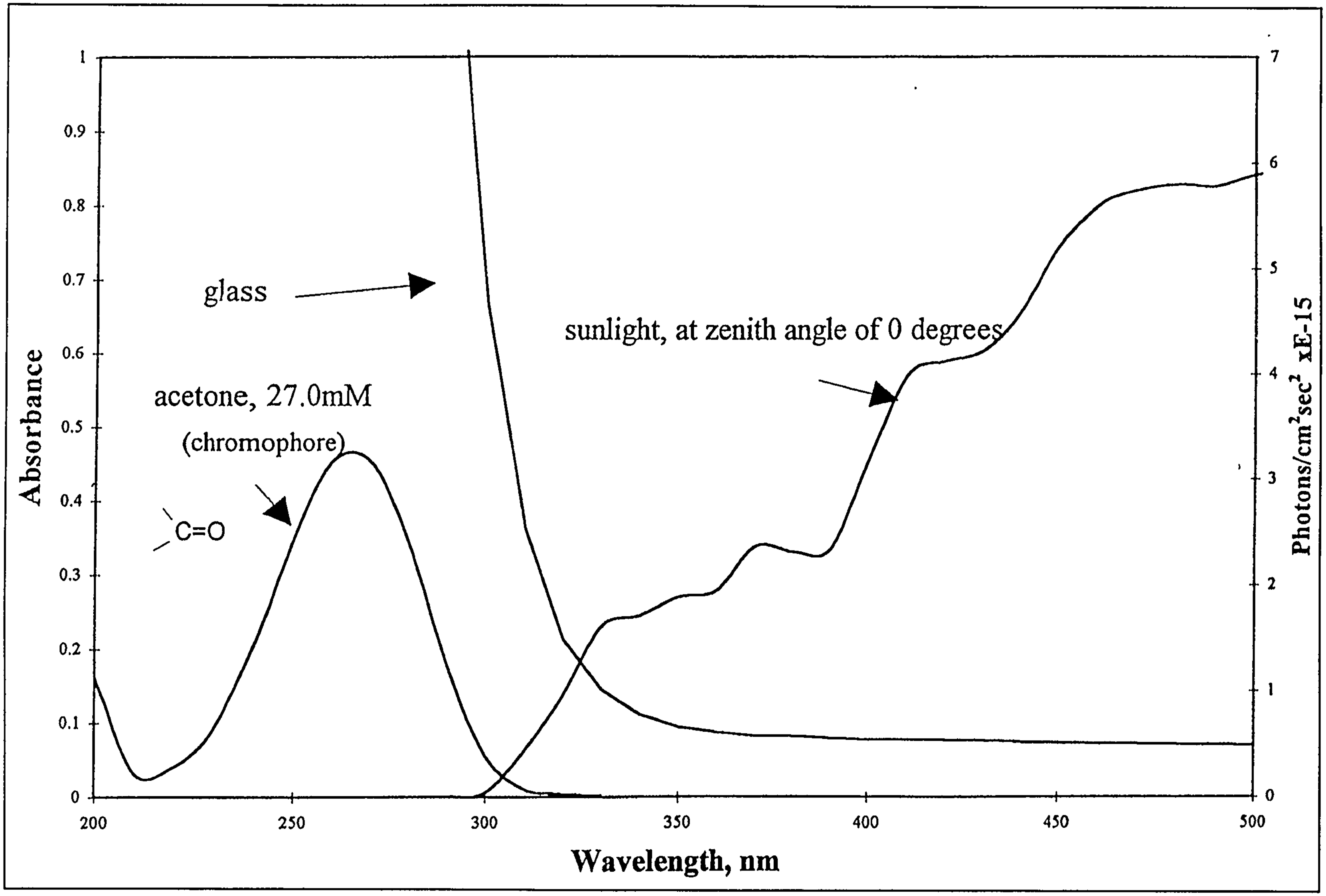

Fig. 11 Sunlight Irradiance and Wavelength-Dependent Light Absorbance by Glass and 27 mM Acetone in water (Data suggest that only a small fraction of incident sunlight is absorbed by acetone in the experiments. Acetone absorbs light primarily in the region 210–310 nm, with a peak absorbance near 260 nm.)

The reaction is initiated by absorption of a photon to yield an excited acetone molecule $(CH_3)_2\,CO^*$, which is thermalized by subsequent reaction with isopropanol and RX. The proposed mechanism accounts, in a general way, for the observed reaction kinetics; that is, the zero-order dependence of rate on CCl_4 would result if the observed reaction rate were dependent on the flux of light of suitable wavelengths to the reactor, and the mechanism acknowledges the general dependence of rate on solvent concentrations.

Assuming the zero-order dependence arises from light limitation, it is possible to calculate a quantum efficiency for CCl_4 and other target dehalogenations. Such calculations were carried out assuming that only photon sorption by acetone can initiate the reaction. Other necessary inputs (beyond the acetone sorption spectrum) included the energy distribution characteristics of the xenon arc lamp in the range of acetone sorption and the total output of light energy in the range $200<\lambda<420$ nm after transmission through the optical fiber. On that basis, quantum efficiencies for CCl_4 dehalogenation between 12 and 13 (molecules converted/photons absorbed) for systems with greater than 0.1 M acetone and 5.68 M isopropanol were rather crudely estimated. Again, values greater than 1.0 suggest that a chain mechanism is responsible for the dehalogenation of CCl_4. Table 2 summarizes quantum efficiencies and reaction rates for other chlorinated targets with acetone concentrations greater than 0.691 M and isopropanol concentrations of 7.60 M. Comparable data for $CHCl_3$ are not available, but observations reveal very slow degradation rates relative to the other chlorinated aliphatics shown.

From Fig. 11, it appears that the component of sunlight that (a) passes through the atmosphere and glass and (b) interacts with acetone is small in comparison to the entire spectrum of the sun's energy. The kinetics of CCl_4 dehalogenation in sunlight (Fig. 7) are all the more impressive.

Table 2 Summary of Reaction Rates and Quantum Efficiencies for Various Targets

Name of Compound	Reaction Rates (mM/min)	Quantum Efficiency (molecules reacted/ photons absorbed)
Carbon tetrachloride (CCl_4)	0.2012	13.2
Pentachloroethane (C_2HCl_5)	0.0625	5.1
1,1,2,2-Tetrachloroethane ($C_2H_2Cl_4$)	No degradation	N/A
1,1,1-Trichloroethane ($C_2H_3Cl_3$)	0.0353	2.9
1,1-Dichloroethane and 1,2-Dichloroethane ($C_2H_4Cl_2$)	No degradation	N/A
Tetrachlorethene (C_2Cl_4)	0.0378	3.1
Trichloroethene (C_2HCl_3)	0.0532	4.3

It is envisioned that a two-solvent system of the type described can be used for disposal or remediation of chlorinated contaminants. For contaminant disposal, or at least conversion to less halogenated forms that are more amenable to alternative treatments, the targets would be added directly to the two-solvent system and irradiated with light. Residuals would be extracted for disposal or further treatment after dehalogenation reactions reached their conclusion or became unacceptably slow. Application within in situ remediation schemes will depend on adequate separation of clean water from the solvents after treatment has occurred. Recent and/or future improvements in membrane separation technologies may eventually support such a treatment scheme.

5 ACKNOWLEDGMENT

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TRAPPING RADIODINE, IN THE FORM OF METHYL IODIDE, ON NUCLEAR CARBON

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ABSTRACT

Studies have been performed on potassium-iodide-impregnated charcoals of the type used in the nuclear industry for trapping radioiodine released during nuclear fission. The effects of various parameters on the trapping efficiency of methyl iodide have been investigated. A variation in particle size within a bulk charcoal caused poor precision in K value measurements because of differences in surface area, pore volume, and bed density, leading to differences in the deposition of the impregnant. Precision is improved by sieving the charcoal to a narrower size because smaller particles have a higher porosity. This finding is supported by surface area and pore measurements. Two methods of impregnation are compared by measuring K values and the deposition of potassium iodide. Charcoal impregnated by rotary evaporation exhibits both higher K values and higher potassium iodide contents than sprayed charcoal. Two designs of spraying drum are compared: a drum with helical vanes allows more efficient deposition and more uniform distribution of impregnant than a drum with axial vanes. A decrease in the K value with increasing humidity correlates with the available surface area. A similar correlation exists between water content and available pore volume. Aging of potassium-iodide-impregnated charcoal, caused by the formation of oxygen complexes on the surface, is associated with significant falls in K value. K values of charcoals also can be restored to at least their original values by heat treatment in the absence of air.

1 INTRODUCTION

Impregnated activated carbons are placed in the filters of nuclear facilities for trapping one of the major fission products, radioiodine. Potassium iodide or triethylenediamine or both are commonly used as impregnants. Activated carbon comes from either coal or coconut shell; coal carbon normally performs better for both impregnants (1).

Each nuclear carbon has a different efficiency for trapping radioiodine. The efficiency can be measured by dosing methyl iodide (I-131), the most difficult form of radioiodine to be removed (2), on a carbon bed sample and measuring the fraction of radioiodine that penetrates the bed. The fractional penetration obtained is usually converted to K value parameter $K = \log_{10}$ (1/FT /stay time), which is a figure of merit (3).

At Liverpool, K value testing of commercial nuclear carbon has been carried out since 1984. From 1984 to 1990, duplicate K values often showed poor precision (Fig. 1). Examination of these test data for the six-year period revealed that the two highest K values recorded (17.9 and 14.7 s^{-1}, respectively) were for charcoal samples in the particle size range 18-52 BSS (British Standard Sieve). Most of the other samples tested consisted of particles within the size range 6-12 BSS, exhibiting K values of between 4 and 12 s^{-1}. Therefore, the variation of particle size within a bulk sample was suspected of being one of the causes of poor precision in K value measurement.

To test this hypothesis, the effect of particle size on the K values of standard charcoal and a commercial sample was studied by grading the charcoals to narrower sizes. K values and other parameters, such as bed density, saturation water content, and level of potassium iodide impregnations, were measured for each charcoal size range and for the bulk charcoals. Also, the effect of particle size on various chemical and physical parameters of the base standard charcoal was studied. These parameters are iodine number, carbon tetrachloride value, surface area, and pore volume.

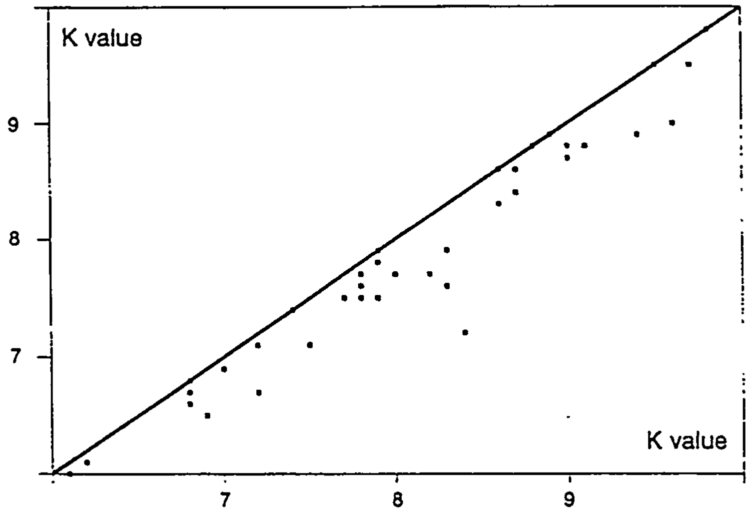

Fig. 1 Relationship between Duplicate K Value for Potassium Charcoals with 6<K<10 Measured between January 1990 and August 1991

An impregnated activated charcoal ages because of surface oxidation, especially in moist air. The oxygen complexes formed during aging reduce the radioiodine trapping efficiency (4, 5). In the present work, K value measurements with particle sizing were repeated on some aged samples archived at Liverpool JM University. Heat treatment of aged samples aids in the reproductivity of the K value.

2 EXPERIMENTAL DETAILS

The rigs for humidification and dosing of impregnated carbon samples and for the in situ preparation of methyl iodide (I-131) have been used to carry out a K value test at Liverpool JM University (formerly Liverpool Polytechnic) for a number of years and have already been described (3, 7). Radioactivities were measured by a Nuclear Enterprises ST6 scintillation counter fitted with NaI/T1 crystal. Iodine-131 as carrier-free iodide (Amersham International) was supplied at a specific activity of 2 mCi mi^{-1}.

2.1 Effect of Particle Size on K Value

The standard activated charcoal of the type 207A, supplied by Sutcliffe Speakman, with a nominal particle size of 8-12 BSS (or 2.0-1.4 mm aperture) was first dry sieved into six fractions, namely, 5–6, 6–8, 8–10, 10–12, 12–14, and >14 BSS. The four central fractions were then impregnated with 1.5% potassium iodide by spraying in a drum with two axial vanes (8). Single measurements of K value, saturation water content, and bed density were made on each de-dusted fraction.

Similar measurements were carried out on a commercial charcoal sample (C 0365) impregnated at Sutcliffe Speakman plant with potassium iodide to a nominal 1.5% . The sample was of type 207B and was described for marketing as having a size range 5–8 BSS. The sample was sieved into five fractions of <5, 5–7, 7–8, 8–10, and >10 BSS, and the potassium iodide content was determined for each fraction by potassium hydroxide extraction followed by flow injection analysis (8).

2.2 Effect of Particle Size on Some Parameters of a Standard Base Charcoal

Approximately 100 g of the standard activated charcoal was dry sieved into fractions of four particle size ranges, 6–8, 8–10, 10–12, and 12–14 BSS. Iodine numbers were determined titrimetrically (9), and carbon tetrachloride uptakes (10) were determined gravimetrically on each fraction at Liverpool. Specific surface areas were determined by nitrogen adsorption, and specific pore volumes were determined by nitrogen adsorption (micropores) and mercury porosimetry (meso- and macropores) at the Sutcliffe Speakman laboratories by using an Omnisorp 100 and a Carlo Erba instrument.

2.3 Comparisons between Sprayed and Rotary Evaporated Samples in K Value and Potassium Iodide Content

Four 100-g batches of standard bulk charcoal were impregnated with potassium iodide to a nominal level of 1.5%. Two of these batches were impregnated by spraying with 20 cm^3 of 7.5% potassium iodide solution and the other two by rotary evaporation of 150 cm^3 of 1% solution (8). After drying in an oven overnight at 110°C, one batch of spray-impregnated charcoal was sieved to produce two main fractions with particle size ranges of 8–10 and 10–12 BSS, respectively. One batch of the charcoal impregnated by rotary evaporation was similarly sieved. The six types of potassium-iodide-impregnated charcoal produced are:

- Sprayed bulk sample,
- Rotary evaporated bulk sample,
- Sprayed 8–10 BSS sample,
- Rotary evaporated 8–10 BSS sample,
- Sprayed 10–12 BSS sample, and
- Rotary evaporated 10–12 BSS sample.

Replicate K value determinations were carried out on each of the six types over a period of four days. Bed densities and saturation water contents were measured in the course of those determinations. Also, the potassium iodide contents of all the sieved samples were determined by flow injection analysis (8).

2.4 Aging

K values of two aged samples commercially produced by Sutcliffe Speakman and archived at Liverpool for 4 and 6 years, namely, LKV 11 and L8 850L, respectively, were measured on their bulks and sieved samples, with the size ranges of 8–10 and 10–12 BSS. The K values of fresh and aged samples were then compared.

3 RESULTS

3.1 Effect of Particle Size

The K values, saturation water contents, and bed densities determined on each fraction of the standard impregnated charcoal samples are shown in Fig. 2.

The data show that (1) the K value increases with decreasing particle size over the size range 6–12 BSS and (2) the saturation water content decreases with increasing particle size and the bed density increases with increasing particle size.

The effects of particle size obtained from the commercial sample are shown in Table 1 and in Fig. 3 and confirm the results obtained from the standard charcoal. In addition, flow injection analysis of the five fractions reveal that potassium iodide content decreases with increasing particle size.

Parameters that indicate the porosity of a charcoal — namely, iodine number, carbon tetrachloride uptake (CTC value), specific surface area, and specific pore volume — were measured on four standard charcoal fractions of different particle size ranges. The results are displayed in Figs. 4a and 4b.

In the comparisons of K value and potassium iodide content between sprayed and rotary evaporated samples, replicate K values of bulk samples and sieved fractions of charcoal impregnated by either spraying or rotary evaporation are shown in Fig. 5.

3.2 Effect of Aging

K values of two commercial bulk samples previously tested were plotted against theft K value results measured for their bulk and sieved samples after aging (Fig. 6). It can be seen that methyl iodide trapping efficiency decreases with time and that particle sizing of the aged charcoal shows that the variation of K value with particle size is retained after aging.

4 DISCUSSION

The increasing of bed density with increasing particle size found in both standard and commercial charcoals was unexpected, and the following explanation for it is advanced. The packing in a charcoal bed for the K value test approximates to the packing of an infinite bed because the charcoal particles are small compared to the size of the bed. If the particles are considered to be uniform spheres, packed in an infinite bed, the void space is independent of the particle radius (11). It follows

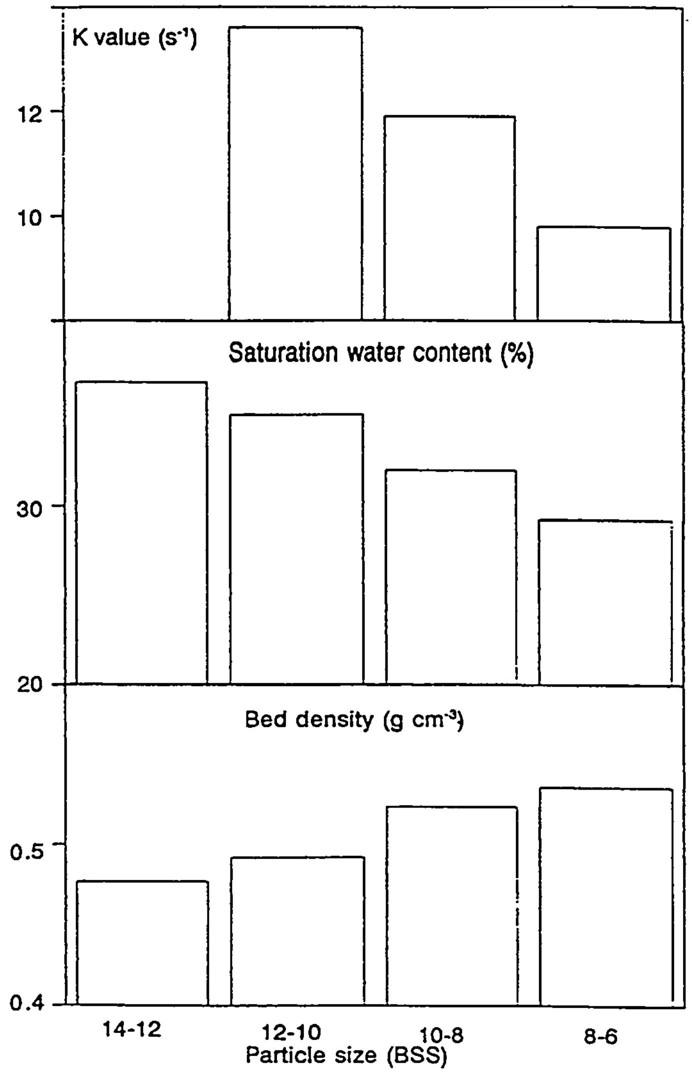

Fig. 2 Effect of Particle Size on K Value, Saturation Water Content, and Bed Density of a Standard Charcoal Impregnated by Spraying with 1.5% Potassium Iodide

that the bed density should be independent of particle size. The results obtained therefore imply that the increase in bed densities with increasing particle size must be due to an increase in the intrinsic density of charcoals. This can be confirmed by data (iodine number, carbon tetrachloride uptake, specific surface area, and specific pore volume) obtained from standard base charcoal fractions (Figs. 4a and 4b).

Table 1 K Value, Saturation Water Contents, Bed Densities, and Potassium Iodine Contents of Different Particle Size Ranges of a Commercial Charcoal C0365

Fraction	Aperture (mm)	BSS	Percent of Total Sample	K Value Day 1	K Value Day 2	Saturation H_2O Content (%) Day 1	Saturation H_2O Content (%) Day 2	Bed Density (g cm^{-1})	KI (%)
1	>3.35	<5	0.7	-	-	-	-	-	0.64
2	3.35-2.36	5-7	33.8	6.0	5.8	30.7	31.5	0.553	1.06
3	2.36-2.00	7-8	37.7	7.2	7.2	32.6	33.4	0.527	1.16
4	2.00-1.70	8-10	17.1	8.9	8.9	33.4	34.1	-0.515	1.56
5	<1.70	>10	10.8	-	-	-	-	-	3.00
Total	-	-	-	6.9	7.2	32.7	-	-	-

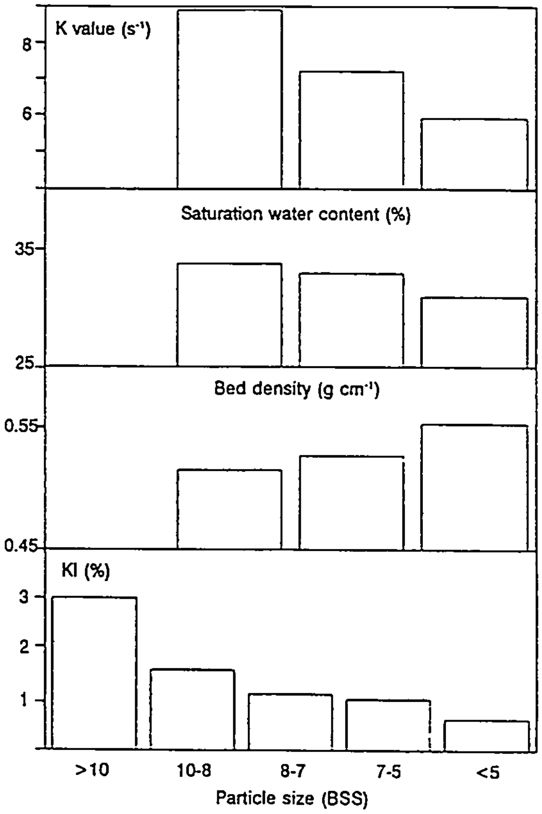

Fig. 3 Effect of Particle Size on K Value, Saturation Water Content, Bed Density, and KI Content of a Commercial Charcoal Sample

The results displayed in Figs. 4a and 4b clearly demonstrate that porosity of activated charcoal particles from a particular batch increases with decreasing particle size. The most probable explanation for charcoal porosity to be decreased with increasing particle size is that in the activation process, particles of various sizes fall by gravity through a heating zone; the time spent by all particles in the zone is the same, irrespective of size. Under these conditions, the porosity in a single particle would vary inversely with depth, and larger particles would therefore have a lower average porosity than smaller ones.

K value, saturation water content, and deposited potassium iodide all vary inversely with particle size. As size increases, charcoal becomes more dense (less porous); therefore, fewer sites are available for the sorption of potassium iodide on the surface of base charcoal and for the trapping of radioiodine, in the form of methyl iodide, and the sorption of water on the surface of impregnated charcoal.

A comparison between sprayed and rotary evaporated samples in K value and potassium iodide content is one example of the effect of particle size. The results obtained from the bulk charcoal shown in Fig. 5a are imprecise and inconclusive due to the variation in particle size within the charcoal, which causes the portions taken for K value measurement to be nonrepresentative. No meaningful comparison between the two methods of impregnation could be made on the basis of these results. But the K value results for the sieved fractions in Fig. 5b show clearly that the performance of the charcoal after impregnation by rotary evaporation is better than its performance after impregnation by spraying.

The data indicate that in a particular size range, rotary-evaporated samples exhibit both a higher K value and a higher potassium iodide content than corresponding sprayed samples. Therefore, there is a correlation between the K value and the amount of potassium iodide deposited onto a charcoal surface. The results indicate that charcoal impregnated by rotary evaporation performs better than the same charcoal impregnated by spraying, because there is more impregnant available on the surface of charcoal impregnated by rotary evaporation than on the surface of spray-impregnated charcoal. The better performance of rotary-evaporated charcoal can also be due to the fuller penetration of the pore structure under reduced pressure. By contrast, the deposition of sprayed potassium iodide onto a charcoal surface is more superficial. The results also indicate that there is very little less of potassium iodide during impregnation by rotary evaporation than there is during impregnation by spraying. During spraying, some loss of potassium iodide must occur at the aperture and on the wall of the drum.

The results imply that rotary evaporation is the better method of impregnation. However, the spray-impregnation method used industrially for the production of commercial charcoal may be more efficient than the spray-impregnation method used in the laboratories at Liverpool and Leigh.

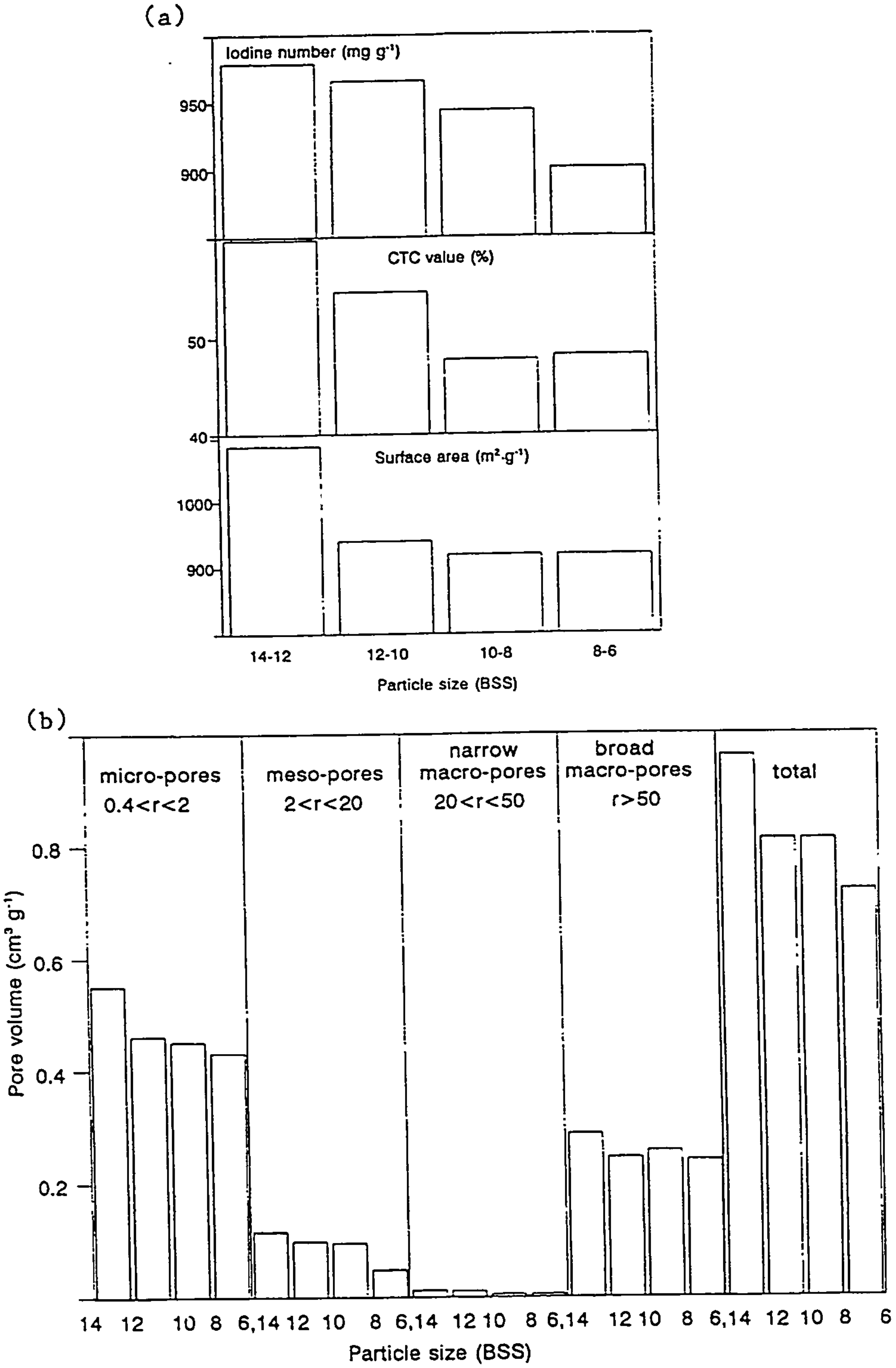

Fig. 4 Effect of Particle Size on Parameters of a Standard Activated Charcoal for (a) Iodine Number, CTC Value, and Surface Area and (b) Specific Pore Value (Radius r in nanometers)

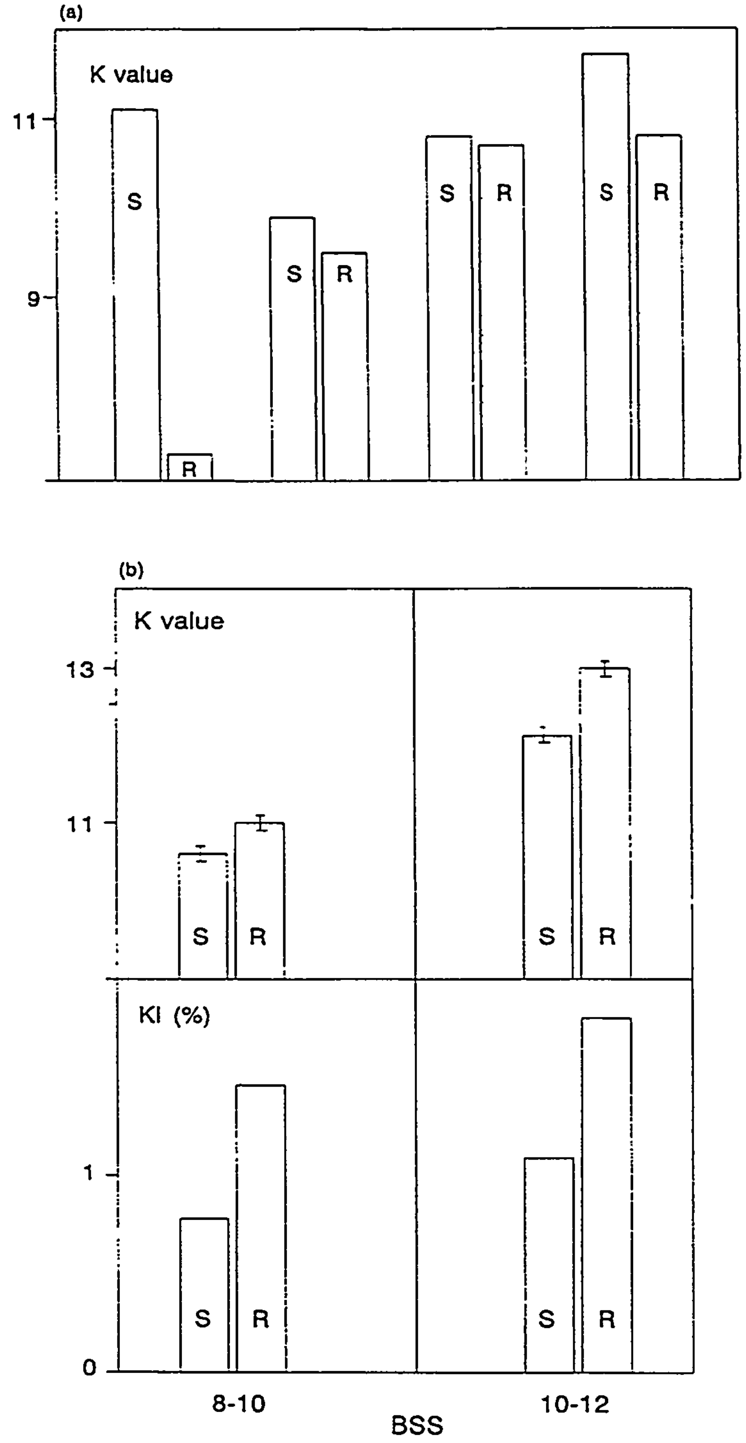

Fig. 5(a) Replicate K Values Obtained from a Bulk Standard Charcoal Impregnated by Spraying (S) or by Rotary Evaporation (R) and (b) Comparison between K Value and KI Contents of Sprayed and Rotary-Evaporated Samples in Two Particle Size Ranges

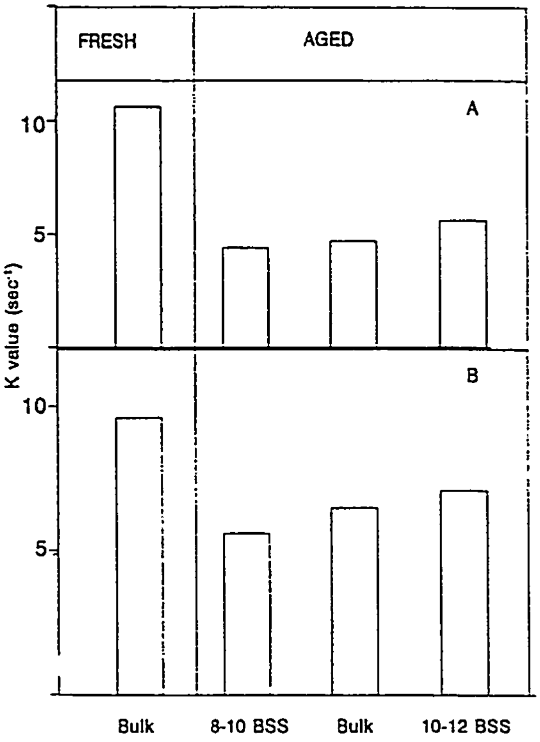

Fig. 6 K Values of Fresh and Aged Charcoals Aged for (a) Four Years and (b) Six Years

The results in Fig. 5b also confirm the results obtained from the commercial sample C0365 (Fig. 3), namely, that K value and potassium iodide content both decrease with increasing particle size.

Because particle size has a significant effect on parameters that govern the K value, precise K values can be obtained only if test samples are representative or if all the particles lie within a narrow size range. Therefore, the quality assurance of potassium-iodide-impregnated charcoals can be improved by reducing the particle size range of the product. It is highly likely that a similar improvement in quality assurance could be achieved for triethylenediamine-impregnated charcoals.

K value results remeasured on bulk and sieved samples, LKV 11 (4 years) and L8 850L (6 years), were plotted in Fig. 6 against their previous K values measured on fresh bulk samples. It is found that (1) aging over about five years causes a substantial reduction in K value and (2) particle sizing of the aged charcoal shows that the variation of K value with particle size is retained after aging.

The K value falls with age because oxygen complexes from on carbon surfaces when air and water vapor are present for long periods (4, 5). No significant decrease of iodide content of impregnated carbon occurs with time (12), so the oxide groups formed must occupy sites that were free when the impregnated charcoal was fresh, or the migration of methyl iodide to iodide sites where exchange may take place, or both. Evidence shows that the oxide groups are destroyed by heating the aged carbon in an inert atmosphere; the sorbed oxygen is desorbed as carbon dioxide at about 220°C and 600°C and as CO above 760°C, indicating that at least two types of oxygen groups are formed. It follows that it is possible to restore the K value of aged potassium-iodide-impregnated charcoal by heat treatment. Some regeneration experiments have already been carried out at Sutcliffe Speakman but are proprietary.

5 ACKNOWLEDGMENT

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DECONTAMINATION OF CESIUM, STRONTIUM, AND COBALT FROM AQUEOUS SOLUTIONS BY BENTONITE

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ABSTRACT

Sorption studies of cesium, strontium, and cobalt (Cs, Sr, and Co) on bentonite under various experimental conditions, such as contact time, pH, sorbent and sorbate concentration, and temperature, have been performed. The sorption data for all these metals have been interpreted in terms of Freundlich, Langmuir, and Dubinin-Radushkevich equations. Thermodynamics parameters, such as heat of sorption ΔH°, free energy change ΔG°, and entropy change ΔS°, for the sorption of these metals on bentonite have been calculated. The value of ΔH° shows that the sorption of Cs was exothermic, while the sorption of Sr and Co on bentonite were endothermic in nature. The value of ΔG° for their sorption was negative, showing the spontaneity of the process. The maximum loading capacity of Cs, Sr, and Co were 75.5, 22, and 27.5 meq, respectively, for 100 g of bentonite. The mean free energy E of Cs, Sr, and Co sorption on bentonite was 14.5, 9, and 7.7 kJ/mol, respectively. The value of E indicates that ion exchange may be the predominant mode of sorption for these radionuclides. The desorption studies with 0.01 M $CaCl_2$ and groundwater at low-metal loading on bentonite showed that about 95% of Cs, 85–90% of Sr, and 97% of Co were irreversibly sorbed. Bentonite could be effectively used for the decontamination of wastewater effluent containing low concentrations of radioactive nuclides of Cs, Sr, and Co.

1 INTRODUCTION

At present, Pakistan has a few nuclear facilities. Because of the energy shortage, the country has planned to construct more power generating nuclear reactors and other allied facilities. The fissioning of uranium in a nuclear reactor produces numerous fission products having varying half-lives. Their percentage yield depends on the mode of fission under specific nuclear reactor conditions. As the process of fission continues, more and more fission products are produced and accumulate. After some time, the fissioning efficiency of the nuclear fuel, because of the accumulation of fission products, becomes low and requires reprocessing. The spent fuel is processed generally by using solvent extraction procedures to separate the unused uranium from the fission products, nuclides formed through nuclear reactions, and their decay products. The chemical processing of nuclear fuel yield radioactive waste.

Radionuclides of Cs and Sr, because of their greater yield in the nuclear fission process and longer half-lives, are among the most hazardous radionuclides in the nuclear waste. Cobalt-60 is formed in a nuclear reactor by (n-γ) reaction and can also be present in the waste water effluents.

For nuclear waste management, an understanding of the sorption behavior of long-lived radioisotopes on various geological formations, rocks, minerals, and clays is essential [1-4].

To evaluate the feasibility of using some local soils and clays as decontaminants for low-level radioactive wastewater effluents containing metallic pollutants, the sorption of Ce, Sr, and Co from aqueous solutions has been studied on local bentonite under various experimental conditions, i.e., contact time, pH, sorbent and sorbate concentration, and temperature. Sorption data in terms of distribution coefficients (K_d) and percentage sorption have been interpreted in terms of Freundlich, Langmuir, and Dubinin-Radushkevich equations. Various thermodynamic parameters, mean free energy of sorption, and sorption capacity of the bentonite for each metal have been determined. Desorption experiments were also carried out to determine the mechanism of sorption. Based on the experimental data, the conditions for the decontamination of wastewater effluents containing these radioactive pollutants have been established.

2 EXPERIMENTAL DETAILS

2.1 Adsorbent

Various bentonite samples were obtained through local clay contractors. The samples were chosen at random from individual large lots of bentonite from various locales. The samples were individually processed. First, the bentonite sample was crushed in a thoroughly clean jaw crusher. A steel roller was used to homogenize the bentonite, which was then subjected to sampling by coning and quartering. Finally, it was pulverized in a ball mill and sieved through a 250 mesh screen. Various physical, chemical, and other structural properties of all the samples were determined.

On the basis of x-ray diffraction analysis and other characteristic properties, bentonite was selected for study. The bentonite came from Shina Bagh, Kala Chita Forest, Attock, Pakistan. The sample contained montmorillonite as a major constituent and also some quartz. In addition, it contained 24% clay, 74% silt, and 2% sand. All other samples contained either mixed clays or had sandier contents. Bentonite was used without any heat or chemical treatment for the sorption studies reported here.

2.2 Chemicals

Individual standard stock solutions of the metals were prepared by dissolving calculated amounts of their nitrate salts of > 99% purity in distilled water.

Cesium-134 ($t_{1/2} = 2.05$ yr) and Sr-85 ($t_{1/2} = 65$ d) were supplied by the Pakistan Institute of Nuclear Science and Technology, Islamabad. Cesium radiotracer contained 4.166 mg of Cs in 4 cm^3 of 0.01 M HNO_3 solution, and the activity of the solution, was 55.5 M Bq. Strontium radiotracer contained 80 mg of Sr in 10 cm^3 of 0.01 M HNO_3, and its activity was 3.7×10^4 Bq. Cobalt-60 ($t_{1/2} = 5.26$ yr) was obtained from the Radiochemical Centre, Amersham, U.K., as cobalt (II) chloride in 0.1 M HCl solution. The concentration of Co was 0.0029 $\mu g/cm^3$ of the solution, and the activity of ^{60}Co was 18.5 M Bq/cm^3.

Various spiked standard solutions of the metals were prepared by taking a known aliquot of the appropriate stock solution in a volumetric flask, adding a known volume of the radioactive tracer solution, and adding distilled water to the mark.

2.3 Instruments

The pH of the solution was measured by using microprocessor pH meter model H18417 by Hanna Instruments. The shaking was carried out in a thermostated shaker water bath by Precision USA, model 25. The centrifugation was done with a Wirowka Type WE-1 Centrifuge machine at 4,500 rpm. NaI (Tl) detector crystal size 3 × 3 in., coupled either with a complete counting assembly or 2 K multichannel γ spectrometer and an IBM computer from EG&G ORTEC USA, was used for gamma counting.

3 METHOD

The sorption of metal on bentonite was studied by batch technique. The general method used for these studies is described below.

A known weight, i.e., 0.5 g of bentonite, was equilibrated with 10 cm^3 of the spiked metal solution of known concentration in a stoppered Pyrex glass flask at a fixed temperature for a predetermined amount of time in a shaker water bath that had a thermometer. The flasks containing the weighed amounts of bentonite and metal solutions were separately kept in the bath before mixing for a sufficient time to attain the desired experimental temperature. After equilibration the suspension was centrifuged in a stoppered tube for 15 min at 4,500 rpm. Gross gamma activity, in 1 cm^3 of the supernatant was determined by scintillation counter. The activity of 1 cm^3 of the reference solution was recorded at the same time. Counting of the sample solutions always occurred at a certain time so that counts would lie within 1–2% of statistical accuracy. All the sorption experiments, except where the pH was varied, were at pH 7.3, which was obtained naturally at a solution-to-clay ratio of 20:1. The pH of the suspension in one set of experiments was adjusted by using NaOH and HNO_3. The pH of the solution was that of the supernatant obtained after equilibration. The amount of metal adsorbed x and the equilibrium metal concentration in the solution C_e was always determined radiometrically, i.e., on the basis of the initial activity in the reference solution and the activity left in the solution after equilibrium. Adsorption of metal on the walls of glass flasks and centrifuge tubes was determined by running the blank experiments; this was found to be negligible. Sorption of metal on bentonite was determined in terms of distribution coefficients K_d, percentage adsorption, or amount sorbed per unit weight of the sorbent x/m.

The distribution coefficient K_d is defined as the concentration of a species sorbed per gram of the sorbent divided by its concentration per cubic centimeter in the liquid phase:

$$K_d = \frac{m_s/M}{m_e/V} \quad (\mathrm{cm^3/g}) \quad , \tag{1}$$

where

m_s, m_e = masses of nuclide sorbed and in solution, respectively,
M = mass of the sorbent (g),
V = volume of the solution ($\mathrm{cm^3}$).

In the present study, K_d values were determined radiometrically by using the following equation:

$$K_d = \frac{A_i - A_e}{A_e} \times \frac{V}{W} \quad (\mathrm{cm^3/g}) \quad , \tag{2}$$

where

A_i, A_e = activities of radionuclide in solution at the beginning and end of sorption, respectively,
V = volume of the solution used for equilibration ($\mathrm{cm^3}$),
W = weight of adsorbent (g).

The percentage adsorption was calculated from K_d by using the following equation:

$$\% = \frac{100 \times K_d}{K_d + V/W} \ . \tag{3}$$

The amount of the metal adsorbed per unit weight of the bentonite *x/m* was calculated radiometrically from the initial (known metal concentrations) and final activities of the solutions.

4 RESULTS AND DISCUSSION

The percentage sorption of metals on bentonite as a function of equilibrium time was studied for different times ranging from 5 min to 24 h. The metal concentrations used for this purpose were Cs, 1×10^{-2} M; Sr, 1×10^{-3} M; and Co, 5×10^{-4} M. The results in Fig. 1 indicate that the uptake of Cs and Sr was rapid, and equilibrium was reached almost instantaneously, while Co sorption was time dependent. The instantaneous uptake of Cs and Sr by bentonite may be due to adsorption and/or exchange of the metal with some ions on the surface of the adsorbent. The extent of Co sorption in the beginning increased as shaking time lengthened. The percentage sorption attained almost maximum values after about 1 h and did not change afterward up to 16 h. Very rapid intake of Co by bentonite in the beginning and very slow sorption later indicate two sorption processes, i.e., ion exchange in the beginning and a slow adsorption and/or penetration of Co into the crystal lattice of montmorillonite, the main constituent of bentonite. These results are in good agreement with other studies [5]. On the basis of these results, 30 min of shaking time for Cs and Sr and 4 h of shaking time for Co were selected for further sorption studies of these metals on bentonite.

The effect of pH on the sorption of metal on bentonite was studied by varying the pH of the metal solution. The concentration of the solutions of Cs and Sr was 1×10^{-3} M, whereas the concentration of Co solution was 5×10^{-4} M. Figure 2 shows the effect of pH on the percentage sorption of the metals on bentonite. These results indicate that the sorption of Cs, Sr, and Co increased by increasing pH, but shapes of all the curves are different from each other which indicate the different mechanism of their uptake at various pH by the adsorbent. The percentage sorption of Cs, which was about 68% at pH 1.5, increased to about 80% at pH 5.2 after which a sharp increase in the percentage adsorption was observed until the solution became alkaline. It attained maximum value of about 95%, beyond which a very small increase in the percentage uptake was observed up to pH 10. The rapid increase in the uptake of Cs beyond pH 5 may be due to much less H^+ ion competition for ion-exchange sites. These results are in agreement with the sorption for Iron(II) on wallastonite [6].The percentage sorption of Sr was low at low pH but increased with increasing pH and attained about 99% at pH 8.5. The sharp increase in the percentage sorption beyond pH 6 may be due to hydrolytic adsorption because of a reaction between the $Sr(OH)^+$ and OH^- groups on the surface of the adsorbent [7] or through ion exchange because of much less H^+ ion competition for adsorption sites [8]. Above pH 7, precipitation of $SrCO_3$ could also occur. The percentage sorption for Co was low at low pH but increased markedly with increasing pH. The uptake of Co became 98% at pH 8, and at higher pH the percentage sorption attained almost 100% value at around pH 9.5. Cobalt precipitates at pH > 8, and it therefore becomes difficult to distinguish between adsorption and precipitation beyond pH 8. These results indicate that Co^{2+} is better sorbed on bentonite from neutral or slightly alkaline solutions. The enhanced sorption of Co^{2+} on bentonite with increasing pH may be explained either by a mechanism involving prior hydrolysis of the metal ions in solution to give a hydrolysis product (reaction 1), which is more strongly adsorbed (reaction 2), or by a mechanism involving direct exchange of the unhydrolyzed ion (reaction 3) with a specific group on the adsorbing surface.

$$Co^{2+} + H_2O \rightarrow CoOH^{+} + H+ \tag{4}$$

$$CoOH^{+} + X^{-} \rightarrow Co(OH)X \tag{5}$$

$$Co^{2+} + HX \rightarrow Co^{+}X + H^{+} \tag{6}$$

The adsorption of Co by reactions 5 and 6 exhibits the same type of pH dependence. From the known hydrolysis constants, it has been shown that up to pH 8, Co (II) exists mainly as unhydrolyzed ion Co^{2+}, but at pH 10 $[Co(OH)]^{+}$ predominates [9,10]. Further sorption studies were carried out at pH 7.3, and therefore Co^{2+} was the main species in the solution that was sorbed.

The effect of the adsorbent concentration on the percentage sorption was studied by varying the amount of bentonite from 0.05 to 1 g, while keeping the concentration of the metals in the aqueous solution constant. The concentration of Cs and Sr was 1×10^{-3} M and of Co was 5×10^{-4} M.

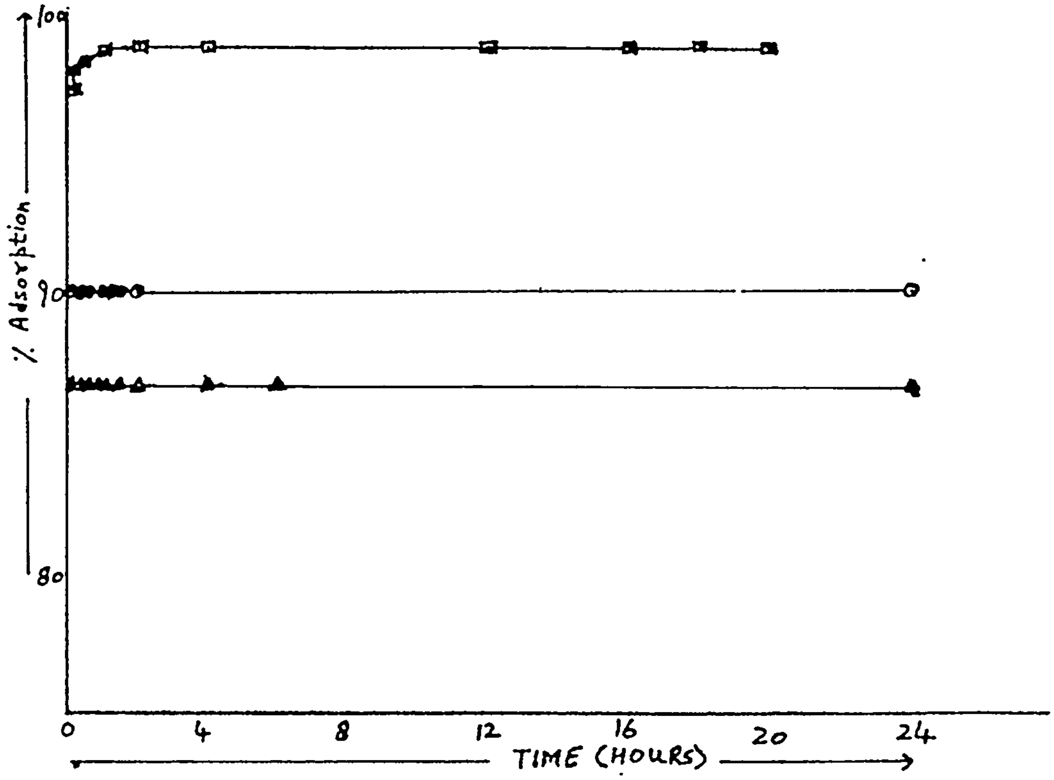

Fig. 1 Effect of Shaking Time on the Sorption of Cs (⊙), Sr (△), and Co (⊡) on Bentonite

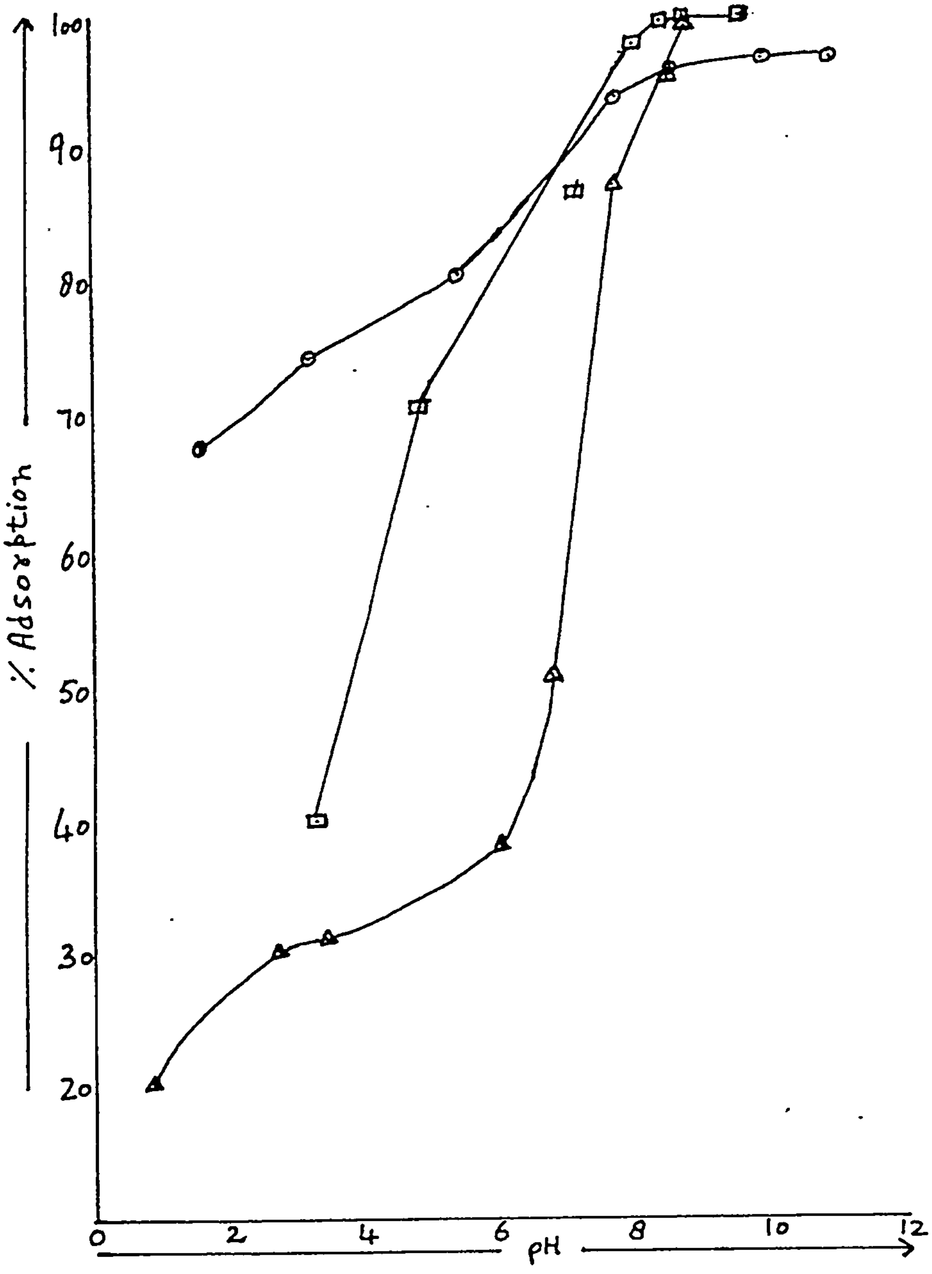

Fig. 2 Effect of pH on the Sorption of Cs (⊙), Sr (△), and Co (⊡) on Bentonite

Figure 3 indicates that the uptake of Cs, Sr, and Co increased with the increasing amount of the bentonite. The percentage sorption increased rapidly with an increasing amount of the adsorbent at beginning, but the percentage sorption curves for all of them almost levels off beyond a certain value of the adsorbent. The maximum percentage adsorption observed was 96.5% for Cs, 92.5% for Sr, and 99.8% for Co. The rapid increase in the percentage adsorption, with increasing amounts of the

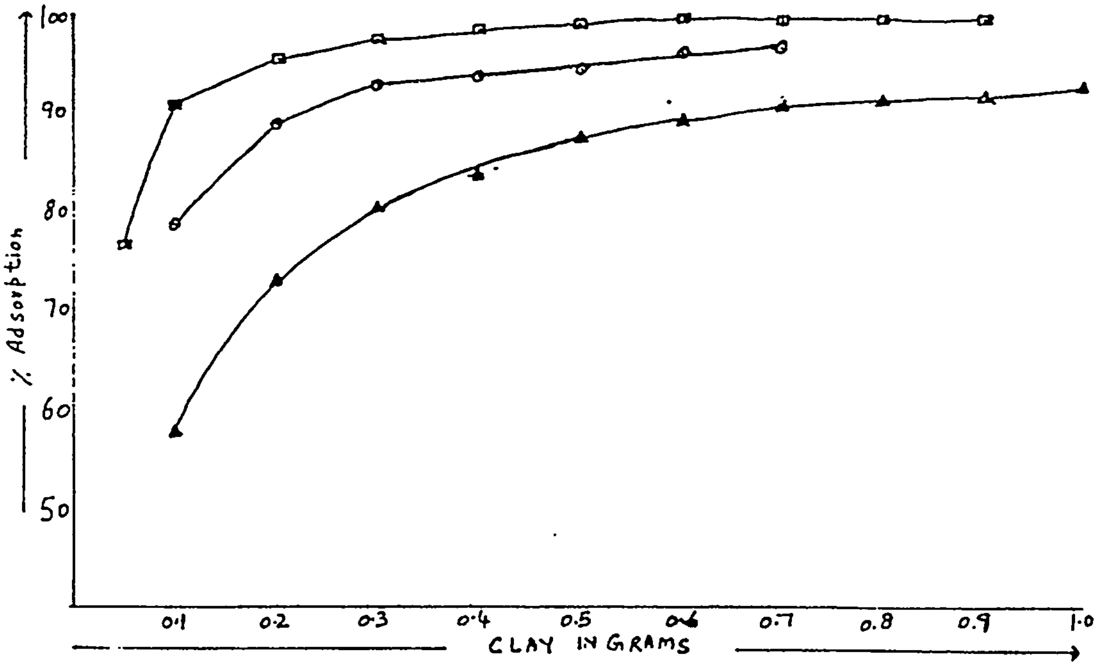

Fig. 3 Effect of Sorbent Concentration on the Sorption of Cs (⊙), Sr (△), and Co (⊡) on Bentonite

adsorbent, occurred because of the greater availability of the exchangeable sites at higher concentrations of the sorbent. Later, the uptake slows down because of the saturation of the adsorption sites. On the basis of these results, 0.5 g of bentonite was selected as an optimal amount of the sorbent for further sorption studies of these metals.

The effect on the percentage sorption of metal as a function of its concentration was studied by varying the amount of metal, while keeping the amount of the adsorbent constant. The concentrations of the metals studied ranged between 10^{-8} to 10^{-2} M. Figure 4 shows these results. The percentage sorption for Cs, Sr, and Co decreases with increasing metal concentration. The percentage sorption of Cs remains almost constant for metal solution concentrations from 10^{-7} to 10^{-4} mol/dm^3, but it sharply decreases when the metal in the solution is increased beyond 10^{-4} mol/dm^3. The percentage sorption values decrease gradually when the strontium concentration in the solution increases from 10^{-7} to 10^{-4} mol/dm^3, but decrease sharply when the concentration of the metal increases beyond 10^{-4} M. The results suggest that at least two phenomena, adsorption and ion exchange, take place in the range of strontium concentrations examined. These results further suggest that energetically less favorable sites for sorption become involved with increasing concentrations of the metal. Similar behavior has been reported for other metal sorption systems [3,11–13]. The percentage sorption is nearly 100% for concentrations ranging between 10^{-8} and 10^{-5} M, beyond which it decreases. The percentage sorption decreases as the cobalt concentration in the bulk solution increases.

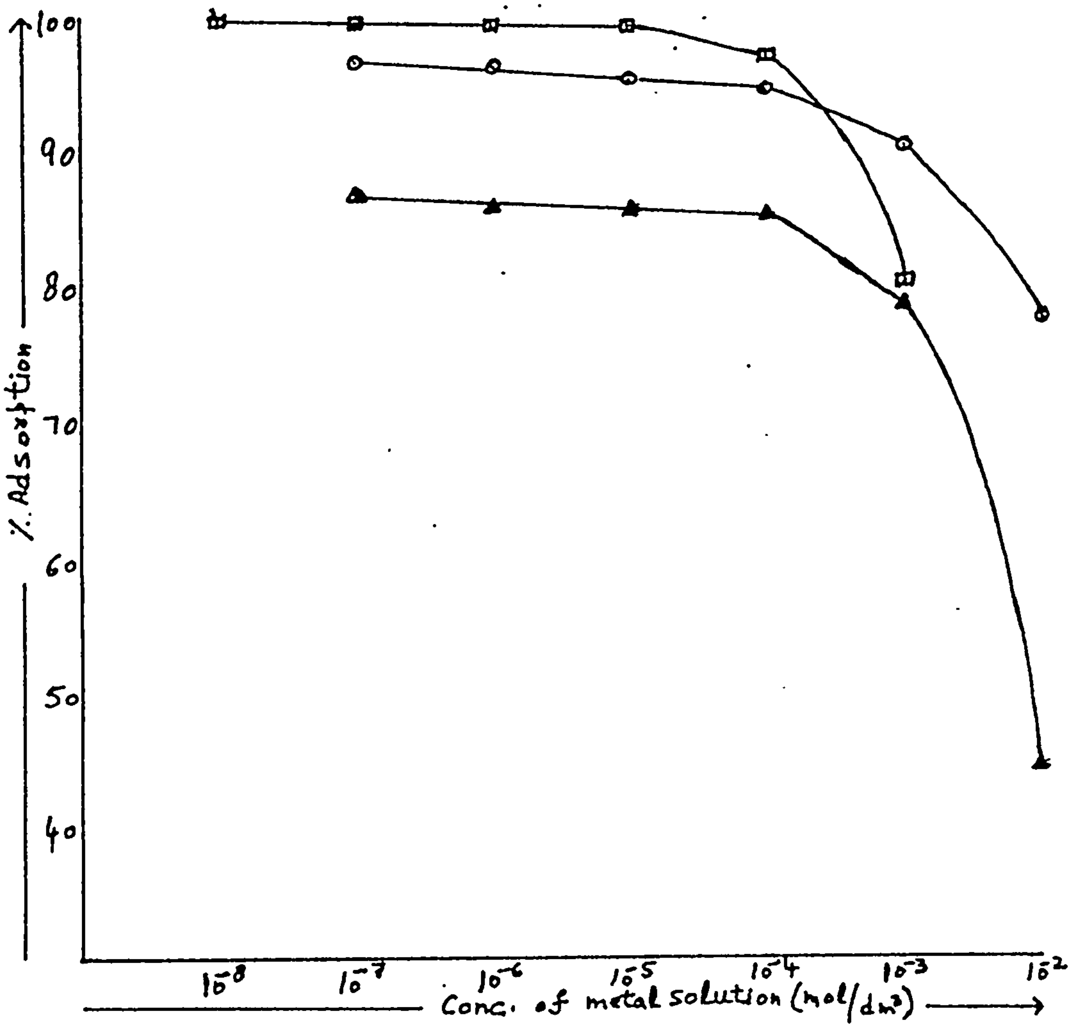

Fig. 4 Effect of Metal Concentration on the Sorption of Cs (⊙), Sr (△), and Co (⊡) on Bentonite

The adsorption isotherms for the sorption of Cs, Sr, and Co on bentonite were obtained at three different temperatures by varying the metal bulk concentration in the solution from 0.01 to 0.3 mol/dm^3, while keeping all other optimum sorption conditions constant, i.e., metal solution to solid ratio 20:1 and pH 7.3. Figures 5–7 show the isotherms of Cs, Sr, and Co, respectively. The data were analyzed in terms of Freundlich, Langmuir, and Dubinin-Radushkevich equations. Various thermodynamic parameters, mean free energy of sorption, and sorption capacity of the bentonite for each metal were determined. The following form of the Freundlich equation was used:

$$\log x/m = \log K + 1/n \log C_e \quad , \tag{7}$$

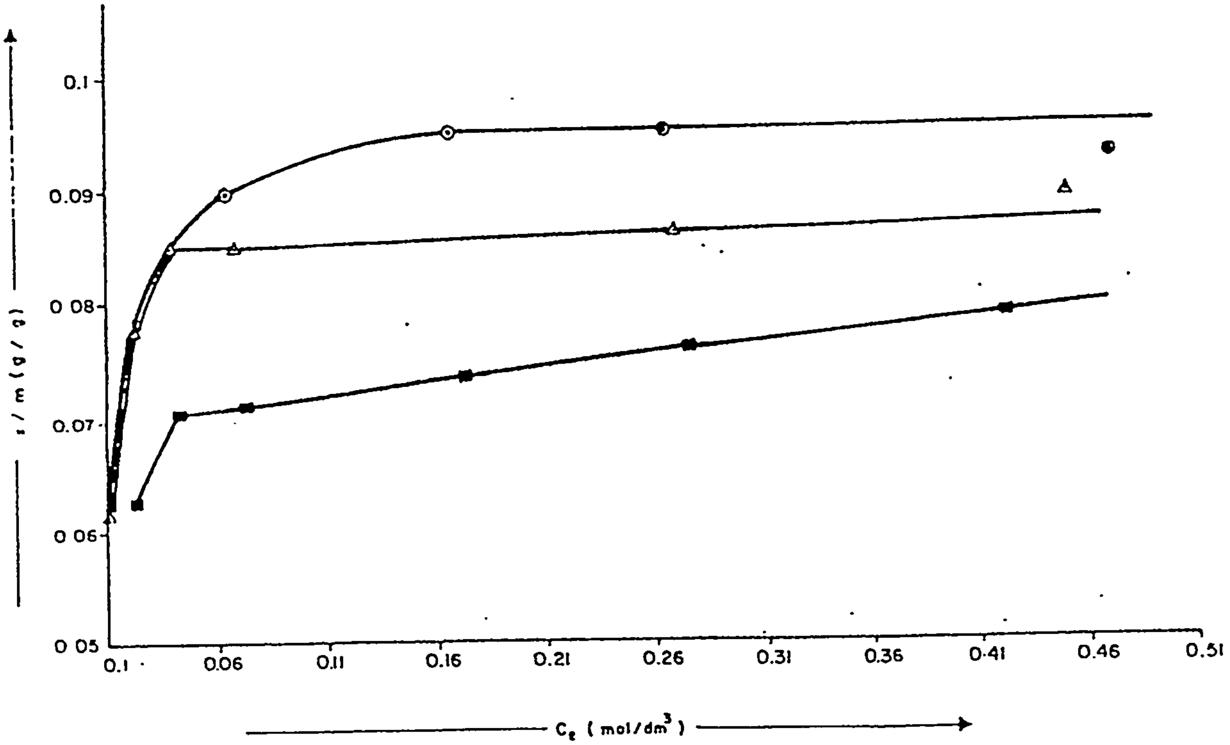

Fig. 5 Isotherms of Cs Sorption on Bentonite at Different Temperatures: 298 K (⊙), 303 K (△), and 308 K (⊡)

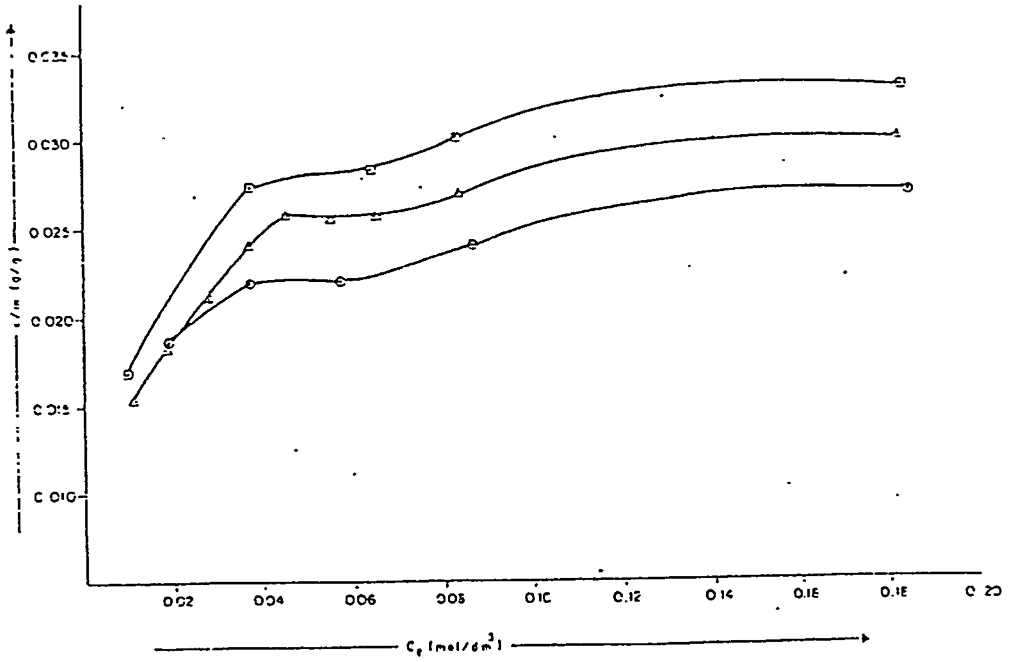

Fig. 6 Isotherms of Sr Sorption on Bentonite at Different Temperatures: 298 K (⊙), 303 K (△), and 308 K (⊡)

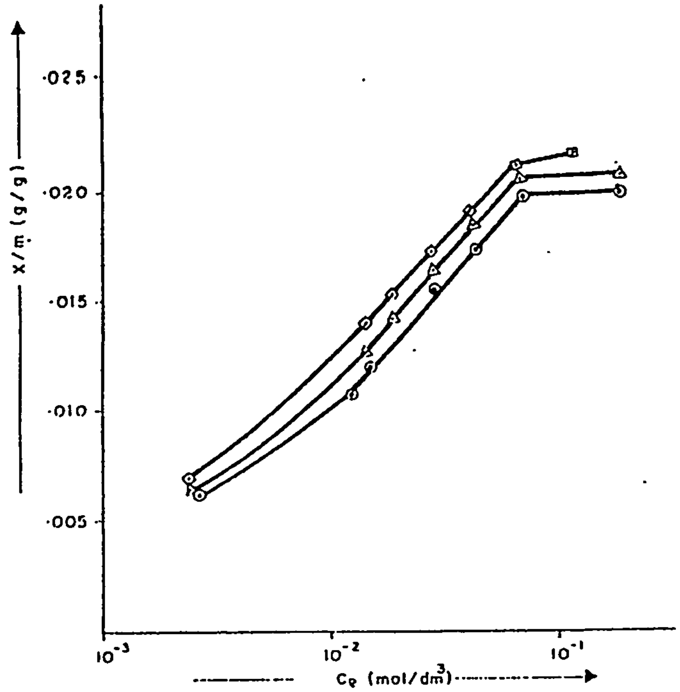

Fig. 7 Isotherms of Co Sorption on Bentonite at Different Temperatures: 298 K (⊙), 303 K (△), and 308 K (⊡)

where

x/m = amount of metal sorbed per unit mass of the sorbent,
C_e = equilibrium concentration of the metal, and
$1/n$, K = constants.

A plot of log x/m against log C_e gives a straight line, the slope, and intercept of which correspond to $1/n$ and log K, respectively. The Freundlich plot for Cs/Sr/Co sorption on bentonite was a straight line. Linear regression gives a slope less than 1, indicating a concentration-dependent sorption of the metal in the concentration range used. The value of the Freundlich exponent $1/n$ was 0.85 for Cs, 0.96 for Sr, and 0.74 for Co.

The following well-known form of the Langmuir equation was used for the interpreting the sorption data:

$$C_e/x/m = 1/K\ V_m + C_e/V_m \quad , \tag{8}$$

where

x/m = amount adsorbed per unit mass of adsorbent,
C_e = equilibrium concentration of adsorbate in solution,
V_m = monolayer capacity,
K = binding constant related to the heat of adsorption by equation:

$$K = K_0 \exp(-q/RT) \quad , \tag{9}$$

where q is the heat of adsorption.

The equilibrium concentration of the metals was 0.02–0.47 mol/dm^3 for Cs, 0.01–0.185 mol/dm^3 for Sr, and 4×10^{-3}–2.8×10^{-1} mol/dm^3 for Co.

A straight line was obtained by plotting $C_e/x/m$ against C_e for the sorption of Cs, Sr, and Co on bentonite. The constants involved in the equation were calculated. These are given in Table 1.

Thermodynamic parameters, such as free energy and enthalpy of metal sorption, were calculated from the values of the binding constant K obtained from Langmuir's equation by using the following relations:

$$\Delta G^\circ = -RT \ln K \tag{10}$$

and

$$\ln K = \frac{-\Delta H^\circ}{RT} + \text{Constant} \quad . \tag{11}$$

The value of ΔH° was calculated from the slope of the linear variation of ln K versus $1/T$. The values of ΔS° were calculated by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \, \Delta S^\circ \quad . \tag{12}$$

The experimentally determined values of ΔH°, ΔS°, and ΔG° for the metal-bentonite system calculated from binding constant are given in Table 2.

The values of the monolayer capacity V_m calculated from the Langmuir's plot was 72.55 meq/100 g for Cs, 16.3 meq/100 g for Sr, and 17.43 meq/100 g for Co, which is 94.1%, 21.1%, and 23% for cesium, strontium, and cobalt, respectively, of the total cation exchange capacity of the sorbent. The negative values for both heat of sorption ΔH° and free energy change ΔG° at 298 K suggest that the sorption of Cs on bentonite is an exothermic and a spontaneous process. ΔG° becomes less negative at higher temperatures, and therefore less Cs is sorbed at higher temperatures. The positive

Table 1 Values of Langmuir Constants for Cs, Sr, and Co Sorption on Bentonite

Metal	Temperature (K)	K	V_m (mol/g)
Cs	298	203.3 ± 2[a]	$7.25 \times 10^{-4} \pm 8 \times 10^{-6}$
	303	183.6 + 2	$6.68 \times 10^{-4} \pm 7 \times 10^{-6}$
	308	136.1 ± 1	$5.89 \times 10^{-4} \pm 7 \times 10^{-6}$
Sr	298	74.8 ± 0.6	$3.27 \times 10^{-4} \pm 1 \times 10^{-6}$
	303	91.4 ± 0.02	$3.48 \times 10^{-4} \pm 1 \times 10^{-6}$
	308	112 ± 0.5	$3.76 \times 10^{-4} \pm 4 \times 10^{-6}$
Co	298	76.8 ± 0.7	$3.48 \times 10^{-4} \pm 9 \times 10^{-7}$
	303	87.9 ± 0.6	$3.43 \times 10^{-4} \pm 7 \times 10^{-7}$
	308	102 ± 0.4	$3.52 \times 10^{-4} \pm 7 \times 10^{-7}$

[a] Mean ± standard deviation.

Table 2 Values of the Thermodynamic Parameters for Cs, Sr, and Co Sorption on Bentonite

			ΔG° (kJ/mol)		
Metal	ΔH° (kJ/mol)	ΔS° (kJ K^{-1} mol^{-1})	298 K	303 K	308 K
Cs	-32.29 ± 0.4[a]	0.150 ± 0.003	13.16 ± 0.03	13.13 ± 0.07	12.58 ± 0.05
Sr	30.62 ± 0.3	0.139 ± 0.002	10.69 ± 0.02	11.37 ± 0.05	12.08 ± 0.01
Co	22.08 ± 0.2	0.110 ± 0.007	10.75 ± 0.002	11.28 ± 0.002	11.85 ± 0.01

[a] Mean ± standard deviation.

values of the $\triangle H°$ and the negative values of $\triangle G°$ for the sorption of strontium and cobalt, respectively, at 298 K on bentonite show that both these processes are endothermic and spontaneous in nature. The value of $\triangle G°$ becomes more negative with increasing temperature, which shows that sorption of Sr and Co on bentonite is favored at higher temperatures.

The sorption mean free energy *E*, defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution, was calculated by using equation [14]:

$$E = (-2K)^{-1/2} \quad . \tag{13}$$

The value of *K* was determined from the D-R isotherm equation:

$$\ln X = \ln Xm - K\varepsilon^2 \quad , \tag{14}$$

where

X = amount of solute adsorbed per unit mass of solid (mol/g),
X_m = sorption capacity of adsorbent per unit mass (mol/g),
ε = polanyi potential, $RT \ln (1 + 1/C)$,
C = equilibrium solute solution concentration (mol/dm^3),
R = gas constant (kJ/deg mol),
T = temperature (K), and
K = constant related to the sorption energy (mol^2/kJ^2).

The values of X_m and *K* were calculated from the intercept and the slopes of these plots of log *X* against ε^2. The values of *E* were calculated from *K* values. The magnitude of *E* can indicate the type of sorption occurring. The parameters obtained from the fitting of sorption data to D-R isotherm are shown in Table 3.

The mean free energy *E* for Cs, Sr, and Co sorption on bentonite was 14.5, 9, and 7.7 kJ/mol, respectively, which is within the energy range for ion-exchange reaction, i.e., 8–16 kJ/mol [15, 16]. The maximum sorption capacity found by using the D-R equation for Cs, Sr, and Co was 75.5, 22, and 27.5 meq, respectively, for 100 g of the bentonite. This corresponds to about 97.9%, 29%, and 35.67% of the total cation exchange capacity of bentonite, i.e., 77.1 meq/100 g, respectively. The value of *E* indicates that ion exchange may be the predominant mode of sorption for these radionuclides.

The desorption studies with 0.01 M $CaCl_2$ and groundwater at low metal loading on bentonite showed that about 95% of Cs, 85–90% of Sr, and 97% of Co were irreversibly sorbed.

Table 3 Values of the D-R Parameters for Sorption of Cs, Sr, and Co on Bentonite

Metal	Temperature (K)	K (mol^2/kJ^2)	X_m (mol/g)	E (kJ/mol)
Cs	298	$-2.49 \times 10^{-3} \pm 4 \times 10^{-6}$[a]	$7.55 \times 10^{-4} \pm 6 \times 10^{-6}$	14.2 ± 0.08
	303	$-2.29 \times 10^{-3} \pm 5 \times 10^{-6}$	$6.72 \times 10^{-4} \pm 5 \times 10^{-6}$	14.8 ± 0.07
	308	$-2.39 \times 10^{-3} \pm 2 \times 10^{-6}$	$5.91 \times 10^{-4} \pm 4 \times 10^{-6}$	14.5 ± 0.07
Sr	298	$-6.57 \times 10^{-3} \pm 9 \times 10^{-6}$	$3.54 \times 10^{-4} \pm 2 \times 10^{-6}$	8.72 ± 0.06
	303	$-6.19 \times 10^{-3} \pm 3 \times 10^{-6}$	$3.97 \times 10^{-4} \pm 2 \times 10^{-6}$	8.99 ± 0.03
	308	$-5.93 \times 10^{-3} \pm 5 \times 10^{-6}$	$4.40 \times 10^{-4} \pm 4 \times 10^{-6}$	9.18 ± 0.04
Co	298	$-9.09 \times 10^{-3} \pm 5 \times 10^{-6}$	$4.703 \times 10^{-4} \pm 1 \times 10^{-6}$	7.41 ± 0.02
	303	$-8.77 \times 10^{-3} \pm 8 \times 10^{-6}$	$4.988 \times 10^{-4} \pm 1 \times 10^{-6}$	7.55 ± 0.03
	308	$-8.39 \times 10^{-3} \pm 8 \times 10^{-5}$	$5.499 \times 10^{-4} \pm 1 \times 10^{-6}$	7.72 ± 0.04

[a] Mean ± standard deviation.

These results indicate that local bentonite can effectively be used for decontaminating wastewater effluents containing low concentration of radionuclides of Cs, Sr, and Co.

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BIOTECHNOLOGICAL REDUCTION OF SULFIDE IN AN INDUSTRIAL PRIMARY WASTEWATER TREATMENT SYSTEM: A SUSTAINABLE AND SUCCESSFUL CASE STUDY

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ABSTRACT

The leather industry is an important export-oriented industry in India, with more than 3,000 tanneries located in different clusters. Sodium sulfide, a toxic chemical, is used in large quantities to remove hair and excess flesh from hides and skins. Most of the sodium sulfide used in the process is discharged as waste in the effluent, which causes serious environmental problems. Reduction of sulfide in the effluent is generally achieved by means of chemicals in the pretreatment system, which involves aerobic mixing using large amounts of chemicals and high energy, and generating large volumes of sludge. A simple biotechnological system that uses the residual biosludge from the secondary settling tank was developed, and the commercial-scale application established that more than 90% of the sulfide could be reduced in the primary treatment system. In addition to the reduction of sulfide, foul smells, BOD and COD are reduced to a considerable level.

1 INTRODUCTION

The treatment of industrial effluent with high concentrations of sulfide is one of the difficult tasks required for successful results from conventional physio-chemical treatment systems. India has more than 3,000 tanneries located in different clusters. Together, these tanneries process 700,000 tons of hides and skins per year.

Sodium sulfide is a toxic chemical used in large quantities in tanneries — about 25,000 ton/yr. During the leather-making process, most of the sodium sulfide is discharged as waste in effluent, which causes serious environmental problems. The sulfide in the effluent is generally reduced by treatment using such chemicals as manganous sulfate in the primary treatment under aerobic mixed conditions. Foul smells, the high cost of chemical treatment for reducing sulfide, and the large volume of sludge disposal are the major constraints in the operation and maintenance (O&M) of tannery effluent treatment plants. Therefore, development of a suitable biomass at the source for biotechnological application was considered necessary to reduce the sulfide concentration in the primary treatment.

Based on laboratory- and field-scale studies, a suitable biomass was developed using the residual bio sludge from the secondary treatment system and applied in the primary treatment under mixed aerobic conditions. The field application established that more than 90% of the sulfide could be reduced in the pretreatment system. It is also resulted in the reduction of BOD, COD, and sludge generation from the primary treatment system. The O&M cost in the primary treatment was reduced by 40%, and foul odors in the effluent treatment plant area were nearly eliminated. This commercial-scale biotechnological application for sulfide reduction is working successfully in a full-scale treatment plant with a capacity of 400,000 L/day for the past three years.

2 TANNING PROCESS AND WASTEWATER DISCHARGE

The processing of raw salted hides and skins into finished leather involves a number of primary operations, such as soaking, sulfide liming, deliming, etc., to clean the material before chrome tanning. Soaking is done in pits or paddles to remove salt and rehydrate the raw material to its original condition. After soaking, sulfide liming is done in pits or paddles. Sulfide liming is an important operation for removing the hair and excess flesh and to open up the fiber structure of the skins and hides by suitable plumping and swelling. For this process, 20 – 40 kg of sodium sulfide, along with 80 – 150 kg of calcium hydroxide (lime), is applied per ton of raw material in a float of 300% to 400% water. Major amounts of sodium sulfide and lime used in the process are discharged as waste in the effluent. In some organized tanneries, it is possible to decrease the sodium sulfide usage to less than 10 kg/ton of raw material by using enzymes and other process controls. However, enzyme usage is not practical in most Indian tanneries because of the existing facilities and work force capabilities.

The wastewater discharge from the sulfide liming operation is 3,000–4,000 L of the total volume of 30,000–40,000 L/tonne of hides and skins processed from raw to finished leather. The characteristics of the wastewater from lime sulfide operations and overall composite tannery wastewater are given in Table 1.

3 NEED FOR BIOTECHNOLOGICAL APPLICATION FOR REDUCTION OF SULFIDE

The concentration of sulfide (S) in the sectional waste stream ranges from 1,000 to 2,000 mg/L and in the composite stream from 100–250 mg/L, as given in Table 1, compared with the environmental permissible discharge limit of 2 mg/L. It is estimated that 20,000 ton/yr of sulfide is discharged as waste, along with 25,000 million liters of wastewater from Indian tanneries, and this causes serious environmental problems. Sulfide in the effluent is generally reduced by treatment with chemicals,

Table 1 Characteristics of Sectional and Composite Tannery Wastewater

Parameter	Soaking	Sulfide Liming	Deliming	Pickling	Chrome Tanning	Wet Finish	Composite (including washings)
Volume of effluent/ton of hides/skins	6–9 m^3	3–4 m^3	1–2 m^3	0.5–1 m^3	1–2 m^3	5–10 m^3	30–40 m^3
pH	7.5–8.0	9.8–12.8	7.0–9.0	2.0–3.0	2.5–4.0	3.5–4.5	7.0–9.0
BOD 5 days at 20°C	1,100–2,500	5,000–10,000	1,000–3,000	400–700	350–800	1,000–2,000	1,000–3,000
COD	3,000–6,000	10,000–25,000	2,500–7,000	1,000–3,000	1,000–2,500	2,500–7,000	2,500–8,000
Sulfide (S)	–	1,000–2,000	100–300	–	–	–	100–250
Total solids	35,000–55,000	30,000–50,000	4,000–10,000	35,000–70,000	30,000–60,000	4,000–10,000	15,000–25,000
Dissolved solids	32,000–48,000	24,000–30,000	2,500–6,000	34,000–67,000	29,000–57,500	3,400–9,000	13,000–21,000
Suspended solids	3,000–7,000	6,000–20,000	1,500–4,000	1,000–3,000	1,000–2,500	600–1,000	2,000–4,000
Total chromium (Cr)	–	–	–	–	2,000–5,000	40–100	100–250

Note: All values except pH are expressed in milligrams per liter. Chrome recovery and reuse are not taken into account.

like manganous sulfate, in the primary treatment system under aerobic mixing conditions. In this treatment, chemical dosage at a concentration of 200–400 mg/L is required under aerobic mixing for 8–12 hours. This dosage causes large chemical consumption, high-energy requirements, generation of large volumes of sludge, and increases in total dissolved solids (TDS) in the treated effluent. Chemical treatment is often ineffective due to the variation in the quality and quantity of wastewater discharged from the batch operations of the tannery. The foul smell due to the liberation of hydrogen sulfide and expensive chemical treatment are other constraints. Therefore, development of a suitable biomass that is easily available at the source was considered necessary for biotechnological application to reduce the sulfide concentration in the primary treatment.

4 FIELD STUDY ON BIOTECHNOLOGICAL APPLICATION OF SULFIDE REDUCTION

A commercial conventional tannery effluent treatment system with a capacity of 400,000 L/day was selected for biotechnological application of sulfide in primary treatment. This treatment system consists of equalization cum mixing tank, chemical treatment for pH control and sulfide reduction, primary settling, a sludge dewatering system, and a secondary biological system with provisions for recirculating biosludge from the secondary settling tank, as shown in Fig. 1.

Some of the constraints associated with the O&M of a conventional treatment system are large amounts of chemical dosing in the equalization cum mixing tank for sulfide oxidation, large volumes of primary sludge generation, dewatering of the excess biosludge from the secondary settling tank, and foul smells due to the liberation of hydrogen sulfide. On the basis of laboratory and field experiments, the excess biosludge generated from the secondary settling tank was collected and improved by adding micronutrients and discharging in the equalization tank under aerobic conditions. The existing facilities were used for mixing. The chemical dosing for sulfide oxidation was slowly reduced and completely eliminated in a period of two weeks. The pH, volume, and concentration of biomass and reaction time are the important factors in reducing sulfide. The sulfide concentration from an average level of 200 mg/L is reduced to less than 15 mg/L in the treated effluent from the primary treatment.

Further biological oxidation of sulfide occurs in the secondary biological system, and the sulfide concentration in the final treated effluent *is less* than 2 mg/L. The significant achievement is the complete reduction of foul smells in the effluent treatment plant area. In the O&M area, the cost of chemical usage is reduced by 80%, and the primary sludge volume by about 15%. The dewatering problem of the excess biosludge from the secondary settling tank is solved. The overall O&M cost is reduced by 20%. This system has successfully worked for the past three years.

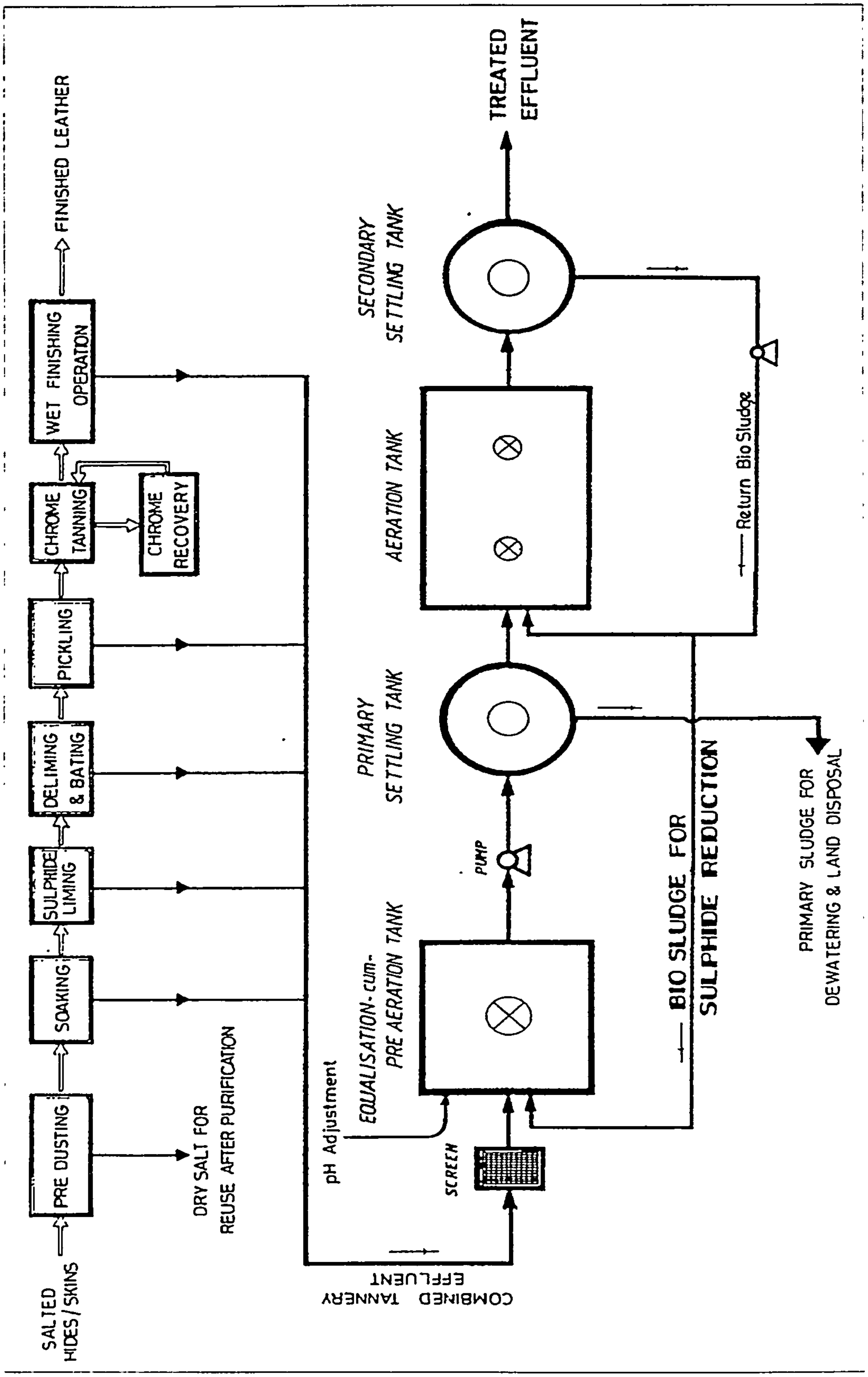

Fig. 1 Biotechnological Reduction of Sulfide in a Primary Wastewater Treatment System

In addition to implementing the biotechnological application to reduce sulfide, a simple and cost-effective chrome recovery and reuse system was introduced in the tannery. The process flow diagram of the chrome recovery and reuse system is shown in Fig. 2. The payback period for the entire chrome recovery system is only about two years. The implementation of the chrome recovery and reuse system reduced the chromium waste by 90%, and the O&M cost of the effluent treatment system was also further reduced. The disposal problem of the chromium containing sludge was also minimized, as the chromium concentration as Cr in the sludge was reduced from an average level of 3% to less than 0.5% on dry solid matter.

5 CONCLUSIONS

The commercial-scale biotechnological application that uses residual biosludge for reducing sulfide in primary treatment systems without adding chemicals is appropriate and first of its kind in India. Based on the success of this process, many industries with effluent treatment systems adopted this technology. The chrome recovery and reuse system is also becoming popular, and many tanners willingly adopted this system in India.

6 ACKNOWLEDGMENTS

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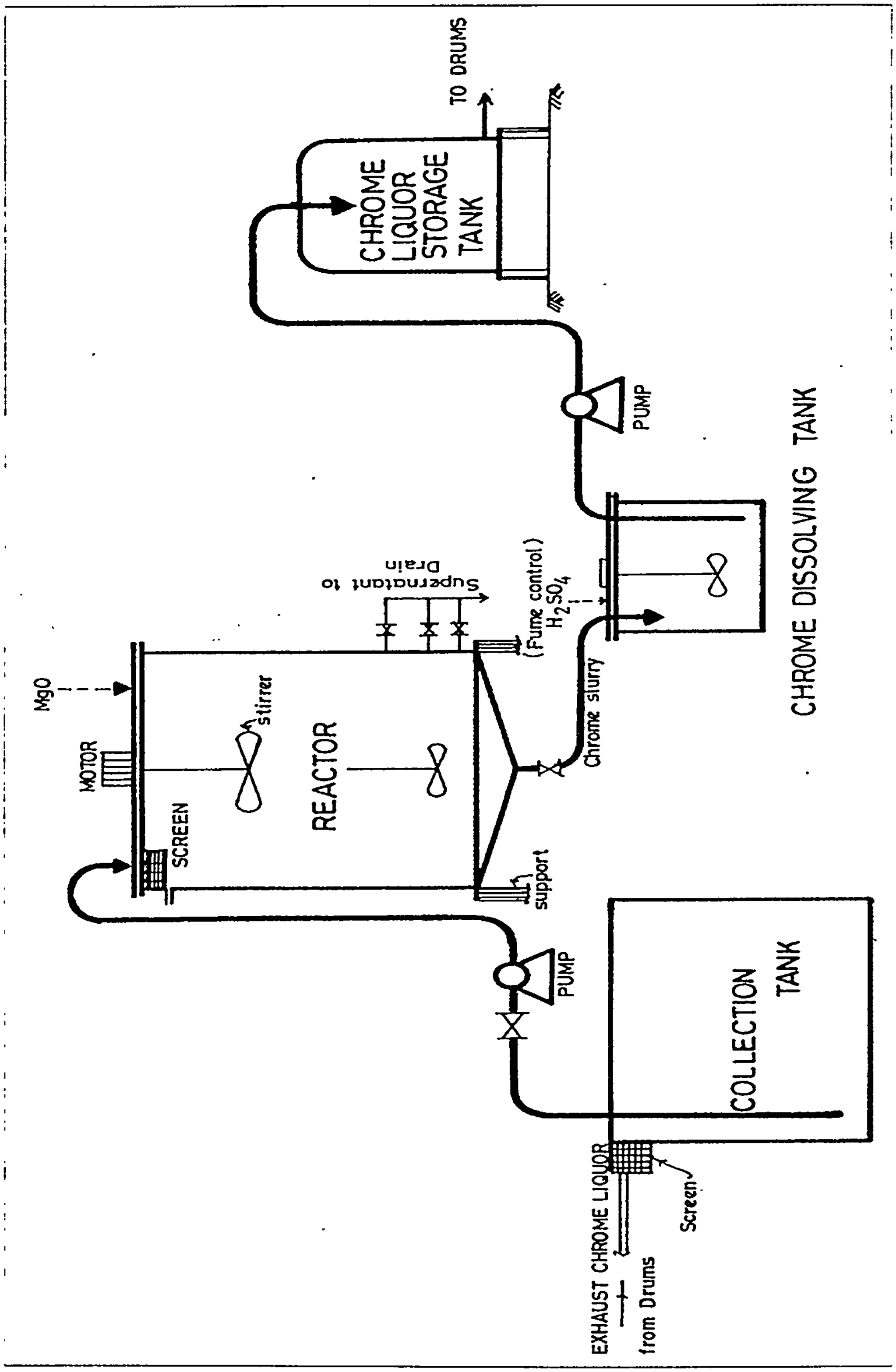

Fig. 2 Process Flow Diagram of Chrome Recovery and Reuse

POPULATION DYNAMICS OF DECHLORINATORS AND FACTORS AFFECTING THE LEVEL AND PRODUCTS OF PCB DECHLORINATION IN SEDIMENTS

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ABSTRACT

Microbial dechlorination of polychlorinated biphenyls (PCBs) generates lower chlorinated products through the selective removal of *meta* and *para*-chlorines. However, dechlorination often stops at a level where a significant number of removable chlorines remain. To determine the reason for the apparent cessation, we investigated the potential limitation of organic carbon, PCB bioavailability, and inhibition by metabolic products. Enrichment with various carbon sources, known to enhance dechlorination, did not induce any additional dechlorination, indicating the plateau was not due to the depletion of organic carbon in sediments. The bioavailability of PCBs was also not limiting, since a sub-critical micelle concentration of the nonionic surfactant Tween 20, which enhanced PCB desorption without inhibiting dechlorinating microorganisms, also failed to lower the plateau level. Neither was it due to the accumulation of metabolites, since no additional dechlorination was detected when plateau sediments were incubated further with fresh medium. Similarly, dechlorination was not inhibited in freshly spiked Aroclor 1248 sediment slurries made with the old supernatant. Interestingly, dechlorination always ended up at the same level with nearly identical congener profiles, regardless of treatment. These results indicate that the cessation of dechlorination was due to the accumulation of daughter congeners, which cannot be utilized as electron acceptors by the present microbial population. To determine whether this decreasing availability affected the dechlorinating microorganisms, we, for the first time, determined the population dynamics of dechlorinators using the most probable number technique. The growth dynamics of the dechlorinators mirrored the time course of dechlorination. It started when the dechlorinating population increased by two orders of magnitude. Once dechlorination stopped, reaching a low plateau, the dechlorinating population also began to decrease. However, when the dechlorinators were inoculated into PCB-free sediments, the population decreased over time from their initial level. The decrease of the dechlorinator population as

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dechlorination ceased confirms that the diminishing availability of suitable congeners to be used as electron acceptors was the reason for the incomplete dechlorination. Recent findings have shown that a second phase of dechlorination of certain congeners can occur after a long lag.

1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are among the most ubiquitous and persistent environmental contaminants because of their widespread industrial use and improper disposal. Concerns over their toxicity and bioaccumulation potential have emphasized the need to remediate contaminated sites. Recently, interest in the biodegradation of PCBs has increased because it may provide a cost-effective alternative to existing remedial technologies.

Many chlorinated compounds are transformed in anaerobic environments through microbially mediated reductive dechlorination (Mohn and Tiedje 1992; Rhee and Sokol 1994; Bedard and Quensen 1995). This naturally occurring process, which is carried out by as yet undefined microorganisms or consortia of microorganisms for PCBs, reduces the degree of chlorination by preferentially removing *meta* and *para* chlorines from the biphenyl ring (Quensen et al. 1990; Rhee et al. 1993a). The dechlorination products are often less toxic, less likely to bioaccumulate, and more susceptible to further microbial degradation by oxidative processes. However, a complete transformation to biphenyl has not been reported for Aroclor mixtures since chlorines at the *ortho* position are rarely removed (Quensen et al. 1990; Rhee et al. 1993a).

Dechlorination is often incomplete or limited even after taking into account the absence of dechlorination of *ortho*-substituted chlorines. A typical time course of PCB dechlorination in the laboratory has an initial lag followed by a relatively rapid dechlorination and then a plateau showing no further change with continued incubation. However, this process often stops at a point where a significant number of *meta* and *para* chlorines remain (Rhee et al. 1993b; Liu et al. 1996). From a bioremediation point of view, it is important to understand what sets this apparent lower limit of dechlorination. Our recent research has therefore focused on uncovering factors responsible for this limitation. These investigations centered on the bioavailability of PCBs; limitation of electron donors; accumulation of metabolic products, which are inhibitory to dechlorinating microorganisms or consortia of microorganisms; and the decline of competent populations.

2 FACTORS LIMITING DECHLORINATION

PCBs are extremely hydrophobic with high partition coefficients and tend to be tightly sorbed to sediment particles. This partitioning may make PCBs less available to microorganisms for degradation; for example, the degradation of hexachlorocyclohexane (Rijnaarts et al. 1990), 1,2-dibromomethane (Steinberg et al. 1987), 2,4-D (2,4-dichlorophenoxy)-acetic acid (Ogram et al. 1985), naphthalene (Mihelcic and Luthy 1991), and other PAHs (Weissenfels et al. 1992) was greatly reduced by the sorption of these compounds to sediment or soil particles. In addition, the bioavailability of hydrophobic organic contaminants (HOCs) may further decrease with increasing age of sediment contamination (Scribner et al. 1992; Hatzinger and Alexander 1995).

Since dechlorinating microorganisms do not metabolize the biphenyl skeleton, they require a source of electrons for their growth. In addition, electron acceptors are often limiting in anaerobic sediment environments. Evidence indicates that PCBs are utilized as alternate electron acceptors. Recent thermodynamic calculations have also shown that dechlorinators can obtain energy from the reductive removal of chlorines (Dolfing and Harrison 1992; Holmes et al. 1993). Therefore, dechlorination activity may become limited in sediments through the exhaustion of a supply of appropriate electron donors and/or acceptors.

The formation and accumulation of metabolites can also decrease and even inhibit biodegradation. End-product inhibition is well known in the degradation of many HOCs (Adams et al. 1992; Sondossi et al. 1992; Arensdorf and Focht 1994; Lloyd-Jones et al. 1995), including the aerobic degradation of PCBs (Barriault and Sylvestre 1993). Biodegradation of HOCs can also involve interactions of different microbial populations. In the mineralization of a phenol and *p*-nitrophenol mixture by two different strains of *Pseudomonas*, degradation of one substrate produced products that were inhibitory to the population acting on the second (Murakami and Alexander 1989). The anaerobic degradation of 2,4-dichlorophenol into methane and CO_2 by sediment microorganisms required sequential actions involving at least five different populations (Zhang and Wiegel 1990). It is unclear whether dechlorination involves a single organism or a consortium of organisms. Nonetheless, it is possible that intermediate metabolic products of PCBs or other substrates can accumulate to inhibit further dechlorination. If the competent population is eliminated by shifting environmental conditions as the dechlorination reaction occurs, the biotransformation could then be prematurely terminated.

2.1 Bioavailability of PCBs

The use of surfactants is one way to enhance the bioavailability of sorbed HOCs. The addition of surfactants can increase the aqueous concentration of these compounds, thereby potentially increasing the amount available for uptake and biodegradation (Tsomides et al. 1995; Volkering et al. 1995). In fact, surfactant-facilitated desorption promoted the aerobic degradation of PCBs (Aronstein and Paterek 1995) and was also found to enhance the biodegradation of other HOCs, such as PAHs (Aronstein et al. 1991; Aronstein and Alexander 1992, 1993; Weissenfels et al. 1992). Therefore, to determine whether the cessation of dechlorination at the plateau was due to PCB bioavailability, we chose the nonionic surfactant Tween 20 (polyoxyethylene sorbitan monolaurate).

Since most surfactants are toxic to microorganisms above their critical micelle concentration (CMC) (Laha and Luthy 1991), a sub-CMC might be necessary for the experiments. Therefore, we conducted preliminary experiments, using [^{14}C]-labeled 2,4,5-2',4',5'-hexachlorobiphenyl (HCBP)-spiked sediments, to determine whether PCB desorption could be increased with sub-CMC levels of Tween 20. The results demonstrated that PCB desorption increased proportionally with increasing concentrations of Tween 20 up to 0.1% (v/v). With a 0.05% (v/v) concentration, approximately 35% of 2,4,5-2',4',5'-HCBP was in the aqueous phase, while less than 1% was detectable without the addition of Tween (Liu et al. 1996). This concentration is below Tween 20's CMC. A second experiment was carried out to determine whether any of these sub-CMCs were toxic to the dechlorinating microorganisms. The results showed that concentrations of Tween 20 up to 0.1% (v/v) had no inhibitory effect on PCB dechlorination (Kwon et al. 1995). We therefore chose a concentration of 0.05% (v/v) to determine whether surfactant addition could increase the extent of dechlorination at the plateau.

To investigate the effect of Tween 20 at the low plateau, dechlorination cultures were set up in PCB-free sediments from the Grasse River (a tributary of the St. Lawrence River, New York), which were spiked with Aroclor 1248 and inoculated with St. Lawrence River sediment microorganisms from the Reynolds site (see Sokol et al. 1994 for site description). This culture reached a low plateau level after 15 weeks of incubation, resulting in a 33% reduction in total chlorines (Fig. 1). Once the cessation of dechlorination was confirmed after 24 weeks, Tween 20 (0.05% v/v) was added to these plateau sediments with and without replacing the supernatant with fresh reduced anaerobic media.

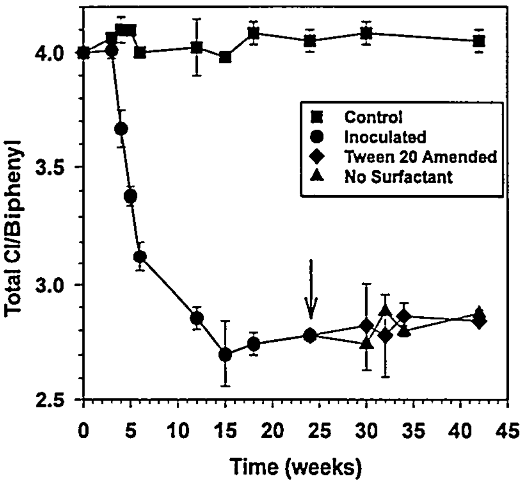

Fig. 1 Time Course of Aroclor 1248 Dechlorination in Control (■) and Inoculated (●) Sediments (The arrow indicates when vials were divided and amended with a sub-CMC of Tween 20 [0.05%] (◆) or left untreated (▲) [from Liu et al. 1996].)

Continued incubation for up to 18 weeks showed no enhancement of dechlorination when compared with unamended sediments (Fig. 1; Liu et al. 1996).

In a parallel set of experiments, Tween 20 was added to Aroclor 1248 sediment slurries at the time of inoculation and also periodically every 6 weeks. The periodic amendment slightly enhanced the rate of dechlorination, while the single addition had no effect on the rate or lag period. However, the overall extent and final congener pattern in each treatment were similar to the untreated control (Kwon et al. 1995).

These results show that addition of a sub-CMC of Tween 20 to sediments at the plateau did not bring about any additional dechlorination even though the aqueous-phase PCB concentration was enhanced. Recent investigations have shown that even sub-CMCs were effective in enhancing the biodegradation of various sorbed HOCs (Aronstein et al. 1991; Aronstein and Alexander 1993), probably because, even at these levels, HOCs can partition to nonionic surfactant monomers, effecting an increase in their apparent aqueous-phase concentrations (Kile and Chiou 1989; Edwards et al. 1992). Therefore, the apparent cessation of dechlorination does not appear to be due to the bioavailability of PCBs to the dechlorinating microorganisms. Laboratory dechlorination studies of preexisting PCBs in sediments also suggested that bioavailability might not be a major limitation (Sokol et al. 1996; Abramowicz et al. 1993; Alder et al. 1993).

2.2 Electron Donors

In search for suitable organic carbon/energy sources, we tested dried algal cells, since algal carbon is a major source of organic matter in sediments. When this algal carbon was added to a sediment-free system, it supported the dechlorination of the single test congener 2,3,4-trichlorobiphenyl (Rhee, unpublished). To determine whether an enrichment with this carbon source would enhance dechlorination or restart the process when dechlorination leveled off, in one experiment, sediments were prepared with algal carbon and in another the carbon was added when dechlorination reached a plateau. PCBs in sediment slurries initially prepared with the algal carbon were dechlorinated to the same level with the identical congener pattern as the untreated control sediments. Addition of the algal carbon to the plateau sediments did not stimulate any additional dechlorination (Kwon et al. 1995). Amendment of plateau sediments with the fatty acids acetate and formate, which are substrates for methanogens, also failed to restart dechlorination (Sokol and Rhee, unpublished). (Methanogens have been implicated to play a role in the dechlorination of PCBs [Ye et al. 1995]). In another experiment, addition of pyruvate and malate to sediments at the time of inoculation slightly inhibited the dechlorination of Aroclor 1248 (Rhee and Kwon, unpublished). Thus, the limitation of electron donors does not appear to be the cause of the restricted dechlorination.

Attempts to enhance PCB dechlorination through enrichment with carbon/energy sources have in general increased the rate or reduced the lag period but have failed to increase the overall extent of dechlorination (Nies and Vogel 1990; Morris et al. 1992). The addition of a fatty-acid mixture resulted in a similar rate enhancement in Hudson River sediments, but not in sediments from the New Bedford Harbor or Silver Lake, which in general had high organic content (Alder et al. 1993).

2.3 Inhibition by Metabolites

To determine whether the plateau in dechlorination might be due to the accumulation of any soluble metabolic products from members of the dechlorinating consortia, the following experiment was set up. The supernatant, from vials containing sediment slurries that had reached a low plateau level of dechlorination after 24 weeks of incubation, were removed, and the sediments split into two portions. One portion received fresh media, while the second had the original supernatant replaced. Continued incubation of these sediments with either fresh media (old sediment; new media) or the original supernatant (old sediment; old media) did not result in any further dechlorination. Analysis of the sediments after an additional 6, 8, 10, and 18 weeks of incubation showed that the total chlorines per biphenyl remained constant at approximately 2.7 (Fig. 2a). A detailed examination of the congener profile also revealed no change in the congener pattern in either treatment. These results indicate that the limit of dechlorination was not set by the production of any inhibitory metabolites by the sediment microorganisms.

To determine whether the old supernatant might affect the dechlorination of fresh Aroclor 1248, sediment slurries, spiked with fresh Aroclor 1248, were prepared with either the 24-week-old supernatant or new anaerobic media, and their dechlorination was compared. After 14 weeks of incubation, the total chlorines per biphenyl in both treatments were reduced to 2.7, showing no further change out to the end of the experiment at 18 weeks (Fig. 2b). Both the time course and final extent of dechlorination were similar to those found in the initial experiment. Regardless of the media differences in the two treatments, both the pattern and extent of dechlorination were the same. The results show no metabolic products in the dechlorinated sediments at the plateau that would inhibit dechlorination of fresh Aroclor 1248.

Metabolites produced during the biodegradation of other xenobiotics have been found to inhibit their further transformation. For instance, the biodegradation of 3-chlorobenzoate (Suflita et al. 1983), trichloroethylene (Alvarez-Cohen and McCarty 1991) and phenol (Murakami and Alexander 1989) was inhibited by intermediate metabolites from the respective compounds. However, the production of metabolic products by dechlorinating microorganisms does not appear to be responsible for the limitation of Aroclor dechlorination.

A comparison of the dechlorination profiles between all four treatments after 18 weeks of incubation revealed that the congener patterns were almost identical, regardless of the sediment-media combination (Fig. 3). When partially dechlorinated St. Lawrence River sediments (originally contaminated by Aroclor 1248) were incubated further in the laboratory, dechlorination continued,

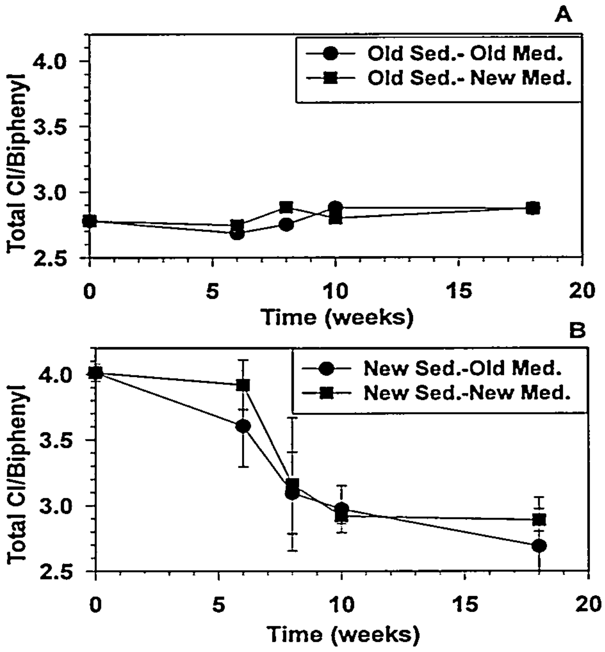

Fig. 2 Comparison of Dechlorination between (A) Plateau Sediments with the Addition of Fresh Anaerobic Media (old sed.-new media) and the Original Supernatant (old sed.-old media) (B) Fresh Aroclor 1248 Spiked Sediments Prepared with the Supernatant from Plateau Sediments (new sed.-old media) and New Anaerobic Media (new sed.-new media). (The final congener pattern was the same in all treatments regardless of sediment-media combination [from Liu et al. 1996].)

ending eventually at a low plateau. Interestingly, both the extent and final congener pattern at this plateau were almost identical to those of the laboratory-spiked sediments (Fig. 4; Sokol et al. 1996). This finding, along with the fact that no amendment was able to enhance dechlorination beyond the observed plateau level, suggests that the cessation was due to the accumulation of daughter congeners with chlorine substitution patterns that could not be utilized as electron acceptors by the present microbial population (Liu et al. 1996).

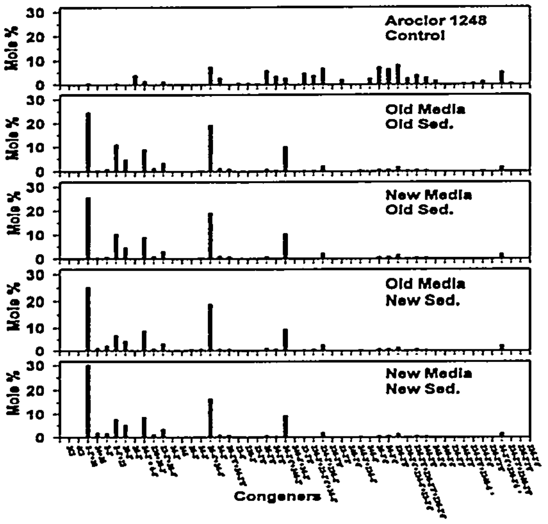

Fig. 3 Mole Percent Comparison of Congeners between Old Sediment:Old Media, Old Sediment:New Media, New Sediment:Old Media, and New Sediment:New Media Treatments after 18 weeks of Incubation (from Liu et al. 1996)

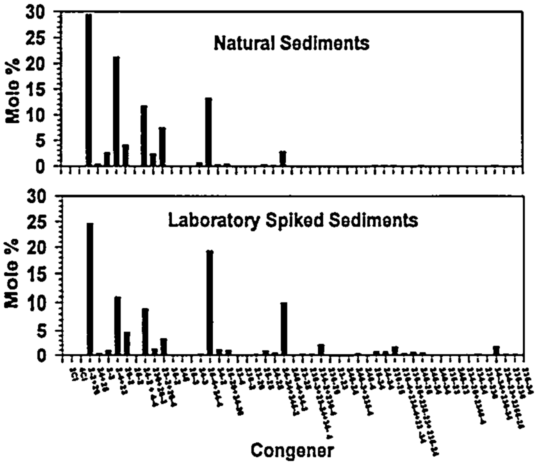

Fig. 4 Mole Percent Comparison of Congeners in Partially Dechlorinated St. Lawrence River Sediments and PCB-Free Sediments Spiked with Aroclor 1248 after 4 Months of Incubation in the Laboratory (from Sokol et al. 1996)

3 POPULATION DYNAMICS OF PCB-DECHLORINATORS

If the declining availability of suitable electron acceptors was indeed the reason why dechlorination slowed and eventually stopped at the plateau level, the dechlorinating microorganisms, which depend on these suitable congeners, should also decrease following a similar pattern. However, despite their environmental significance, little is known about the microorganisms or consortia of microorganisms responsible for PCB dechlorination. Efforts to isolate and characterize them have so far failed. However, we, for the first time, were able to determine their population dynamics by adapting the most probable number (MPN) technique. This statistical method is based on the serial dilution of microorganisms, which permits the estimation of population density measuring a characteristic transformation in a given dilution. Since it relies on the measurement of a population's transformation characteristics, an actual count of single cells or colonies is not required. The presence of dechlorinators is based on their ability to dechlorinate two test congeners (2,3,4- and 2,5-3',4'-chlorobiphenyls) coated on PCB-free sediment. (Previous work in our laboratory has shown that these two congeners are readily dechlorinated [Rhee et al. 1993c; Sokol et al. 1994].) Sulfate-reducing bacteria and methanogens, which have been implicated in certain types of dechlorination, were also counted using the same technique; the former were recognized by the formation of a black FeS precipitate in the MPN vials, and the latter were detected through the measurement of methane gas in the vial's headspace.

When microorganisms from the General Motors (GM) Superfund site in the St. Lawrence River, New York, were inoculated into Aroclor 1248-spiked sediments, dechlorination began after a 3-week lag period (Fig. 5). The start of dechlorination coincided with an increase in the dechlorinating population by two orders of magnitude to 4.6 × 10^7 cells g^{-1} sediment. Dechlorination continued until the sixth week, reducing the average number of chlorines per biphenyl by 28%, from 3.89 to 2.79. After this time, dechlorination reached a low plateau, showing no further change. Once dechlorination reached this plateau and ceased, the number of dechlorinators also began to decrease, returning to a level similar to the initial inoculum size after 18 weeks of incubation. Therefore, the lower plateau in the dechlorination was due to the exhaustion of suitable electron acceptors for the dechlorinating populations.

Interestingly, we also found that when the same inoculum was placed into PCB-free sediments, the dechlorinating population size decreased over time from their initial level (Fig. 5). These results suggest that PCBs are required for the selective enrichment of dechlorinators. Recent evidence suggests that dechlorinating microorganisms can use PCBs as an alternate electron acceptor and gain sufficient energy to support their growth (Dolfing and Harrison 1992; Holmes et al. 1993). Electron acceptors are often limiting in anaerobic environments, and thus chlorinated substrates represent a resource for any microorganisms capable of transferring electrons to them. The decrease of the dechlorinator population as dechlorination subsided can then reflect the diminishing availability of electron acceptors to the population. Therefore, the availability of PCB congeners can provide a selective advantage for the growth of the dechlorinating population.

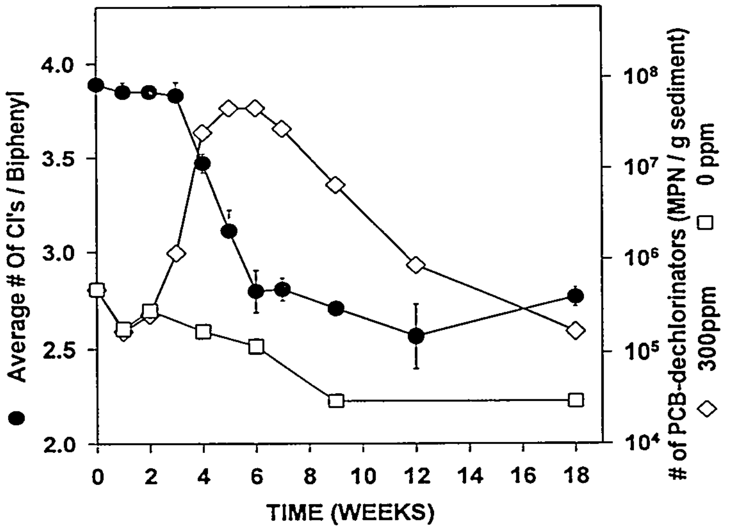

Fig. 5 Time Course of Aroclor 1248 Dechlorination (●) and Population Dynamics of PCB Dechlorinators in PCB Amended (◇) and Unamended (□) Control Sediments. (from Kim and Rhee 1996)

The population dynamics of methanogens and sulfate reducers were also followed in the same sediments using the MPN technique. The sulfate reducers grew rapidly, reaching their highest population density 3 weeks earlier than the dechlorinators (Fig. 6). In addition, their population size was about an order of magnitude higher than that of the dechlorinators (Kim and Rhee 1996). On the other hand, the methanogen population had a growth curve very similar to that of the dechlorinators and reached similar population densities. However, unlike the dechlorinators, the size of both the methanogen and sulfate-reducing populations remained high even after dechlorination ceased at the plateau level (Fig. 6). Furthermore, the population dynamics of these two groups remained the same even in PCB-free sediments (Kim and Rhee 1996). It is still unclear, however, how these two groups of sediment bacteria are actually involved in the dechlorination process.

These results demonstrate that the growth of PCB-dechlorinators requires the presence of PCBs. Dechlorination potential, as measured by the length of the lag before PCB dechlorination in laboratory cultures, also depended on the PCB concentration in sediments from which the inoculum came (Sokol et al. 1995). Taken together, these results imply (1) a possible correlation between PCB concentration and dechlorinator population size and (2) that PCB concentration may have to be above a certain threshold level to maintain the growth of dechlorinators.

4 SECOND PHASE OF DECHLORINATION

Recent work suggests that with prolonged incubation, a shift in the dechlorinating community composition can lead to a second phase of dechlorination. When the native St. Lawrence River

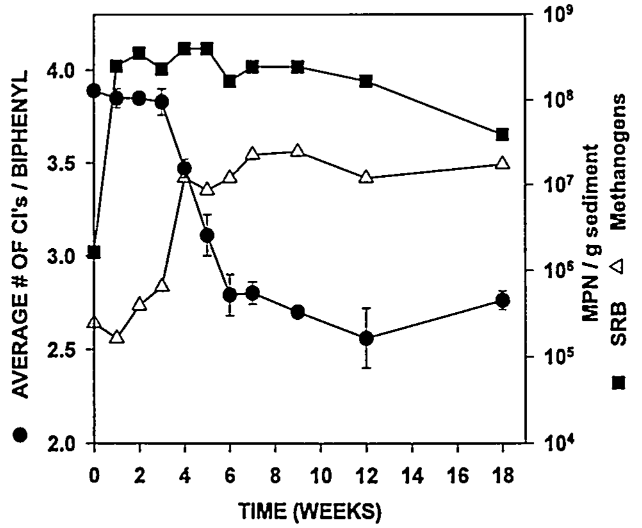

Fig. 6 Population Dynamics of Methanogens (△) and Sulfate-Reducing Bacteria {SRB} (■) in Relation to PCB Dechlorination (●) (from Kim and Rhee 1996)

sediments were incubated further after the initial plateau, a second phase of dechlorination ensued, resulting in a secondary plateau, after 15 months (Fig. 7; Sokol et al. 1996). The observed reduction in total chlorines was due to the further dechlorination of a single major product, 2,4-4'- and 2,4-5'-trichlorobiphenyl (Fig. 8). Loss of this peak was balanced by accumulation of 2-4'+4-4'-dichlorobiphenyl, indicating *para* chlorine removal. This second phase was congener-specific, since there was no further dechlorination of 2-4'+4-4' or other *para*-rich parent compounds, such as 2,4-2',4'-tetrachlorobiphenyl (Sokol et al. 1996). These results suggest that, after a lag period, a new population of dechlorinators developed that could use these specific congeners as their electron acceptors. The long lag before the dechlorination of these congeners also implies that the new population was entirely different from those transforming the original congeners. Although it is unclear why 2,5-4' +2,4-4'-trichlorobiphenyl, which was present from the beginning, did not select these populations earlier, it is possible that competition between other populations prevented them from reaching an effective density, and only after the initial population declined (see above) were they able to grow. It is not known, however, how far this kind of apparent microbial succession can remove chlorines from the biphenyl ring of PCBs.

5 ACKNOWLEDGMENTS

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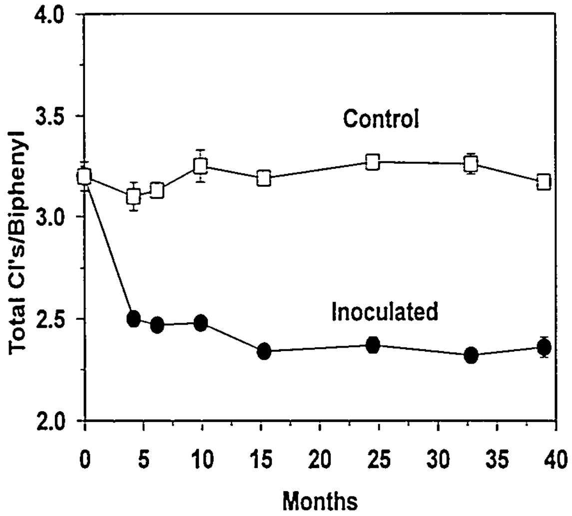

Fig. 7 Time Course of Dechlorination of Preexisting PCBs in St. Lawrence River Sediments over a Three-Year Period of Laboratory Incubation (from Sokol et al. 1996)

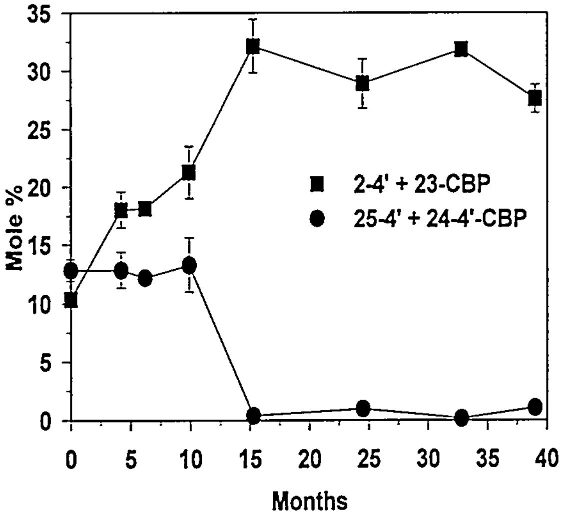

Fig. 8 Dechlorination of 25-4'+24-4'-CBP and Accumulation of 2-4'+23-CBP in St. Lawrence River Sediments with Extended Laboratory Incubation (from Sokol et al. 1996)

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THERMAL TREATMENT

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RECOVERY OF HEAVY METALS FROM INTRACTABLE WASTES: A THERMAL APPROACH

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ABSTRACT

The generation of industrial solid wastes containing leachable species of environmental concern is a problem for developing and developed nations alike. These materials arise from direct processing of mineral ores, from production of metals and minerals, from manufacturing operations, and from air and water pollution treatment processes. The general characteristics that make these wastes intractable is that their content of hazardous species is not easily liberated from the waste yet is not bound so tightly that they are safe for landfill disposal or industrial use. The approach taken in this work is a thermal treatment that separates the inorganic contaminants from the wastes. The objective is to provide recovery and reuse of both the residual solids and liberated contaminants. The results from operating this technique using two very different types of waste are described. The reasons that the process will work for a wide variety of wastes are explored. By using the knowledge of the thermodynamic stability of the phases found from the characterization analyses, a thermal regime was found that allowed separation of the contaminants without capturing the matrix materials. Bench scale studies were carried out using a tube furnace. Samples of the wastes were heated in crucible boats from 750 to 1150°C in the presence of various chlorinating agents. The offgas contained $90^{+}\%$ of the targeted contaminants despite their complex matrix form. The residue was free of contamination. As a result of the efficient concentrating mechanism of the process, the contaminants in the offgas solids are attractive for reuse in metallurgical industries. As an additional benefit, the organic contaminants of the residues were eliminated. Dioxin traces in the solids before treatment were absent after treatment.

1 BACKGROUND

The challenge for minimizing hazardous wastes for disposal is directly linked to the cost of processing. Wastes that have concentrations of hazardous components at or below those of crustal abundances will never be able to be processed cost effectively. Only those wastes that have been significantly enriched above crustal levels should be considered for recovery or processing. Even with enrichment, there still remains a considerable technological challenge to effectively separate the species of environmental concern. For most organic contaminants in solid wastes, there is no market for the organics, and the only option is destruction of the contaminant. Many technologies have been proposed for the destruction, including oxidation, combustion, thermal degradation, and reduction. Since organic molecules are not stable above 600°C, there is no doubt that destruction of the offending molecules can be carried out. Apart from ensuring that the treatment completes the destruction and that reformation of organochlorine compounds does not occur, the major obstacles are cost and public concern over siting and technology reliability. With inorganic contaminants, the challenges are much greater and have yet to be resolved, since destruction of the elemental species is not possible.

Many "treatment" technologies have been proposed for wastes containing inorganic species, such as lead, arsenic, cadmium, chromium, and mercury. Most of these involve immobilizing the hazardous components to minimize the risk of disposal of the waste. Binders, cement, glassifying, and slagging have all been tested for immobilizing the inorganic components. While immobilization can be achieved in the short term, there are difficulties in predicting long-term consequences. Despite the use of currently acceptable waste disposal practices, the long-term storage of hazardous wastes in disposal sites still carries long-term liabilities. Regulations can change, waste disposal operations can fail financially, sites can leak, land-use guidelines can change, and new forms of environmental damage can be discovered. Love Canal in the United States is an example of how liability can arise unexpectedly.

Site remediation is enormously expensive if environmental damage is found to be associated with the waste. Even multinational companies, such as Union Carbide and Exxon, can find the legal, environmental, and public image costs associated with site cleanup sufficient to endanger the viability of the company. Thus, the only certain way to avoid long-term risk is to not dispose of hazardous wastes. The removal of the hazardous inorganic constituents from the complex wastes would render the waste nonhazardous and, hence, eliminate the liability associated with the waste. Yet, the very nature of a waste indicates that it has little if any value, so that the separation technology must be efficient, selective, and cost-effective. Various leaching and extraction methods have been proposed, but in all cases they generate complex aqueous streams containing the hazardous contaminants and many co-extracted common elements. Thus, the hazardous components have been transposed from one media to another, where they may be equally difficult to contain or recover. This paper describes a separation technology that has been developed to satisfy the requirements for recovery of hazardous contaminants from complex wastes.

2 EXPERIMENTAL DESCRIPTION

2.1 Heating Apparatus and Analytical Instruments

For this experiment, we used the following: a tube furnace, Carbolite Model TZF 12/75, with a programmed temperature controller, Model 808 P; a quartz tube, 100 cm long and 3 cm inside diameter, to contain the sample boat and confine the heating space; a gas absorber; air supply from a cylinder; Teflon beakers, 30 mL; graphite crucibles, 8 mL; atomic absorption spectrometer, Perkin Elmer Model 703; an inductively coupled plasma spectrometer, Spectro Analytical Instruments Model Spectroflame P; and an x-ray diffractometer.

2.2 Reagents

All chemicals were of reagent grade, and water was pretreated by Reverse Osmosis before deionization. Chemicals included nitric acid, hydrofluoric acid, perchloric acid, lithium metaborate, 1,000 parts per million (ppm) standard solutions of Pb, Cu, Zn, Cd, Cr, and Mn.

2.3 Samples

The steel samples were from a steel company using a basic oxygen furnace (BOF) and were collected as dry dusts from an electrostatic precipitator and as wet sludges from a water quench and scrubber.

The fly ash used in this study was from a municipal solid waste (MSW) energy-from-waste incineration plant. Grab samples of the ash collected from the electrostatic precipitators were passed through a 20-mesh sieve and well mixed by a tumbling mixer in this laboratory.

2.4 Procedure for Thermal Treatment of Samples

Samples (approximately 3 g) and a solid chloridizing agent (a chloride salt, such as sodium) were weighed. They were well mixed and transferred to a sample boat. The sample boat was then pushed with a rod into the mid-section of the quartz tube in the furnace. The general arrangement of the thermal system is shown in Fig. 1. A gentle flow of air across the sample boat carried the volatilized components out of the furnace and into the absorber. Analysis of the captured volatiles and the residue in the furnace provided a mass balance for confirming analyses.

2.5 Characterization of Samples and Products

A wide variety of analytical procedures were used. Liquid samples were analyzed by inductively coupled plasma (ICP) and AA spectroscopy. Solids were analyzed by microscopic techniques, such as optical phase identification, SEM/EDS, XRD for phase confirmation, and elemental analysis using ICP analysis through the digestion steps described below.

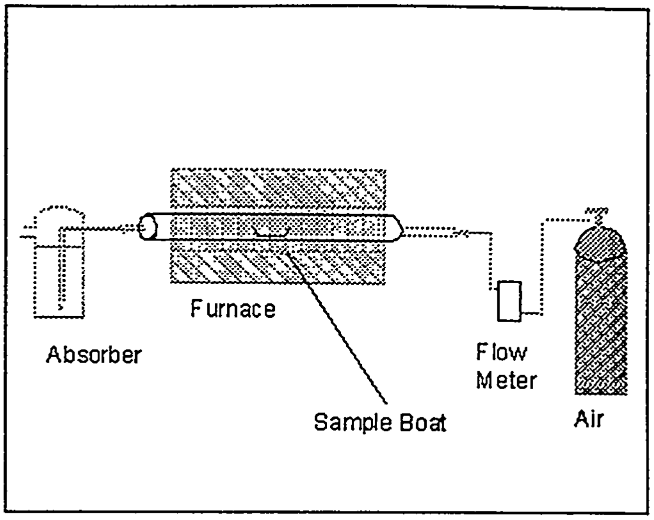

Fig. 1 Schematic of Thermal Equipment

2.6 Digestion

An aliquot of the steel dust or fly ash residue was digested with an acid mixture HNO_3 : HF : $HClO_4$ (4:2:1), and the solution was diluted with 5% HNO_3. The fly ash residue cannot be completely dissolved by digestion with the acid mixture. The acid-resistant matter contains many refractory chemicals that should be accounted for if a complete analysis is desired. The undissolved residue was filtered out and dried. It was transferred to an 8-mL graphite crucible and mixed with 0.5 g of lithium metaborate ($LiBO_2$). The mixture was fused at 9,500°C for 5 min. The molten bead was poured into a beaker containing 30 mL of 5% (v/v) HNO_3 and dissolved with the aid of a magnetic stirrer. These solutions were used to determine the chemical elements by ICP spectrometry.

3 RESULTS AND DISCUSSION

The two samples investigated in this work represent very different types of chemistries. The steel dust is primarily iron oxide enriched in elements such as zinc, lead, sodium, and potassium. (See Table 1 for analysis.) The zinc inhibits its use as an iron oxide feedstock to the blast furnace. The contaminants become volatile under the high temperatures of the furnace, causing fouling in the furnace, while zinc may also be incorporated into the steel, degrading its properties. Despite the activity in the furnace, the zinc component is surprisingly difficult to remove from the dust by conventional leaching techniques. The reason is that zinc exists in the steel dusts as refractory zinc ferrite ($ZnFe_2O_4$). In the zinc industry where the residues contain substantial zinc ferrite values, hot sulfuric acid leaching is practiced to extract zinc, but this operation does solubilize iron and create a very significant environmental problem.

The fly ash sample (Table 1) is primarily a silicate residue enriched in lead and cadmium. Detailed morphological studies (Graydon and Kirk 1992) have shown that the contaminants are held as readily leachable salts on the surfaces of fly ash particles, such as glassy spheres of silica,

Table 1 Composition of Waste Samples

Analysis of Wastes (Major Species)	
Steel Dust	Fly Ash
Magnetite Fe_3O_4 (75%)	Silica SiO_2 (39%)
Calcium oxide and carbonate $CaO + CaCO_3$ (13.3%)	Calcium oxide and sulfate $CaO + CaSO_4$ (15%)
Periclase MgO (3.5%)	Alumina Al_2O_3 (13.6%)
Quartz SiO_2	Magnetite Fe_3O_4 (3%)
Zinc ferrite $ZnFe_2O_4$	Titanium dioxide TiO_2 (3%)

aluminosilicate, and titanium dioxide, and as ions incorporated into the silicate substrates. Aggressive leaching of these materials to remove the contaminants results in solutions containing soluble silicates, which are notoriously difficult to filter (Gong and Kirk 1994). Thus, the contaminants show both short- and long-term leaching, making encapsulation/stabilization the only commercial practice for disposal.

The effect of thermal treatment of the steel dust sample at 1,000°C for 180 min is shown in Table 2. As can be seen from the analysis, the principal component is iron (as hematite), with the major contaminant being zinc at 5%.

Heating the untreated sample resulted in volatilization of <50% of the lead and almost none of the other components. With the addition of a chlorinating agent, the volatilization of zinc and lead became essentially complete. Despite the refractory nature of the zinc ferrite, the thermal separation was carried out under simple oxidizing conditions.

The fly ash sample was treated in a similar manner. The sample was heated to 1,000°C for 180 min under a low flow of air. The analysis of the experiment is shown in Table 3. Many more elements contribute to the composition of the matrix. Although not shown in the analysis, silica is the primary component (40%) and, as expected, is not volatile under the conditions of the test.

There was good recovery of the elements Pb, Zn, Cu, Cd, Na, and K. X-ray powder diffraction (XRPD) analysis, using copper Kα radiation (34 kV, 20 mA), showed that more crystalline compounds existed in the heat-treated fly ash sample than in the untreated one. A chemical phase of $Ca(Mg, Fe)Si_2O_6$ was identified in the heat-treated sample, which was not found in the untreated fly ash.

Table 2 Thermal Treatment of a Steel Dust Sample at 1,000°C for 3 h

		Volatilized with or without Chlorinating Agent (μg/g)	
Element	Content (μg/g)	With Chlorinating Agent	Without Chlorinating Agent
Zn[a]	50,200	49,600	38
Pb	7,460	7,470	4,440
Na	680	413	[a]
Cu	270	120	6
Cd	120	45	2
Fe	582,000	0	0
Ca	47,800	470	[a]
Mn	10,120	50	[a]

[a] Zinc was identified as zinc ferrite ($ZnFe_2O_4$).

Table 3 Fly Ash Sample Thermal Treatment at 1000°C for 3 h

Element	Content (μg/g)	Volatilized (μg/g) with the Addition of a Chlorinating Agent
Zn[a]	9,470	9,130
Pb	3,870	3,670
Cu	1,030	930
Cd	140	140
K	24,400	23,000
Na	49,500	37,300
Fe	18,700	83
Ca	105,900	152
Mg	12,300	4
Al	71,100	0
Ti	18,600	0
Mn	1,910	750

[a] Zinc was identified as zinc ferrite ($ZnFe_2O_4$).

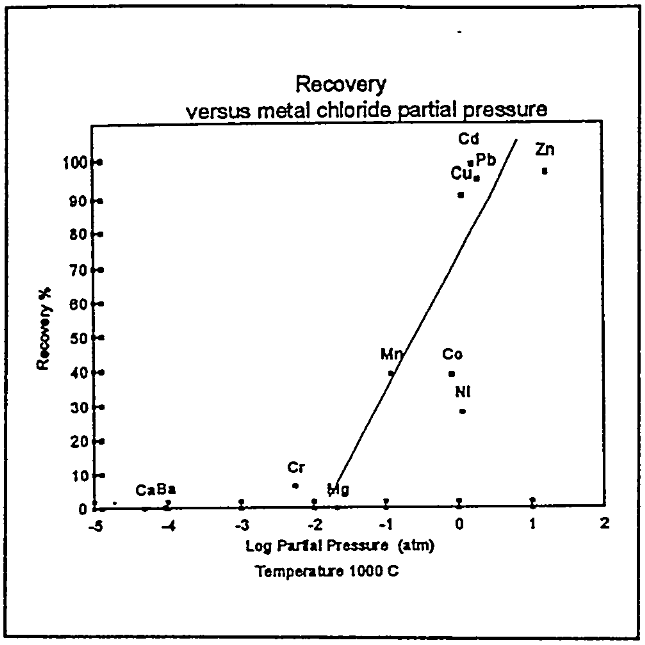

Fig. 2 Recovery of Metals as a Function of Metal Chloride Volatility

From the results of Table 2, the importance of the chlorinating agent is clear. In particular, the recovery of the zinc increases to essentially complete volatilization. Without the availability of a chlorinating agent, only lead can be partially volatilized. From Table 3, a more complete list of elements that have volatility in the presence of a chlorinating agent is given. Lead, zinc, copper, cadmium, potassium, and sodium all show good volatility in the presence of a chlorinating agent. Thus, there is reason to suspect that these metals in both the oxide and silicate matrices react with the chlorinating agent to form volatile chlorides.

In Fig. 2, the correlation of partial pressure of various metal chlorides is plotted against the recovery of metals found from thermally heating the fly ash sample with a chlorinating agent at 1,000°C for 180 min. The values were determined from Gibbs energy values for volatilizing the liquid salt and using $\Delta G^\circ = -RT \ln p$.

As can be seen in Fig. 2, the elements having high recovery correspond to those with substantial chloride salt vapor pressure at 1,000°C. Furthermore, an anion analysis of the scrubber solution revealed that chloride was the dominant anion (>88%). Quenching the offgas from the roaster and performing XRD analyses on the collected salts revealed chloride salts of zinc, lead, and potassium. Thus, the mechanism for recovery of the contaminant metal species should be

$$M_1\mathrm{O} + M_2\mathrm{Cl}_2 = M_1\mathrm{Cl}_2 + M_2\mathrm{O}\,,$$

where M_1 is the oxide of the heavy metal and M_2 is the chlorinating agent. Since the system is operated in a steady-state mode, the flow of air across the heated sample boat continuously transports the volatile chlorides to the collector/scrubber. The results of high recovery being associated with high metal chloride vapor pressure suggest that the rate of volatilization might be the rate controlling step. It is possible for many of the metal oxides to calculate the Gibbs energy for the conversion of the metal oxide to the metal chloride vapor at the furnace reaction temperature. In this work, F*A*C*T, a thermodynamic modeling package, was used to calculate the Gibbs energy for the reaction, and the values were plotted against experimental recovery. The results are shown in Fig. 3. The elements that have good recoveries have negative values for the Gibbs energy (indicating a favorable reaction). The elements having positive Gibbs energy values (indicating no reaction should be possible under standard conditions) are not recovered.

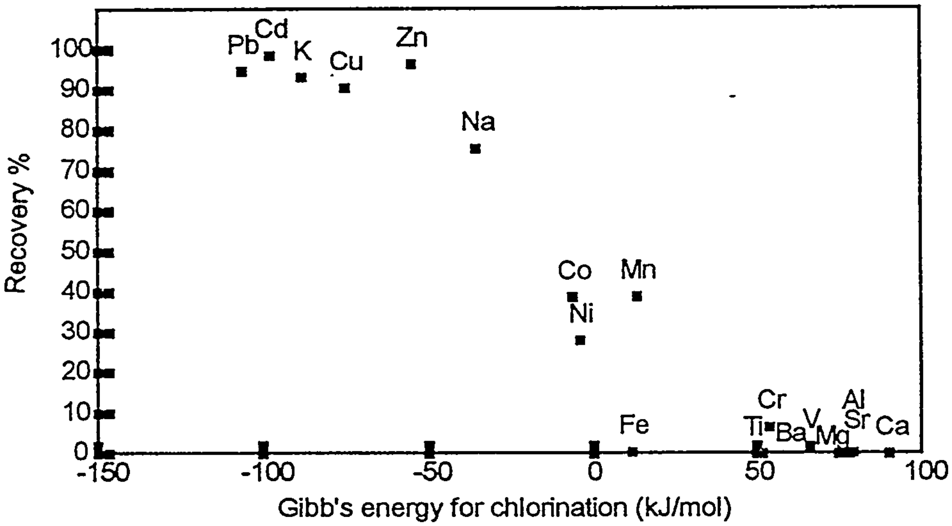

Fig. 3 Recovery at 1,000°C for 180 min as a Function of Gibbs Energy for Metal Chloride Formation

A question remains about those elements whose recoveries are incomplete, such as Co, Ni, Mn, and Na. There is also a concern about zinc, since if the Gibbs energy for zinc ferrate rather than zinc oxide is calculated, the value is + 59 kJ, indicating no recovery should be found in contrast to the experimental results. The difficulty lies in assuming that standard conditions are necessary for recovery. Certainly large negative or positive Gibbs energy values are good indicators for volatility potential or inertness. For those compounds with negative values, the degree of recovery may depend on kinetic factors, such as reactant mass transfer to the solid phase. For those compounds having positive values, however, a closer inspection of the assumptions made for the calculations is necessary. For the reaction,

$$ZnFe_2O_4 + CaCl_2 = Zn\,Cl_2 + CaO + Fe_2O_3 \ ,$$

the physical states of the reactants may change with temperature, and the Gibbs energy for each of the species is temperature dependent. Furthermore, the activity of a volatile species such as $ZnCl_2$ is directly related to its vapor pressure. To recover zinc, there must be some vapor pressure, but not necessarily 1 atm. An analogy is the evaporation of water at temperatures less than 100°C by passing unsaturated air over the surface of the water. The vapor pressure of the water is less than 1 atm, so that evaporation is not as rapid as at the boiling point but does take place. The Gibbs energy for the above reaction was calculated for 1,000°C and various partial pressures of $ZnCl_2$. The results are shown in Fig. 4.

Fig. 4 clearly shows that the reaction can generate 0.001 atm of $ZnCl_2$ at 1,000°C. With continual removal of the zinc chloride vapor by the air stream in the furnace, complete evaporation of the chloride content is possible.

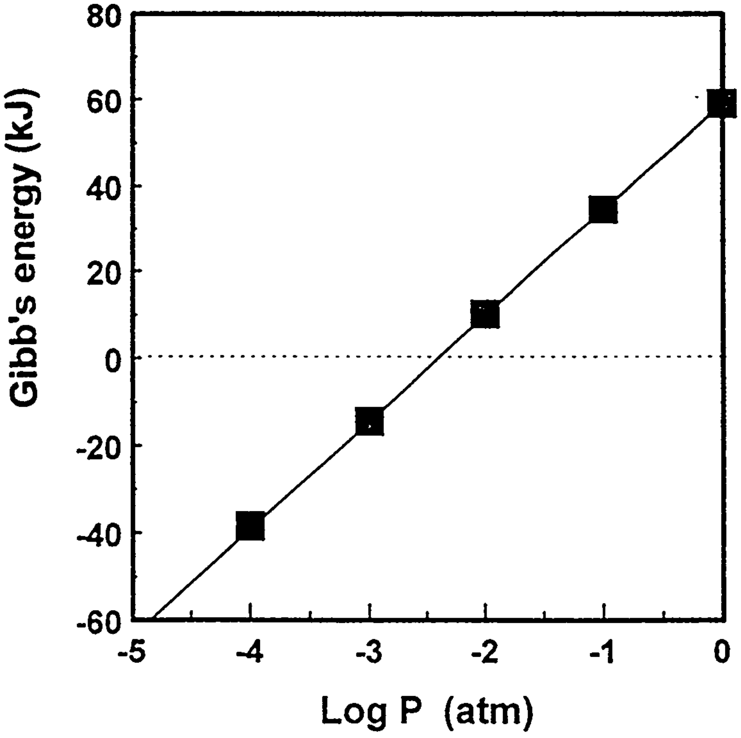

Fig. 4 Gibbs Energy for Zinc Ferrite Conversion to Zinc Chloride as a Function of Partial Pressure at 1,000°C

It has been reported by Jakob et al., who studied volatility of metals from fly ash, that incomplete recovery of zinc is found at high temperatures under oxidizing conditions due to the formation of $Zn_2Si_2O_4$ and $ZnAl_2O_4$. In contrast, in this work, excellent recoveries were found for the fly ash and steel dust samples. We suspect that part of the reason is that the chloridizing agent decomposes as shown below:

$$CaCl_2(l) + 1/2\ O_2 = CaO + Cl_{2\,(g)}\ .$$

The chlorine gas is more mobile than the chloride salt and is able to more efficiently convert the oxides and silicates to the volatile metal chlorides:

$$ZnO + Cl_2 = ZnCl_2 + 1/2\ O_2\ .$$

Research using chlorine gas (not reported in this paper) has shown it to be very aggressive in recovering metal values from fly ash and supports the possibility of the two-step mechanism.

A concern is sometimes raised when a process uses chlorine because of the potential for producing organochlorine compounds. For the wastes in this study, the matrices were inorganic, and there is no possibility of generating organic compounds. For the fly ash sample, it is possible that the ash collected organochlorines from the flue gas. For this reason, the sample was analyzed for dioxins and furans. A sample of the fly ash after being treated with a chloridizing agent and thermally processed at 1,000°C was also analyzed. The results are shown in Table 4. The toxins in the fly ash sample were extracted in refluxing toluene for 16 h using a Soxhlet extractor. The interfering organic compounds were removed from the sample extract by using open-column liquid-solid chromatography. The toxins in the extract were then analyzed by gas chromatography/mass spectrometry.

As can be seen from Table 4 (which follows Sec. 6), traces of the dioxins and furans are in the fly ash sample. The treatment of the fly ash sample for removal of the heavy metals also eliminates the organochlorines from the residue. Thus, the use of chloridizing salts does not cause stabilization or formation of dioxins or furans in the fly ash sample.

4 SUMMARY

Overall, the thermal treatment process allows separation and recovery of a variety of metals, such as Pb, Zn, Cu, Cd, Na, and K, from both oxide- and silicate-type wastes. The mechanism for removal is suggested to be the conversion of the metal contaminant to a volatile chloride salt that can be captured from the furnace offgas. The chemistry functions in an oxidizing atmosphere, which is a substantial benefit for industrial application. The chemistry would appear to be applicable to a large number of wastes and will be the subject of continuing investigation.

Table 4 Dioxin and Furan Analysis of a Fly Ash Sample before and after Treatment

Toxin	Fly Ash Sample (pg/g)	Heat-Treated Sample (pg/g)
Tetrachlorofuran	16,000	1
Tetrachlorodioxin	8,100	1
Pentachlorofuran	31,000	1
Pentachlorodioxin	30,000	3
Hexachlorofuran	43,000	2
Hexachlorodioxin	79,000	3
Heptachlorofuran	50,000	2
Heptachlorodioxin	120,000	4
Octachlorofuran	16,000	2
Octachlorodioxin	170,000	20
2378-tetrachlorofuran	3,000	1
2378-tetrachlorodioxin	450	1
12378-pentachlorofuran	1,700	1
23478-pentachlorofuran	2,800	1
12378-pentachlorodioxin	2,800	1
123478-hexachlorofuran	7,700	2
123678-hexachlorofuran	5,100	1
234678-hexachlorofuran	5,700	2
123789-hexachlorofuran	370	2
123478-hexachlorodioxin	5,300	3
123678-hexachlorodioxin	6,300	3
123789-hexachlorodioxin	11,000	3
1234678-heptachlorofuran	33,000	2
1234789-heptachlorofuran	2,500	2
1234678-heptachlorodioxin	65,000	4

5 ACKNOWLEDGMENTS

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SOLIDIFICATION/STABILIZATION

Chair: Wee Tee Tan, Universiti Pertainian Malaysia, Malaysia

PORE SIZE DISTRIBUTION, STRENGTH, AND MICROSTRUCTURE OF PORTLAND CEMENT PASTE CONTAINING METAL HYDROXIDE WASTE

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ABSTRACT

Stabilization/solidification of hazardous wastes is used to convert hazardous metal hydroxide waste sludge into a solid mass with better handling properties. This study investigated the pore size development of ordinary portland cement pastes containing metal hydroxide waste sludge and rice husk ash using mercury intrusion porosimetry. The effects of age and the addition of rice husk ash on pore size development and strength were studied. It was found that the pore structures of mixes changed significantly with curing age. The pore size shifted from 1,204 to 324 Å for 3-day old cement paste, and from 956 to 263 Å for a 7-day old sample. A reduction in pore size distribution for different curing ages was also observed in the other mixtures. From this limited study, no conclusion could be made as to any correlation between strength development and porosity.

1 INTRODUCTION

Treatment technologies such as cement-based stabilization/solidification (S/S) are important in the treatment of certain hazardous materials such as metal-based inorganic waste streams. As a proven technology for the treatment of hazardous waste and hazardous waste sites (USEPA, 1989), it is commonly used to convert hazardous liquid or solid wastes into less hazardous or nonhazardous solids before they are disposed in a landfill. The process involves the blending of cement or cement and pozzolanic materials with waste to produce a structurally stable product with reduced porosity, permeability, metal solubility, and mobility.

Porosity and pore size distribution of hardened cement paste have been widely studied because of their influence on some mechanical properties of cement (Parcevaux, 1984). Total porosity and pore size distribution of a solid affect the physiomechanical properties and permeability characteristics of a solid and can be utilized as potential indicators of the physicomechanical properties and leaching potential of S/S wastes (Gress and El-Korchi, 1993). Bishop et al. (1992) studied the effect of leaching on the pore size of S/S waste and found that the pore structure varied depending upon the mix formulation used. Therefore, study of the pore size distribution of a solidified waste sample is important in assessing the durability of the resulting product.

The pore size distribution in the hardened samples can be examined by mercury porosimetry, whereby the volume of mercury penetrating the sample is measured as a function of increasing pressure, p. Pressure is related to the diameter, d, of the pores penetrated at that pressure by the following equation:

$$p = 4\gamma \cos \theta / d,$$

where

γ = surface tension of Hg,
θ = advancing contact angle with the solid,
d = equivalent diameter of the intruded pores.

The mercury porisimetry technique involves enclosing a porous sample in a chamber, surrounding it with mercury, applying monitored increments of pressure, and measuring the volume of mercury forced into the sample. Information on the pore size distribution, density, and specific surface area of porous material can be obtained from mercury intrusion porosimetry (MIP) studies. MIP among others gives a curve of cumulative pore volume versus bore size. The pore size distribution is approximated by estimating the intruded volume of mercury under pressure. The total porosity can also be approximated from such a curve in order to determine a characteristic pore size as well as to indicate material character (Cook and Hover, 1993).

MIP was used to study the microstructure (pore size distribution) of the solidified sample. The aim was to obtain a better understanding of the pore size development of the solidified waste sample with and without the addition of rice husk ash at different curing ages.

2 MATERIALS AND METHODS

2.1 Raw Materials

The stabilized waste was obtained from a semiconductor factory. The liquid effluent waste, which is inorganic in nature, contains high concentrations of Cu, Fe, Pb, Ni, Zn, Sn, and Mn. Stabilization was carried out at the treatment facility of the factory by the addition of NaOH and flocculants at a controlled pH of approximately 9.5. The resulting sludge was sent to a filter press to remove excess liquid before storing the stabilized filter cake in the factory premises. The resulting filter cake contained approximately 20–30% insoluble residue. Typical concentration of metals in the stabilized waste filter cake are shown in Table l.

TABLE 1 Metal Concentration in Stabilized Waste

Metal	Concentration (mg/kg)
Copper	257,797.0
Manganese	334.0
Nickel	5,556.0
Lead	39,441.0
Tin	520.0
Iron	12,004.0
Zinc	960.0

Type I portland cement conforming to BS12 was used throughout the investigation. The cement used was stored in steel drums with an epoxy lining and tightened with steel rims to prevent the cement from hardening. Rice husk obtained from Kuala Selangor was burned in a furnace to obtain the ash and stored similarly. Deionized water was used as the mixing water.

2.2 Solidification of Stabilized Waste

Solidification was initiated by mixing cement and waste at a fixed water/solid ratio of 0.4. When rice husk ash was used, it was added before the addition of waste. Mixing was done in a 25-L Hobart type mixer until mixture appeared homogeneous. The mixture was then cast into 50 x 50 x 50 film Perspex cubes in three layers, with each layer being compacted by means of a vibrating table. The samples were then covered with a Perspex cover to reduce the evaporation of water. Samples were removed after 1 to 3 days, depending on the state of the solidified samples. Samples containing waste and cement only were usually removed 3 days after casting. The samples were then air-cured at room temperature.

Samples for porosity studies were oven dried at 105°C overnight and stored in a vacuum dessicator until examined. The pore size distribution of each sample was determined using a Micromeritics Autopore III, which is capable of intrusion pressures up to 60,000 psi (407 mPa). The surface tension of mercury was taken at 485.0 dynes/cm and contact was chosen at 130.0 degrees. An equilibrium time of 60 seconds was applied for each step of the high-pressure run.

Unconfined compressive strength of the solidified products was taken at 3, 7, and 28 days curing. Table 2 shows the mix formulations and unconfined compressive strength of the samples.

3 RESULTS AND DISCUSSIONS

Figures 1(a) through 1(c) show a comparison of the cumulative intrusion volumes for cement paste, cement plus waste, and cement plus rice husk ash plus waste samples at 3 days. Samples containing cement, rice husk ash, and waste had the highest total intruded volume. This could be attributed to the presence of rice husk ash, which has a porous structure, and the pozzolanic reaction between the ash and calcium hydroxide left because of cement hydration that has not taken place.

Figures 2(a) and 2(b) show the dominant pore sizes for cement paste samples at 3 and 7 days. These bar graphs show the incremental intrusion volumes at different pore diameters. For comparison purposes, the incremental intrusion volume at the selected diameter is normalized to total intrusion volume and expressed in percentage on the *y*-axis. At 3 days, most of the pore volume of cement paste is contributed by pores with diameters from 2,135 to 263 Å, while at 7 days the pore volume for Mix A is contributed by pores with diameters from 1,818 to 324 Å.

The major hydration products of cement are calcium hydroxide and calcium silicate hydrate (C-S-H) gel which consists of thin, densely packed silicate fibrils radiating from cement particles and interlacing with one another (Walsh et al., 1974). The shift to smaller pore diameter is expected because continuing hydration of the clinker progressively fills and subdivides the pores (Bye, 1983).

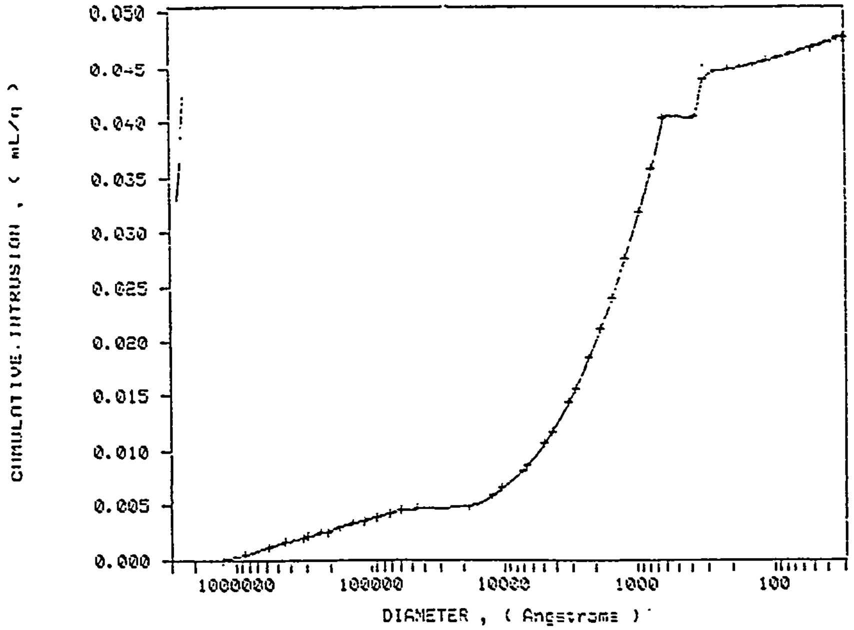
Figures 3(a) and 3(b) show the incremental intrusion volume for Mix B at 7 and 28 days. At 7 days, most of the pore volume is dominated by pores with diameters from 3804 to 1,660 Å. As shown in Fig. 3(b), at 28 days the pore size has shifted to smaller regimes, and pore volume is contributed by pores with diameters from 1,199 to 326 Å. This measurement implies that the slow pozzolanic reaction between the rice husk ash particles and calcium hydroxide takes place between 7 and 28 days, contributing to the pore refinement of the solidified sample. Comparing Fig. 1(b) and Fig. 3(a), the large shift in pore diameter is brought about by the presence of rice husk ash which has a cellular structure, thus contributing to the high porosity.

Figures 4(a) and 4(b) show the incremental intrusion volume for Mix C at 3 and 7 days. At 3 days the pore volume of Mix C is contributed by pores with diameters from 263 to 73 Å, while at 7 days pores with diameters from 326 to 52 Å contributed to the pore volume. From Fig. 3(a) and Fig. 4(b), pore size shifted to smaller regimes upon the addition of metal hydroxide waste, i.e. from pores with diameters between 3,804 and 1,660 Å, to pores with diameters of 326 to 52 Å. This drastic shift to smaller pore radii could be attributed to the presence of the metal hydroxide waste, which partly filled the cellular structures of rice husk ash. The slow pozzolanic reaction between rice husk ash particles and $Ca(OH)_2$ to form silicate hydrates, as mentioned earlier, can also contribute to this shift.

TABLE 2 Mixture Formulations and Strengths

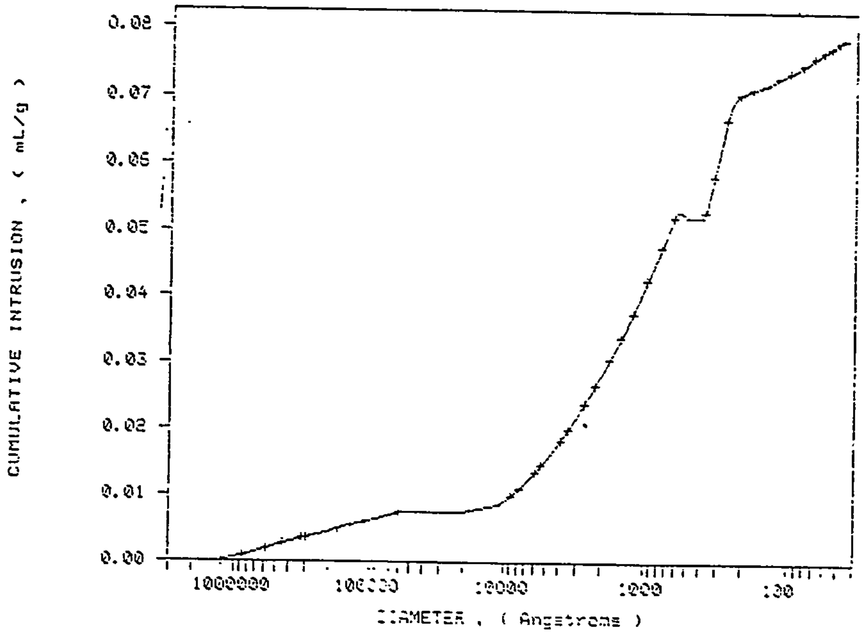
Mixture (% w/w)	Composition	Unconfined Compressive Strength (N/mm^2)
A	Cement, deionized water	
70% OPC	3 days	56.1
30% H_2O	7 days	63.4
	28 days	83.7
B	Cement, rice husk ash	
53% OPC	3 days	22.4
17% RHA	7 days	28.8
30% H_2O	28 days	38.6
C	Cement, rice husk ash, metal hydroxide waste sludge	
23% OPC	3 days	9.02×10^{-2}
17% RHA	7 days	1.35×10^{-1}
30% Waste	28 days	2.71×10^{-1}
30% H_2O		

OPC = ordinary portland cement
RHA = rice hush ash

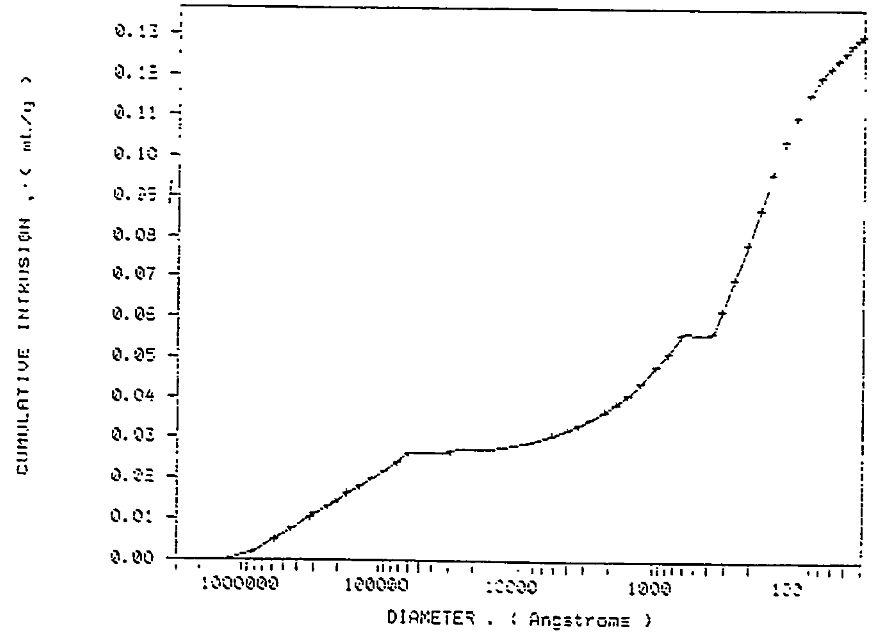


(a) Cement Paste

Fig. 1 Comparison of Cumulative Total Intrusion Volumes for Samples at 3 Days

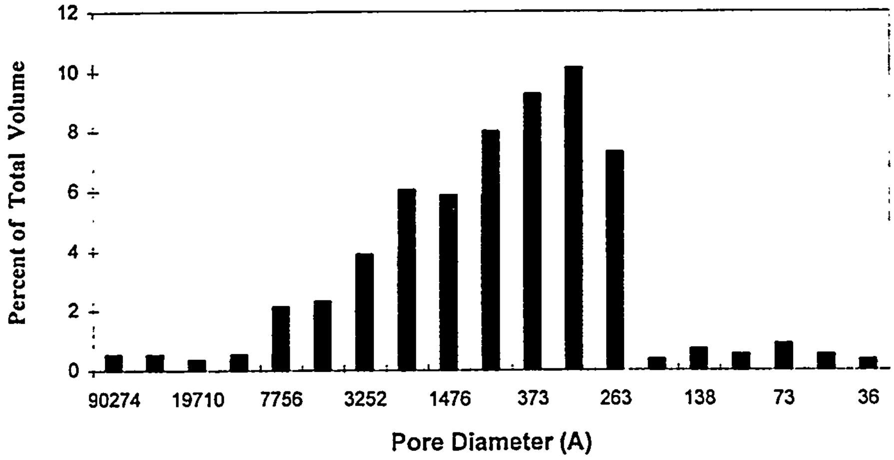


(b) Cement + Waste

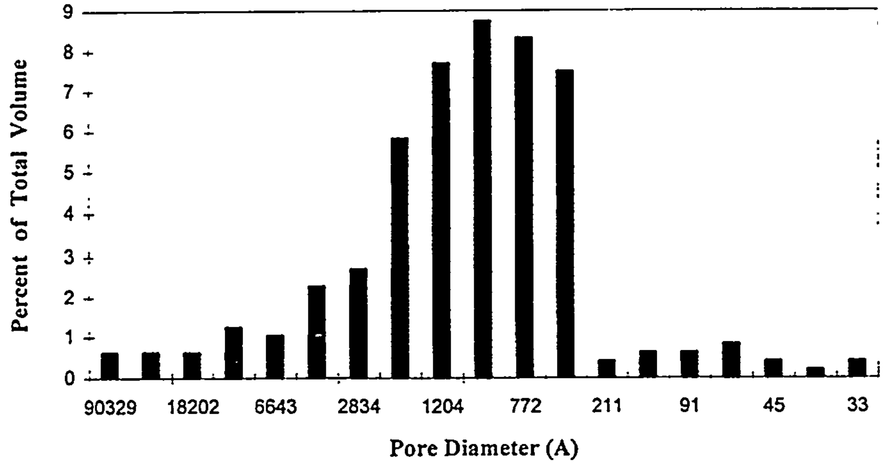


(c) Cement + Rice Husk Ash + Waste

Fig. 1 (Cont.) Comparison of Cumulative Total Intrusion Volumes for Samples at 3 Days

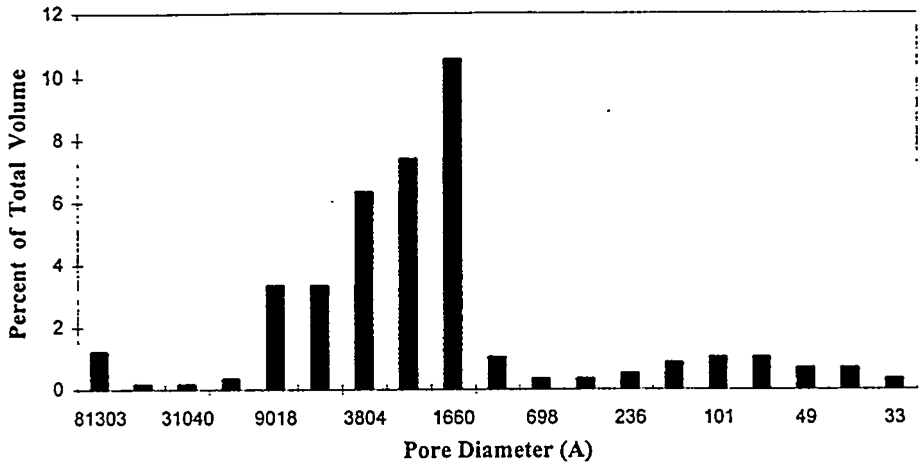


(a) Cement Paste - 3 days

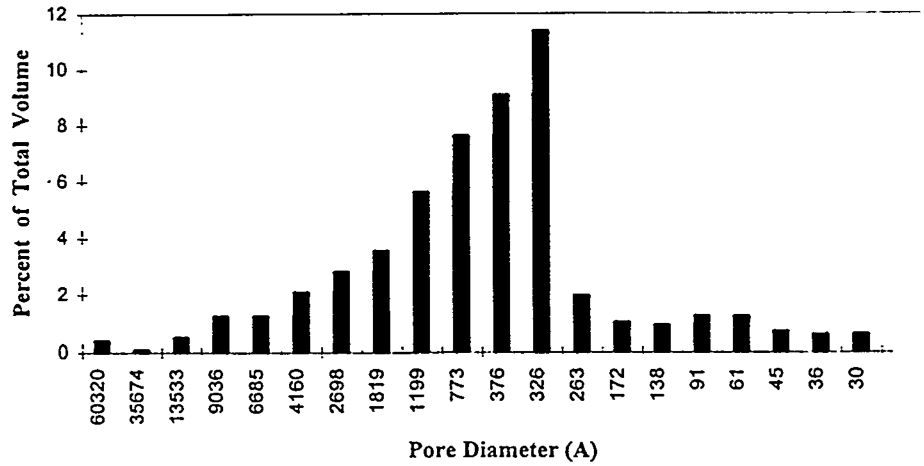


(b) Cement Paste - 7 days

Fig. 2 Incremental Intrusion Volume for Cement Paste at 3 and 7 days

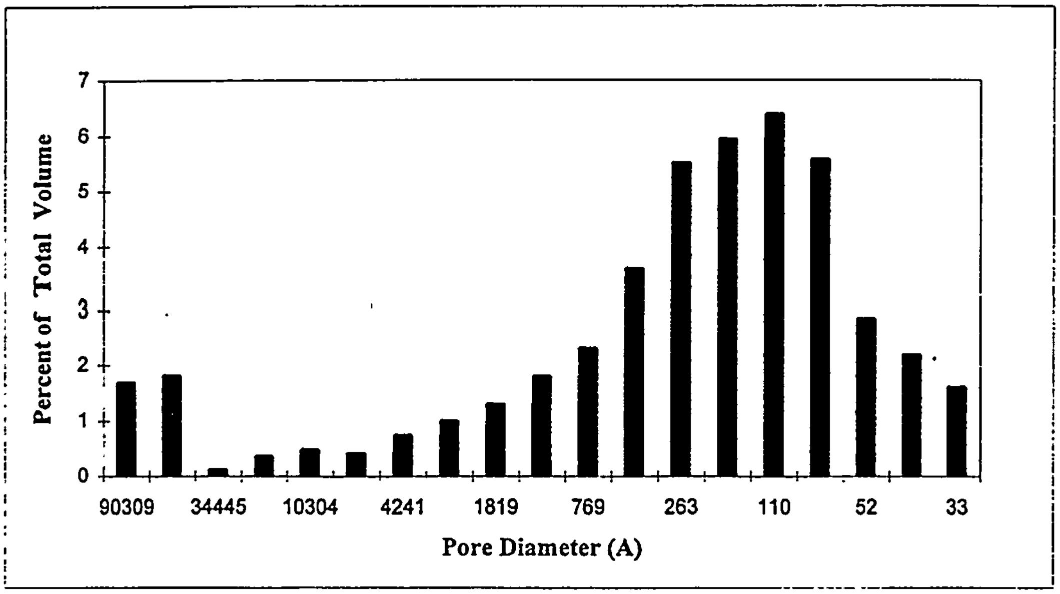


(a) Cement + Rice Husk Ash - 7 days

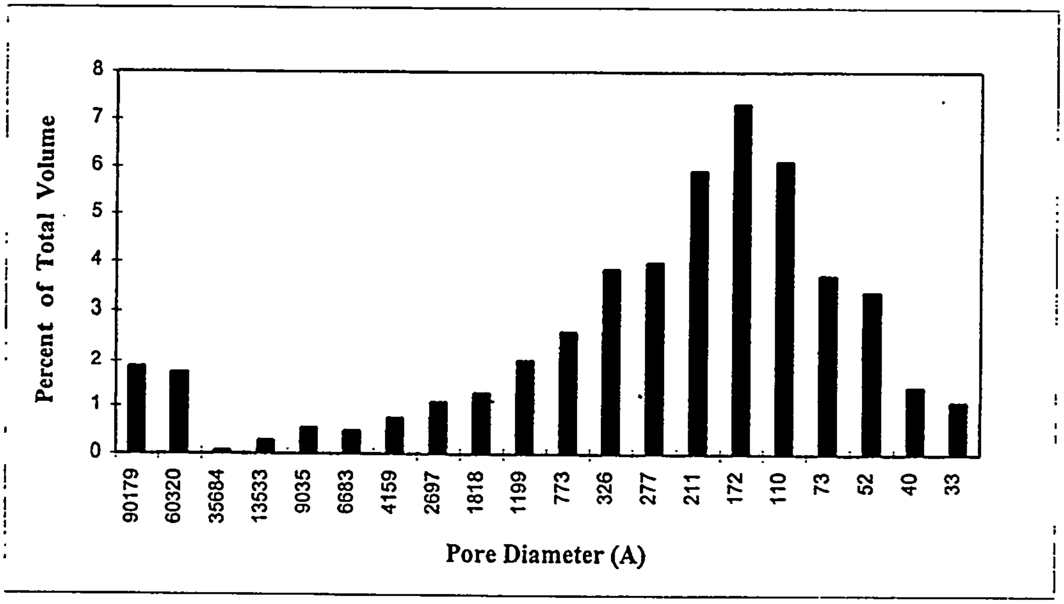


(b) Cement + Rice Husk Ash - 28 days

Fig. 3 Incremental Intrusion Volume for Cement + Rice Husk Ash



(a) Cement + Rice Husk Ash + Waste - 3 days



(b) Cement + Rice Husk Ash + Waste - 7 days

Fig. 4 Incremental Intrusion Volume of Cement + Rice Husk Ash + Waste

Figure 5 shows the pore size distribution of cement with 30% waste at 3 days. No particular trend is observed except that the pore size making up the pore volume varies considerably, namely from 3,890 to 211 Å. However, comparing Fig. 4a and Fig. 5, the pore sizes contributing to pore volume decrease when the mix contains cement, rice husk ash, and waste. Again this shows that the mixture of metal hydroxide waste, rice husk ash, and cement results in smaller pore radii compared to a mixture of cement and waste or cement and rice husk ash.

From Table 2 the strengths for cement paste, and cement plus rice husk ash plus waste, at 3 days are 56.1 N/mm^2 and 9.02 × 10^{-2} N/mm^2, respectively. The pore sizes contributing to the pore volume of these samples are 1,204 to 324 Å and 3,890 to 211 Å, respectively. At 7 days, strengths of Mixes A, B, and C are 63.4, 28.8, and 1.35 × 10-2 N/mm^2. In terms of pore size distribution, Mixes A and B have higher pore size distribution compared to Mix C. For samples cured for 3 days and 7 days, the greater the pore size distribution the higher the strength. Further tests have to be done to confirm this relationship.

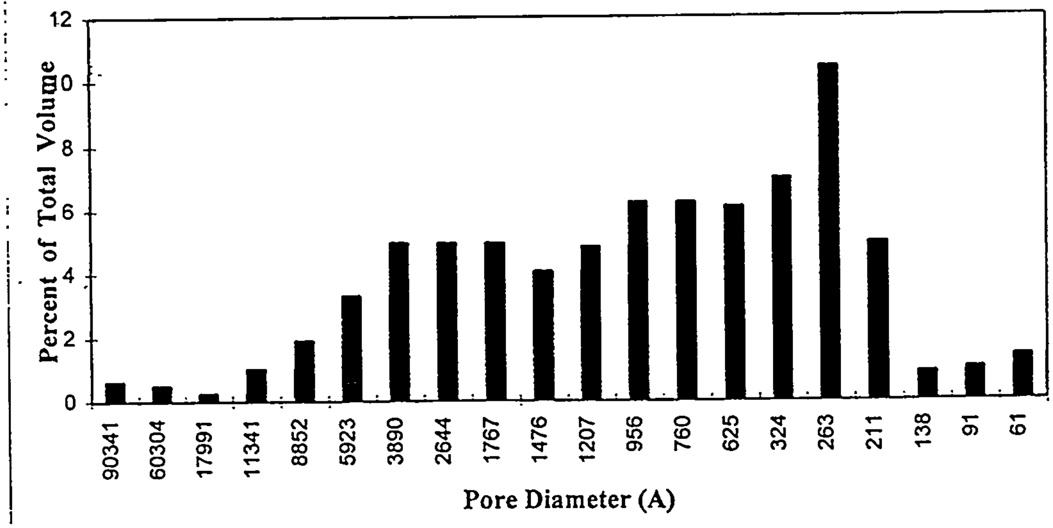


Fig. 5 **Incremental Intrusion Volume of Cement + 30% Waste at 3 days**

3.1 Pore Size and Waste Content

The pore size distribution of samples containing ordinary portland cement and 30 and 35% waste at 1 year were also studied. The water/cement ratios of these mixes were 0.6. Table 3 shows the cumulative intrusion volume and strength for mixture containing 30 and 35% of the waste at 1 year, and Figures 6(a) and 6(b) show the incremental intrusion volume for the above samples. There is not much difference in the pore size distribution of the two samples containing 30 and 35% waste. As indicated in Table 3, strength at 1 year is quite similar for both these samples. These results suggest that irrespective of the quantity of waste, stabilization of the waste can be done successfully with the S/S technique.

TABLE 3 Cumulative Intrusion and Unconfined Compressive Strength at 1 year

Mix	Cumulative Intrusion Volume (mL/g)	Unconfined Compressive Strength (N/mm^2)
OPC + 30% Waste w/c = 0.6	0.1708	33.5
OPC + 35% Waste w/c = 0.6	0.1445	34.5

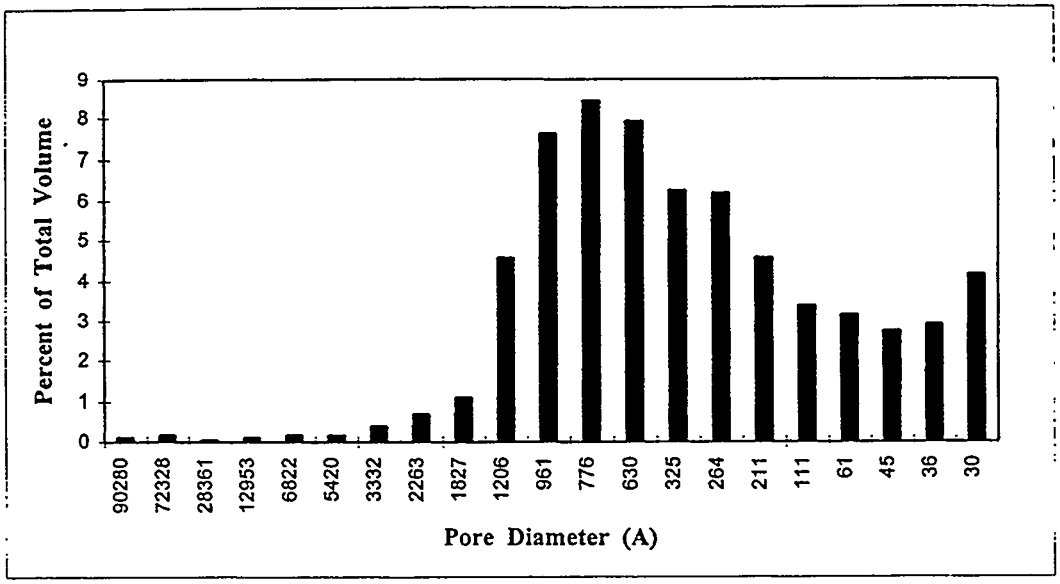
OPC = ordinary portland cement

3.2 Data Reliability

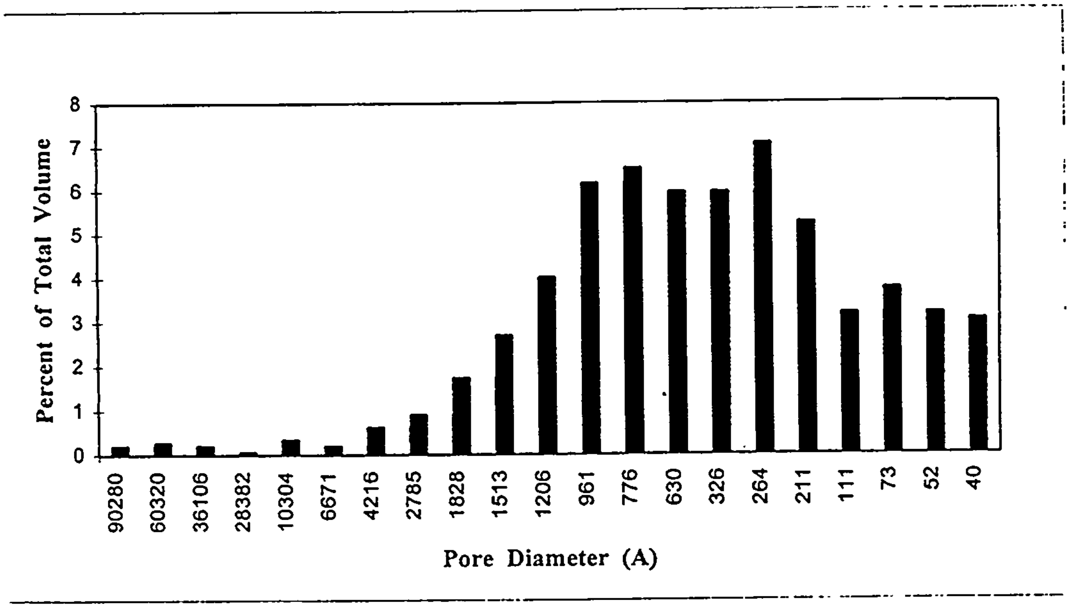
Variations in results are expected from the heterogeneous nature of the samples used. Triplicate tests were conducted in order to minimize errors associated with the measurements made. It should be emphasized that the reliability of pore structure studied is limited by the test method used. The limitations include the usual assumptions that the pores are cylindrical when the actual pore structure has a more complex shape. Interpretation of the results is also complicated by the presence of "ink bottle" shaped pores, since the whole volume penetrated is then recorded as belonging to pores with a diameter equal to that of the neck (Bye, 1983). Pore structure could be destroyed during the preparation of the samples. On the other hand, this in general affects the submicrometer structural features, so MIP provides a reasonable guide to pore distribution and connectivity, especially of the larger macro- and mesopores (Glasser, 1990). The method has also been used to study the pore size distribution of portland cement (Parcevaux, 1984; Kjellsen, et al., 1990; Hughes, 1985).

4 CONCLUSIONS

From the limited study of samples containing cement, cement plus waste, and cement plus rice husk ash plus waste, it appears that the pore sizes that make up the total volume of the pores vary



(a) Cement + 30% Waste



(b) Cement + 35% Waste

Fig. 6 Incremental Intrusion Volume at 1 year significantly with curing age. The study showed that the pore size can be minimized by incorporating rice husk ash in the cement and waste mixture. Although the strength of this sample is reduced at 3 and 7 days, improvement in pore size distribution as compared to the sample without rice husk ash was noted. Further investigations will be carried out to ascertain the relationship between strength and pore size distribution in the samples studied.

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ROLE OF UNSATURATED SOIL IN A WASTE CONTAINMENT SYSTEM

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ABSTRACT

The role of the unsaturated properties of sand as a drainage layer in a composite liner system for landfills is investigated. The effect of the unsaturated properties of coarse-grained soil on contaminant migration was evaluated by means of a series of simulations using a one-dimensional model of a two- and a three-layer soil liner system for advection and diffusion, respectively. The results showed that under seepage conditions, the effect of an unsaturated sand layer on the advancement of the concentration front was quite insignificant. The arrival time of the $C/C_o = 0.5$ concentration front increased from 651 days for the case with no sand layer to approximately 951 days for the case with a 1.0-m sand layer. A steady-state flow condition was ultimately established in the sand, and this fact suggests that the capillary action might not be effective. For diffusion, the arrival time of the concentration front increased nonlinearly with a decrease in the degree of saturation and linearly with increasing depths of the sand layer. At a residual degree of saturation, the arrival times of the $C/C_o = 0.01$ and 0.5 concentration front at the base of the 1-m sand layer were 26.9 and 877.4 years as compared to 1.52 and 2.62 years by advection, respectively.

1 INTRODUCTION

In many shallow waste containment systems, a compacted clayey soil liner is often used as a barrier to prevent leachate migration from the waste site into the surrounding geologic environment. The key characteristics of a clay liner are the low hydraulic conductivity and high adsorption potential associated with fine-grained soil, and the presence of clay minerals. Quigley et al. (1980), however, have shown that under low seepage conditions, diffusion can be a dominant transport process. Hence, unless both the advective and diffusive components of the transport phenomenon are eliminated, leachate migration is ineluctable.

The hydraulic properties of soils, and particularly sand and gravel, are known to decrease with decreases in the degree of saturation. At saturation, the hydraulic conductivity of coarse-grained soils is considerably higher than fine-grained soils. However, as the soil desaturates beyond a threshold suction value, the hydraulic conductivity for coarse-grained soil can be smaller than that for fine-grained soil by a few orders of magnitude.

In the case of diffusion, studies reported by soil scientists showed that desaturation of the soil was also accompanied by a reduction in the effective diffusion coefficient for soils of differing textures. The form of the functional between the effective diffusion coefficient and the volumetric water content for glass beads, sand, and gravel was nonlinear (Klute and Letey, 1958; Romken and Bruce, 1964; Conca and Wright, 1990), while that for loamy and silty soils was either slightly nonlinear or linear (Porter et al., 1960; Rowell et al., 1967; Barraclough and Tinker, 1981).

Consequently, a number of numerical studies on the use of unsaturated coarse-grained soil as a moisture and diffusion barrier have been initiated and investigated. The lateral moisture migration along the interface between a saturated fine-grained soil and an unsaturated coarse-grained soil was first investigated by Corey and Horton (1969) for a steady-state system. This lateral migration along the interface or the "wicking effect" was attributed to the capillary barrier effect associated with coarse-gained soil under very dry conditions. This wicking effect was later reexamined by Frind et al. (1976) in the design of a composite silt loam, sand, and gravel system for radioactive waste storage facilities.

Other examples include the use of an unsaturated gravel as a moisture and diffusive barrier around a nuclear waste repository proposed by Allison and Bergmen (1988) and Conca and Wright (1990). A numerical analysis of the wicking effect in a two-layer soil liner system has been reported by Yeh et al. (1995). The simulations, however, were based on a point source leakage from the landfill to the liner. More recently, a laboratory-scale experimental study on contaminant transport through a soil liner underlain by an unsaturated stone collection layer was undertaken by Badv and Rowe (1996). The results showed that a uniform concentration profile was almost established throughout the 0.38 m in a thick, unsaturated clear stone layer after approximately 160 days, which would suggest that the capillary action might not be effective.

The objective of this paper is to examine the role of an unsaturated granular drainage layer in a composite liner system for landfills as a moisture and diffusive barrier under a constant head of leachate. A series of simulations modeling both the advective and the diffusive transport through a typical composite soil liner system for landfills was performed in this study. The effect of the unsaturated properties of coarse-grained soil on contaminant migration was evaluated using a simple one-dimensional model of a two-layer soil liner system for advection and a three-layer soil liner system for diffusion.

2 DESCRIPTION OF THE PHYSICAL PROBLEM

The one-dimensional models for advective and diffusive transport chosen for this study are given in Fig. 1. Both models are simplistic representations of a typical composite liner system as shown in Fig. 2. The one-dimensional model for advection consisted of a 0.5-m-thick silt layer overlying a sand layer, and the water table was set at the base of the sand layer. The effect of the capillary barrier, which depends on the contrast in hydraulic conductivity between silt and sand, was investigated by varying the thickness of the sand layer. A change in the depth of the sand is equivalent to effecting a change in the suction value and a corresponding increase in the contrast in hydraulic conductivity between the saturated silt and the unsaturated sand. In the case of diffusion, the seepage fluxes were assumed to be negligible.

The one-dimensional model for diffusion consisted of a 0.5-m-thick silt layer overlying a sand layer underlain by a 1-m-thick silt layer. The effect of the unsaturated diffusive properties on contaminant migration was examined by varying the degree of saturation and the depth of the sand layer.

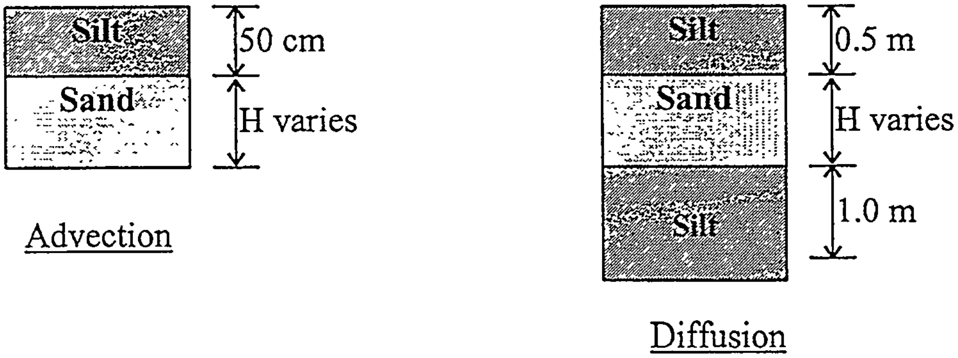

Fig. 1 Schematic Representation of the Two-Layer Soil Liner System

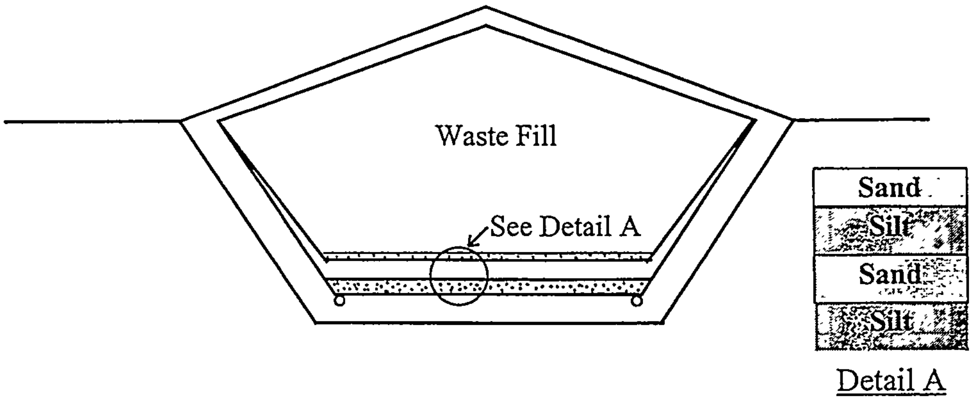

Fig. 2 Schematic of a Double-Lined Waste Containment System

3 MATERIAL PROPERTIES

The coarse- and fine-grained soils selected for this study were based on the sand and the silt used by Lim (1995). The sand was an olive brown, oxidized, clean, uniform, fine-to-medium sand with low water retention characteristics, whereas the silt was a light brown, clean, uniform, coarse-to-medium silt. The soil-water retention characteristics for the sand and the silt are given in Fig. 3. The theoretical soil water-suction and hydraulic conductivity-suction relationships for the sand and the silt calculated on the basis of the van Genuchten model (1978) are given in Equations 1 and 2:

$$\theta(\psi) = (\theta_s - \theta_r)\,[1 + (\alpha\psi)^n]^{-m} + \theta_r \quad , \tag{1}$$

$$K(\psi) = K_s \, \frac{\{1 - (\alpha\psi)^{n-1}\,[1 + (\alpha\psi)^n]^{-m}\}^2}{[1 + (\alpha\psi)^n]^{m/2}} \quad , \tag{2}$$

where

K_s = saturated hydraulic conductivity,
ψ = suction,
θ_s = volumetric water content at saturation,
θ = volumetric water content at residual degree of saturation,
α, n = parameters controlling the curvature of the functional, and
m = $(1\text{-}1/n)$.

The theoretical hydraulic conductivity-suction relationships for the sand and the silt are shown in Fig. 4. The saturated hydraulic conductivities for the sand and the silt were arbitrarily set equal to 1×10^{-5} and 1×10^{-9} m/s, respectively. These values were chosen on the basis of the lower range for fine sand and silt. The results for the sand showed a steep decrease in hydraulic conductivity beyond the air-entry value. Beyond a threshold suction value of 4.5 kPa, the hydraulic conductivity for the sand was smaller than the value for the silt; the contrast in hydraulic conductivity between the sand and the silt intensified with increasing suction.

The functional relationship for the effective diffusion coefficient for the sand and the silt reported by Lim (1995) is given in Fig. 5. The effective diffusion coefficients were determined using a potassium ion as the tracer. The functional relationship between the effective diffusion coefficient, normalized with respect to the effective diffusion coefficient at saturation, and the degree of saturation for the sand and the silt was nonlinear. The reduction in the normalized effective diffusion coefficient from saturation up to near the residual degree of saturation for the sand and the silt was less than one order of magnitude.

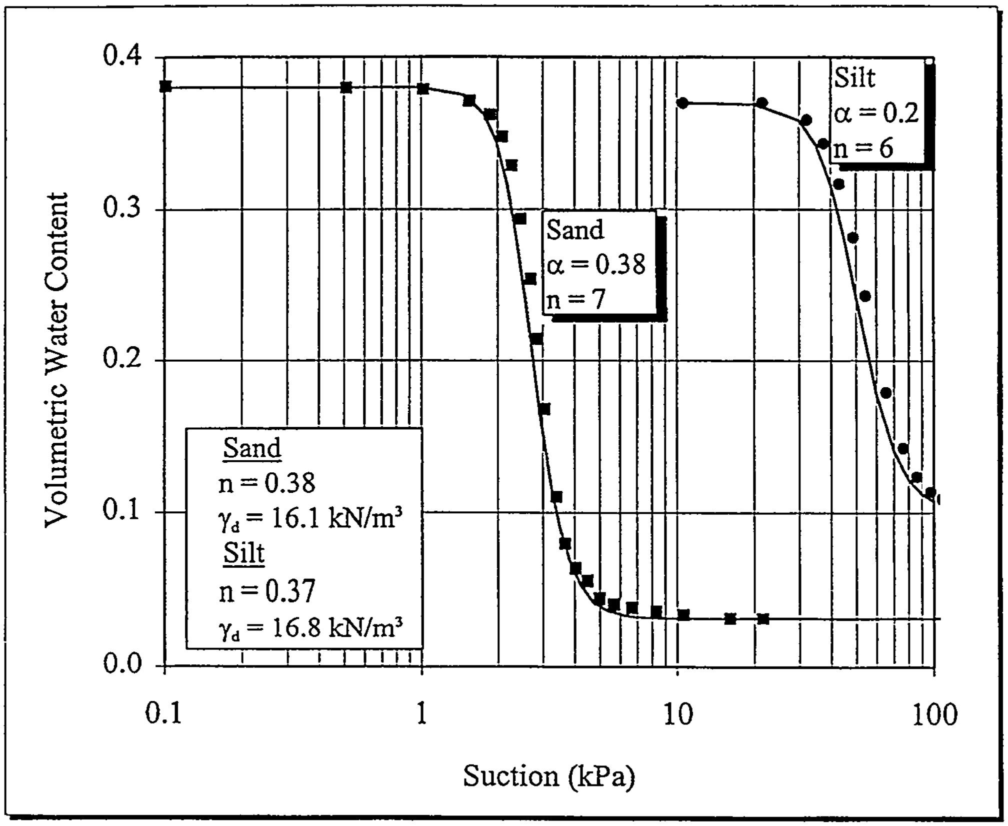

Fig. 3 Water Content versus Suction Relationships for the Sand and the Silt

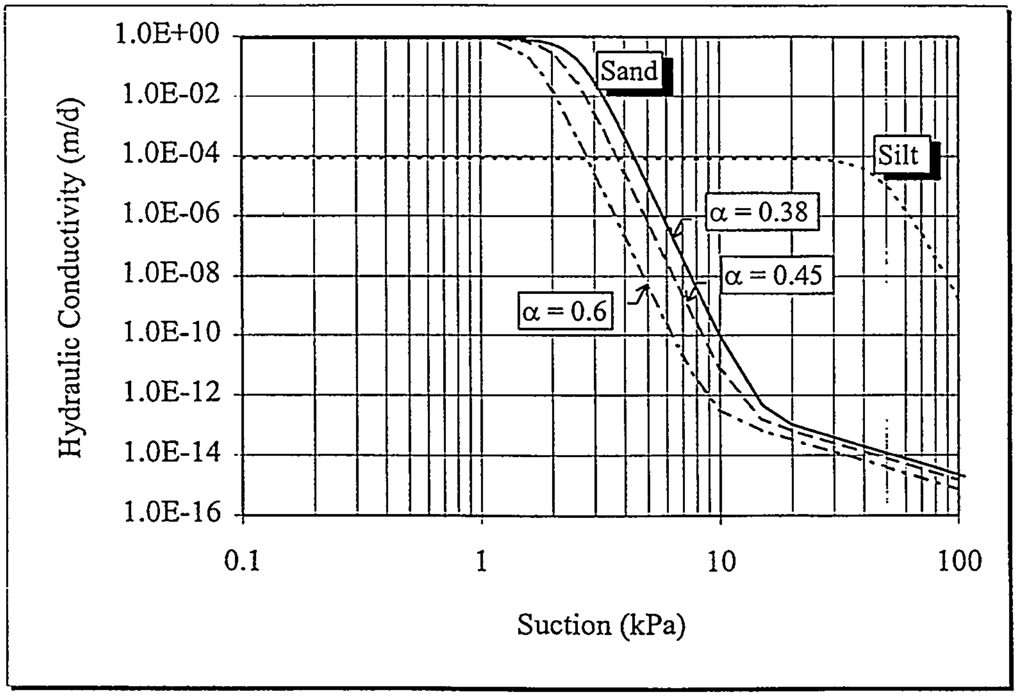

Fig. 4 Hydraulic Conductivity versus Suction Relationship for the Sand and the Silt

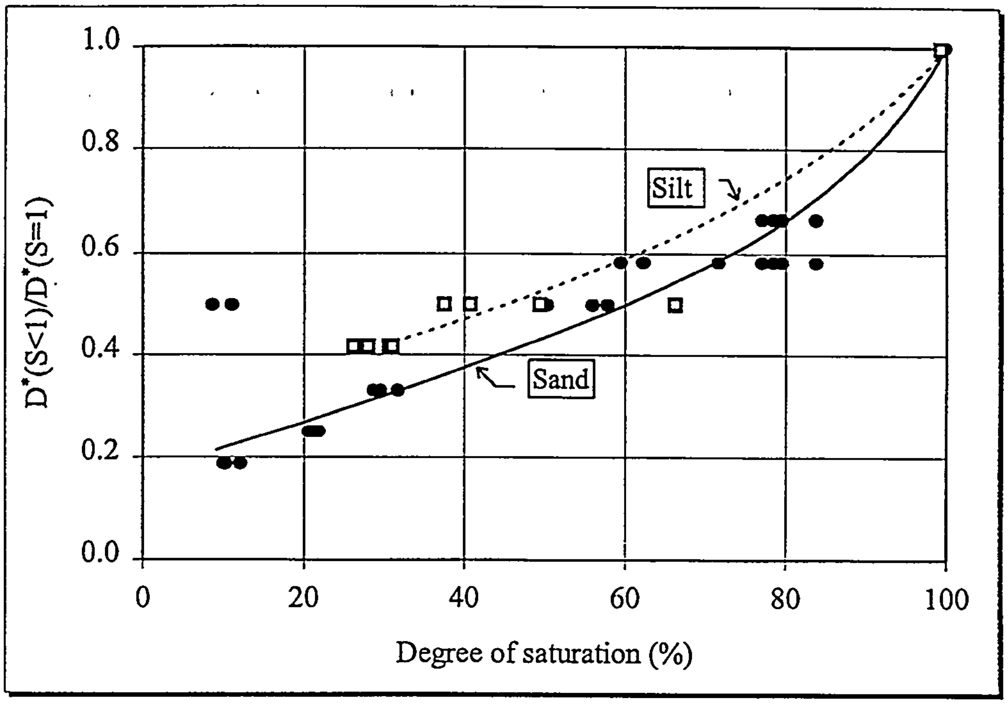

Fig. 5 Effective Diffusion Coefficient versus Suction Relationships for the Sand and the Silt

4 NUMERICAL MODEL

The sand and the silt layers were discretized into a column of 50 × 50 mm eight nodes quadrilateral elements. Simulations of the flow through the two-layer soil liner and the migration of the concentration front were performed using SEEP/W (1991) and CTRAN/W (1991), respectively. Both SEEP/W and CTRAN/W are proprietary computer software based on a finite element formulation and have been developed by and are distributed by Geo-Slope International Ltd., Calgary, Alberta, Canada. A state of hydrostatic equilibrium or a condition of no moisture movement was assumed as the initial condition. The initial head at all nodes was established by running a steady-state analysis with the hydraulic head set equal to zero along the top and bottom boundaries. Boundary conditions of the two-layer soil liner model were assigned as follows: no flow along the left and right boundaries, and a constant hydraulic head of 1 and 0 m along the top and lower boundaries of the cross-section, respectively. The water content-suction relationship and the conductivity functions for the sand and the silt are given in Figs. 3 and 4.

The effect of the contrast in hydraulic conductivity on the advancement of the moisture and the concentration front was investigated by varying the depth of the sand layer while maintaining the water table at the lower boundary. The simulations assumed a constant dispersivity of 0.025 m in order to satisfy the Peclet number criterion of less than or equal to 2. Additional simulations based on a steeper conductivity function for the sand were also performed to examine the effect of the shape of the functional relationship. The slope of the conductivity function was arbitrarily altered by setting α equal to 0.45 and 0.6. Plots of the conductivity functions corresponding to α-values of 0.45 and 0.6 are shown in Fig. 4.

The diffusive transport for cases of different degrees of saturation and depth of the sand layer was determined using POLLUTE, which is a semi-analytical solution for the advective-diffusive transport equation developed by Rowe and Booker (1983). POLLUTE was used for analysis because of its simplicity and short runtime. The boundary conditions assigned to the diffusion model were as follows: a concentration source with a constant unit concentration along the top boundary and zero flux along the right, left, and lower boundaries of the cross-section. The effective diffusion coefficient for the sand at various degrees of saturation was based on the idealized function given in Fig. 5. For the silt, the effective diffusion coefficient at saturation was adopted in all the simulations, assuming that the silt remained saturated over the range of suction values for the sand.

5 RESULTS

The results of the simulations of the advective and diffusive transport for cases of different depths of the sand layer, shapes of conductivity function, and degrees of saturation are discussed in Sections 5.1 and 5.2.

5.1 Effect of Contrasting Hydraulic Conductivity on Advective Transport

The arrival times of the $C/C_o = 0.5$ and 0.01 concentration front at the base of the sand layer for cases of 0-, 0.5-, 0.75-, and 1.0-m-thick sand layer are given in Fig. 6. The results were determined on the basis of the conductivity function corresponding to an α-value of 0.38 for the sand. The results showed that the arrival time increased with increasing thickness of the sand layer. The arrival time of the $C/C_o = 0.5$ concentration was delayed by approximately 217 days, as the sand layer increased from 0 to 0.5 m. However, with a further increase in the depth of the sand layer, the retardation of the arrival time decreased to 97 days for every 0.5-m increment. Although results for the $C/C_o = 0.01$ concentration front showed a much earlier arrival time, the trend was similar to that of the $C/C_o = 0.5$ concentration front.

Simulations of the cases with depths greater than 1.0 m and that corresponding to an α-value of 0.6 were evaluated; however, the solutions were unsatisfactory because of problems of nonconvergence. One interesting observation was that, regardless of the methods of analysis, the predicted arrival times determined using the transient and steady-state analyses were almost identical for the various cases of differing sand thickness. In addition, the predicted arrival times for the

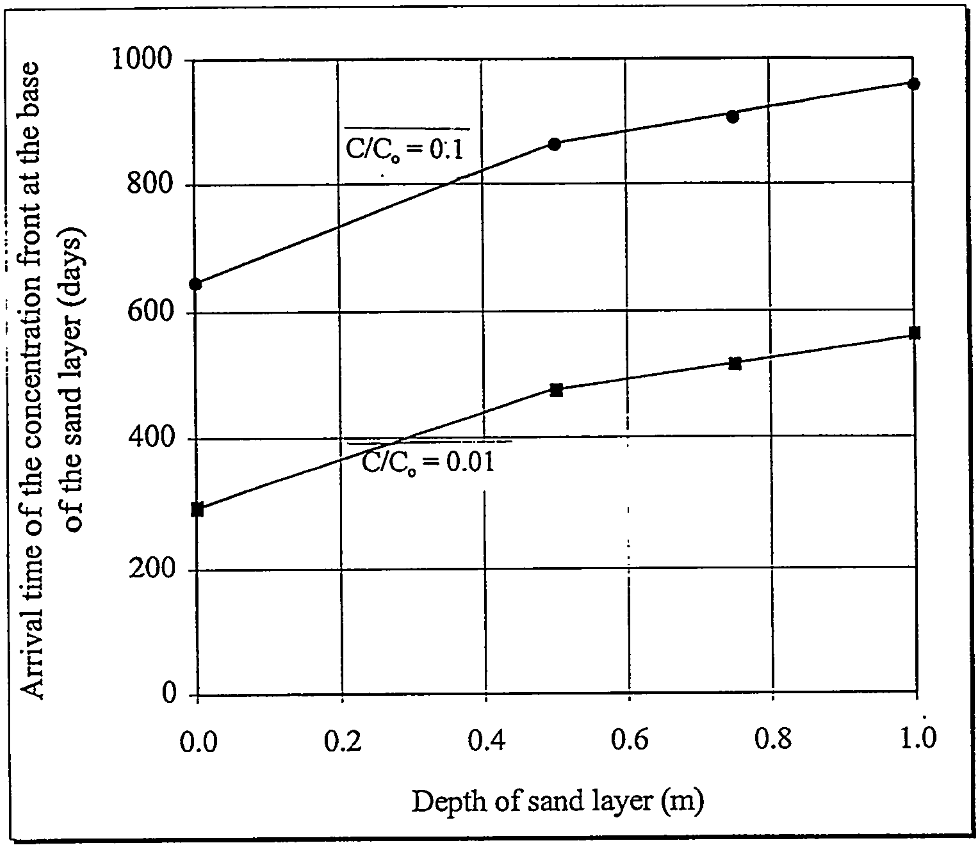

Fig. 6 The Effect of the Contrast in Hydraulic Conductivity on the Arrival Time of the Concentration Front at the Base of the Sand Layer

different conductivity functions were approximately the same. Additional data pertaining to the time at which a steady-state condition was fully established may provide some useful information to help interpret the results.

The times corresponding to the establishment of steady-state flow conditions for cases of 0-, 0.5-, 0.75-, and 1.0-m-thick sand layers with different conductivity functions are presented on a semi-logarithmic plot in Fig. 7. The results show that the relationship between the time at steady state and the thickness of the sand layer was linear for cases with α equal to 0.38 but was slightly nonlinear for α equal to 0.45. This may suggest that the time to reach steady-state conditions increases exponentially with increasing depth of the sand layer, and the steeper the conductivity function, the greater would be the degree of nonlinearity.

Plots of hydraulic conductivity versus depth of the sand layer for cases of different thickness and conductivity functions are provided in Fig. 8. The results show that the shapes of the various hydraulic conductivity versus depth profiles were similar. More important, the results showed that

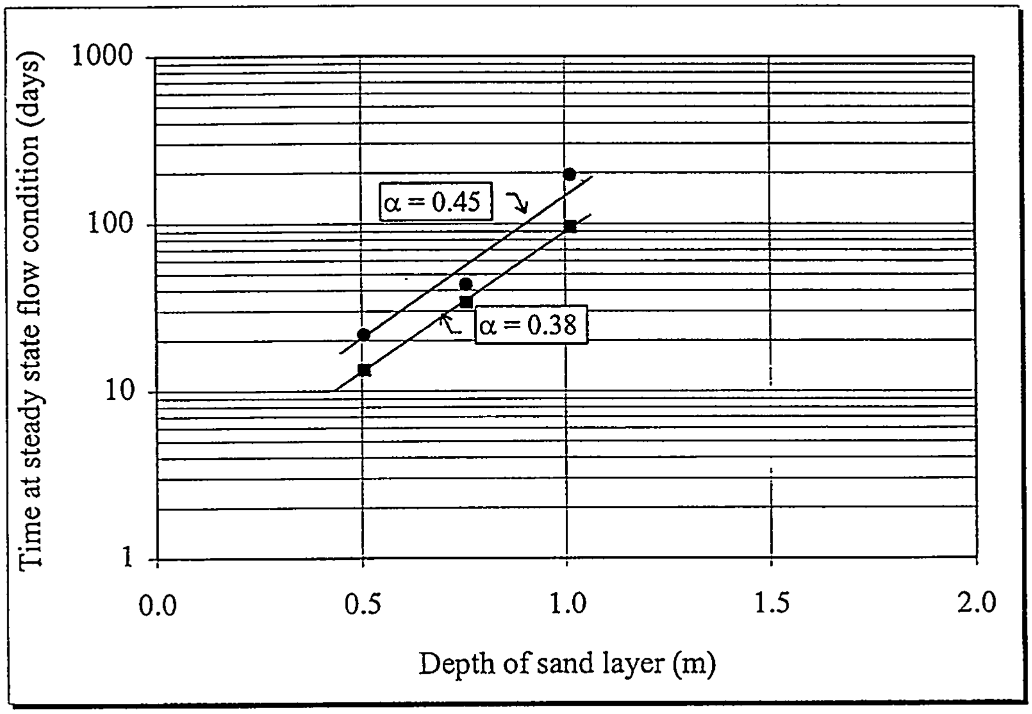

Fig. 7 The Effect of the Contrast in Hydraulic Conductivity on the Time Required for the Establishment of Steady State Condition

the hydraulic conductivity of the sand layer at steady state was much higher than the silt, regardless of the depth and shape of the conductivity functions. Also, the seepage fluxes at steady state for the various cases were the same. The steady-state fluxes for cases with the sand layer were actually higher than for the case without the sand layer. The steady-state seepage fluxes for cases with the sand layer were 3.31×10^{-4} $m^3/day/m^2$ as compared to 2.59×10^{-4} $m^3/day/m^2$ for the case with no sand layer.

Hence, the unsaturated hydraulic property of coarse-grained soil is only advantageous under transient conditions. Once steady-state conditions are established, the hydraulic conductivity of the sand layer, although less than the saturated value, would be higher than the silt. This permeable sand layer would increase the overall hydraulic conductivity of the system and, consequently, cause a higher seepage flux at steady state.

5.2 Effect of Unsaturated Effective Diffusion Coefficient on Diffusive Transport

The influence of the degree of saturation on the arrival time of the $C/C_o = 0.01$ and $C/C_o = 0.1$ concentration front at the base of the sand layer is shown in Fig. 9. The simulations were based on a 1.0-m-thick sand layer. The predicted arrival times given in Fig. 9 were normalized with respect

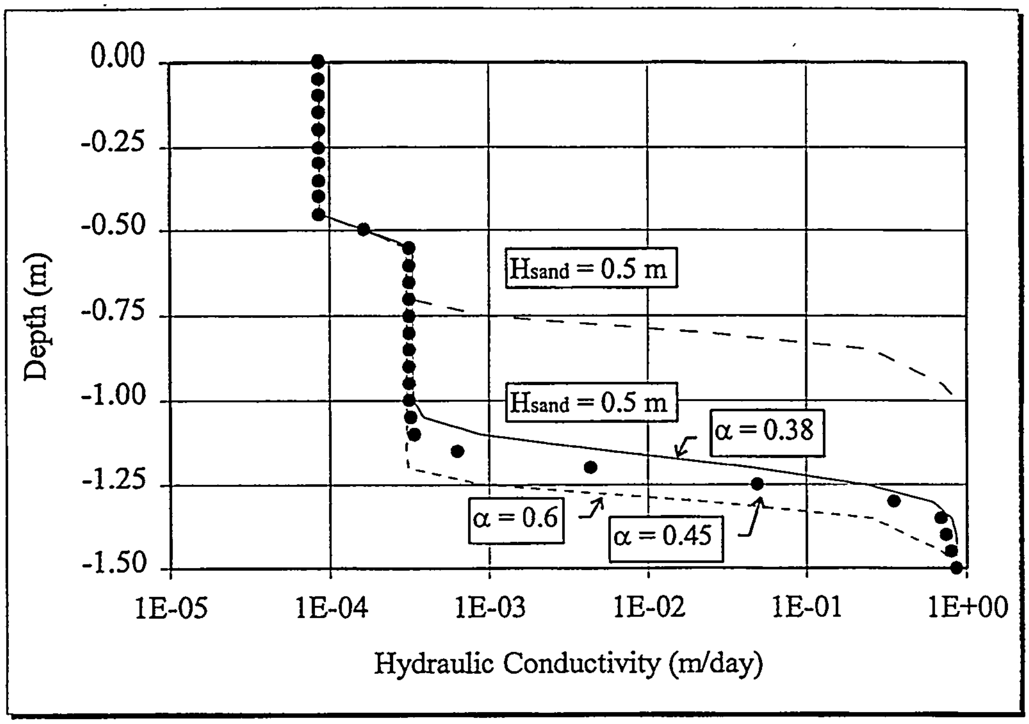

Fig. 8 The Hydraulic Conductivity Profile at Steady-State Flow Conditions

to the arrival time of the $C/C_0 = 0.01$ concentration front for the case with 100% saturation. The arrival time of the $C/C_0 = 0.01$ concentration front at 100% saturation was approximately 4.5 years. For the case of the 0.01 concentration front, the results showed a gradual increase in arrival time as the soil desaturated from a degree of saturation of 100% to near the residual degree of saturation. The effect of the degree of saturation on the arrival time was more significant for cases with $C/C_0 = 0.1$; the arrival time increased exponentially with a decrease in the degree of saturation.

The effect of the depth of the sand layer on migration of the $C/C_0 = 0.01$ and $C/C_0 = 0.1$ concentration front was also investigated; the results are provided in Fig. 10. The simulations were based on a degree of saturation of 10%. The predicted arrival times given in Fig. 10 were normalized with respect to the arrival time of the $C/C_0 = 0.01$ concentration front based on the 0.5-m-thick sand layer. The arrival time of the $C/C_0 = 0.01$ concentration front for the 0.5-m sand layer was approximately 9.15 years. The results showed the arrival time of both concentration fronts increased linearly with increasing thickness of the sand layer. For any given depth, the arrival time of the $C/C_0 = 0.1$ concentration front was consistently longer than that for the $C/C_0 = 0.01$ concentration front. The slope of the function for the $C/C_0 = 0.1$ concentration front is at least 3.5 times steeper than that for the $C/C_0 = 0.01$ concentration front.

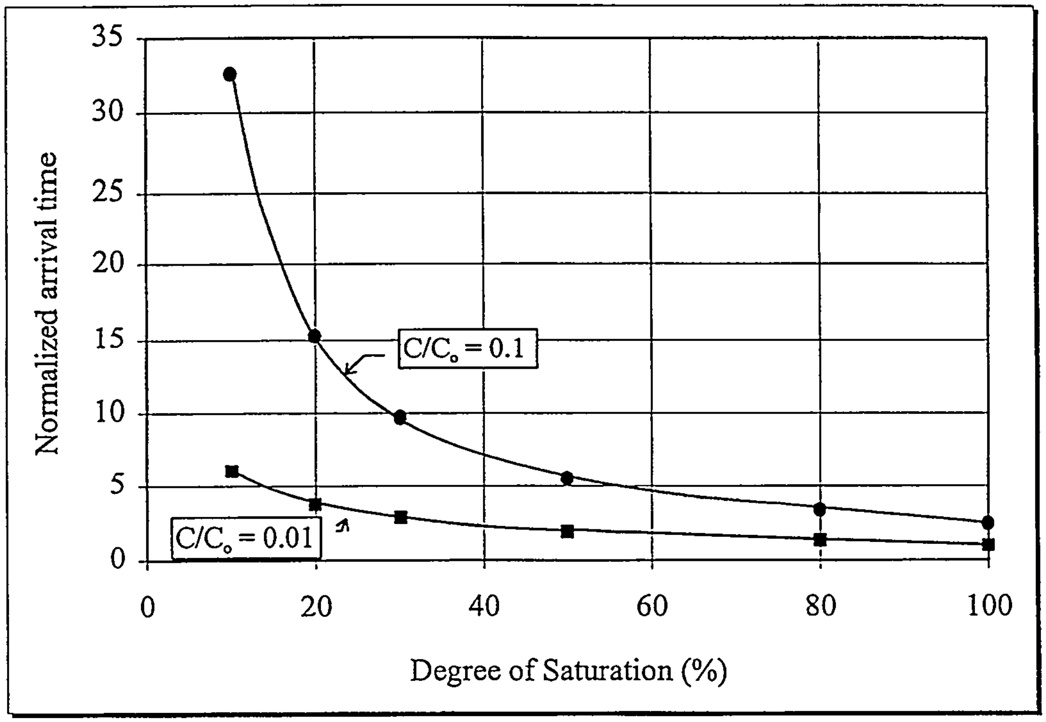

Fig. 9 Effect of the Degree of Saturation on the Arrival Time of the Concentration Front

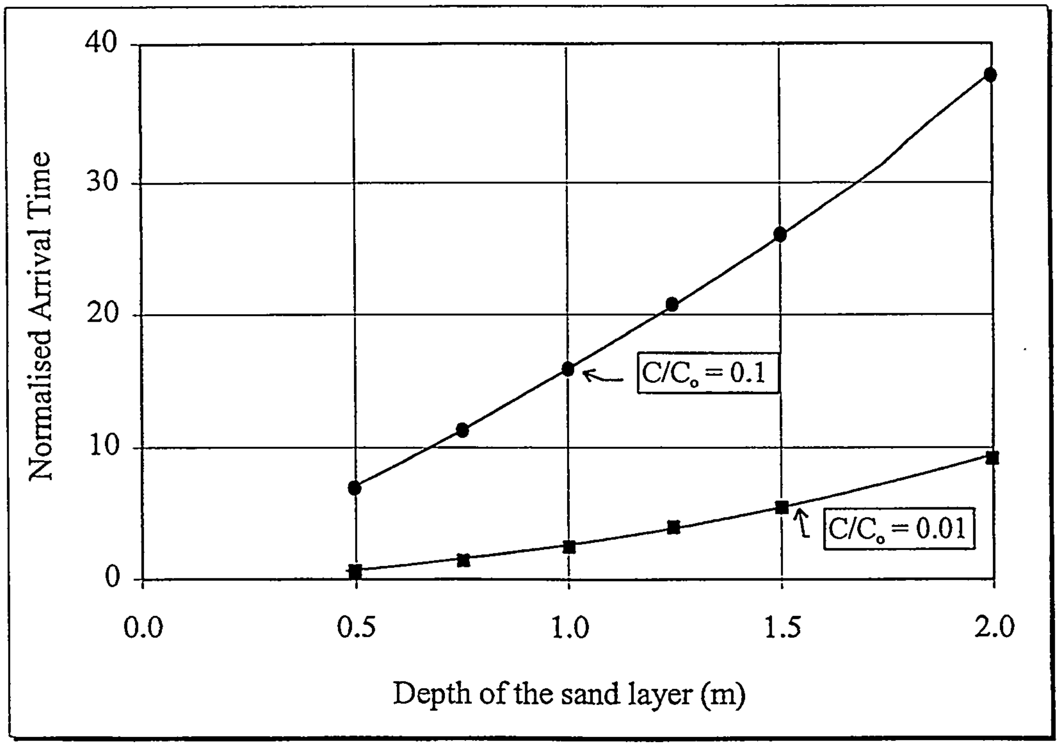

Fig. 10 Effect of the Thickness of the Sand Layer on the Arrival Time of the Concentration Front at the Base of the Sand Layer

The arrival times of various concentration fronts corresponding to C/C_o values of 0.01, 0.1, 0.25, and 0.5 for cases with a degree of saturation of 100% and 10% are shown in Fig. 11. The increase in arrival time for the different concentration fronts was small for cases at saturation, while for the cases with a degree of saturation of 10%, the results showed a significant delay in the arrival time with progressing concentration front.

Diffusive transport through just the 0.5 m silt layer without the sand layer was evaluated, and the simulations showed that the $C/C_o = 0.01$ and 0.1 concentration fronts arrived at the base of the silt layer at approximately 0.5 years and 1.22 years, respectively. These were comparatively very much faster than the arrival times of 4.5 years and 11 years for the case of the 1.0-m-thick saturated sand layer.

Hence, under low or zero seepage condition, diffusive transport can be a very slow process. The delay in the arrival of the concentration front at the base of the sand layer is quite significant, particularly at near the residual degree of saturation and as the concentration front progresses. However, for the unsaturated diffusive property to be effective, a well-drained condition must be maintained in the drainage layer. Clogging of the drainage layer will cause the water level to build up within the drainage layer.

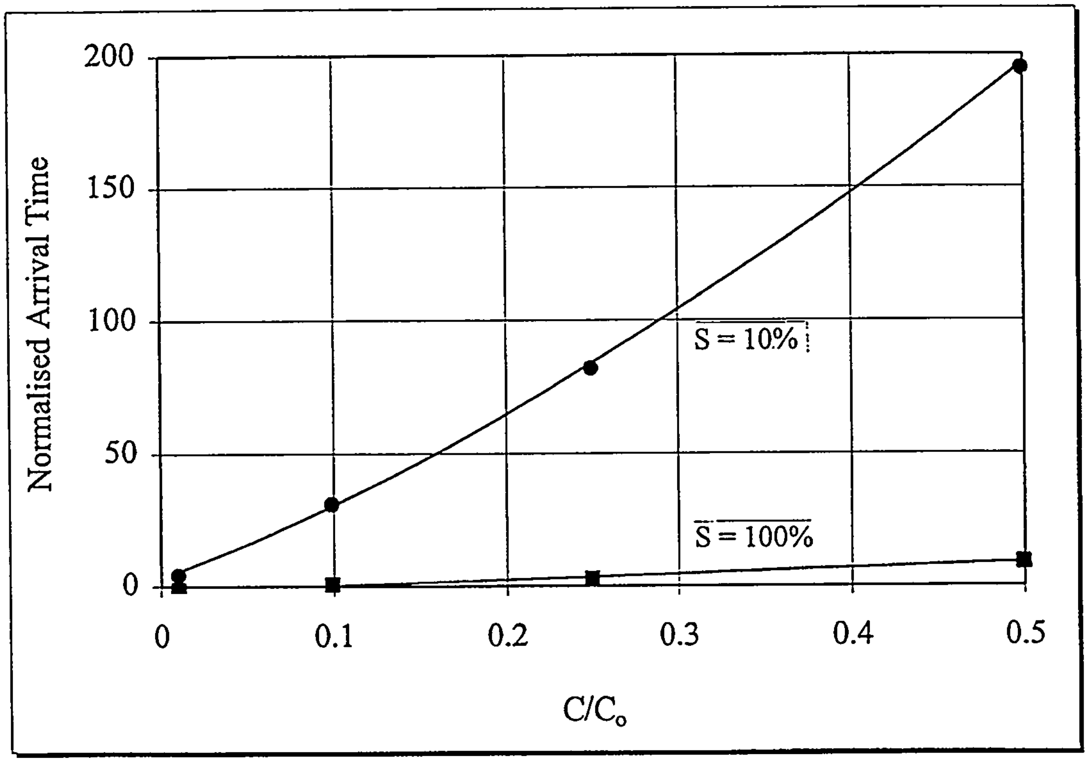

Fig. 11 Arrival of the Different Concentration Fronts at the Base of the Sand Layer

6 CONCLUSIONS

The series of simulations on the flow through a saturated silt and an unsaturated sand showed that, although the arrival time of the concentration front increases with increasing depth of the sand layer, the increase is not significant. The arrival time of the $C/C_o = 0.5$ concentration front increases from 651 days for the case with no sand layer to approximately 951 days for the case with a 1.0-m-thick sand layer.

At steady-state flow conditions, the seepage fluxes are higher than for the case with no sand layer, regardless of depth of the sand layer and the shape of the conductivity function. The hydraulic conductivity of the sand at steady state is also higher than that for the silt but less than the saturated value. Therefore, as long as seepage conditions prevail, a steady-state flow would ultimately be established in the unsaturated sand layer. Hence, the unsaturated sand layer might not be an effective capillary barrier to flow and migration of contaminants.

The results for cases of extreme contrasting hydraulic conductivity are not conclusive. Further experimental studies would be useful to verify the capillary action of the unsaturated properties of sand or gravel under dry conditions and to calibrate the numerical models.

In the case of diffusion, the results showed an increase in arrival time of the concentration front with increasing degrees of saturation and depths of the sand layer. The arrival time varies nonlinearly as the soil desaturates but fairly linearly with increasing depth.

At a residual degree of saturation, the time taken for the $C/C_o = 0.01$ and 0.5 concentration fronts to arrive at the base of the 1 m sand layer by diffusion were 26.9 years and 877.4 years as compared to 1.52 years and 2.62 years by advection, respectively.

Under low or zero seepage condition, diffusive transport can be a very slow process. The delay in the arrival of the concentration front at the base of the sand layer is quite significant, particularly near the residual degree of saturation and as the concentration front progresses. A well-drained condition, however, must be properly engineered in order to maintain an unsaturated condition within the drainage layer.

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FINAL DISPOSAL

Chair: M.A. Badri, MAB Environmental Consultants, Malaysia

ATTENUATION OF HEAVY METAL LEACHING FROM HAZARDOUS WASTES BY CO-DISPOSAL OF WASTES

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ABSTRACT

The potential hazard of landfill wastes was previously evaluated by examining the extraction procedures for individual waste, although various wastes were co-disposed of in actual landfills. This paper investigates the reduction of extraction-procedure toxicity by co-disposing various combinations of two wastes. When two wastes are mixed homogeneously, the extraction of heavy metals from the waste mixture is critically affected by the extract pH. Thus, co-disposal wastes will have a resultant pH between the pH values of its constituent. The lower the resultant pH, the lower the concentrations of heavy metals in the extract. When these wastes are extracted sequentially, the latter extracted waste has a stronger influence on the final concentration of heavy metals in the extract. Small-scale lysimeter experiments confirm that when heavy-metal-bearing leachates generated from hazardous-waste lysimeters are passed through a nonhazardous-waste lysimeter filled with compost, briquette ash, or refuse-incineration ashes, the heavy-metal concentration in the final leachates decreases significantly. Thus, the heavy-metal leaching could be attenuated if a less extraction-procedure-toxic waste were placed at the bottom of a landfill.

1 INTRODUCTION

The most common disposal method for inorganic hazardous wastes, such as sludges or electric-arc-furnace (EAF) dusts, is landfill. Potential hazards from such landfill wastes can be evaluated in advance through either extraction procedures (EPs) or the Toxicity Characteristic Leaching Procedure (TCLP) (*Federal Register* 1986). In extraction procedures, wastes are tested individually, although various wastes are co-disposed of in landfill sites. In Korea, for instance, hazardous wastes, such as EAF dusts, incineration residues, and sludges from industrial wastewater treatment or manufacturing processes, are disposed of together in designated public landfill sites.

Because the EP toxicity for a mixture of wastes can differ from the sum of the EP toxicity of individual wastes, an extraction or leaching test for the mixture of wastes is needed for proper evaluation of the potential hazard of the wastes. Furthermore, a landfill can be designed to minimize the EP toxicity by manipulating or avoiding co-disposal of wastes according to the characteristics of the wastes to be landfilled. So far, little research has addressed this issue in spite of its high practical implications. This paper investigates the reduction of EP toxicity by co-disposal of two wastes of various combinations: (1) co-disposal of two different hazardous wastes and (2) co-disposal of a hazardous waste with nonhazardous compost, briquette ash, or refuse-incineration ashes.

2 MATERIALS AND METHODS

2.1 Waste Samples

Four hazardous wastes—two EAF dusts and two plating wastewater treatment sludges—were selected for this experiment. The nonhazardous wastes used for testing the co-disposal effects were three ashes and a compost material. The ashes included the briquette ash generated from individual heating furnaces and bottom and fly ashes generated from a refuse incinerator. The total heavy-metal content of the hazardous wastes, and the extractable concentrations of heavy metals in the nonhazardous wastes, is given in Table 1. The extraction concentrations in Table 1 were determined by the Korean extraction test procedures in which a wet sample (100 g) and distilled water (1 L) are shaken for 6 h (MOE 1991).

Table 1 Total Content and Extraction Concentration of Waste Samples

Content/Concentration	Waste	Heavy Metal				pH
		Cu	Pb	Cd	Zn	
Total content (mg/kg)	Dust 1	1,740	10,700	273	9,840	11.6
	Dust 2	1,340	8,690	335	6,990	6.2
	Sludge 1	26,600	17	4.6	985	7.3
	Sludge 2	23,800	186	4.3	11,800	8.6
Extraction concentration (mg/L)	Briquette ash	ND[a]	0.16	0.01	ND	8.9
	Bottom ash	1.00	0.14	0.01	0.13	10.3
	Fly ash	0.06	0.63	0.11	0.06	9.6
	Compost	0.32	0.12	0.00	1.08	8.1

[a] Not determined.

2.2 Extraction Experiments

2.2.1 Extraction of Mixed Waste

The EAF dusts were extracted with various amounts of nonhazardous wastes: 100 g of dust sample was mixed with 0, 10, 25, 50, 75, or 100 g of bottom ash, fly ash, briquette ash, or compost. The mixture was extracted with 2 L of extraction fluid, either TCLP 2 fluid (acetic acid solution, pH 2.9) or distilled water. The extraction was made according to TCLP methods.

2.2.2 Sequential Extraction of Wastes

Two hazardous wastes were extracted sequentially to see which waste in the extraction sequence was more influential in terms of metal leaching. In each combination, one waste (e.g., waste A) was extracted first; the other waste (e.g., waste B) was then extracted, using the extract obtained from the first extraction. The sequence of extraction was then reversed (i.e., extract B and then extract A). The composition of the extraction fluids and extraction methods was the same as in the extraction of mixed wastes.

2.2.3 Sequential Leaching with Lysimeters

To test the attenuation of heavy-metal leaching by nonhazardous wastes, a system of two-stage lysimeters (a top hazardous lysimeter and a bottom nonhazardous lysimeter) was designed and operated. Details and experimental procedures are given with the experiment results (Sec. 3).

2.3 Analysis

The concentrations of Cu, Pb, Cd, and Zn were measured for the heavy-metal components, according to the Korea Standard Test Methods for Wastes (MOE 1991). An atomic absorption spectrophotometer (Perkin-Elmer, Model 5100PC) was used for the metal determination.

3 RESULTS AND DISCUSSION

3.1 Extraction of Mixture of Two Wastes

When the mixture of dust 2 and various amounts of bottom ash was extracted using distilled water, the heavy-metal concentration in the extraction fluid strongly correlated with the mixture pH

(Fig. 1). As the pH increased as bottom ash was added, the heavy-metal concentration decreased in log scale, which is the typical shape of the metal solubility-pH curves (Bae 1992).

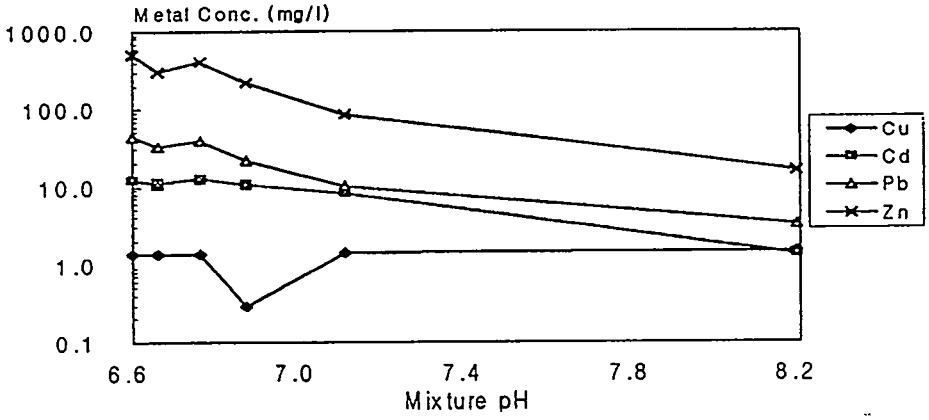

Fig. 1 Heavy-Metal Concentration in the Extract of Waste Mixture (Dust 2 + Bottom Ash) Versus Mixture pH

The possibility of adsorption of the heavy metals onto the surface of ash particles was small because the metal concentration did not decrease with the addition of ash when the pH change was small (Table 2). Table 2 shows that the zinc concentration in the extract of dust 1 + bottom ash mixture did not decrease as bottom ash was added. Instead, it increased significantly, most likely because of the slight decrease of the mixture pH.

Table 2 Comparison of Zinc Concentrations in the Extract of Waste Mixtures

		Bottom Ash Added to 100 g of Dust					
Dust No.	Component	0 g	10 g	25 g	50 g	75 g	100 g
2	pH	6.60	6.66	6.76	6.87	7.11	8.19
	Zn (mg/L)	510	312	416	219	85	16
1	pH	11.36	11.35	11.29	11.25	11.211	11.16
	Zn (mg/L)	3.6	3.7	4.2	8.4	17.8	15.6

Note: The extraction fluid was distilled water.

Figure 2 shows the data for the waste mixture extractions (dust 2 + nonhazardous wastes). Although the data are somewhat scattered, the trend clearly indicates that the metal extraction decreased as the pH of the mixture increased, which was caused by adding nonhazardous wastes.

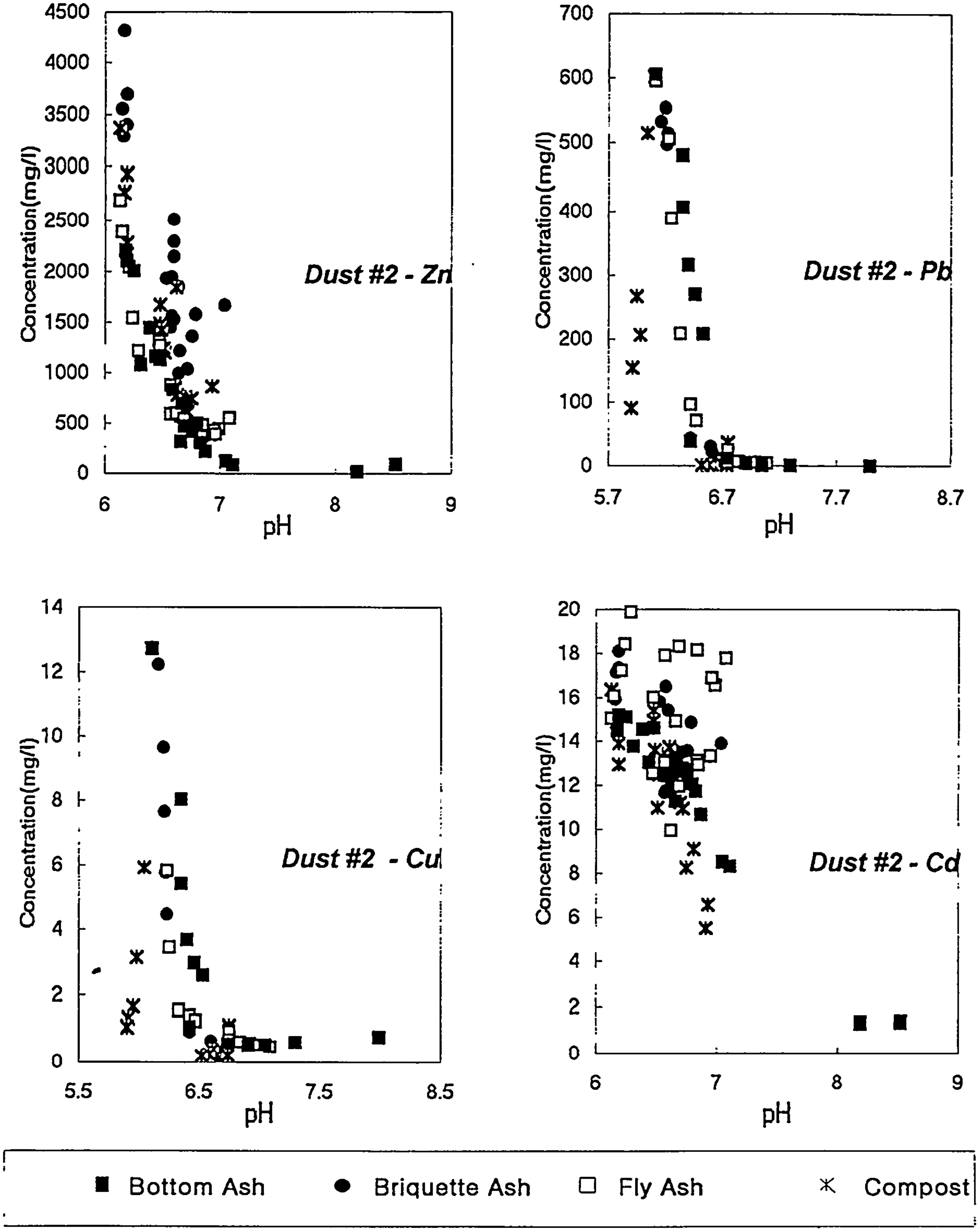

Fig. 2 Extract Metal Concentration Compared with pH in the Waste Mixtures

A similar pH effect was observed in a mixture of two hazardous wastes. Table 3 shows the co-disposal effect of dust samples 1 and 2. The samples had very different pH potential. When the dust samples were extracted independently, dust 2, which had more acidic pH, gave higher metal concentrations than did dust 1. When the dust samples were mixed and extracted together (solid:liquid = 100 g:2 L), the extracted metal concentration was lower than the sum of the extracted metal concentrations from the individual extractions (solid:liquid = 50 g:2 L in each extraction). This could be easily explained from the difference of the medium pH: as pH increased in the mixture, the extraction decreased. The results in Table 3 indicate that when two heavy-metal-bearing wastes that have significantly different pH potential are to be landfilled, environmental risk can be reduced by disposing them in a mixture.

Table 3 Comparison of Potential Hazards among Individual and Co-Disposal of Two EAF Dust Samples

	Individual Disposal		Sum of Individual	
Component	Dust 1	Dust 2	Dust 1 + Dust 2	Co-Disposal
Cu	0.06	0.50	0.55	0.18
Pb	8.27	18.96	27.24	1.07
Cd	0.12	3.84	3.97	2.64
Zn	0.28	137.61	137.89	36.27
pH	11.5	6.7	-	7.4

3.2 Sequential Extraction of Two Wastes

Two hazardous wastes were extracted sequentially to see which waste in the extraction sequence had a greater influence on metal leaching. Table 4 gives the results of the experiment. In each combination of two wastes, one waste was extracted first, and then the other waste was extracted, using the extract obtained from the first extraction. The reversed sequence of extraction was also made. The final metal concentrations obtained from the two extraction sequences were compared, and the less risky sequence is presented in Table 4. Symbols indicate the waste that gives higher (H) or lower (L) extraction concentration when extracted alone. In short, H represents more toxic waste, and L represents less toxic waste. Therefore, the expression "HL" in Table 4 means extracting the less toxic waste later gave a lower final metal concentration in the extract. In Table 4, all combinations except one case (dust 1 + sludge 2 experiment for Cu) showed an HL concentration. This indicates the latter extracted waste influenced more strongly the final concentration of heavy metals in the extract. This finding implies that when two wastes are co-disposed of layer by layer, forming strata, the EP toxicity of the bottom-layered waste can play a major role in terms of the

Table 4 Extraction Sequence for Less Heavy-Metal Leaching

Metal	Dust 1 + Dust 2	Dust 1 + Sludge 1	Dust 1 + Sludge 2	Dust 2 + Sludge 1	Dust 2 + Sludge 2	Sludge 1 + Sludge 2
Cu	HL	HL	HL	HL	HL	HL
Cd	HL	HL	*LH*	HL	HL	HL
Pb	HL	HL	HL	HL	HL	HL
Zn	HL	HL	HL	HL	HL	HL

overall EP toxicity. Thus, the heavy-metal leaching would be attenuated if a less EP toxic waste were placed at the bottom, compared to the opposite case.

3.3 Sequential Leaching with Lysimeters

From the results of the sequential extraction experiments, it was postulated that a nonhazardous waste would attenuate heavy-metal leaching in a landfill if it were placed at the bottom of a hazardous waste layer. To test this hypothesis, a system of two-stage lysimeters, which consisted of a top lysimeter (TL) and a bottom lysimeter (BL), was designed and operated. The TL contained hazardous wastes, while the BL contained nonhazardous wastes. The leachate collected from the TL was fed into the BL, and the change of heavy-metal concentration in the leachate was monitored.

The TL was made of an acrylic tube, 50 cm high and 25 cm in diameter. The leachate was filtered through a bottom filter system. The BL was similar in shape to the TL, but smaller: 12.5 cm high and approximately 10 cm in diameter. A synthetic rain (pH = 5) was made by using sulfuric acid and nitric acid at the ratio of 6:4. The synthetic rain was put into the TL once a day and left for 18 h and was then percolated. The percolated leachate was fed to the BL once a day. The BL was left for 18 h before its leachate percolated. By maintaining the lysimeters saturated for 18 h, it partially simulated the natural moisture change in landfills.

The results are given in Fig. 3 (for dust 1) and Fig. 4 (for dust 2) for copper and lead. A substantial attenuation was observed in most cases. The difference between the cumulative input amount and the cumulative leached amount from each BL was the amount of metal retarded by the nonhazardous wastes in the BL. However, no attenuation was achieved when the waste in the BL contained leachable metals more than or as much as the waste in the TL did (see Cu curves in Fig. 3).

Table 5 Average Amount of Metal Attenuated by Nonhazardous Wastes

	Nonhazardous Waste (mg/kg)			
Metal	Compost	Briquette Ash	Bottom Ash	Fly Ash
Cu	90	106	97	95
Cd	-96	-13	40	-24
Pb	206	180	168	191
Zn	1,563	784	2,126	1,490

The average rate of attenuation for various heavy metals in milligrams of metal removed per kilogram of nonhazardous waste is shown in Table 5. The average attenuation ranged from 90 to 106 for Cu, 168 to 206 for Pb, and 784 to 2,126 for Zn, according to the type of nonhazardous wastes in the BL. Unexpectedly, the Cd was not attenuated in most cases, although the nonhazardous wastes did not contain large amounts of cadmium. An analytical error might have been involved in determination of cadmium.

4 CONCLUSIONS

The following conclusions were derived from our evaluation of the potential attenuation of heavy-metal leaching from EAF dusts and hazardous sludges by co-disposal of hazardous and nonhazardous wastes:

- When hazardous and nonhazardous wastes were mixed homogeneously, the extraction of heavy metals from the waste mixture was most critically affected by the extract pH. As pH fell, the concentration of heavy metals in the extract increased sharply, as expected from the solubility of metal hydroxides. The pH effects on the heavy-metal extraction were similar when two hazardous wastes were mixed homogeneously.

- When two wastes were extracted sequentially, that is, extract waste A and then extract waste B, using the filtered extract of waste A, the latter had a stronger influence on the final concentration of heavy metals in the extract. Thus, the heavy-metal leaching would be attenuated if a less EP toxic waste were placed at the bottom of a hazardous layer in a landfill.

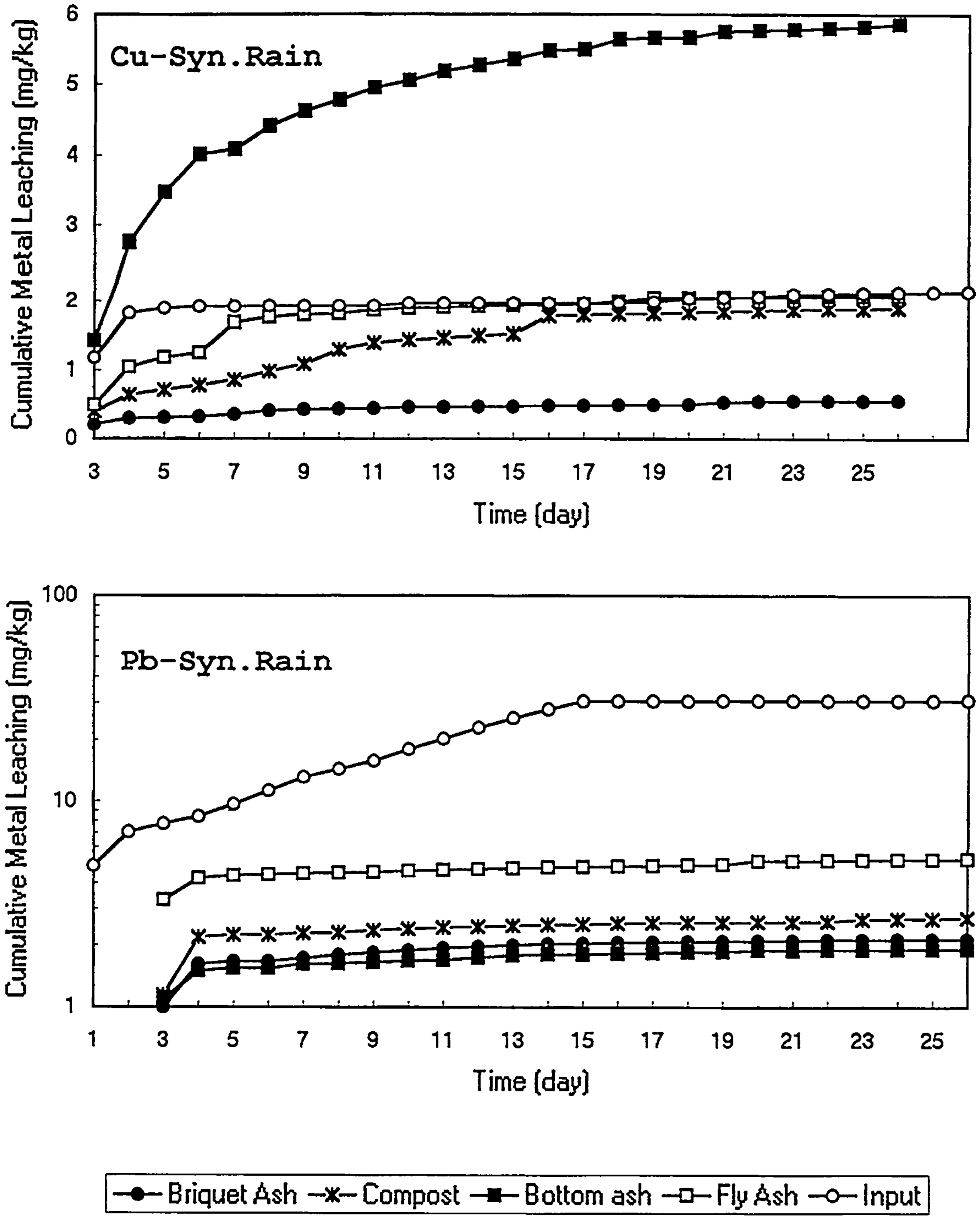

Fig. 3 Attenuation of Heavy-Metal Leaching from Dust 1 by Nonhazardous Wastes

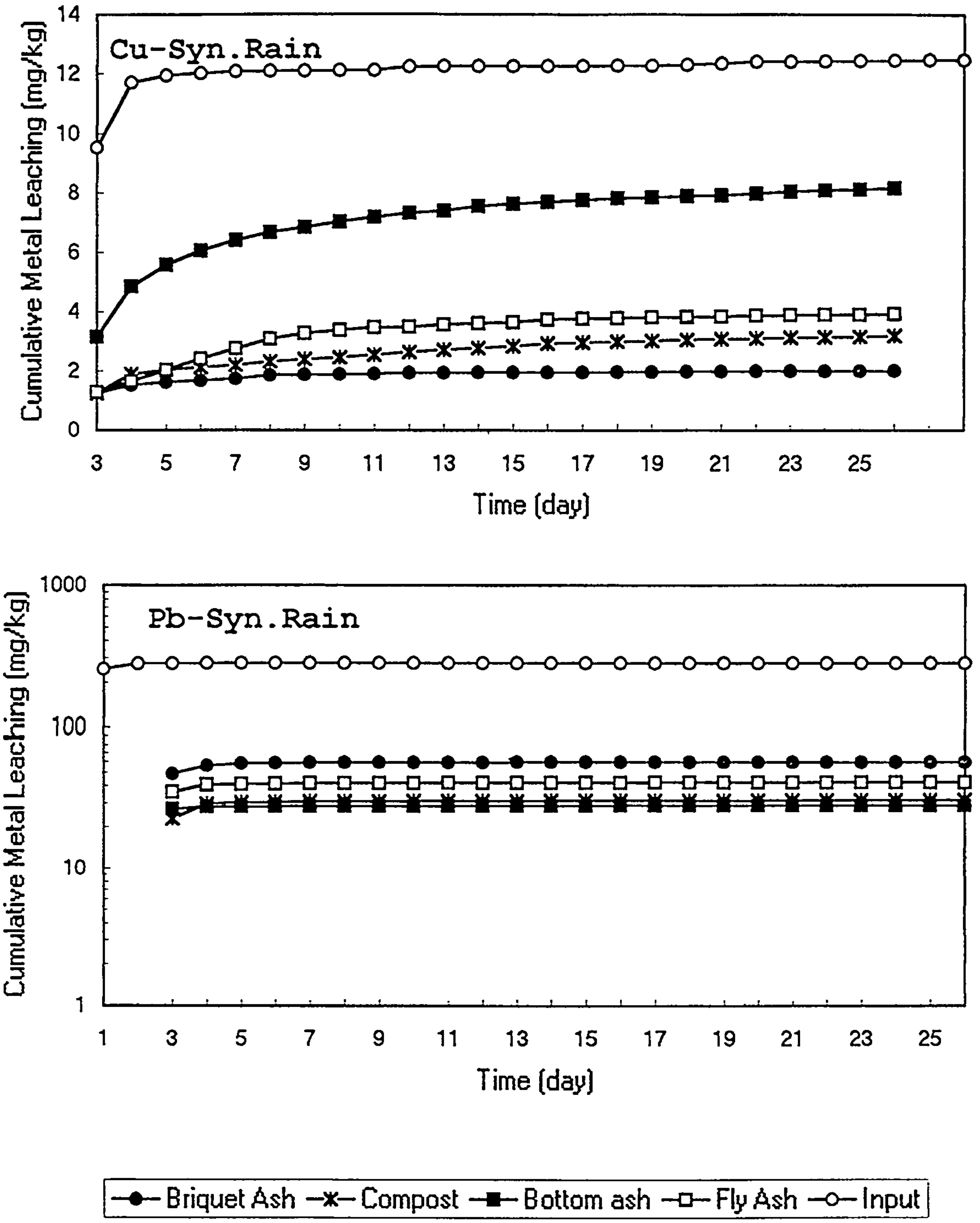

Fig. 4 Attenuation of Heavy-Metal Leaching from Dust 2 by Nonhazardous Wastes

- When heavy-metal-bearing leachates generated from hazardous-waste lysimeters were passed through a nonhazardous-waste lysimeter filled with compost, briquette ash, or refuse-incineration ashes, the heavy-metal concentration in the final leachates decreased significantly.

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MOE, *Standard Test Methods for Wastes*, Ministry of Environment, Republic of Korea, 1991.

The area analyzed was 235 ha of the first working area (total 396 ha), excluding the stockyard for briquette ash and construction debris. Precipitation, temperature, and solar radiation during 1984 and 1994 at the Incheon area, where the landfill is located, were used in the HELP model analysis. The input soil property parameters are shown in Table 1.

Table 1 Soil Characteristics of Intermediate, Waste, and Barrier Layers

Layer	Total Porosity	Field Capacity	Wilting Point
Intermediate	0.473	0.222	0.104
Waste	0.501	0.292	0.071
Barrier	0.427	0.418	0.367

A waste layer porosity of 0.501 was applied instead of 0.671 due to the compaction of 0.4 ton/m^3 to 0.9 ton/m^3. The inputs for the slope of the drainage layer and the drainage length were 0.1% and 20 m, respectively, because metropolitan landfill is on the natural barrier layer (Figure 1).

2.2 Continuous Calibration Results with Hydraulic Conductivity

HELP analyses were performed with varying saturated hydraulic conductivities (K) of waste and intermediate layers due to the great uncertainty of the property. The results were compared with field data from February 1993 to June 1995. Cases according to the landfill lifts (1st, 2nd, and 3rd) and with/without cover layer were also analyzed as shown in Figure 2.

The results are summarized in Figure 3(a)-(e) and Table 2. The waste layer has hydraulic conductivities varying between 2.0×10^{-5} cm/sec and 2.5×10^{-5} cm/sec, while the intermediate layer has a constant hydraulic conductivity value of 5.0×10^{-5} cm/sec. This demonstrates that the much thinner cover layer (0.5 m) affects the analytical results far less than does a waste layer of 4.5 m.

Calibration showed that infiltration was 30% averaged throughout the stages. These values were used in the water balance analysis in Section 2.3 (Figure 4).

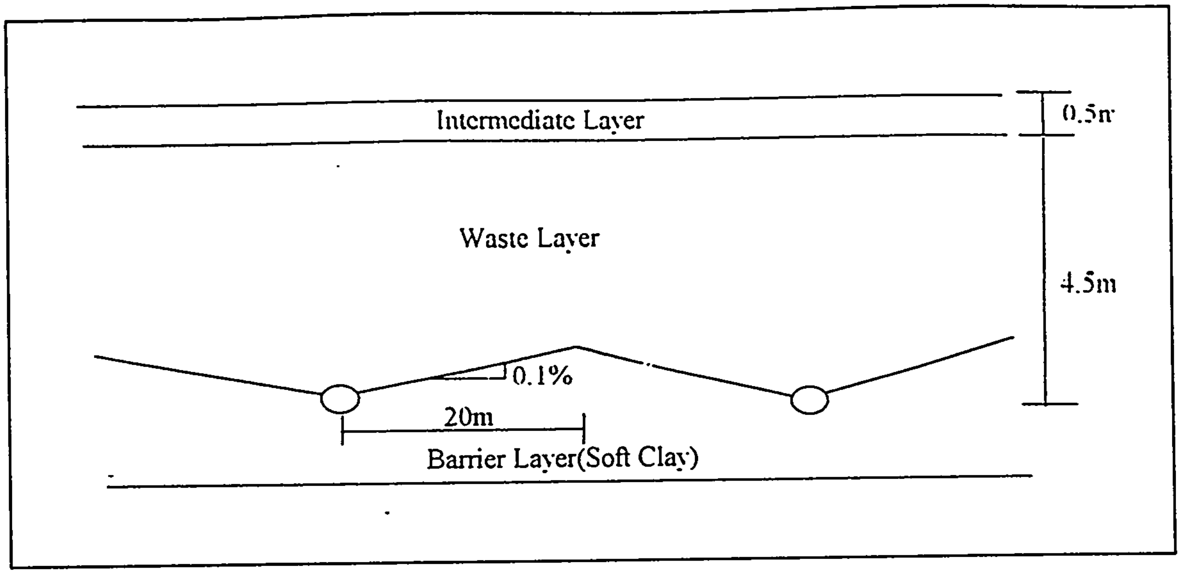

Fig. 1 Model Input Data for Landfill Design

Table 2 Calibrated Saturated Hydraulic Conductivity (K)

Step of Disposal[a]		Calibrated Saturated Hydraulic Conductivity (K, c/s)
1st lift	Inter ×	Waste layer $K = 2.0 \times 10^{-5}$
	Inter O	Intermediate layer $K = 5.0 \times 10^{-5}$
2nd lift	Inter ×	Waste layer $K = 2.5 \times 10^{-5}$
	Inter O	Intermediate layer $K = 5.0 \times 10^{-5}$
3rd lift	Inter ×	Waste layer $K = 2.5 \times 10^{-5}$

[a] Inter = intermediate layer.
× = without intermediate layer.
O = with intermediate layer.

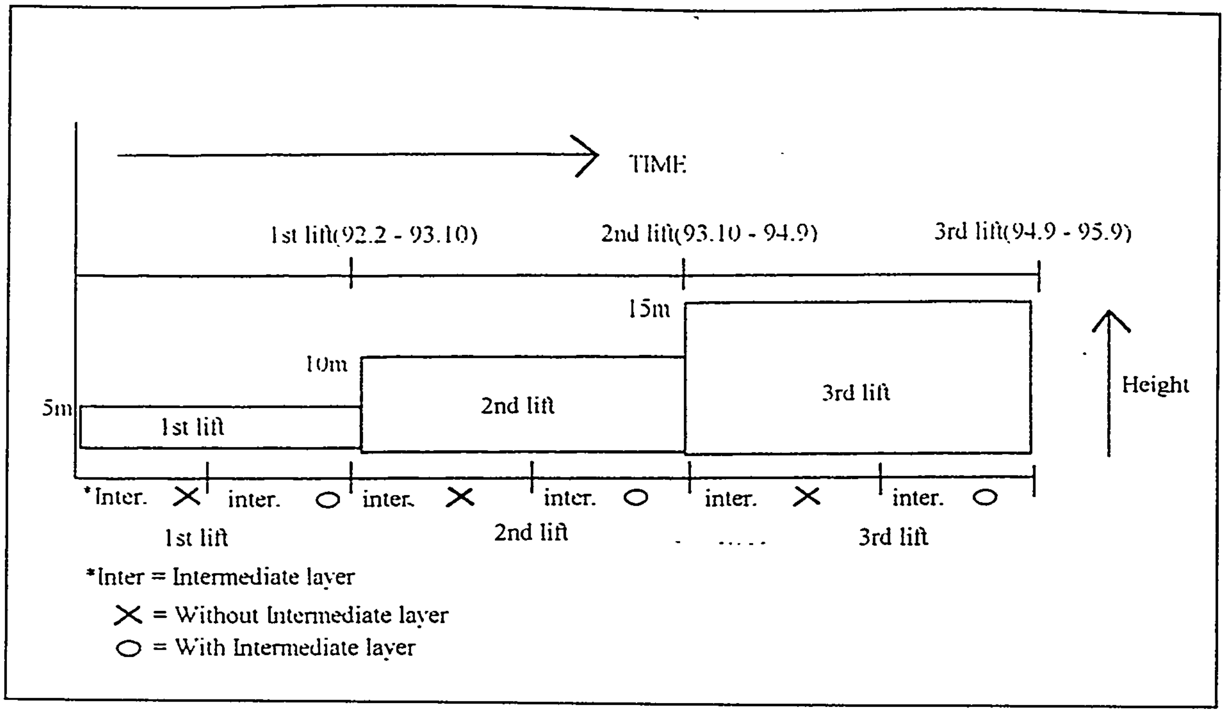

Fig. 2 Procedure of HELP Model Analysis

2.3 Total Water Balance Analysis

For total water balance analysis, we used equation (1). However, run-off and evapotranspiration in the K landfill site were not measured, so we used HELP model results for these values. From the HELP model results we found the infiltration ratio into the landfill site is 30%, assuming a 100% precipitation ratio (Fig. 4).

$$p-e-r+s+w_0=L+H \ , \qquad (1)$$

where

p = precipitation
e = evapotranspiration
r = run-off
s = water into the landfill by consolidation settlement
w_0 = initial wastewater content
L = quantity of leachate production from drainage pipe
H = quantity of leachate level (area × H = volume [m^3])

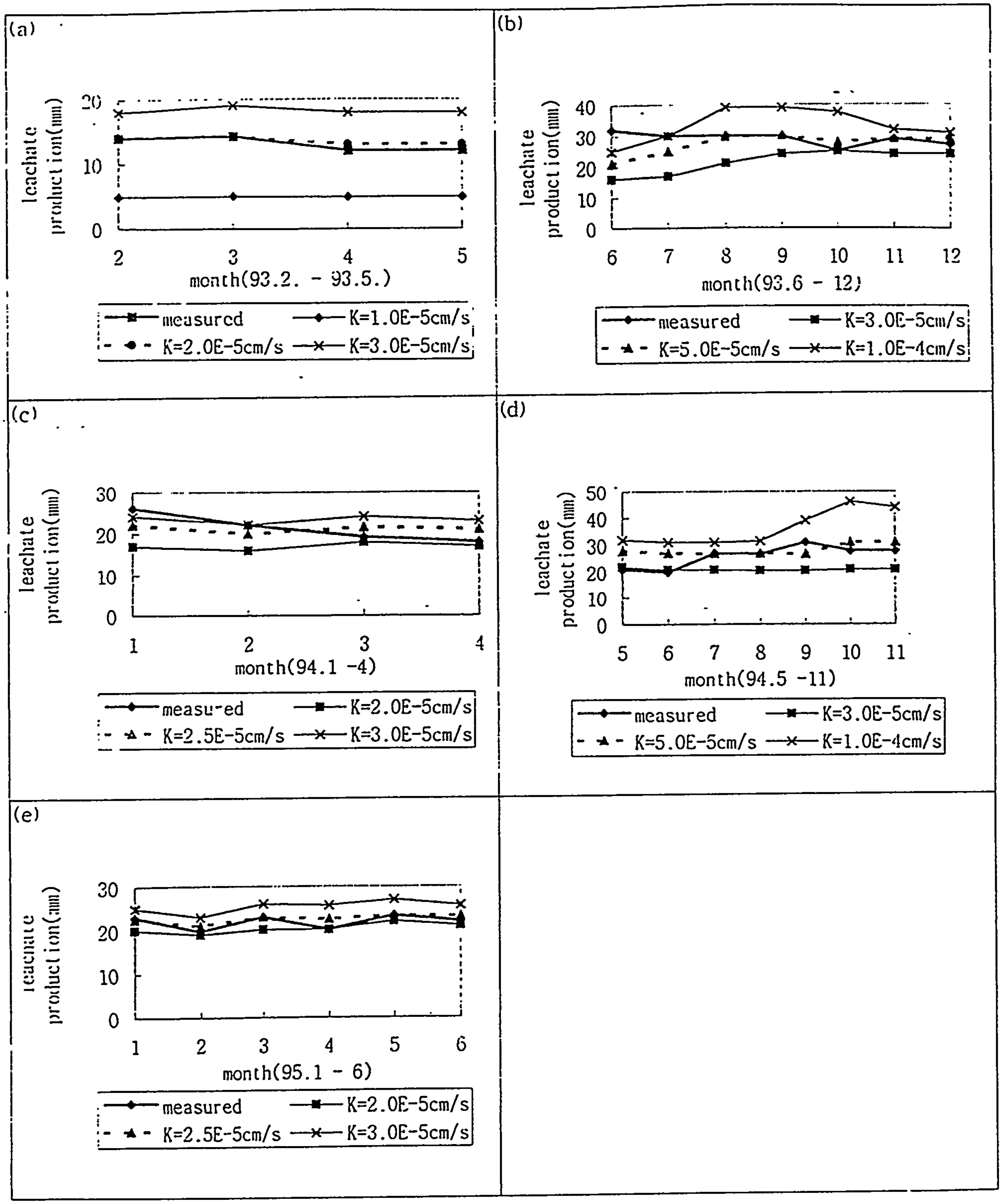

Fig. 3 Results When the HELP Model Is Calibrated with Hydraulic Conductivity: (a) Calibration of Waste Layer (1st lift, Inter×); (b) Calibration of Intermediate Layer (1st lift, InterO); (c) Calibration of Waste Layer (2nd lift, Inter×); (d) Calibration of Intermediate Layer (2nd lift, InterO); (e) Calibration of Waste Layer (3rd lift, Inter×)

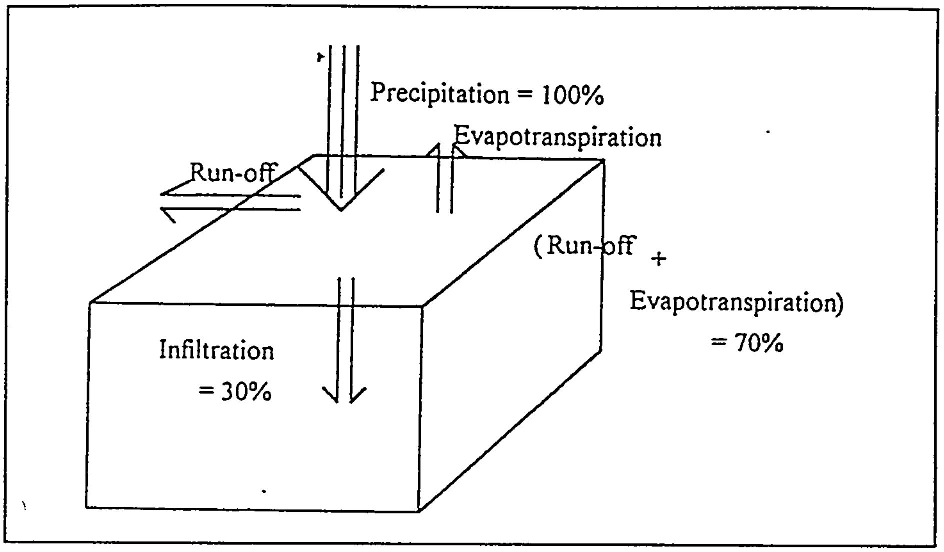

Fig. 4 Infiltration Ratio in Landfill Site (%)

The results of the cumulative total water balance analysis are shown in Fig. 5(a). During the first-lift landfilling until September 1993, the precipitation proportion of the total input is 62% and the proportion of initial wastewater content is 36%. In this case, the quantity of leachate level is 50% of the output and the quantity of leachate production from the drainage pipe is 6.4%. So, we will predict an increasing leachate level in the landfill site.

Figure 5(b) presents the cumulative results through the second-lift landfilling. The precipitation proportion of the total input is 55%, which is smaller than the results for the first-lift landfilling, but the initial wastewater content is increased to 41%. The high water content in the waste increased the quantity of leachate level, so in this lift the quantity of leachate level proportion is 60.5%, an increase of 10.5% over the first-lift landfilling.

Figure 5(c) gives the cumulative results of the third-lift landfilling. In this case, both the precipitation and the initial wastewater content proportions are 48.2%. These results show a decreasing rate of precipitation to 20% and an increasing rate of initial wastewater content to 12.4% in proportion to the total input. During the third-lift landfilling, the quantity of leachate level and the leachate production from the drainage pipe are 55% and 11% in proportion to the total output, respectively.

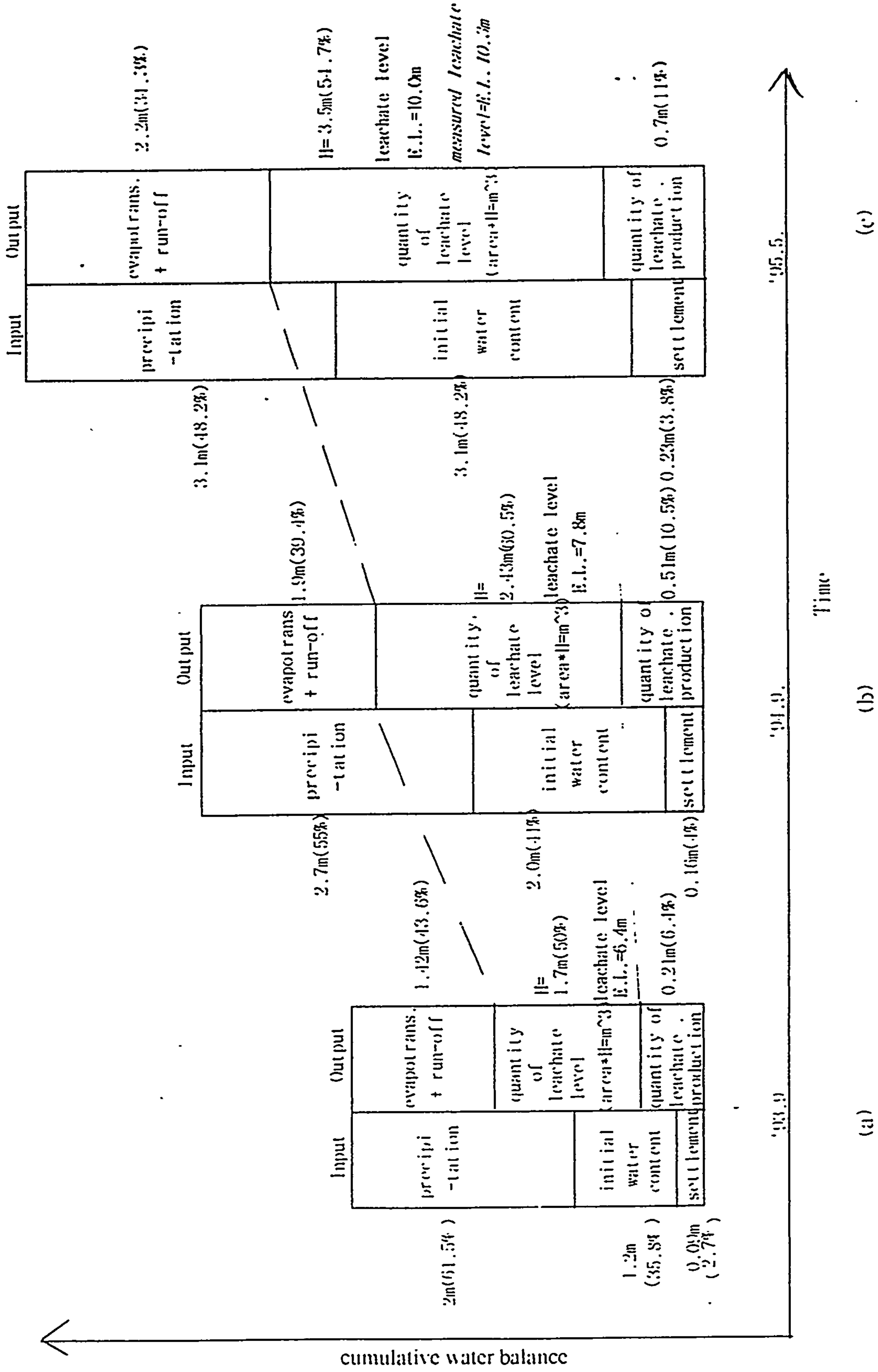

Fig. 5 Cumulative Results of Total Water Balance Analysis: (a) Until First-Lift Landfilling; (b) Through Second-Lift Landfilling; (c) Through Third-Lift Landfilling

This means that the water content of the waste is a very important factor for the production of leachate in the K landfill site. The results of the total water balance analysis of the K landfill indicate that only 11% of the leachate was collected from the drainage pipe and 55% of the leachate contributed to the increasing leachate level in the landfill. The measured and calculated leachate levels are E.L. 10.3 m and E.L. 10.0 m, respectively, so prediction of leachate level by total water balance analysis is feasible.

2.4 Prediction of Leachate Level by the Total Water Balance

To estimate the change of the leachate level in the future, the total water balances with different leachate discharge rates of 3,000, 3,500, and 5,000 m^3/day were analyzed.

In so doing, we can predict a leachate level in the future and estimate a stability of slope. Figure 6 shows the variation in leachate level at each step of disposal for different wastewater contents at a 3,000 m^3/day discharge rate. After the final disposal step, the leachate level increased to E.L. 18 m with a wastewater content of 45%. But, in this case, the safety factor for slope stability is less than 1.3 (i.e., E.L. 11.5 m). Even if the discharge rate is 3,500 m^3/day and the wastewater content continues to be 45% at the end of landfilling, the leachate level is increased to 17.8 m. Therefore, we did not continue more landfilling after the 4th lift (Figure 7).

Figure 8 shows the case of a 5,000 m^3/day discharge rate. At the end of landfilling the leachate level reached 15 m. This result does not satisfy the safety factor requirements for slope stability analysis. Only a 25% wastewater content and 5,000 m^3/day discharge rate satisfied the safety factor requirements for stability of slope.

3 RESULTS AND DISCUSSION

In this study, we used a successive calibration analysis with each layer's hydraulic conductivity and compared that with field-measured data from February 1993 to June 1995. To verify the HELP model analysis, we analyzed total water balance using field-measured data and achieved a good result for the leachate level. Based on this analysis, we predicted future leachate levels according to the landfill stage (4th, 5th, 6th, 7th, and 8th lift landfilling) for the different discharge rates and compared these results with a slope stability analysis. The results of this study follow:

- The calibration results for each layer (see Table 2).
- From the total water balance analysis, the initial wastewater content is 48.2% of the total input. This point is very important to Korea, as compared to a country that typically has a low wastewater content in its landfills.

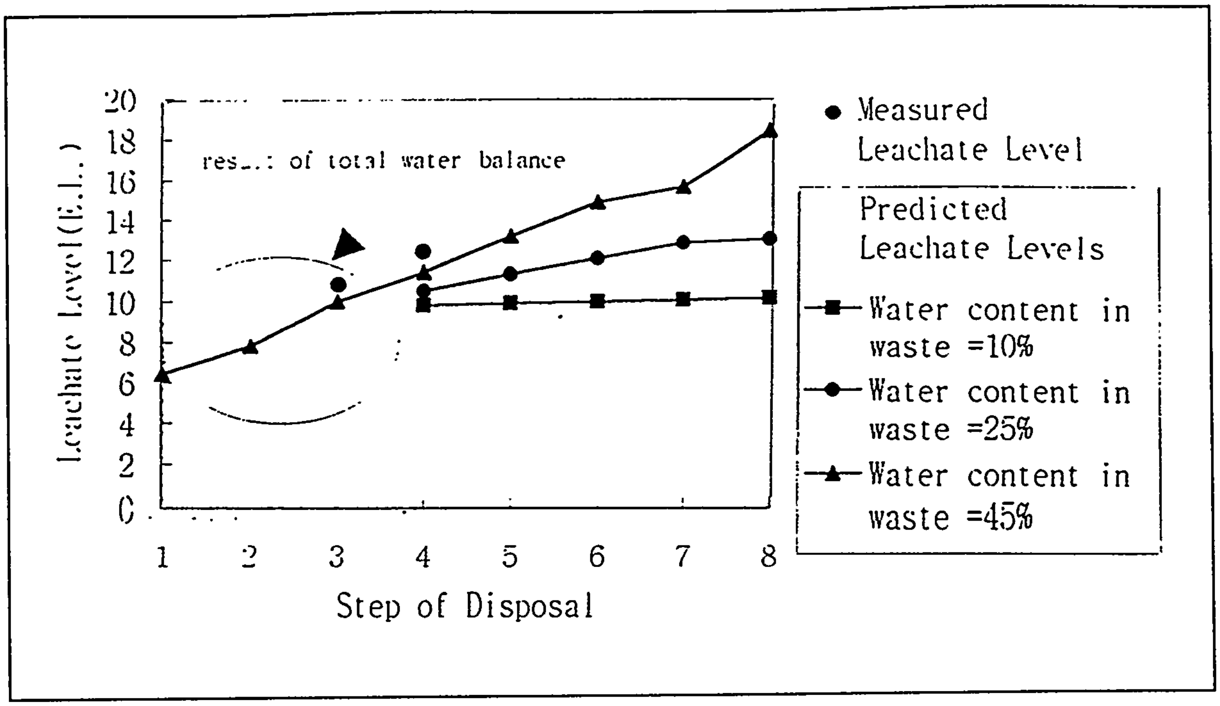

Fig. 6 Variation of Leachate Level with Various Wastewater Contents (discharge rate = 3,000 m^3/day)

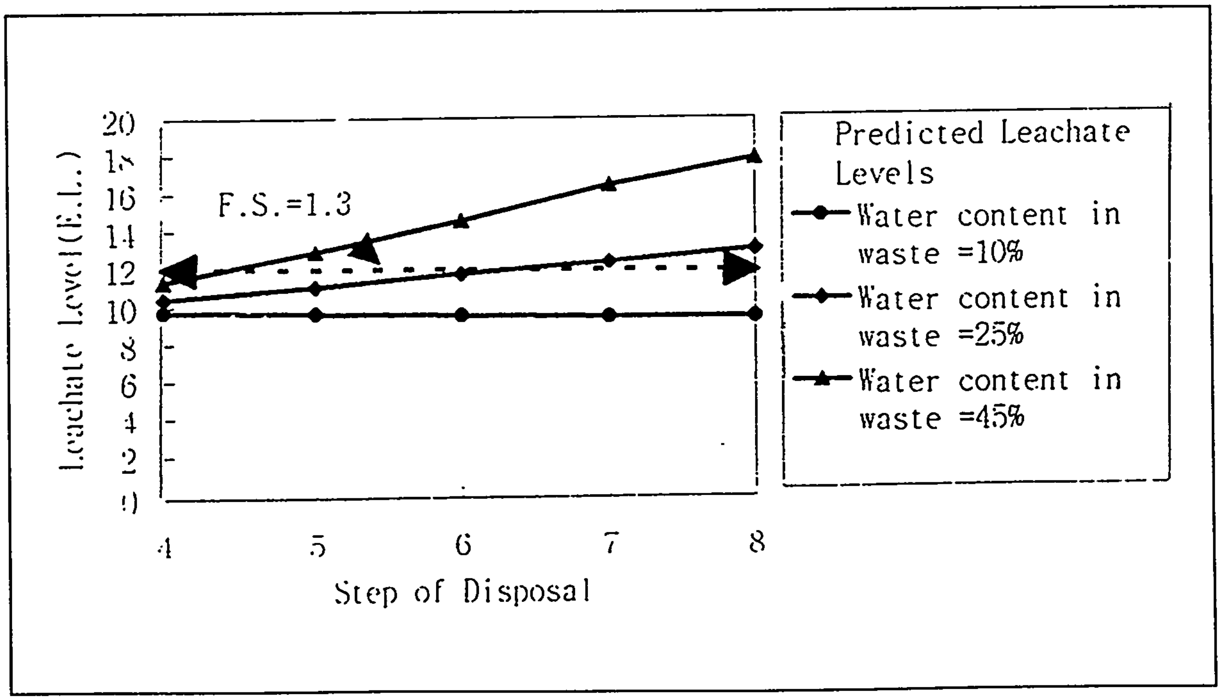

Fig. 7 Variation of Leachate Level with Various Waste Water Contents (discharge rate = 3,500 m^3/day)

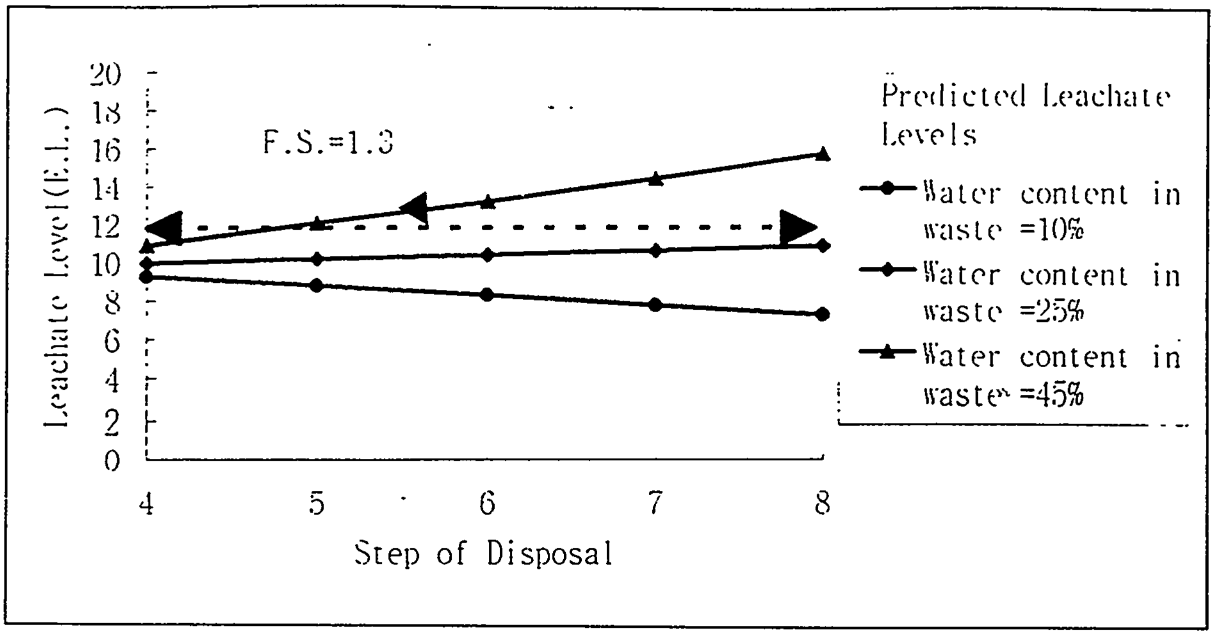

Fig. 8 Variation of Leachate Level with Various Wastewater Contents (discharge rate = 5,000 m^3/day)

- At the end of landfilling, to achieve a safety factor of 1.3 for slope stability, the discharge rate is continued at 5,000 m^3/day and the initial wastewater content is below 25%. The cause of the increasing leachate level is a very high percentage (55%) of cumulative leachate in the landfill site through the 3rd-lift landfilling, as compared with leachate production from the drainage pipe (11%).

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CLEANUP AND REMEDIATION

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WASTE SITE CHARACTERIZATION AND REMEDIATION: PROBLEMS IN DEVELOPING COUNTRIES

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ABSTRACT

Increased industrial activities in developing countries have degraded the environment, and the impact on the environment is further magnified because of an ever-increasing population, the prime receptors. Independent of the geographical location, it is possible to adopt effective strategies to solve environmental problems. In the United States, waste characterization and remediation practices are commonly used for quantifying toxic contaminants in air, water, and soil. Previously, such procedures were extraneous, ineffective, and cost-intensive. Reconciliation between the government and stakeholders, reinforced by valid data analysis and environmental exposure assessments, has allowed the "Brownfields" to be a successful approach. Certified reference materials and standard reference materials from the National Institute of Standards (NIST) are indispensable tools for solving environmental problems and help to validate data quality and the demands of legal metrology. Certified reference materials are commonly available, essential tools for developing good quality secondary and in-house reference materials that also enhance analytical quality. This paper cites examples of environmental conditions in developing countries, i.e., industrial pollution problems in India, polluted beaches in Brazil, and deteriorating air quality in countries, such as Korea, China, and Japan. The paper also highlights practical and effective approaches for remediating these problems.

1 INTRODUCTION

Increased industrial activities in developed countries have contributed to degradation in the quality of the environment. While this statement is also true for developing countries, the impact on the environment is further magnified because of the pressures of an increasing population. Whether a country is developed or developing, such conditions primarily affect local populations. As industrial activity intensifies, it tends to change previously moderate polluting conditions to more serious proportions, e.g., from textile, wood, and food processing to metal, chemical, and paper industries. Adjoining water bodies are likely receptors of pollutants, as industries have found rivers, streams, and lakes to be convenient disposal/discharge media to dilute wastes. Recipient water bodies extend the danger of contamination beyond local boundaries. This paper presents contrasting examples of industrial pollution problems in both developed and developing countries. Further, effective solutions for remediating such potential problems are discussed.

2 COMPARISON OF ENVIRONMENTAL SCENARIOS (DEVELOPED VS. DEVELOPING COUNTRIES)

In most developing countries, it is common for the economically poorer segments to become receptors of environmental degradation. The "not-in-my backyard (NIMBY)" syndrome does not seem to be a critical concern of the poor and their children in developing countries, as survival depends on coping with the changing economy and aspirations for a better future. Furthermore, such pollution problems have reached the backyards of the middle- and high-income communities in metropolitan cities. Though environmental problems in developed and developing countries are similar in many ways (1), they remain unique to the local infrastructure and the awareness of the community. For example, in the United States, it is possible to strategize an evacuation effort in a hypothetical catastrophic environmental situation, i.e., a chemical explosion, as the infrastructure and procedures established through existing laws allow for emergency response and remedial actions (3). On the other hand, in Asia, Latin America, and Eastern Europe, such actions are often impractical because of haphazard infrastructural growth patterns dominated by local conditions. These chronic conditions disregard or ignore chemical hazards that lead to undesired health effects, e.g., industrial accidents. This situation is further compounded by the inability of various governments to act coherently on environmental concerns.

Most of these problems are attributable to lack of proper characterization and monitoring principles and demand effective collaborations and partnerships between industry and government to address environmental concerns. In this paper, examples are given of specific situations, such as the industrial pollution problems in Gujerat, India; the polluted shorelines in Santos Beach, Brazil; and the deteriorating air quality due to pollution concerns in Korea, China, and Japan. Effective solutions and approaches for remediating such problems are also discussed.

2.1 Example 1: Industrial Waste Problems in India

Ankleshwar in Gujerat, India, is one of the largest industrial estates in Asia, and one of the 190 industrial complexes in Gujerat's "Golden Corridor," as shown in Fig. 1. The area gets its name from the revenues generated by rapid development in the region (from Vapi in the South to Mehsana in the North). This 450-km industrial corridor is described as "a region not far from the Bhopal tragedy that had shaken the world on industrial safety and waste management concerns" (4). Industrial regions in the area are described as covered with foul-smelling chemicals, unpleasant

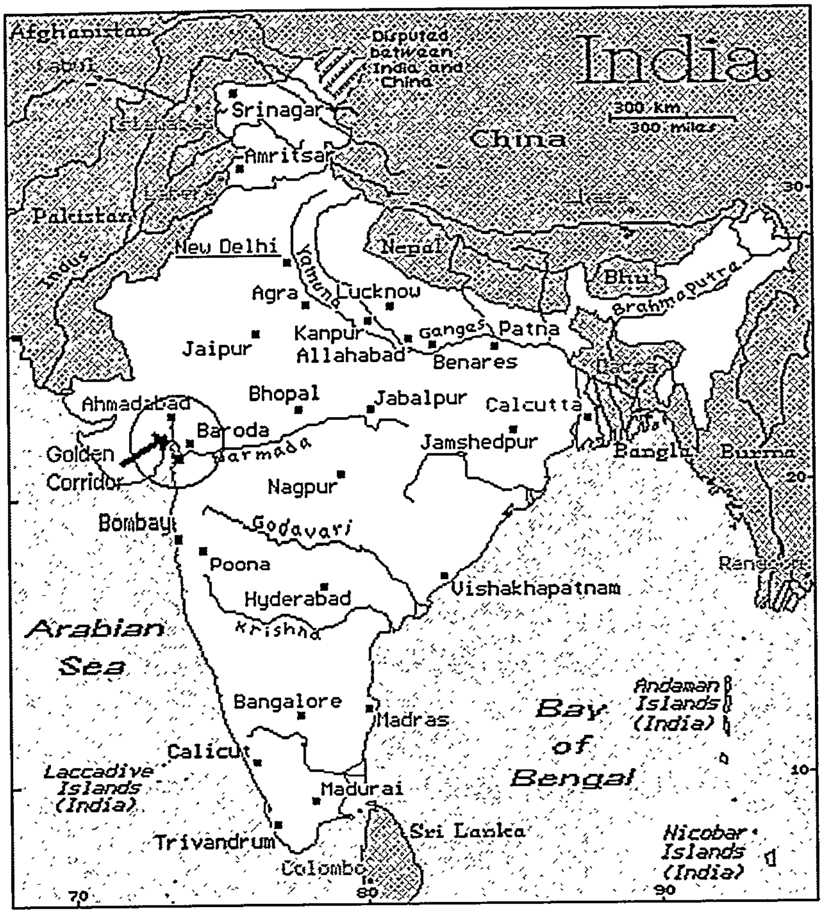

Fig. 1 The Golden Corridor, Gujerat, India (Source: Modified from Microsoft Encarta 96)

effluents that flow through the *unlined* run-off ditches and that tend to clog the drains, and heaps of solid waste that lie scattered about the area, both inside and outside the plant gates. The area is inhabited with workers and residents who are either employed at the industrial facilities or a part of the system in support organizations. Cattle roam the industrial area, and children play casually in the open areas not far from the industrial plants. Ankleshwar consists of some 3,000 industries, with nearly 1,500 chemical units operating in a 65-km^2 complex. Chemical production processes and products at Ankleshwar include paints, fertilizers, dyes, pulp and paper, pharmaceuticals, and pesticides. Hazardous waste generation quantities are estimated to be 250–270 million liters of liquid waste per day and nearly 50,000 tonnes of solid hazardous waste per year. Notwithstanding such conditions, the government is poised to invest an additional Rs. 25,000 crore for industrial expansions by the year 2000 (3).

Groundwater monitoring in the Golden Corridor region revealed no significant levels of pollutants (5). Although the investigative report indicated that some analytes were not detected, the approach used in the process appears to be inadequate. Therefore, the conclusions of the report at best are incomplete, since they do not advocate proper tracing and fingerprinting of the problem. Also, the need for further sampling and analysis of environmental media, such as sediments and surface waters, has not been identified in the groundwater report.

When sampling and analyzing for specific constituents, it is vital to understand the nature and behavioral patterns of compounds to effectively characterize the problem. It is also necessary to establish proper quality controls and chain-of-custody procedures through efficient record-keeping procedures. With the extent of industrial activity in the Golden Corridor region and its situation along the Gulf of Khambhat, it is likely that there is a significant level of contamination beyond the detection capabilities of such techniques available at site. Other environmental receptors also can be probable indicators. Potential discrepancies and deficiencies in groundwater characterization efforts indicate improper placement of groundwater monitoring wells. For example, groundwater contamination in the area was reported at a depth of 150 ft (4). Groundwater reports indicate that the wells in the area were installed in the upper aquifer zone, ranging from 37 ft to 80 ft (5). This clear evidence shows that characterization was not incompatible with the requirements of the problem, thus disqualifying the information for risk and exposure assessment.

To remediate the present hazardous waste problems at Ankleshwar, the Industrial Development Corporation in Gujerat and the Ankleshwar Industrial Association have agreed to construct a secured hazardous waste landfill (4). Secured landfills are excellent waste repositories and, if constructed with proper control measures, are excellent for controlling migratory problems. However, it is very important to keep in mind that hazardous waste landfills can be a problem, if proper security or surveillance measures are not in place. Further, secured landfills have a life expectancy of 15–20 years and are not a permanent solution to the problem. Ownership, operation, and maintenance of the landfills also have serious legal implications. To curb the problems at Ankleshwar and minimize exposure, a hazardous waste landfill may be a solution but may fall short of being effective.

An illustration of the problems associated with landfills can be as inconspicuous as the one discussed below. Recent landfill problems at a Superfund site and codisposal facility in the central United States show that landfill gases violate regulatory compliance requirements (6). Volatile organic compounds (VOCs) and semivolatiles exist in high concentrations within the landfill leachate. Because of their chemical behavior, such VOCs tend to migrate in the form of gases through the underlying layers of the landfill and partition with the groundwater. Further, CO_2 and methane, commonly produced within the landfill, tend to create high-pressure conditions with time and tend to migrate into the groundwater table. This situation is particularly true for landfills with a low-permeability layer and cap, wherein the upward migration of gases is restricted. Recent findings show that several California solid waste landfills revealed the presence of nine VOCs in groundwater at concentrations higher than that stipulated by regulatory requirements. Compounds identified in groundwater samples for 43 solid and hazardous landfills sites are presented in Fig. 2.

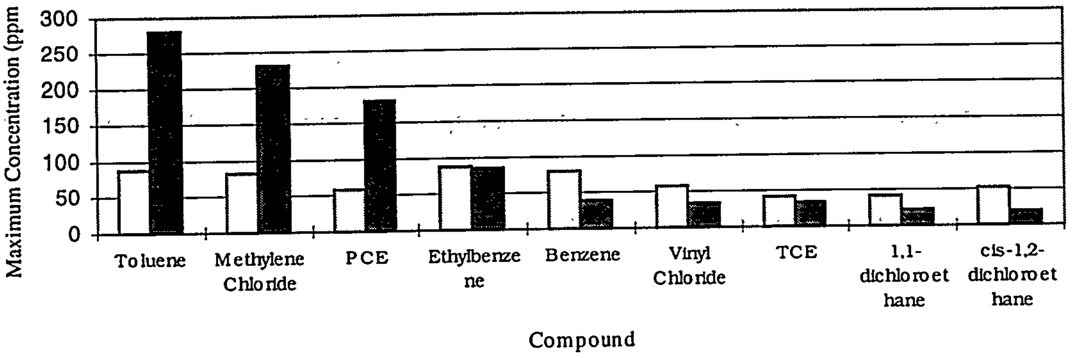

Fig. 2 Volatile Organic Compounds in Groundwater at Landfill Sites (Modified from Ref. 6)

In addition to generic engineering and design principles for the construction of landfills, it is important to consider other site-specific factors, such as local industrial practices; waste receiving, treatment, and disposal options; issues relating to potential migration and time-dependent release of wastes; and the logistics associated with both short- and long-term monitoring and surveillance.

2.2 Example 2: Municipal Sewage Problems in Santos Beach, Brazil

Municipalities in developing countries face unique challenges when trying to reduce pollution from sewerage systems. Overcrowding in urban areas results in problems related to infrastructure planning and development.

Until 1950, Santos was the most important beach resort on the coast of the state of Sao Paulo, Brazil (Fig. 3). However, increasing levels of coastal pollution from local industrial activity and inadequate sewerage and wastewater treatment systems gradually eroded the coast, leading to a decrease in local tourism. In the 1970s, Santos suffered from a deep economic recession, due primarily to the reduction of the tourist business. In 1990, a major survey revealed high levels of fecal coliform at several locations within the city of Santos. Characterization of the area and sources from the Sao Paulo region indicate that the pollution came from within the city. Illegal installation of drain pipes from the city allowed raw sewage to be dumped to the ocean, rather than to the municipal sewerage system (7). The Santos Beach Recovery Program was developed in 1991 as a cooperative project between the local and state governments, with distinct responsibilities for sewerage and storm water systems operated in the municipality. To remediate the situation, a program that integrated intergovernmental cooperation and academic participation was initiated.

Significant infrastructural changes from 1991 to 1993 improved the water quality at Santos Beach by reducing fecal coliform levels by 50%. Tourism has increased, and community awareness programs on environmental consciousness have been established. The problems at Santos Beach are

Fig. 3 Santos Beach, Santos, Brazil (Source: Modified from Microsoft Encarta 96)

common to most beaches and tourist resorts in developing countries. It is not clear from this example whether sediments and sludges along the beaches have been contaminated with industrial chemicals, particularly organics that may have been transported through sewage and sludges discharged through commercial and industrial outfalls. Santos Beach may have more serious problems than the high fecal coliform levels reported.

Recent concerns over the environmental impact of applying sewage sludge to agricultural land has drawn particular attention to the wide range of organic chemical contaminants that can enter sewage treatment process and persist in biosolids for disposal (8). Organic chemical contaminants can be transformed or lost through a variety of processes during wastewater treatment and end up in sludge samples. Since sewage sludge samples yield complex mixtures of organic compounds, it is essential that the various organic fractions be segregated prior to analysis, through specific sample cleanup procedures. Cleanup procedures not performed on samples will result in inferences and erroneous results. Figures 4 and 5 indicate the high levels of organic chemical contaminants in sewage sludge.

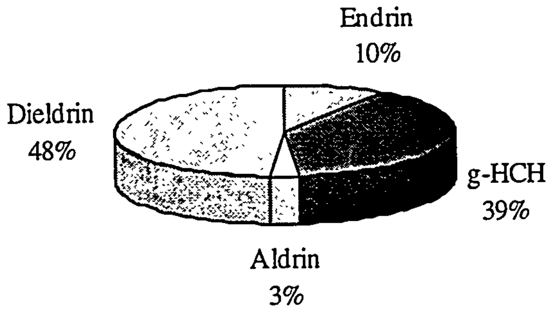

Fig. 4 Mean Percentage Concentration of PCBs and Organochlorine Pesticides in U.K. Sewage Sludges (Modified from Ref. 8)

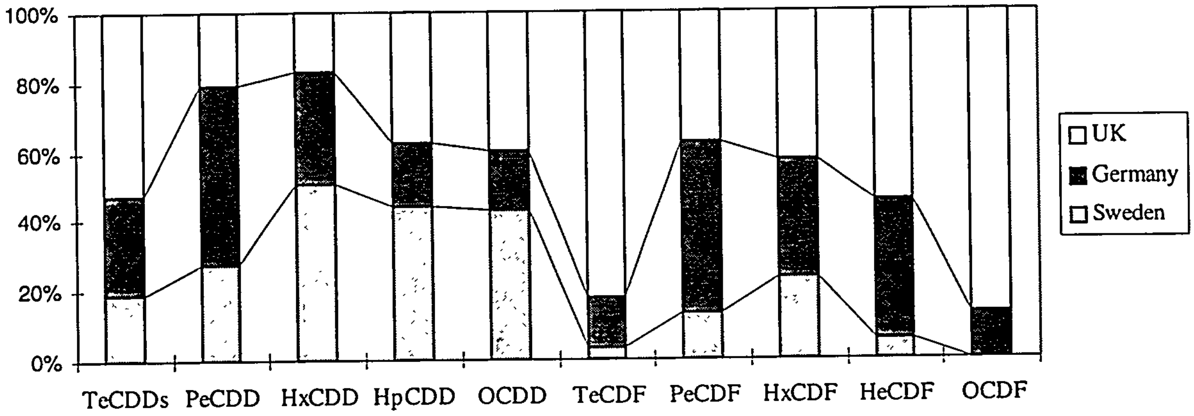

Fig. 5 Percent Concentrations of PCDDs (Dioxins) and PCDF (Furans) in Sewage Sludges from Various Countries (Modified from Ref. 8)

Other contaminants found in sludge samples include herbicides and phenolic compounds and specific pharmaceutical chemicals.

The cooperative community cleanup efforts at Santos Beach are highly commendable but address only the short-term objectives. The long-term residual effects of industrial wastes and sewage on environmental receptors have to be understood and resolved, e.g., by establishing a program to monitor the contaminated sediments.

2.3 Example 3: Air Pollution and Acid Rain Concerns in Korea

From 1970 to 1990, the period of Korea's economic boom, little attention was given to the damaging effects of rapid industrialization on the environment (8). It was not until the 1980s that Korea recognized environmental issues. They discovered that the problems had arisen so quickly that the Korean government was unable to manage them. Industrial emissions contributed heavily to the acid precipitation problems in South Korea.

The Ulsan region (southeastern Korea) is known for its heavy industrialization and attracts major Korean companies. Approximately 200 industries operate in the Ulsan and Onsan industrial region. The main issue of concern for South Korea and Japan is China's rapid economic growth; i.e., their environmental pollution is crossing the boundaries into these two countries. China is the largest emitter of air pollution in the region, particularly SO_2 (8). Further, weather conditions in China influence the effects of acid rain on Japan and South Korea. Studies have shown that plants that grow in heavily polluted areas have appeared in Seoul and nearby cities, indicating the residual effects of the acid rain problem. Also, acid rain in the Pacific region is affecting cultural artifacts (i.e., historical buildings and temples), destroying vegetation, polluting water bodies, and affecting wildlife (17). Figure 6 displays the region of concern.

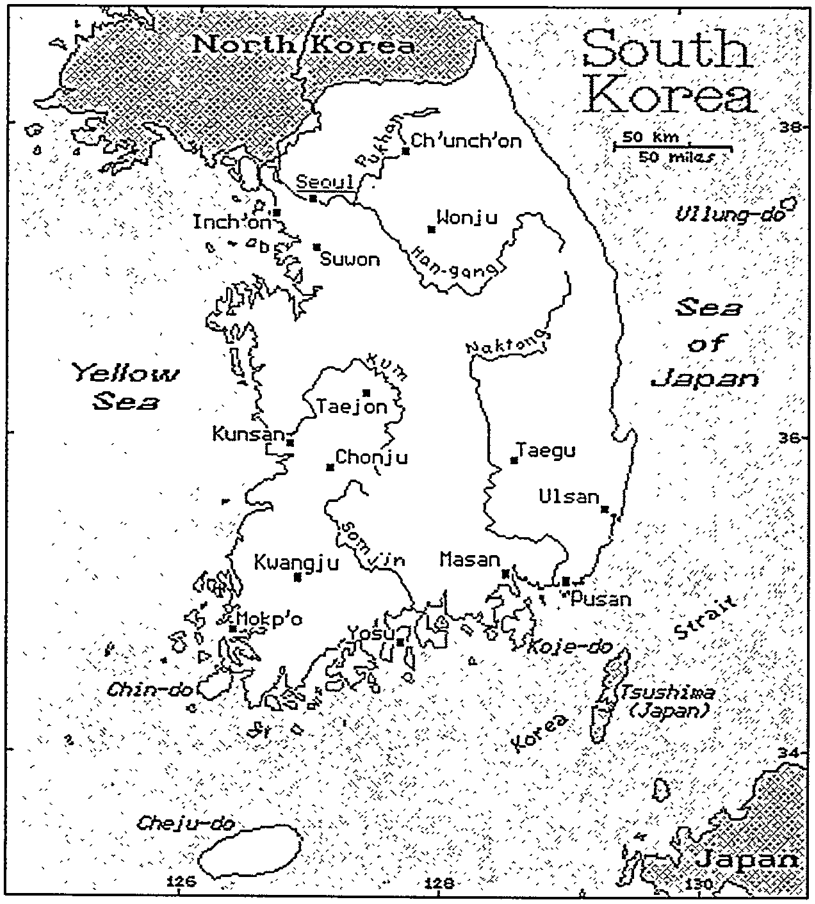

Fig. 6 Air Pollution Concerns in South Korea and the Sea of Japan (Source: Modified from Microsoft Encarta 96)

Without air pollution control measures, lakes and streams, groundwater, soils, and forests continue to acidify, which causes economic and aesthetic damage. Air pollution problems resulting from the rapid industrialization in China is believed to be the cause for acid rain in East Asia; three of the world's most polluted cities are Beijing, Seoul, and Shanghai (16). Prevailing winds from China during November and April have transported contaminants as far as Japan.

Based on these findings, South Korea imposed regulations to implement controls to reduce 26 kinds of gases and particulate matter. As a result, South Korea witnessed a drastic reduction in SO_2 emission through the consumption of low sulfur fuels for industries. However, standards set by the Korean government still exceed those of advanced countries, especially in the winter when mass consumption of fossil fuels occurs. Furthermore, a common and aggravating problem in Seoul is auto emissions and exhaust fumes from motorcycles. It was estimated that at the end of 1993, the number of automobiles on the roads was 6.27 million, up from just 40,000 in 1965. In 1993, motor vehicles emitted 1.84 million tons of all pollution (16). Further, 60% of air pollutants in Seoul come from exhaust emissions, even though more stringent emission standards are in place and fuel quality has improved. The Korean market for air pollution control equipment, which totaled $557 million in 1992, climbed to US$ 910 million in 1993. This market is expected reach $1.4 billion by the end of 1997 (12).

Accelerated development of the substantial fossil fuel systems, propelled by high economic and population growth rates, has increased atmospheric emissions of acidifying compounds and greenhouse gases. The total projected SO_2 emissions for the Asian countries in year 2010 (76 million tons) exceeds the projected emissions of North America and Eastern and Western Europe combined. This problem will increase demands for monitoring activities, which will lead to enhanced laboratory measurement efforts.

3 WASTE SITE CHARACTERIZATION AND REMEDIATION: LESSONS LEARNED IN THE UNITED STATES

In the United States, site characterization is a common procedure required to assess and quantify hazardous and toxic contaminants in air, water, and soil at a disposal site. Generally, characterization efforts involve several steps and procedures that demand extensive manpower and financial resources. In the past, cost escalation was the most common element in such characterization efforts. This was mainly due to the cumbersome procedures required under the regulatory framework. From 1980 to 1993, characterization and remediation efforts in the United States have been affected by extensive regulations and complex procedures that require assessing various environmental media and satisfying cleanup requirements imposed by federal, state, and local agencies. Cleanup action goals and objectives require lengthy negotiations among government authorities, public, and the responsible private parties. Negotiations involved concurring on standards and applicable, relevant, and appropriate requirements (ARARs) for planning site characterization and remediation strategies.

Once these standards were established, it was essential to meet the set requirements through remediation and cleanup efforts. Over time, most federal agencies and state and local governments have recognized that remediation and cleanup efforts did not meet the set criteria and were no longer cost-effective. Also, progress on cleanup was delayed due to regulatory constraints and approvals required by various government agencies, stakeholders, and communities. These requirements, along with other conditional barriers within the regulations and historical conditions, resulted in contractual delays.

Today, after harsh lessons learned and extensive efforts by the states and federal agencies, the United States has taken the "Brownfields" redevelopment approach for remediating abandoned waste sites. A Brownfields site is a site or a portion thereof that has actual or perceived contamination but has potential for restoration. To the owner of a contaminated industrial site, cleanup is often necessary to sell the property and return it to productive use. To the public, cleanup of contaminated industrial sites is crucial to reducing economic, environmental, and health problems. The government and the public are overcoming many disincentives and barriers inherent in existing federal and state policies through state voluntary investigation and cleanup (VIC) programs that encourage the cleanup of contaminated industrial sites by eliminating many procedural and economic stumbling blocks. The programs provide a number of incentives for companies to volunteer to clean up sites that would otherwise remain contaminated and unused. VIC programs offer advantages to participants, including technical assistance, flexibility in cleanup standards, and liability assurances. These Brownfields have set an example on how regulatory policies, engineering principles, and local stakeholders can work together by integrating strong scientific knowledge with proper analytical methods.

4 SURVEILLANCE NEEDS OF THE BROWNFIELDS CONCEPT

The Brownfields concept and the VIC program embody the need for ongoing surveillance and monitoring of remediation sites. Useful approaches are based on environmental monitoring principles. Some of these efforts involve laboratory measurements concerned with environmental and biological receptors. In meeting the statuary guidelines and promulgations under the USEPA, two kinds of measurements are needed. One is for continuous emission monitoring (i.e., real-time monitoring) for gases, particulates, air, or groundwater at a remediated site. The other is long-term monitoring (LTM), which also requires development of newer methodologies, and efforts to reform existing methods and conduct research for newer methods capable of quantification to meet baseline requirements. Generally, methods development requires extensive analytical skills and laboratory work, and specific tools for methods development and validation. In this context, certified reference materials (CRMs) are indispensable tools — useful to validate data quality, provide a framework for meeting legal metrology requirements, and mitigate liability aspects. Thus, linking the CRM usage with monitoring activities of Brownfields is beneficial in the long term.

5 METHODS DEVELOPMENT FOR FUTURE USE

As new chemicals enter the environment, it is imperative to develop new and effective analytical methods. The analyst is challenged to develop methods to address ultratrace concentrations of highly toxic compounds, such as dioxins. For chemical contaminants, such as pesticides, PAHs, halogenated hydrocarbons, and heavy metals, there is still room for methods development. Any methods development effort requires a tool to test and validate the analytical procedure. Thus, as the analytical challenge intensifies, more pressure to develop appropriate CRMs occurs.

CRMs are available for both organic and inorganic analytical needs. The usefulness of CRMs in supporting analytical quality control requirements are recognized (19). As more complex problems arise, matrix-specific CRMs will be needed. These may be in the form of liquids and solids that cater to various industrial cleanup action requirements. One of the critical elements for resolving environmental disputes is data quality and validation procedures that support data collection efforts. Many developing countries face numerous limitations in their efforts to introduce adequate analytical quality control measures. Based on the pressing requirements for environmental actions, it is most effective to build on matrix-specific secondary reference materials, as the preparation and certification of CRMs is expensive and time-consuming. Good quality secondary reference materials (RMs) can fulfill the normal requirements of quality assurance (QA) of an analytical scheme; frequent use of such QA materials should be encouraged. Further, RMs can be developed to suit site-specific scenarios and conditions that meet national and regional guidelines. Recognizing the analytical quality control problems in developing countries, it is tempting to suggest RM-related technical activities at the regional level (19). Illustrations demonstrating the usefulness of CRMs for field problems are presented in the following sections.

5.1 CRMs for Inorganic Analysis

5.1.1 Lead in Our Living Environment

The insidious human health risks of lead are well documented. Sufficient evidence links health exposures to lead (as low as <100 μg/L blood-Pb) that produces adverse results in the vulnerable segment of the population (i.e., the fetus *in utero*, infants, children, and the elderly). Enough evidence exists that relates the adsorption of lead in the children as being higher than adults (20). Since lead poisoning is a global concern, the need exists to develop CRMs for lead (paint, dust, soil, and drinking water). Analysis for lead compounds in ambient air samples, water, soil, and sediments may be a local exigency based on a field assessment. A CRM for lead will be commensurate with national or local laboratory requirements for quality control from which secondary reference materials can be developed to meet site-specific conditions.

5.1.2 Impact of Industrial Emissions

In a similar context, waste residues and solids to be disposed at a hazardous waste landfill may require field sampling and analysis. If the landfill accepts a significant volume of power plant wastes, such as fly ash, it is essential that the facility be sampled for selenium (Se). Mineral oil contains about 0.2 μg/g of Se and coal contains up to μg/g of Se (21). Coal ash, which contains up to several hundred micrograms per gram of Se, is transported over long distances, distributed widely in soils, and adsorbed into plants depending on soil characteristics (degree of alkalinity). Soil and environmental factors in China have been reported as the reason for Se toxicity in neighboring countries and in Se-deficient areas of northeastern China, with an end result of 50% mortality rate in some villages. The source of this Se is the pebbly coal, with a Se concentration of 300 μg/g. Selenium uptake was high in plants due to the traditional use of lime as a fertilizer. To understand the chemistry of emitted particulates, CRMs such as coal fly ash have been developed. These are exhibited in Table 1.

5.2 CRMs for Organic Analysis

5.2.1 CRMs for Landfill Sites

Figure 7 displays CRMs and RMs that are applicable for long-term landfill site characterization; RMs may be developed that meet specific local requirements.

Selected CRMs for organic analysis are available through a variety of sources identified in Table 1. CRMs selected from these sources are used as a baseline to meet local analytical requirements. These include sediments, soils, air, marine sediments, and fauna. Selective CRMs pertaining to the case examples discussed above have been provided.

5.2.2 Organics in Whale Blubber

This RM is a frozen whale blubber homogenate intended for use in evaluating analytical methods for the determination of selected congeners and chlorinated pesticides. Whale blubber was collected from an adult female pilot whale that became stranded in Cape Cod, USA, in 1991. The blubber tissue was frozen, cryogenically pulverized, homogenized, bottled, and stored at -80°C. This CRM is labeled as SRM 1945 and is available through the NIST.

Table 1 Certified Reference Materials and Standard Reference Materials for Environmental Analysis (Modified from Ref. 18 and 19)

Certified Reference Material	Description	Origin	Case Example
CRM - 429	Polychlorodibenzo-p-dioxins and polychlorodibenzo furans in fly ash extract	Community Bureau of Reference (BCR) Reference Materials, Brussels, Belgium	1, 3
SRM - 1633b	Trace elements in fly ash	National Institute of Standards and Technology (1993) SRM 1633 (b), Gaithersburg, MD, USA	1, 3
NIES 8	Vehicle exhaust particulates	National Institute for Environmental Studies Ibaraki, 305, Japan (1987)	3
SRM - 1650	Diesel particulate matter	National Institute of Standards and Technology (1991), Gaithersburg, MD, USA	3
CS-1, HS-1 and HS-2	PCBs in marine sediments	National Research Council (Canada)	2, 1
DX-1, DX-2	Dioxins and furans in sediment	National Water Research Institute (Canada)	2, 1
IAEA - 356	Trace elements in polluted marine sediments	International Atomic Energy Agency (Austria)	2, 1
CRM - 088	Polychlorinated aromatic hydrocarbons in sewage sludge	Community Bureau of Reference, Brussels, (Belgium)	2, 1
CRM - 392	PCBs in sewage sludge	Community Bureau of Reference (BCR), Brussels, Belgium	2
CRM - 398 and CRM - 399	Major elements in fresh water	Community Bureau of Reference, Brussels, (Belgium)	1
CRM 145R - 146	Sewage sludges	Community Bureau of Reference, Brussels, (Belgium)	2
SRM - 1581	PCBs in oil	National Institute of Standards and Technology (1991), Gaithersburg, MD, USA	1, 2

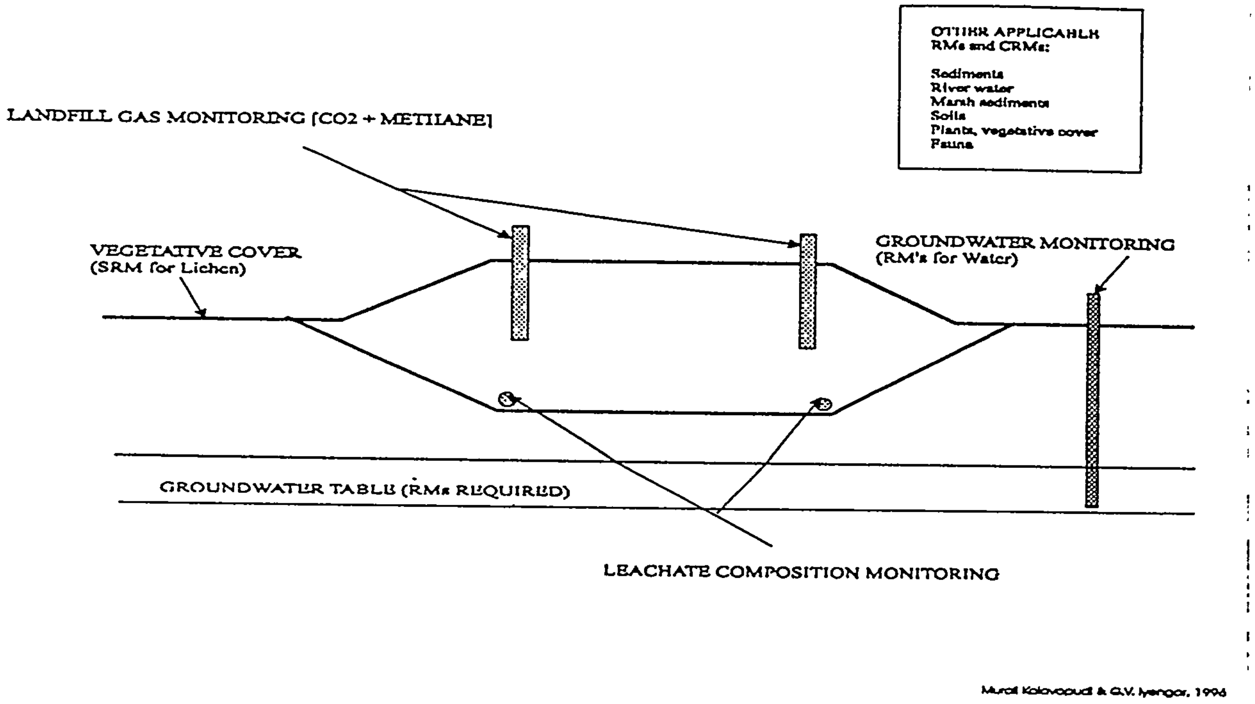

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Fig. 7 CRMs and RMs Applicable for Landfills

5.2.3 Chlorobiphenyls in Industrial Soils

This CRM contains eight constituents and can be obtained from the Community Bureau of Reference (BCR) Reference Materials, Commission of the European Communities, Directorate General for Science, Research and Development, Brussels, Belgium.

6 CONCLUSIONS

Environmental problems have taken a new perspective. Global changes and emerging economies, particularly in Asia, Latin America, and Europe, have not embraced environmental issues as a part of their strategic growth and development. As a result, environmental concerns are growing rapidly and have become a barrier to the quality of living and industrial standards. Health of workers and communities is being threatened constantly by industrial pollution and hazardous chemicals. To effectively combat environmental problems, developing nations should tap into the experiences and technical resources of developed countries through effective partnerships. On a technical level, environmental problems can be solved by following effective strategies that require:

- Initial investments on environmental issues to avoid the long-term problems and associated health effects.

- Strategies to integrate industrial and governmental efforts to promote timely awareness on environmental issues.

- Proper and effective analytical procedures to characterize and remediate waste sites.

- Use of CRMs to address these problems effectively, to validate data quality, and to meet the demands of legal metrology.

- Efforts that promote the development of good quality secondary and in-house RMs to enhance analytical quality.

- An effective regulatory framework to meet local environmental problems and provide specific guidelines for academia, industry, and the community in expediting solutions to environmental problems. Although regulatory models from developed countries are essential, these should not be duplicated but used to build site-specific models through expert guidance.

- Conscientious efforts to educate communities and children on environmental impacts through proper training and awareness workshops.

- Strategic approaches (workshops, seminars, and training courses) to enhance overall industrial quality and environmental awareness. These courses should address specific topics that aid in mitigating environmental problems through the support of stakeholders and the government.

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TURNING A HAZARDOUS WASTE LAGOON INTO RECLAIMED LAND FOR WILDLIFE MANAGEMENT: A CASE STUDY

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ABSTRACT

Brownfields are turning back to green. This paper presents a case study of a former dump site for hazardous waste that has been remediated and will be developed into an enhanced wildlife management habitat. This successful remediation case combined various investigations, remedial designs, risk assessments, ecological studies, and engineering practices.

1 BACKGROUND

The subject site covers a 27-acre area in southeastern Texas in the United States. The site was initially excavated as a soil borrow pit in the early 1910s. Following exhaustion of borrow material, the pits were left open. These open pits were used by a small waste company in the 1940s as chemical waste storage and processing lagoons for liquid hazardous waste. Due to the lack of environmental protection awareness and regulatory requirements at that time, these lagoons were used for liquid waste processing, without any protection, such as lining at the lagoon bottom, leakage control, and air emissions control.

In the early 1970s, a major solid waste management company acquired this site for its expansion into the hazardous waste management market. Soon after the acquisition, the U.S. Environmental Protection Agency promulgated new environmental regulations that required pollution prevention installations, documentation, reporting, and proper waste management procedures. Due to the lack of funding, the site operation was terminated, and no further environmental improvements were implemented.

In 1976, a major flood occurred in the area following a series of heavy rainstorms. The entire site was inundated, and a portion of the liquid hazardous waste was transported off-site with the floodwater. This occurrence caused damage and environmentally impacted the downstream areas. As a consequence of state regulatory agency enforcement and petition by the local residents, a series of environmental site characterizations and remedial investigation activities were initiated.

2 INNOVATIVE SITE INVESTIGATION

Woodward-Clyde International performed a remedial investigation and site characterization program at the site. The investigation program involved collecting stratigraphic and aquifer hydraulic data to identify contaminant migration pathways and the potential of vertical contaminant movement. The groundwater quality investigation involved collection and analysis of samples to delineate the areal and vertical extent of contaminated soil and groundwater.

The technical approach used cone penetrometer testing (CPT) equipment. CPT is a rapid, cost-effective way to assess subsurface conditions. It includes select devices that perform different data collection functions when advanced through soil. In this project, the following CPT devices were used to accomplish the remedial investigation objectives:

- Electric cone - to characterize the site stratigraphy based on the CPT tip resistance and sleeve friction.
- PT push-in soil sampler - to collect discrete soil samples from select target depths.
- PT push-in well screen - to collect groundwater samples without installing monitor wells.
- Push-in piezometers - to install temporary piezometers to monitor groundwater levels.

On the basis of preliminary soil and groundwater quality data, certain permanent groundwater monitor wells were installed at strategic locations for monitoring groundwater quality data trends. Aquifer pump tests were conducted to characterize the subsurface hydraulic conditions.

3 RISK-BASED CORRECTIVE ACTION

The newly promulgated risk-based corrective action (RBCA) approach was used to establish the site remedial goals. Risk assessment was conducted with the following primary objectives:

- Identify potential receptor(s) of concern;
- Establish site remedial goals; and
- Ensure the remedial goals protect the human health and environment.

A fate and transport modeling simulated the potential impacts of the identified chemical of concern (COC) to the nearest identified receptor. In this case, a water well located cross-gradient from the contamination source was identified as the nearest potential receptor based on the water well inventory survey conducted in the area.

The risk assessment evaluated several potential exposure scenarios. In each case, the analysis was conducted using a worst-case assumption that the entire mass of COC in the shallow sand instantaneously migrated toward the target receptor. In summary, the risk-based approach established the remedial goals and identified the allowable cleanup level that protects human health and the environment.

These preliminary remedial goals were then presented to the appropriate review experts and regulators within the governing agencies. Subsequent to regulatory approval, the project proceeded to the remedial design phase.

4 REMEDIAL ALTERNATIVES

Two media require remediation: soil and impacted groundwater. Prior to the conceptual design phase, Woodward-Clyde conducted a remedial alternative screening to evaluate the feasibility of various remedial technologies specific to this site. A summary of the remedial alternatives evaluated is presented in Table 1.

Table 1 Summary of Remedial Alternative Screening

Containment	Recovery	In Situ
Slurry wall	Total fluid recovery	Adsorption-absorption
Jet grouting	Vacuum-enhanced pumping	Air sparging
In situ soil mixing	Jet pump	Bioremediation
Cutoff wall	Solvent extraction	Chemical treatment
	Dual-phase extraction	Thermal enhanced recovery

5 SITE REMEDIATION

The final selected remedial system combines remedial technologies to offer effective cleanup to achieve cleanup goals. Figure 1 shows the conceptual plan of the remedial system. The impacted groundwater was pumped to the surface, processed through an aboveground treatment unit, discharged to a bioreactor unit for enrichment of the groundwater with nutrients and an oxygen

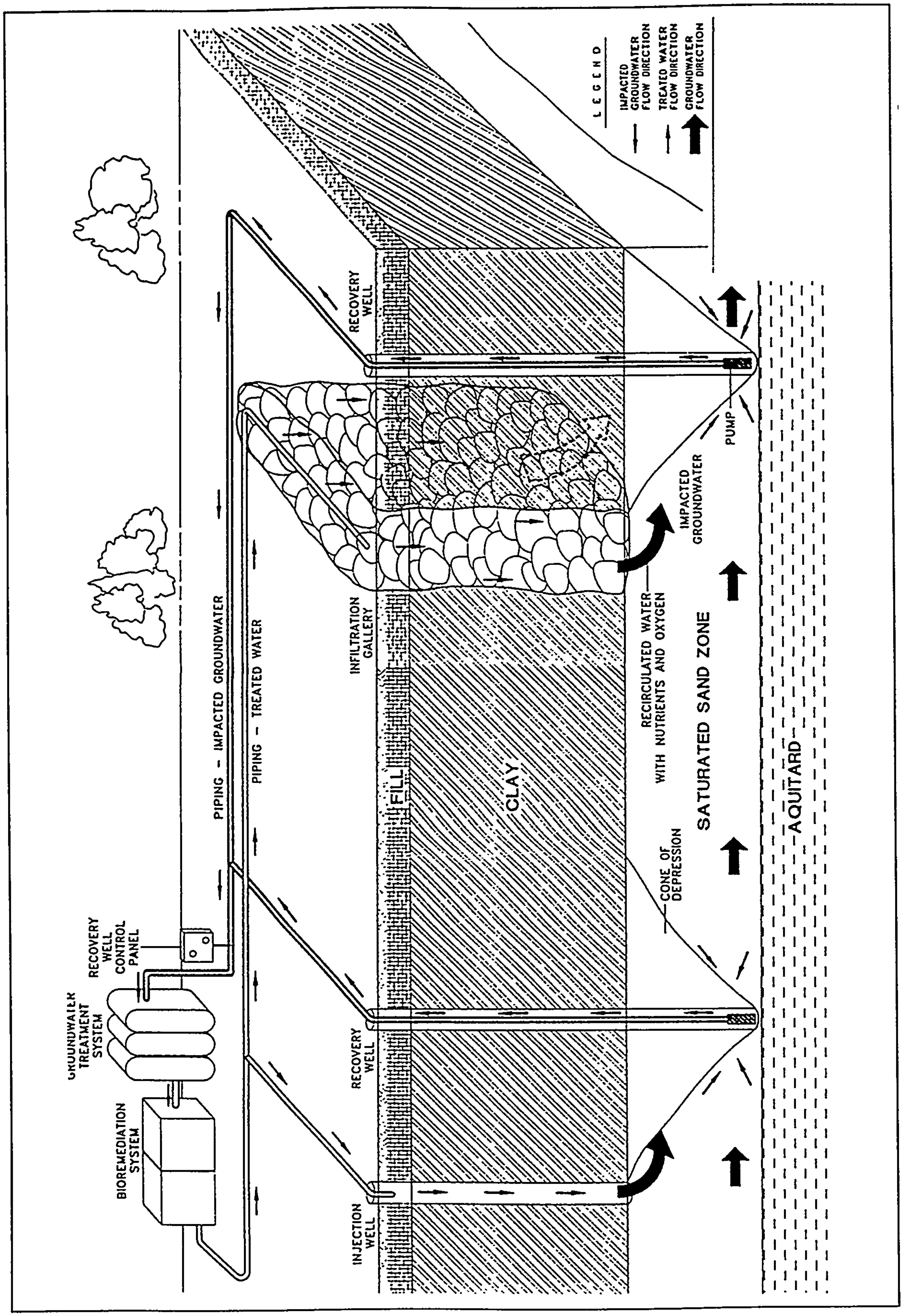

Fig. 1 Conceptual Remedial System Design

source. The stimulated groundwater will then be recirculated to the aquifer for enhancement of in situ biological degradation.

The residual pond bottom liquid was evacuated by vacuum trucks and disposed of to permitted deep injection wells. Contaminated soil and pond bottom sludge were then stabilized, solidified, and eventually landfilled into a properly constructed landfill cell within the site compound.

The ponds were later backfilled to a design grade to ensure proper stormwater drainage. A portion of the site was designed so that it will eventually form a surface pond, with artificial habitat enhancement to attract migratory fowl and ducks commonly found in the area. Vegetation will be planted in other parts of the site so the natural green will blend well with the surrounding environment.

6 CONCLUSION

Many of the contaminated site remediation projects encountered a common question: How clean is clean? Millions of dollars are commonly spent to clean up a contaminated site. With the newly promulgated RBCA, which is gaining significant popularity among industries, effective and reasonable remedial goals can be established. This will also allow the landowner or potential responsible parties to have the flexibility to consider further efforts beyond just the cleanup; that is, turn the once brownfields back into green land.

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TEN-YEAR CLEANUP OF U.S. DEPARTMENT OF ENERGY WEAPON SITES:
The Changing Roles for Technology Development in an Era of Privatization

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1 BACKGROUND

In its beginning, the U.S. Department of Energy (DOE) Office of Environmental Management (EM) viewed private industry as lacking adequate technology know-how to meet demands of hazardous and radioactive waste problems at the DOE's laboratories and nuclear weapons production facilities. In November 1989, EM's Office of Technology Development (recently renamed the Office of Science and Technology) embarked on a bold program of developing and demonstrating "innovative" waste cleanup technologies that would be safer, faster, more effective, and less expensive than the "baseline" commercial methods. This program has engaged DOE sites, national laboratories, and universities to produce *preferred* solutions to the problems of handling and treating DOE wastes. More recently, much of this work has shifted to joint efforts with private industry partners to accelerate the use of newly developed technologies and to enhance existing commercial methods.

To date, the total funding allocation to the Office of Science and Technology program has been about $2.8 billion. If the technology applications' projects of the EM Offices of Environmental Restoration and Waste Management are included, the total funding is closer to $4 billion. Yet, the environmental industry generally has not been very receptive to EM's innovative technology offerings. And, essentially the same can be said for DOE sites. According to the U.S. General Accounting Office in an August 1994 report, "Although DOE has spent a substantial amount to develop waste cleanup technologies, little new technology finds its way into the agency's cleanup actions."

Against this background, the 1996 DOE Baseline Environmental Management Report (BEMR) estimated cleanups of DOE's Cold War legacy of wastes to require the considerable cost of $226 billion over a period of 75 years. The projected cost and time, together with EM's overall lack of progress in cleanup, have caused an impatience in the Congress that has sparked a spirited resolve within EM for affordable near-term results.

2 DOE POLICY SHIFT: THE TEN-YEAR PLAN

2.1 Privatization

In 1993, President Clinton instituted reforms that emphasized competition and "pay-for-performance" in the way the government does its contracting business. In 1994, DOE Secretary Hazel R. O'Leary introduced two major paradigm shifts, *competitive privatization and contract reform,* new ways of doing business meant to become firmly rooted in the Department.

Privatization is regarded as a cost-effective business strategy for accelerating cleanup. The intent is to transfer some portion of the risk and liability to the vendor, who is to deliver an acceptable product or service for a fixed price.

It is anticipated that privatization through competition will save government resources. In his remarks at the Weapons Complex Monitor Decision Makers' Forum on September 27, 1996, Under Secretary of Energy Thomas P. Grumbly emphasized the reason EM must privatize. He said, *"Fundamentally, we have no choice, given the Nation's budgetary constraints."* This has signaled a departure from EM's traditional management and operations (M&O) site contractors who have been responsible for executing cleanup in the past.

Early in 1996, Assistant Secretary Alvin L. Alm, the new head of EM, announced his vision of an ambitious Ten-Year Plan for the Weapons Complex, an initiative to complete cleanup within a decade at most nuclear sites for an estimated savings of $85 billion compared with the BEMR costs! Each site has been required to prepare its own Ten-Year (Site) Plan, describing how it proposes to eliminate most urgent risks, reduce mortgage and support costs, protect workers' health and safety, reduce generation of waste, create a collaborative relationship between DOE and its regulators and stakeholders, focus technology development on cost and risk reduction, and integrate waste treatment and disposal across sites.

Through the Ten-Year Plan, EM has embraced the new DOE reform of performance-based contracting with industry. M&O contractors, who have been paid *reasonable* costs regardless of performance, are being replaced with management and integrating (M&I) contractors, who are paid only on the basis of their performance, largely administered through competitively selected privatized projects.

2.2 Performance-Based Contracting

Performance-based contracting is the centerpiece of the privatization initiative in EM's Ten-Year Plan. The objective of the approach is to identify and develop contracting methods and practices that integrate the ingenuity of industry and the marketplace into governmental procurement and operations. Performance-based contracting ensures that strategic goals and objectives are translated into specific results that can be quantified and measured.

The principal parts of a performance-based contract are (1) a results-oriented Statement of Work (SOW), (2) performance criteria and measures, and (3) performance-based incentives. All aspects of an acquisition are built around the purpose of the work to be performed, including SOW development, contractor selection, contract type (e.g., fixed price), incentives, and contract administration. Again, these contracts emphasize measurable performance requirements as prerequisites for compensation.

3 PRIVATIZATION AND TECHNOLOGY

Performance-based contracting is attractive in the current environment of limited resources because it facilitates increased competition for DOE work, leading to reduced costs. It also radically changes the role of EM with regard to technology. The M&I contractor prescribes the "what," the end results a vendor must achieve, but the vendor is responsible for the "how to" aspect of performance, i.e., the choice of technology or commercial process to be used. *Privatization, through performance-based contracting, would discard EM's traditional practice of stipulating preferred technologies!*

Actually, the practice of prescribing technologies ignored the realities of commercialization and the time-honored manner by which the marketplace delivers products and services to the customer. In the marketplace, emphasis is placed typically on "process," not the technology. Implementation is the course through which a technology is refined until it meets (or fails to meet) the demands of a "commercial process" capable of providing a product or service within the competitive parameters of the marketplace. Therefore, technology implementation is a private-sector function wherein a company with a technology investment develops a process. Even more typical, a company develops *process arts*, its own proprietary approaches for producing and delivering products and services to its customers, hopefully better than that of the competition. The process art of a company, not the technology, attracts a customer to buy, e.g., a particular choice of bread, automobile, or pharmaceutical remedy. A current Breyer's ice cream television commercial says it simply: "It's the taste, not the technology!" It is reasonable to assume the DOE site cleanup marketplace is essentially no different.

For many decades, small businesses, and domestic and global corporations in the chemical, petroleum, mining, and other related industries, have developed or improved technologies and processes for their own purposes. Although the private sector largely has been outside the DOE cleanup activity, it has been adapting its experience and cultivating its expertise in cleanup programs of the U.S. Environmental Protection Agency (USEPA) and the U.S. Department of Defense.

The matrix in Table 1 shows that most EM cleanup categories can be commercially treated by vendor-provided processes that are currently "good enough" to satisfy required cleanup standards. If privatization initiatives are significantly incorporated into the Ten-Year (Site) Plans, it is reasonable to expect the power of private entrepreneurship will be a valuable agent in achieving the overall goals of the EM program.

3.1 Facilitating Privatization

Predating the Ten-Year Plan initiative, EM's Office of Environmental Restoration had been conducting innovative programs to foster the use of commercial technologies and processes and facilitate privatization. These programs are known as TechCon, Innovative Treatment Remediation

TABLE 1 Snapshot Matrix of Technology Resources for the Ten-Year Plan (as of Sept. 1996)

Cleanup Category	Vendor Provides[a]	Vendor & Some Tech Dev Need[b]	Tech Develop Needed[c]	Comments
Low-Level Mixed Waste Treatment and Disposal				Disposal options exist. Also some disposal deficiencies
High-Level Tank Waste Retrieval & Remediation	Remediation		Retrieval	Hanford tanks privatized
Soil Remediation				Numerous projects completed
Groundwater Treatment				Some cost savings needed
Plume Containment and Remediation				Not unique to DOE
DNAPL Remediation				Not unique to DOE
Landfill Containment and Remediation				Hanford landfill privatized

[a] Industry resources satisfy requirements for *most* waste handling in category.

[b] Industry resources satisfy requirements for *some* waste handling in category. Some tech dev needed.

[c] Industry resources *limited.* Technology development needed.

Demonstration (ITRD), Technology Information Exchange (TIE), Video Interactive Teleconferencing (VIT), and the Environmental Cleanup Privatization Products and Services Directory (Directory).

TechCon serves as an advocate for privatization and searches worldwide for companies with documented performance records that can be applied to specific DOE cleanup demands. TechCon brings field managers face to face with worldwide representatives of environmental companies, and assists sites in identifying commercially viable options. This is done through site "opportunity" meetings organized by TechCon, together with site managers and engineers, regulators, industry experts, and stakeholders. At these meetings, strategies are developed with the objective of privatization.

When it is necessary to validate a particular commercial alternative of interest, the ITRD program funding may be available to conduct site-specific treatability and pilot tests to determine cost and performance parameters. These tests can assist site managers in learning about a prospective vendor's capability for solving a unique problem. They can help a vendor obtain cost/pricing data important to bid preparation, and they can reassure regulators regarding remediation standards.

The TIE workshop has been a unique annual event. Since 1991, dedicated to "*Using Today's Technologies Better,*" the TIE workshop has been an effective forum for the use of existing technologies, sharing knowledge and information between site personnel who actually work with contaminant problems, industry representatives, and others interested in EM cleanup activities. The *TIE Quarterly* is a publication that continues the TIE process between workshops with information laden articles of timely interest and site-specific emphasis.

The VIT program provided satellite hookups with major DOE sites, which allowed viewers across the Complex to participate in cleanup and demonstration actions at a work site, even while operations were in progress. Viewers could observe details with resolutions within a few inches and were able to interrogate the vendor experts and the site principals in real time. VIT was used effectively at USEPA's King of Prussia Superfund Site and at DOE work sites in Los Angeles, Ohio, and New Mexico.

The Directory serves as a "Yellow Pages" vendor guide to assist site customers in identifying private-sector resources to serve their environmental cleanup needs. It affords users easy access to information on the products and/or services of more than 500 environmental cleanup companies, both domestic and foreign, including contacts for each company.

4 CONCLUSIONS

The $6 billion/year DOE environmental management program is now at its "moment of truth," and its destiny will be determined by the outcomes of the Ten-Year Plan. A key to success will be EM's ability to validate costs, achieve economies, and accomplish its challenges or "stretch" goals.

Privatization, contract reform, and the Ten-Year Plan raise several issues that either augur or evidence a changing EM role with regard to technology development. For example, it is reasonable to assume that the outcome of the Ten-Year Plan will be determined in the first five years, the critical period. This would seem to dictate vigorous privatization activity throughout the Weapons Complex, making use of the ready resources, ingenuity, and cost-effectiveness of the private sector to jump-start cleanup operations on a broad scale.

Under privatization, EM's site managers become the customer, a role substantively different from that of the old M&O structure. They are responsible for defining incentives and results-oriented performance measures and for preparing performance specifications, for example, to avoid contractual pitfalls that could lead to undue liabilities and risks for DOE. Ultimately, vendor accountability must be assured.

Many site personnel who are to perform these functions will require assistance in the form of expert technical guidance and support. Fortunately, that expertise readily exists. Such technical support represents a potential new role ideally suited for the national laboratories, which have amassed a wealth of technical and site data knowledge through EM's Science and Technology program.

On the subject of innovative technologies, those currently in the EM inventory that are not already field tested will require three to five years for market readiness, after industry acceptance. Therefore, these technologies likely will not be commercially available to EM, at least during the critical phase of the Ten-Year Plan. Moreover, both the EM/Office of Energy Research newly funded fundamental science program and EM's technology development activities that are focused on the long term are beyond the scope of the Plan.

On the other hand, EM has reportedly developed 170 new or improved cleanup technologies that will reduce risks and costs. The Plan can benefit from the increasing share of EM technology development funding now being focused on industry partnerships to accelerate the availability of EM-developed technologies currently in the commercial implementation pipeline.

Table 1 showed that most EM cleanup needs can be met by industry processes that are good enough, particularly when coupled with compatible land-use scenarios.

In fact, the private sector has been developing a greater than generally recognized cleanup expertise and capability. The TechCon program has identified approximately 2,000 commercially available waste cleanup technologies and processes. Even so, TechCon estimates this number to be only 25% of the worldwide total, ranging from developmental demonstrations to large-scale cleanup operations.

The capabilities and potential that privatization can bring to the EM program are being noted as well by DOE senior management. Again, from the recent remarks by Under Secretary Grumbly, "Privatization will also bring innovation, new and improved technologies, methods, and accountability to bear in treating environmental management wastes."

Grumbly continued, "The privatization process provides Environmental Management with a better, more compelling justification for funds in the budget process. Furthermore, privatization efforts will result in new jobs and increased economic activity where they are undertaken."

Finally, as noted earlier, performance-based contracting unalterably places the primary responsibility for technology selection on the private-sector vendor. This is necessary for the vendor to assume risk and to commit to a guaranteed performance for a fixed price.

In summary, the issues cited above collectively indicate a new role for technology development, one that would establish the private sector as the primary resource for innovative and improved cleanup technologies. The extent to which the environmental industry is willing to invest in such a role, however, will depend on how aggressively the DOE sites convert to the privatization way of doing business.

DECONTAMINATION OF SPILLS AND RESIDUES OF SOME PESTICIDES AND OF PROTECTIVE CLOTHING WORN DURING THE HANDLING OF THE PESTICIDES

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ABSTRACT

Users of pesticides may have waste or surplus quantities or spills for disposal. One alternative is to deactivate the pesticide at the handling site by using a straightforward chemical reaction. This option can be practical for those who use relatively small quantities of a large variety of pesticides, for example, greenhouse workers, small farmers, and agricultural researchers. This paper describes practical on-site methods for the disposal of spills or small waste quantities of five commonly used pesticides, Diazinon, Chlorpyrifos, Iprodione, 2,4-D, and Captan. These have been tested in the laboratory for the rate of disappearance of the pesticide, the degree of conversion to nontoxic products, the nature and identity of the products, the practicality of the method, and the ease of reproducibility. Methods selected were shown to be safe for the operator, reliable, and reproducible. Greater than 99% of the starting material had to be reacted under reasonable conditions and length of time. Detailed descriptions of the reactions are presented, so that they can be performed with reproducible results. Protective clothing worn during the handling and application of pesticides may become contaminated. Simple laundering does not always remove all of the pesticide residues. Thus, chronic dermal exposure may result from the pesticide-contaminated clothing. Appropriate methods of laundering using specific pre-treatments have been determined.

1 INTRODUCTION

A large variety of pesticides are used by agricultural workers and researchers. The decontamination of spills of especially concentrated solutions and of small waste quantities of the pesticides can be a difficult and expensive problem. Described here are practical, on-site disposal methods for five pesticides, Diazinon, Chlorpyrifos, Iprodione, 2,4-D, and Captan.

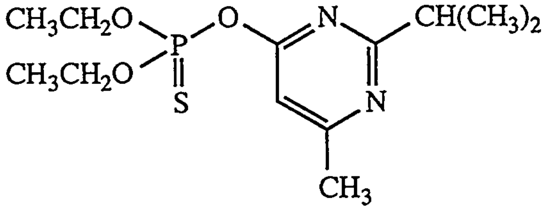
We have developed and tested in the laboratory, disposal procedures for more than 400 hazardous chemicals. About 300 of these are described in Ref. 1. In our continuing effort to provide environmentally acceptable, practical, and reproducible procedures to convert hazardous chemicals to nonhazardous products, we have studied some pesticides. Of the many ways used to dispose of waste pesticides, several are no longer acceptable, including, for example, dilution with water and washing into the sewer. For commercial pesticide applicators, greenhouse workers, and researchers who use a large variety of pesticides in their work, a practical and acceptable alternative is deactivation by a straightforward chemical reaction at the handling site. Such a procedure can also be used for decontamination of equipment and cleanup of spills, which are important to the health of all workers on the job site. The literature has a considerable amount of information about reactions that degrade certain types of pesticides; however this information often does not provide specific instructions for individual pesticides, including the quantities and concentrations of reagents, times of reaction, and conditions required to yield reproducible results; nor does it indicate the products formed from the reaction. One of the objectives of our work is to determine such information.

For each pesticide, potential reactions for their destruction are tried in the laboratory and, as far as possible, the products are identified. An appropriate reaction is then chosen. The quantities of reagents, the time, and the details of the reaction are documented in such a way that the procedure can be performed safely and with reproducible results.

Also of importance to workers is whether laundering the protective clothing worn while applying pesticides removes all of the contaminant. It has been shown that simple laundering does not always remove all of the pesticide residue. This can result in dermal exposure from the contaminated clothing. The best laundering procedures for removing pesticide residues from clothing have been investigated.

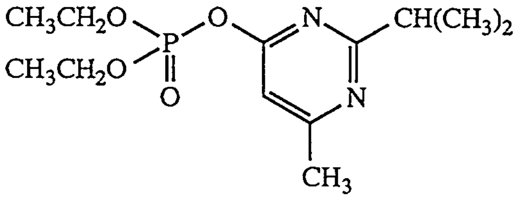
2 RESULTS AND DISCUSSION

2.1 Diazinon

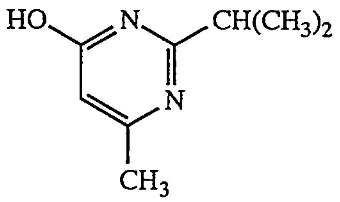


Diazinon

Diazinon is an insecticide used to control sucking and chewing insects on a wide variety of crops. The reactions of Diazinon were investigated with (1) synthetic detergent (prepared by mixing 25 mL of 95% ethanol, 25 mL of water, 2 g of sodium hydroxide pellets, 0.48 g of sodium pyrophosphate, and 1 mL of Triton X100), (2) 6% sodium hypochlorite (household bleach), (3) sulfuric acid (3*M*), and (4) acidic potassium permanganate. Reactions with the synthetic detergent and the sodium hypochlorite were performed at both room temperature and at 55°C. The synthetic detergent was not effective in decomposing Diazinon. Similarly, treatment with 3*M* sulfuric acid did not completely decompose Diazinon in a reasonable length of time. The reaction of pure Diazinon with sodium hypochlorite yielded both transient and persistent products that were identified. The formation and disappearance of products were followed by thin layer chromatography and gas chromatography, and the products were identified by gas chromatography/mass spectrometry. In the presence of sodium hypochlorite, Diazinon is immediately converted to diazoxon:

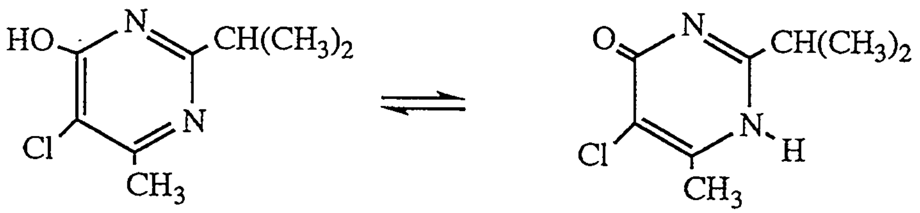


diazoxon

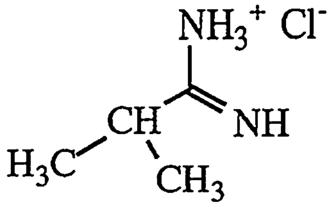


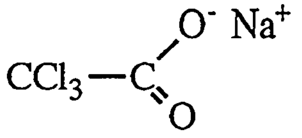
2-isopropyl-4-methyl-6-pyrimidinol

This product, which is a more potent acetylcholinesterase inhibitor than diazinon, is seen only when a sample of the solution is withdrawn and extracted immediately after the bleach is added. It is rapidly hydrolyzed to 2-isopropyl-4-methyl-6-pyrimidinol, which then gradually disappears from the reaction mixture because it is chlorinated by the hypochlorite solution to form 4-(5-chloro-2-isopropyl-6-methyl)-pyrimidone:



It has been shown that hypochlorite reacts with this material to yield the following ring-opened products:





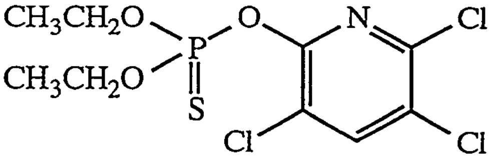
These products have low acute toxicity, especially to aquatic species. However, when the commercial formulation of Diazinon was oxidized with excess sodium hypochlorite under similar conditions, the products were found to be toxic to aquatic species. Therefore, the bleach reacts with an additive or filler in the commercial preparation to yield toxic products.[2]

Oxidation of both the pure and commercial formulation of Diazinon with acidic potassium permanganate rapidly decomposes the pesticide and does not produce toxic products from the commercial material. In this reaction, the diazoxon is not seen, and the hydrolysis product, 2-isopropyl-4-methyl-6-pyrimidinol, is not detectable after 15 minutes. More than 95% of the Diazinon is degraded in less than 1 minute and greater than 99.9% after 15 minutes, since at the end of this time, it is below the level of detection. Thus, the following procedures are recommended for the conversion of Diazinon to nonphysiologically active products.

To 200 mg of pure Diazinon, or 0.5 mL of the commercial liquid concentrate, is added 100 mL of acidic aqueous potassium permanganate solution (17 mL of concentrated sulfuric acid added to about 70 mL of water, then 4.7 g of potassium permanganate dissolved in the aqueous acid and the solution made up to 100 mL with water), and the mixture stiffed at room temperature for 1 hour. If, at the end of the reaction time, no excess permanganate remains (determined by placing a drop of the liquid on a piece of filter paper; the presence of a purple ring around the brown spot indicates permanganate is present), add 1 g of solid potassium permanganate and stir for an additional 15 minutes. Sodium metabisulfite is then added to the stirred solution until a colorless liquid is formed. The pH of the solution is adjusted to between 6 and 8 with solid sodium carbonate (soda ash, add slowly to avoid excess foaming) or 5% sodium hydroxide solution and the liquid poured into the drain.

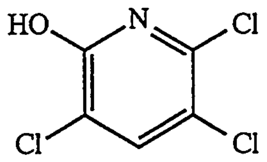
The best laundering procedure to remove residues of Diazinon has already been determined.[3] Thus, when 100% cotton fabric is contaminated with field strength (0.5% active ingredient) Diazinon, a single hot water wash (60°C) removes all but 1% of the Diazinon on the cotton fabric. When cotton is contaminated with concentrated (full-strength, 47.5%) Diazinon and washed in hot water, 4% pesticide residue remains. Further, it was found[4] that when a blend of 50% cotton/50% polyester was contaminated with field-strength Diazinon and given a single warm water wash, 4% of the pesticide remained on the fabric. Pretreating with Spray'n Wash® (a prewash commercial soil and stain remover containing a blend of surfactants and solvents) reduced the pesticide residue to about 1%. Therefore, it is recommended that contaminated clothing should be (1) laundered twice using hot water (60°C) and a heavy-duty detergent or (2) pretreated with a prewash soil/stain remover followed by a warm wash (50°C).

2.2 Chlorpyrifos



Chlorpyrifos

Chlorpyrifos is used to control insects and mites in stored grain and various pests on fruit, vegetables, and other crops. Pure Chlorpyrifos (300 mg, sample used was Pestonal from Caledon Laboratories) was stirred with 100 mL of 6% sodium hypochlorite (household bleach) for 18 hours at room temperature. The solution was tested for the presence of sodium hypochlorite, the oxidizing agent in bleach, at the end of the reaction time by using a potassium iodide test strip. The test was positive, indicating that as desired, an excess of bleach was still present. To determine the nature of the products of the reaction, the excess bleach was reduced by using sodium bisulfite and the solution brought to pH 6 with 5% aqueous sodium hydroxide. The solution was extracted with diethyl ether, the extracts combined, dried over sodium sulfate, and evaporated to dryness by using a rotary evaporator. The recovered products of the reaction represented 1.5% of the starting Chlorpyrifos. Therefore, more than 98% of the residue was water-soluble salts or highly volatile products resulting from the destruction of the pyridine ring by the bleach. In similar experiments, hexane and dichloromethane were used as extraction solvents to recover as many of the organic reaction products as possible. Gas chromatographic analysis of the oily residue indicated that less than 0.06% (the detection limit) of the starting Chlorpyrifos remained and that a large number (at least 30) of product fragments were present. The product mixture was analyzed by gas chromatography/mass spectrometry, and the infrared spectra of the major products were measured after separation by gas chromatography. As expected, one of the products was found to be 2,3,5-trichloro-6-hydroxypyridin-2-ol, but even this product was less than 0.01% of the starting material. Also found was diethyl phosphate from oxidation of the diethyl thiophosphate moiety, which is the other product of base-catalyzed hydrolysis. The remaining products were in even lower



3,5,6-trichloropyridin-2-ol

concentration and were suspected to be oxidation products of the hydroxypyridine after breaking of the ring. Similar results were obtained when the Chlorpyrifos and bleach reaction mixture was extracted with hexane and dichloromethane.

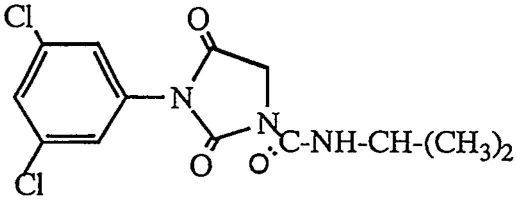
Thus, to decompose Chlorpyrifos, take 300 mg of the pure insecticide or 1 mL of concentrated commercial solution and add 100 mL of 6% sodium hypochlorite solution (household bleach). Allow the mixture to stand at room temperature for at least 18 hours. The solution can then be poured into the drain.

To determine effective laundering procedures, emulsifiable concentrate formulation of Chlorpyrifos, diluted to field strength (1% active ingredient) was used to contaminate 100% cotton and 65% polyester/35% cotton fabric. The best laundry procedure is to presoak the fabric for 3 hours in a washing machine filled with warm water (70 L at 50°C) to which 280 mL of chlorine bleach has been added. After 3 hours, empty the machine and give the fabric a single warm wash (at 50°C). Less than 0.1% of Chlorpyrifos remains on both cotton and polyester/cotton when the bleach presoak is used; however, after a single wash without the bleach presoak, approximately 40% of the Chlorpyrifos remains on the cotton fabric and 28% on the polyester/cotton blend.

The bleach/soak procedure results in color loss which is severe for 100% cotton and less for the polyester/cotton blend; in addition, after 25 bleach/soak launderings, one-third to one-half of the original strength of the 100% cotton is lost, whereas there is no significant strength loss for the 65% polyester/35%cotton blend.[5]

Even after presoaking in bleach and washing, clothing contaminated with concentrated Chlorpyrifos retains approximately 38% of the starting pesticide in the fabric. Therefore, work wear contaminated with the concentrate should be placed in a plastic bag and taken to an approved landfill site.

2.3 Iprodione



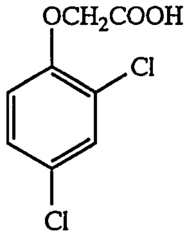
Iprodione

Iprodione is a contact fungicide used to control diseases in lettuce, glasshouse ornamentals, peppers, tomatoes, soft fruit, onions, seed crops, flower crops, and potatoes.

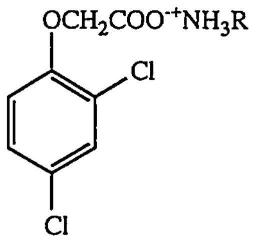
The reactions of Iprodione with acidic potassium permanganate and dilute and concentrated household bleach at both room temperature and 55°C were studied. The residues from the reaction were analyzed by high-performance liquid chromatography and identified by nuclear magnetic resonance spectroscopy and mass spectrometry. Concentrated bleach at room temperature was found to be an effective agent in the degradation of Iprodione. Thus 61.9 mg of pure Iprodione was added to 25 mL of concentrated bleach and the mixture stirred at room temperature for 5 days. The remaining bleach was reduced by the addition of solid sodium bisulfite, the solution was neutralized and extracted with dichloromethane. The extracts were dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue was analyzed by high-performance liquid chromatography and gas chromatography/mass spectrometry, and the results showed that 99.95% of the Iprodione had been degraded. Similarly, it was found that commercial Iprodione could be decomposed under comparable conditions. To 1 g of commercial Iprodione was added 120 mL of undiluted household bleach. The fungicide was completely degraded after 2 days at room temperature or 4 hours at 50°C. The resulting solution can be poured into a drain.

To determine the best laundering procedure for clothing contaminated with Iprodione, the wetable powder formulation of Iprodione was diluted to field strength (0.05% active ingredient) and used to contaminate 100% cotton and 65% polyester/35% cotton fabric. A single warm water wash (50°C) leaves approximately 1% residue on the fabric.

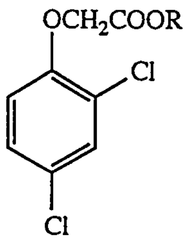
2.4 2,4-D



2,4-D Acid



2,4-D Amine



2,4-D Ester
R = iso-propyl or iso-octyl

2,4-D is widely used for the weeding of cereals and other crops. Its effect is more pronounced on broad-leaved plants, and as a result, it is used to control weeds such as dandelions in lawns. Several forms of 2,4-D are used for this purpose. These include 2,4-D acid, 2,4-D amine, and 2,4-D esters. Currently, the most commonly used ester is iso-octyl ester. We have investigated disposal methods for all of these forms.

2.4.1 2,4-D Acid

To dispose of 2,4-D acid, we wished to use a method that would break the benzene ring to eliminate the risk of the formation of chlorinated phenols or their derivatives. Because 2,4-D acid is a moderately strong acid, we used alkaline potassium permanganate as the reagent to test, so that the acid would be sufficiently soluble to allow the permanganate oxidation reaction to proceed. Thus, 1 g of 2,4-D was dissolved in 200 mL of 10% sodium hydroxide solution. We then added 14 g of potassium permanganate and stirred the mixture at room temperature for 24 hours. The permanganate remaining at the end of the reaction was reduced with sodium bisulfite and the solution acidified with dilute hydrochloric acid. The solution was extracted with diethyl ether, the extract dried over sodium sulfate, and the residue analyzed by thin layer and liquid chromatography. Less than 1% of the 2,4-D acid remained, and we could not find evidence of the formation of higher molecular weight chlorinated organic products. Therefore, the solution remaining after treatment with alkaline permanganate and reduction with sodium bisulfite can be washed into the drain with water, and any residual brown solid (manganese dioxide) can be discarded with regular garbage.

2.4.2 2.4-D Amine

In contrast to 2,4-D acid, 2,4-D amine is basic so that *acidic* potassium permanganate solution was used for its degradation. Thus, 300 mg of 2,4-D ethanolamine salt was treated with 100 mL of acidic potassium permanganate solution (17 mL of concentrated sulfuric acid added to 83 mL of water and 4.7 g of solid potassium permanganate added). After standing at room temperature for 24 hours, the excess permanganate was reduced by adding sodium bisulfite, the solution basified, and extracted with ether. The extract was dried over sodium sulfate, the solvent removed, and the residue analyzed by thin layer and liquid chromatography. No 2,4-D amine could be detected in the residue, indicating that at least 99.9% of the starting material had been decomposed. The solution can be poured into the drain after reduction and neutralization.

2.4.3 2,4-D iso-Octyl ester

A common formulation of 2,4-D is as the iso-octyl ester. This ester is less volatile than the previously used methyl ester so that less of it is lost into the air through evaporation.

It was expected that oxidation of the ester would break down the molecule. The effects of both household bleach and acidic potassium permanganate were tested. After reducing the excess oxidizing agent with sodium metabisulfite and neutralizing the solution, the organic products were extracted with hexane, the solvent was dried and evaporated under reduced pressure. The residue was analyzed by thin layer chromatography, gas chromatography, and liquid chromatography. 2,4-D iso-octyl ester is sparingly soluble in water, much less so than either the acid or the amine, so that its rate of decomposition in aqueous household bleach is slow. For example, after stirring 30.6 mg of pure 2,4-D iso-octyl ester at room temperature with 20 mL of undiluted household bleach for 6 days, high-performance liquid chromatographic analysis of the residue showed that 81% of the starting material remained. However, when 58 mg of pure 2,4-D iso-octyl ester was stirred at room temperature for 4 days with 25 mL of acidic potassium permanganate solution (17 mL of concentrated sulfuric acid and 4.71 g of potassium permanganate added to 83 mL of water), more than 99% of the ester was destroyed. Thus, treatment with acidic potassium permanganate solution is successful is denaturing 2,4-D iso-octyl ester.

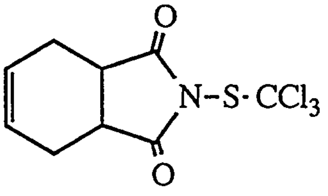
To decompose 2,4-D iso-octyl ester, for each 200 mg of the ester, add 100 mL of acidic potassium permanganate solution (17 mL of concentrated sulfuric acid added to 70 mL of cold water, 4.7 g of potassium permanganate dissolved in the solution, and the volume brought to 100 mL with water). Stir at room temperature for 96 hours. Add solid sodium bisulfite until a colorless liquid is formed. Adjust the pH of the liquid to between 6 and 8 by slowly adding solid sodium carbonate or 5% aqueous sodium hydroxide and pour the resulting liquid into a drain.

2.4.4 Decontamination of Clothing Contaminated with 2,4-D

2,4-D amine or ester formulation was diluted to field strength (1.25%) solution and used to contaminate cotton denim fabric.[6] The amine formulation is highly water soluble and is readily removed with a single wash; it makes no difference whether a cool (30°C) or hot wash (60°C) is used. At both wash temperatures, less than 1% of 2,4-D amine residue remains on the fabric.

When the ester formulation is used, even a hot (60°C) wash leaves a 55% ester residue. A second wash helps to reduce residues; however, they remain high. A 1% active ingredient dilution of 2,4-D iso-octyl ester formulation was used to contaminate 100% cotton and 65% polyester/ 35% cotton fabrics. The best laundry procedure is to pretreat the contaminated clothing with pure limonene or a product containing limonene (undiluted Citrasolve®, an automotive degreaser) for 30 min. and then launder the clothing in warm water (50°C). After this treatment, between 8 and 18% of 2,4-D iso-octyl ester remains on the fabrics.

2.5 Captan



Captan

Captan is used to control a wide range of fungal diseases on fruits and other crops. It can be oxidized with either household bleach or, more rapidly, with acidic potassium permanganate to hydrochloric acid, sulfur dioxide, and carbon dioxide. Details of the two procedures follow.

To 100 mg of pure Captan or commercial wetable powder is added 100 mL of 6% aqueous sodium hypochlorite, and the mixture is stirred at room temperature for 64 hours. Analysis of this mixture by high-performance liquid chromatography showed that after this time, the remaining Captan is below our detection level so that more than 99.95% has been degraded. The solution can be poured into a drain.

Oxidative degradation with potassium permanganate is a more rapid reaction. To 100 mg of pure Captan or commercial wetable powder is added 100 mL of acidic potassium permanganate solution (17 mL of concentrated sulfuric acid added to 70 mL of cold water, 4.7 g of potassium permanganate dissolved in the solution, and the volume brought to 100 mL with water). After stirring at room temperature for 7.5 minutes, no Captan could be detected so that greater than 99.95% had been degraded. It is recommended that the mixture is stirred for 30 minutes. The excess permanganate is then reduced by adding sodium metabisulfite until the solution is colorless. The pH of the solution is adjusted to between 6 and 8 by the careful and slow addition of solid sodium carbonate or 5% aqueous sodium hydroxide and the liquid poured into a drain.

The removal of Captan contamination from a Goretex and a denim fabric has been studied.[7] A single wash with hot water (60°C) results in less than 1% Captan residue remaining on either Goretex or denim when the contaminating solution is an 0.12% aqueous suspension of wetable powder.

3 ACKNOWLEDGMENTS

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ELECTROCHEMICAL PEROXIDATION OF PCBS AND VOCS IN SUPERFUND SITE WATER AND SEDIMENTS

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ABSTRACT

An electrochemical peroxidation (ECP) process has been developed and used to degrade polychlorinated biphenyls (PCB) and volatile organic compounds (VOC)-contaminated water, sludge, and sediments at a New York State Federal and State Superfund Site. The process involves passing an oscillating low-amperage (<10 amps) current through steel electrodes immersed in an acidified water or sediment slurry into which hydrogen peroxide (<1,000 ppm) is added. The generated free radicals attack organic compounds, including organo-metallic complexes and refractory compounds including PCBs. PCB degradation ranged from about 30% to 80% in experiments involving Federal Superfund Site sediments; total PCBs were reduced by ~97% to 68%, respectively, in water and slurry collected from a State Superfund subsurface storage tank. VOC bench-scale experiments involved chloroethane, 1,1-dichloroethane, dichloromethane, 1,1,1-trichloroethane, and acetone and after a 3-min ECP treatment, degradation ranged from >94% to about 99.9%. Results indicate the ECP is a viable process to degrade organic contaminants in water and sediment suspensions. Because the treated water suspensions are acidified, select trace metal sorbed to the particulates is solubilized and therefore can be segregated from the particulates, offering a process that simultaneously degrades organic contaminants and separates trace metals.

1 INTRODUCTION

Advanced oxidative processes (AOPs) use free radicals to spontaneously oxidize a wide range of organic compounds. The effectiveness of the AOP depends on the production and propagation of radical reaction chains. Hydroxyl radicals can be created from hydrogen peroxide by several methods, including the use of heat, iron redox reactions, solvated electrons, sonication, and cavitation, and with the use of electromagnetic radiation, including photocatalysis (1).

Advanced oxidative processes have been used to degrade a variety of organic compounds in liquids; ultraviolet/peroxidation is used commercially to degrade organic contaminants in liquids and air. In this paper, we describe the use of electricity and heat to promote the formation of free radicals from hydrogen peroxide.

More than 100 years ago, Fenton reported (1) on the accelerated decomposition of H_2O_2 in the presence of Fe^{2+}, a reaction known as Fenton's Reagent. In 1934 the process was used to oxidize organic compounds in water (2), and since that time, numerous studies have used Fenton's Reagent to destroy a variety of organic compounds in water. The effectiveness of Fenton's Reagent is related to its ability to create hydroxyl 'free' radicals after Walling (4):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \ . \tag{1}$$

The free radicals produced can participate in reactions, which indiscriminately oxidize available organic matter:

$$R\mathrm{H} + \mathrm{OH}^\bullet \rightarrow \mathrm{H_2O} + R^\bullet \ . \tag{2}$$

The organic radicals ($R^\bullet$) produced in reaction 2 can also be oxidized (reaction 3), dimerized (reaction 4), or reduced (reaction 5), resulting in a variety of possible reaction pathways and products (4):

$$R^\bullet + Fe^{3+} \rightarrow Fe^{2+} + \text{oxidized product} \ , \tag{3}$$

$$2R^\bullet \rightarrow \text{dimer product} \ , \tag{4}$$

and

$$R^\bullet + Fe^{2+} \rightarrow Fe^{3+} + \mathrm{RH} \ . \tag{5}$$

Reaction 3 allows the regeneration of Fe^{2+} and, therefore, propagation of redox chain reactions via Fenton's Reagent (reaction 1).

While AOPs are increasingly being used in the commercial treatment of organic compounds in air and water, relatively little research has emphasized the use of this group of technologies to contaminated solids or slurries. Recent work has confirmed the potential of TiO_2 photocatalysis to degrade highly refractory compounds (pesticides, dioxins, polychlorinated biphenyls [PCBs]) adsorbed on sediments (5–8). Several papers have also demonstrated the application of Fenton's Reagent to degrade contaminants in artificially contaminated sand and soil (9–12).

Much of the preliminary work in the development of this process utilized organic dyes as surrogates for organic contaminants. The use of dyes allowed real-time observation, low-cost analysis, and rapid developmental experimentation.

2 MATERIALS AND METHODS

2.1 Federal Superfund Site

PCB-contaminated sediments were collected from a shallow cove at a federal Superfund site located on the St. Lawrence River near Massena, New York. The sediment consisted of fine sand (~65%), silt, and clay (~35%) and contained a variety of organic and inorganic fragments, including twigs, roots, leaf parts, and gastropod shell fragments. The total PCB concentration was about 65 parts per million (ppm) and, enriched in the ortho chlorinated congeners relative to Aroclor 1248, the compound used at the industrial facility identified as the source of the PCBs. The ortho chlorinated enrichment is attributed to anaerobic microbial degradation, which altered the original Aroclor (13).

2.2 State Superfund Site

Contaminated water and water with suspended sludge (slurry) was collected on three separate occasions from a subsurface storage tank (SST) at a New York State Superfund site located in Oswego, New York. The 3,000-gallon tank was used for septic storage on site and was contaminated by releases of solvents and PCBs during plant operations. Several liters of tank water for the bench-scale experiments were collected by means of a peristaltic pump and teflon tubing. The samples were stored in amber glass at 4°C until used in 500-mL batch experiments. For bench-scale experiments with slurry, the tank water and bottom sediments (sludge) were agitated mechanically and sampled with a peristaltic pump. The presence of sludge was verified visually during sampling as black flocculated particles that settled to the bottom of the sampling container.

The sludge component in all of the slurry experiments was <1% by weight. For the pilot-scale experiments, 200 L of water were pumped directly into a steel drum and treated on site.

3 POLYCHLORINATED BIPHENYL EXPERIMENTS

3.1 Bench-Scale Experiments

Preweighed portions of the sediment collected from the federal Superfund site were added to 500 mL of distilled, deionized water to form sediment slurries that varied from 2% to 20% solids by weight.

The pH of the slurry was adjusted to about 2.5 with 16M sulfuric acid, and the temperature was either maintained at about 25°C or heated to 70°C using a hot plate. Two steel electrodes were immersed in the suspension to induce a current that ranged from 0 to 500 mA, and the system was continuously mixed with a teflon-coated magnetic stirrer. Duplicate control samples (20 mL) were collected by using a syringe and teflon tube. Hydrogen peroxide, ranging from 84 to 840 ppm, was added to the slurry; after 1–10 minute exposures, duplicate experimental samples were collected.

For the experiments involving the state Superfund SST, four PCB bench-scale experiments were conducted utilizing 500 mL of tank water and slurry. These experiments were conducted in precleaned 600-mL beakers. Teflon-coated magnetic stir bars were used to mix the solution. After addition of the tank water or slurry, the temperature was raised to 70°C using a hot plate. The pH of the solution was adjusted to about 2 by the addition of H_2SO_4. Two steel electrodes (6 × 8 cm) were immersed in the solution, and a small current of ~500 mA applied for 2 minutes during which the current polarity was reversed every 5 s. At the end of the 2-min 'charge' period, the entire contents of one beaker of tank water and a beaker of slurry were extracted as controls. The four treated samples received 1 mL of 30% H_2O_2 (840 ppm) immediately after charging and were allowed to react for 5 minutes. After the reaction, the entire contents of each beaker were extracted for analysis. Duplicate degradation experiments were completed on both subsurface tank water and slurry. The results and operating parameters of each experiment are shown in Table 1.

Table 1 Experimental Conditions and Results of ECP Treatment of PCB-contaminated Sediments Collected from the Federal Superfund Site Located near Massena, New York (The initial PCB concentration was 65 ppm and the sediment consisted primarily of fine sand; silt and clay comprised about 35%.)

	Experiment Number					
Parameter	1	2	3	4	5	6
Solids (wt%)	2	2	2	2	2	20
Temperature (°C)	70	70	25	25	70	25
Current (mA)	500	0	500	0	500	500
Treatment time (min)	1	1	1	1	1	10
H_2O_2 (ppm)	840	840	840	840	84	420
Degradation (%)	78	81	70	31	69	57

3.2 Pilot-Scale Experiments

The two PCB pilot-scale experiments were conducted on the state Superfund site SST and used 200 L of tank water pumped into a steel drum. The water was stirred by an electric mixer and treated at ambient temperatures (-1 5°C). The pH was adjusted to 2 with 250 mL of H_2SO_4. Two steel electrodes (30 × 90 cm) were immersed into the solution, and a current of 20 A was applied for 5 minutes with polarity reversal every 10 seconds. Following the 5-minute charge time, duplicate 500-mL control samples were taken for analysis. Immediately after collection of the control samples, 25 mL of 50% H_2O_2 (87.5 ppm) was injected into the drum and allowed to react. After 5 minutes, duplicate 500-mL samples were collected for analysis. The results and operating parameters of each experiment are given in Table 2.

Table 2 Results of ECP Bench-scale Experiments on PCB-Contaminated Subsurface Storage Tank Water and Slurry from the State Superfund Site (The controls were the starting concentrations [pretreated]; two separate experiments were conducted on each medium.)

	Water			Slurry	
Experiment	PCBs (µg/L)	DCB Recovery (%)	Experiment	PCBs (µg/L)	DCB Recovery (%)
Control A	19.8	76.8	Control B	99.0	86.4
1	0.3	84.0	3	34.5	87.9
2	0.8	74.5	4	28.5	87.3
Degradation (%)	97.2	-	Degradation (%)	68.2	-

4 VOLATILE ORGANIC COMPOUND EXPERIMENTS

4.1 Bench-Scale Experiments

Two volatile organic compound (VOC) bench-scale experiments were conducted on the state Superfund site SST water and slurry. First, 580 mL of tank water and slurry was poured into precleaned 600-mL glass beakers. The beaker's contents were then stirred with a teflon-coated magnetic stir bar. The temperature was 5°C, and the pH was adjusted to 2.5 by using H_2SO_4. Steel electrodes (6 × 8 cm) were immersed in the beaker and charged at 500 mA with polarity reversal every 5 seconds for 2 minutes. Two duplicate 40-mL control samples were then withdrawn by using a glass syringe and teflon tube and added to precleaned vials. Three consecutive, minute-long treatments utilizing incremental additions of 2 mL of 30% H_2O_2 (1,680 ppm), 120 mg of

$FeSO_4 \cdot 7 H_2O$, and periodically reversed current were applied. A 40-mL subsample was withdrawn 1 minute after the application of each treatment. A 'trip blank' composed of double distilled laboratory water was added to a precleaned 40-mL vial and submitted for analysis. All samples were immediately refrigerated in the dark until analyzed. The results and operating parameters of each experiment are presented in Table 3.

Table 3 Results of ECP Pilot-scale Experiments on PCB-Contaminated Tank Water (Controls A and B represent the pretreated samples; two separate experiments were conducted on the contents of the subsurface storage tank located at the state Superfund site.)

	Pilot Test 1		Pilot Test 2	
Experiment	PCBs (μg/L)	DCB Recovery (%)	PCBs (μg/L)	DCB Recovery (%)
Control A	16.41	94.3	13.71	94.0
Control B	16.18	93.3	13.57	95.9
Treated A	2.00	92.9	2.01	95.5
Treated B	1.95	98.3	2.04	94.2
Degradation (%)	87.9	-	85.2	-
Field Blank A	0.04	-	-	-
Field Blank B	0.03	-	-	-

5 ANALYTICAL METHODS

5.1 PCB Analysis

All PCB analyses were conducted at the Environmental Research Center of the State University of New York, Oswego, and were congener specific. All samples were stored in the dark at 4°C until analyzed. Samples were extracted with a separatory funnel using three sequential hexane extractions of 50 mL. Triplicate hexane rinses of the interior of the beakers were also combined with the hexane extract. The hexane extract was dried, using sodium sulfate, and oxidized with sulfuric acid. Elemental sulfur and polar compounds, if present, were removed using tetrabutylammonium sulfate and 4% activated Florisil columns, respectively. The clean hexane extract was condensed and stored at 4°C until analyzed. Congener-specific PCB analysis was performed on an HP5890 gas chromatograph using a Ni^{63} electron capture detector and an Ultra DB-5 column. Decachlorobiphenyl (DCB) was used as a surrogate to monitor PCB recovery. The gas chromatograph was calibrated using a mixed Aroclor standard prepared by the New York State Department of Health Wadsworth Laboratory.

5.2 VOC Analysis

VOC analyses were conducted by a state-certified laboratory — O'Brien and Gere Laboratories, Inc., of Syracuse, New York. Glass 40-mL vials were delivered to O'Brien and Gere Laboratories within 2 hours after completion of the ECP treatment. The samples were stored in the dark at 4°C until analysis, which occurred within five days of receipt. Samples were analyzed by gas chromatography using the U.S. Environmental Protection Agency EPA Method 601/602 for purgeable organics, modified to allow quantitation of acetone.

6 RESULTS

6.1 Federal Superfund Sediments

PCB degradation of the Massena area sediment slurries ranged from 31% to 81% of the original concentration of about 65 ppm. The experimental data suggest that degradation was affected by the temperature of the slurry and the application of a low-amperage current. As noted from Table 1 (experiments 1 and 2), application of a weak current made little difference in heated slurries, whereas at 25°C, the low-amperage current increased degradation from about 31% to 70%, as noted in experiments 3 and 4, Table 1. Heating of the slurry also significantly increased the effectiveness of the hydrogen peroxide, as noted from experiments 1 and 2, where the degree of degradation was similar (~80%) compared to about 69% in experiment 5 even though the H_2O_2 concentration varied by an order of magnitude. Minimal degradation was noted at ambient temperatures, and lower H_2O_2 concentrations as can be seen from experiment 4, Table 1. The process degraded more than 50% of the total PCBs at solids concentrations of about 20% even at lower H_2O_2 concentration, although the rate of degradation is reduced, as evidenced in experiment 6, Table 1.

6.2 State Superfund Site

Bench-scale laboratory experiments (500 mL) were conducted separately on VOCs and PCBs in SST water and slurry collected from a state Superfund site located in Oswego, New York. Tank water and slurry samples contained a variety of organic contaminants, including, but not limited to, PCBs and VOCs. All of the contaminants experienced significant degradation (68–99%) in comparison to control samples during ECP treatments ranging from 3 to 5 minutes (Tables 2–3).

In separate bench-scale experiments, total PCBs were reduced by ~97% in tank water and ~68% in slurry containing sludge after a 5-minute treatment with 1 mL of 30% H_2O_2 and 500 mA.

The tank water used in the subsurface tank experiments had a PCB content of 19.8 parts per billion (ppb). Two experiments using the same water contained 0.3 and 0.8 ppb PCBs after a 5-minute ECP treatment, corresponding to an average reduction in PCBs of ~97% (Table 2). The difference between the level of treatment attained (0.8 vs. 0.3 ppb PCBs after ECP treatment) is probably related to the current applied; experiment 1 had more than three times the current of experiment 2 because a different power supply was used.

Figures 1a and lb illustrate the extent of congener degradation for ECP bench-scale experiments with tank water and water with sludge. Figure 1a shows nearly complete destruction of all congeners. However, a systematic tailing off in degradation at higher retention times is evident; congeners with gas chromatograph retention times in excess of 30 minutes were degraded to 85% relative to the control sample. The higher chlorinated PCB congeners were degraded to a lesser extent in slurry than in tank water alone, suggestive of solubility-imposed constraints in slurry systems; the more soluble, lower chlorinated congeners are more readily degraded, and associated suspended sediments affect the rates and degree of degradation.

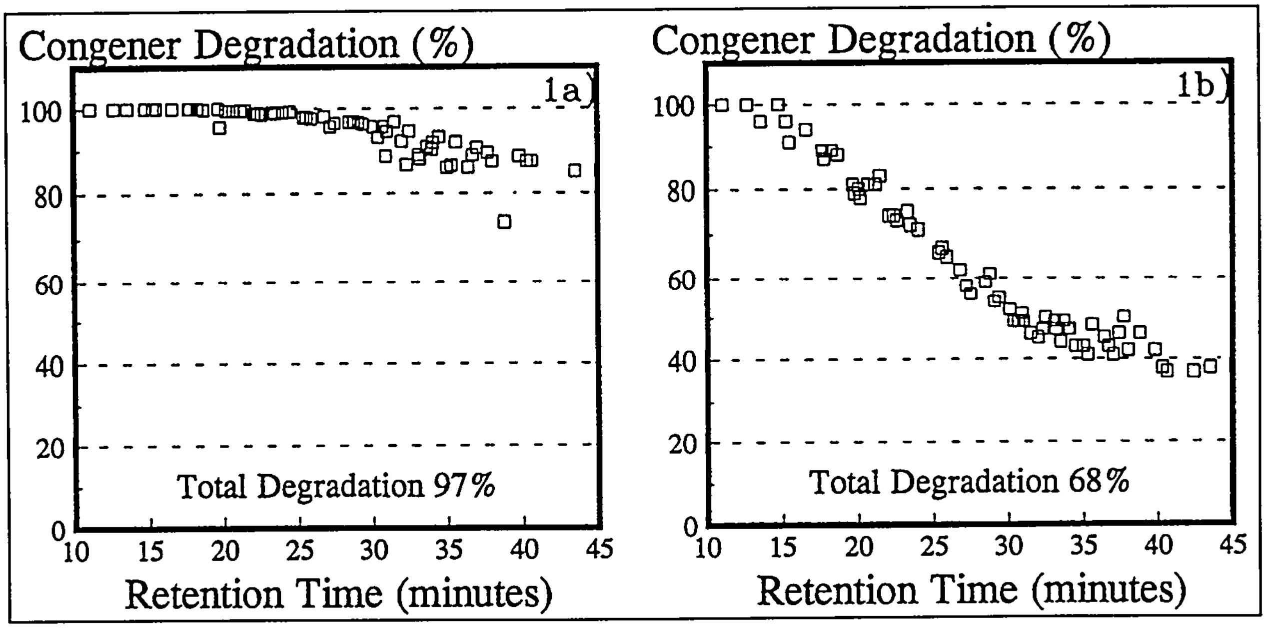

Fig. 1 (a) ECP Degradation of PCB-Contaminated Water and (b) Water with <1% Sludge from a State Superfund Subsurface Storage Tank

6.3 PCB Pilot-scale ECP Results

Duplicate 200-L ECP pilot-scale experiments were conducted on subsurface tank water. The first experiment involved duplicate control samples of 16.4 and 16.2 ppb PCBs (Table 3). After treatment, the PCB concentrations were reduced to about 2 ppb, corresponding to a PCB reduction of about 88%.

The SST slurry contained less than 1% solids and a PCB content of 99 ppb, approximately five times the concentration of the tank water without the suspended sludge. Two slurry experiments, 3 and 4, contained 34.5 and 28.5 ppb PCBs after a 5-minute ECP treatment, corresponding to an average reduction in PCBs of ~68%.

The second experiment was conducted with identical parameters (Table 3); however, the concentration of the duplicate control samples was 13.7 and 13.6 ppb PCBs. After ECP treatment, about 2 ppb remained, corresponding to a reduction of ~85%.

A duplicate pilot-scale assessment of PCB destruction was conducted on 200 L of SST water and resulted in ~85% (87.9% and 85.2%) reduction within 5 minutes of treatment with 25 mL of 50% H_2O_2 and 20 A of current (Table 3). These results indicate the electrochemical peroxidation process can rapidly degrade a variety of organic compounds, including PCBs and VOCs in water and slurry suspensions, with the use of minimal amounts of electricity and reagents. Upscaling the process from bench- to pilot-scale (400x) resulted in minor losses in efficiency, most likely related to proportional differences in electrode surface area or electrode spacing.

6.4 VOC Bench-scale Electrochemical Peroxidation

A bench-scale (500-mL) experiment conducted on SST water and slurry used a 3-minute reaction time with three incremental additions of reagents (Table 4). Note that these experiments included the addition of ferrous sulfate and hydrogen peroxide. Both experiments were subsampled three times, 1 minute after each incremental reagent addition.

The data presented in Table 4 show >95% degradation of chloroethane, dichloromethane, 1,1-dichloroethane, and acetone during the 3-minute ECP treatment of each medium. Incremental additions of reagents resulted in the progressive destruction of each contaminant.

The extent of contaminant degradation was nearly linear on log/linear plots of concentration versus peroxide dosage for all VOCs detected. Overall degradation of measured compounds (USEPA 601/602 + acetone) was ~95% after three 1-minute treatments with 2 mL of 30% H_2O_2 (840 ppm), 40 ppm ferrous iron, and 500 mA. Several compounds, including chloroethane, 1,1-dichloroethane, and methylene chloride, were reduced to nondetectable levels.

Table 4 ECP Treatment of VOCs in Tank Water (A) and Water + Sludge (B) from the State Superfund Site Subsurface Storage Tank (ND means not detected.)

Parameter	Chloroethane (μg/L)		Dichloro-methane (μg/L)		1,1-Dichloroethane (μg/L)		1,1,1-Trichloroethane (μg/L)		Acetone (μg/L)	
Media	A	B	A	B	A	B	A	B	A	B
Control	1,750	2,150	<100	130	170	185	<100	<100	73,000	<9,999
Treatment 1	80	<5	10	<5	51	6	47	14	29,000	<500
Treatment 2	33	<1	15	<1	<10	<1	18	5	10,000	<100
Treatment 3	<10	<1	11	<1	<10	<1	12	6	3,300	659
Degradation (%)	>99.4	>99.9	-	>99.2	>94.1	>99.4	-	-	95.5	-
Trip Blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

7 DISCUSSION

Experimental results indicate that PCBs and VOCs can be rapidly degraded by the ECP process. ECP can be applied to purely aqueous wastes or effluents and admixed sediment, sludge, or soil. The process was upscaled 400 times with only minor losses in efficiency in the destruction of PCBs and VOCs in subsurface storage tank water and slurry.

Polychlorinated biphenyls represent a class of compounds with isomers or congeners that can contain from 1 to 10 chlorines. As a consequence, congeners have a wide range in solubility, volatility, and hydrophobicity, which influences degradation rates and pathways. The relationship between PCB degradation relative to gas chromatograph retention time illustrates this correlation. Figure 1 depicted the results of the ECP experiment on subsurface storage tank water and sludge and demonstrates this relationship; the lower chlorinated and earliest eluting congeners were completely degraded and those with the longest retention times about 40% degradation. A similar trend has been noted by Chiarenzelli et al. (8) and was produced by the TiO_2 photocatalysis of PCBs adsorbed on contaminated sediments. Pignatello and Chapa (18) showed a degradation pattern nearly identical to the one plotted for tank water (Figure 1a) from their studies on the destruction of Aroclor 1242 by the ferric ion, hydrogen peroxide, and ultraviolet light in aqueous suspension.

The reduced degradation of highly chlorinated congeners by the ECP process in the presence of suspended solids is believed to be directly related to the degree of chlorination and lower solubility. The solubility of individual PCB congeners varies by nearly eight orders of magnitude (19) and may control the availability of PCBs to radical attack. The more soluble PCBs will readily partition into the aqueous phase, whereas the most hydrophobic congeners may become effectively shielded by sequestering in solid particles (13).

Larger amounts of PCBs were destroyed in tank water than in the slurry system containing a small percentage of sludge; however, the opposite is true for VOCs (Table 4). For PCBs, high concentrations of organic materials, anticipated in septic system sludge, can limit the destruction of target compounds by competition for radicals or by sequestering highly hydrophobic compounds during the aging process (13).

At this time, little is known about the mechanisms or kinetics of the ECP process. However, some preliminary observations can be made. Because little or no degradation of organic compounds occurs when electrodes other than mild steel are used, iron is considered critical to the process. Similarly, because little or no degradation occurs when hydrogen peroxide is absent, it is also a critical reactant. The dominant reaction in the ECP process is Fenton's Reagent (2), requiring the reaction of ferrous iron and hydrogen peroxide either on the electrode surface or in solution. The relationship of degradation rates to pH suggests that iron from the electrodes is dissolved during the charge period and reacts with the added hydrogen peroxide. Iron is substantially more soluble at lower pH. The length of the charge period is also critical to the rate of reactions (1 or 2 minutes is optimal, with little further gains with additional charging). The charge period enables the dissolution of iron from the electrodes. This has been verified by measuring the amount of weight loss of the electrodes after ECP treatment. Based on electrode weight loss in 500-mL experiments, as much as 100 ppm iron is introduced to the solution during the charging period. When stainless steel electrodes were used, no degradation was observed, even at low pH.

The relative effects of other electrochemical reactions are more subtle but may be important for some compounds or intermediates. The ECP reactions are not entirely controlled by Fenton's Reagent because periodic current reversal, and the configuration, number, and spacing of the electrodes affecting the current density influence the rates of degradation.

A number of anodic oxidation or cathodic reduction reactions and reactions with solvated electrons (reactions 6 and 7) can contribute to the oxidation of organic compounds or reduction of metals:

$$e^- + H_2O_2 \rightarrow OH^\bullet + OH^- \ , \tag{6}$$

and

$$e^- + Cr^{+4} \rightarrow Cr^{+3} \ . \tag{7}$$

Several papers have addressed the electrochemical regeneration or electrogeneration of Fenton's Reagent. In one study (14), a phenolic effluent was oxidatively degraded in a ferrous sulfate catholyte utilizing hydrogen peroxide. The hydrogen peroxide was generated by electroreduction of oxygen at lower pH with a graphite cathode and platinum anode:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \; . \tag{8}$$

Tzedakis et al. (15) used a mercury pool cathode and platinized titanium plate anode in an electrochemical reduction process to regenerate the ferrous ion (reaction 9). Using this process made it possible to control the rate of hydroxyl radical production, the rate of phenol production from benzene by hydroxylation, and the side reactions that decreased the efficiency of the process (reactions 10–12) or generated undesirable products. They concluded that current yields of phenol production could exceed 100% at the cathode if phenol can be rapidly extracted from the system to avoid further degradation by free radical attack. Measured current yields of 70% were attributed to numerous side and chain reactions that could not be totally suppressed.

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \; , \tag{9}$$

$$2\,OH^\bullet \rightarrow H_2O_2 \; , \tag{10}$$

$$OH^\bullet + Fe^{+2} \rightarrow OH^- + Fe^{+3} \; , \tag{11}$$

and

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \; . \tag{12}$$

The difference between the ECP process and the large number of studies on the use of Fenton's Reagent to destroy organic contaminants in the aqueous phase (3) appears to be the time required for degradation. Treatment by Fenton's Reagent often requires hours, whereas PCB and VOC disappearance and dye decoloration occurs within minutes or seconds. This difference may be more apparent than real, in that in our studies on PCBs, VOCs, and dyes, the production of intermediates and liberation of CO_2 or Cl^- has not been measured. Compounds that degrade rapidly (seconds) by Fenton's Reagent require hours for complete mineralization or alternative or supplemental treatment. Atrazine, for example, was degraded in less than 30 seconds by the use of Fenton's Reagent, but produced several products that required further treatment (16). In addition, Pignatello (17) has shown that 2,4-D and 2,4,5-T were rapidly destroyed by Fenton's Reagent in 1 minute or less; mineralization was achieved by the photo-assisted reaction between ferric iron and hydrogen peroxide; however, this process required from 1 to 2 hours. The oxidative dechlorination of PCBs in aqueous suspension required 20 hours to reach 88% PCB degradation and 66% Cl^- yield by the photo-assisted ferric reaction of Pignatello and Chapa (18). In contrast, oxidative dechlorination of PCBs using ECP degradation occurred within minutes. Additional work is needed to elucidate the production of intermediates and determine the extent of mineralization possible by the use of the ECP process.

7.1 Metals Removal

Hydrous ferric iron phases form as a by-product of the ECP treatment by the oxidation of ferrous iron by Fenton's Reagent. Iron hydroxides and sesquioxides can adsorb and immobilize a variety of metals. Subsequent pH adjustment can enhance the settling, separation, and recovery of ferric iron complexes and associated adsorbed trace metals. Similar metal recovery processes are currently used by the plating industry to facilitate metals recovery and meet wastewater standards. They could be integrated into the ECP process to enable simultaneous treatment of effluents with organic and inorganic contaminants.

8 SUMMARY

An electrochemical peroxidation process that rapidly degrades organic contaminants in water and slurry has been developed by using hydrogen peroxide, electricity, and steel electrodes. The process has been used to degrade PCB-contaminated sediments from a federal Superfund site and PCBs and VOCs in subsurface storage tank wastewaters from a state Superfund site at the bench- and pilot-scales. Pilot-scale tests with 200 L of tank water indicate the process is efficient at ambient temperatures and larger volumes. The dominant degradation reaction appears to be a Fenton or Fenton-like reaction. Electrolysis significantly enhances reaction rates; however, reaction mechanisms are yet to be fully elucidated.

9 ACKNOWLEDGMENTS

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BIOREMEDIATION: TECHNOLOGY FOR TREATING HYDROCARBON-CONTAMINATED WASTEWATER

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ABSTRACT

Cutting oil wastewater from an iron and steel factory was applied to the soil windrow. Self-remediation was then compared with remediation with acclimatized indigenous microbes. The incremental reduction rate of the microorganisms and hydrocarbon-degradable microbes was slower in self-remediation than in the latter treatment. Within 30 days, when the acclimatized indigenous microbes were used, there was a significant reduction of the contaminated hydrocarbons, while self-remediation took longer to reduce to the same concentration. Various nitrogen sources were applied to the soil pile, namely, organic compost, chemical fertilizer, ammonium sulfate, and urea. The organic compost induced a high yield of hydrocarbon-degradable microorganisms, but the rate at which the cutting oil in the soil decreased was slower than when other nitrogen sources were used. The results of cutting oil degradation studied by gas chromatography showed the absence of some important hydrocarbons. The increment of the hydrocarbon-degradable microbes in the land treatment ecosystem does not necessarily correspond to the hydrocarbon reduction efficiency.

1 INTRODUCTION

Bioremediation is widely regarded as one of the most promising technologies for the cleanup of sites contaminated by hazardous waste. Organic waste responds well to bioremediation, although complicated structures like long-chain or chlorinated hydrocarbons, are more difficult to degrade by aerobic processes.

Several approaches to bioremediation are available for treating hazardous-waste-contaminated soil and wastewater. They are, for example, the use of natural or engineering organisms, in situ treatment, or after excavation and land or bioreactor treatment. Land treatment methods are applied to remediate excavated contaminated soil or groundwater that has limited amounts of contaminants. In some cases, the treatment needs an area that can be used for arranging the soil pile or soil windrow. The contaminated waste could be applied to the land repeatedly as long as a suitable environment for the acting microbe exists. A well-designed land treatment system can be used for iron and steel factories, where specific oil-contaminated wastewater is produced.

Thailand has more than 10,000 iron and steel factories. Most are small factories that are not required to register with the Department of Industrial Work. These factories use small amounts of wastewater and often discard it with residential wastewater. This wastewater contains soluble cutting oil used as a lubricating agent in machines. Such oils include neat cutting oil, mineral and fatty oil mixtures, sulfurized oils, sulfur oil, etc. Contaminated wastewater causes problems to the environment, as the oil contains long-chain paraffin, naphthenic, and aromatic compounds that are difficult to degrade. Using bioremediation approaches, such as land farming to treat the cutting-oil-contaminated wastewater from an iron and steel factory, mitigates toxic substances to the environment. Proper treatment of cutting-oil-contaminated wastewater governs the good hazardous waste management system, particularly in a small factory. The objective of this paper is to find the appropriate treatment system for cutting-oil-contaminated wastewater. The land treatment method is easy to handle and suitable for the small amounts of water produced. The treatment technology is based on the activity of the acclimatized indigenous microorganisms and the optimization of microbes suitable for the environment in the soil, while the windrow can act as the reactor with daily wastewater loading.

2 METHODOLOGY

2.1 Soil Windrow

Ten kilograms of paddy soil was formed into a windrow to allow good ventilation and air flow. A plastic sheet was used to line the windrow to prevent excess water from escaping. Acclimatized soil was sprayed with cutting oil wastewater, and the moisture content was controlled at 35% for 2 months.

2.2 Wastewater Application

Wastewater from an iron and steel factory was applied to the windrow to keep the primary moisture content at 25%. The moisture content was stabilized afterward by adding distilled water.

2.3 Addition of Nitrogen

The nitrogen source, namely, organic fertilizer, chemical fertilizer, ammonium sulfate, and urea, was used to enhance hydrocarbon degradation.

2.4 Determination of Microorganism

The microorganism in the soil windrow was investigated in terms of the total microbial count and hydrocarbon-degraded microbe (HDM) count. A spread plate technique with plate count agar and mineral medium [1] was developed by adding cutting oil as a carbon source, respectively, as the media.

2.5 Hydrocarbon Analysis

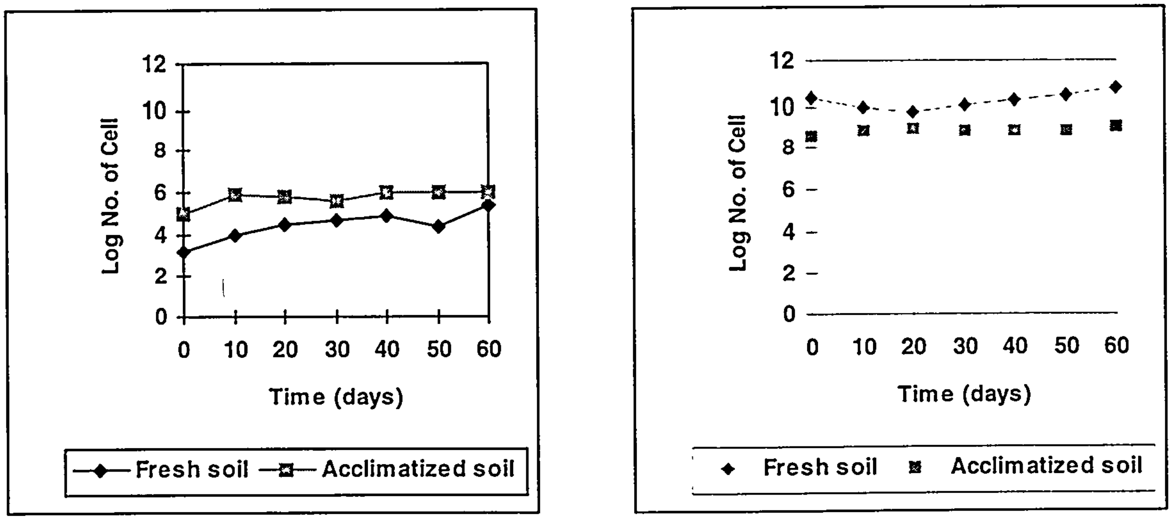
An evaporation technique using hexane extraction [2] was introduced and developed to measure the hydrocarbon remaining in the soil. Aliphatic hydrocarbon and unresolved complex mixture (UCM) were further refined by celite column and silica gel column [3] and measured by gas chromatography. The hydrocarbon reduction efficiency was calculated.

3 RESULTS AND DISCUSSION

3.1 Microbial Change during Remediation

3.1.1 Fresh and Acclimatized Soil

By using both fresh and acclimatized soil as the recipient material for cutting oil degradation, the total microorganisms and HDM were observed. The results are shown in Fig. 1. The number of microorganisms in the fresh soil was higher than in the acclimatized soil, while the number of HDM



A: Hydrocarbon degraded microbe B: Total Count

Fig. 1 Time of Microorganisms in the Cutting Oil Wastewater Added to the Windrow

was lower. High numbers of HDM (mostly bacteria) influenced the cutting oil acclimatization, which also lowered the amount of microorganisms. There was no significant change in the total microorganism count during the 60-day experiment, both in fresh and acclimatized soil windrows. Increased HDM was observed after 10 days of the experiments.

3.1.2 Application of Nitrogen Source

Four nitrogen sources were applied to the acclimatized soil windrow, namely, organic fertilizer, chemical fertilizer, ammonium sulfate, and urea. The microorganism variation during 60 days of the experiment is shown in Fig. 2. The organic fertilizer enhanced HDM, while there was no change in the total count. The result of the urea addition windrow was the opposite: HDM increased slowly, and the total count increased gradually. The other nitrogen sources showed patterns similar to the control pattern.

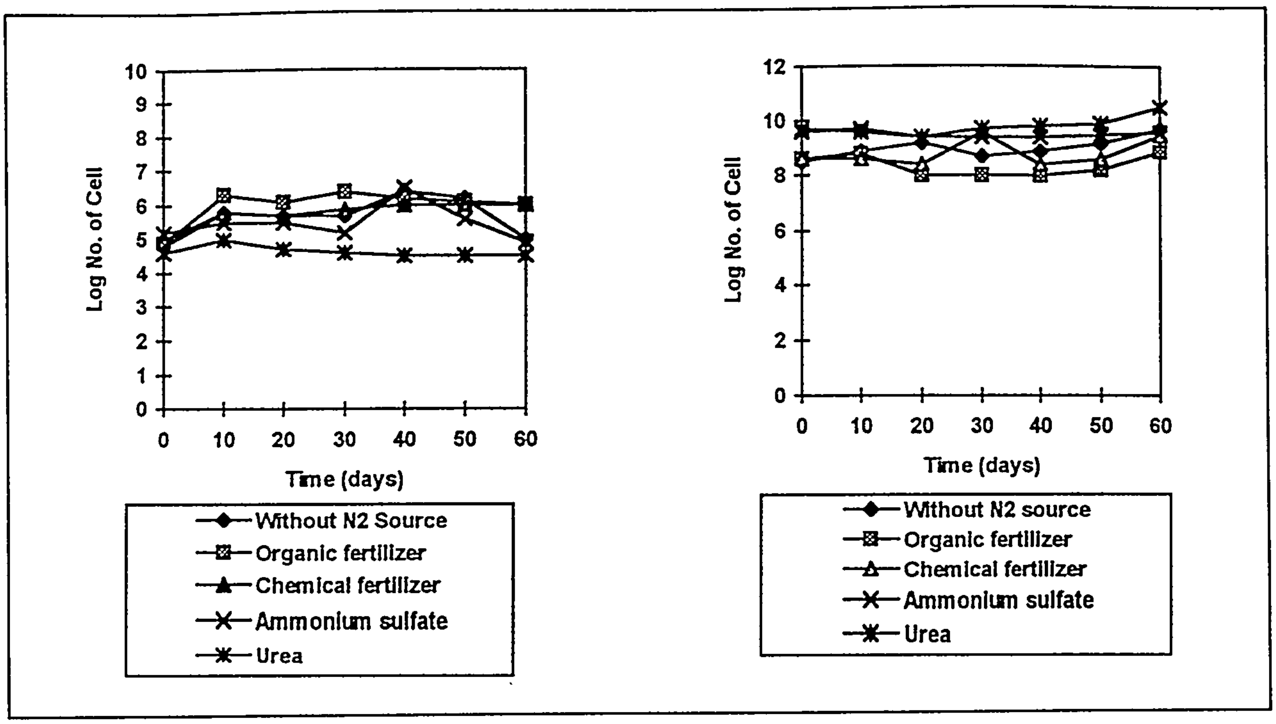
3.2 Hydrocarbon Reduction

It was clear that the bioremediation of the acclimatized soil was more efficient in reducing hydrocarbons in term of aliphatic hydrocarbon (including UCM) than the original soil. After 60 days of treatment, the reduction stabilized at 43% while the acclimatized soil showed reductions (after 60 and 100 days) of 51% and 72%, respectively, as shown in Fig. 3.

The addition of three nitrogen sources (chemical fertilizer, ammonium sulfate, and urea) resulted in a reduction hydrocarbons of greater than 60% within 20 days of the treatment. However, the rate decreased after that. Less hydrocarbon reduction was found when organic fertilizer was used as the nitrogen source; a reduction of only 40% was achieved at 20 days; this increased to 62% after 60 days. Urea was the most effective nitrogen source, with 81% reduction after 60 days.

3.3 Microbe and Hydrocarbon Reduction

Although acclimatized soil had low levels of total microbes, higher hydrocarbon reduction was observed, which may have been caused by the activities from increasing HDM. This phenomenon was different when urea was used as the nitrogen source. High efficiency of degradation was observed despite the use of less HDM, but the total count gradually increased. The addition of urea introduced a slightly alkaline level to the soil windrow (pH 8.0) during 2 weeks of the treatment, which may have led to the slow increase in HDM. However, after 20 days, pH dropped to 7.5, while



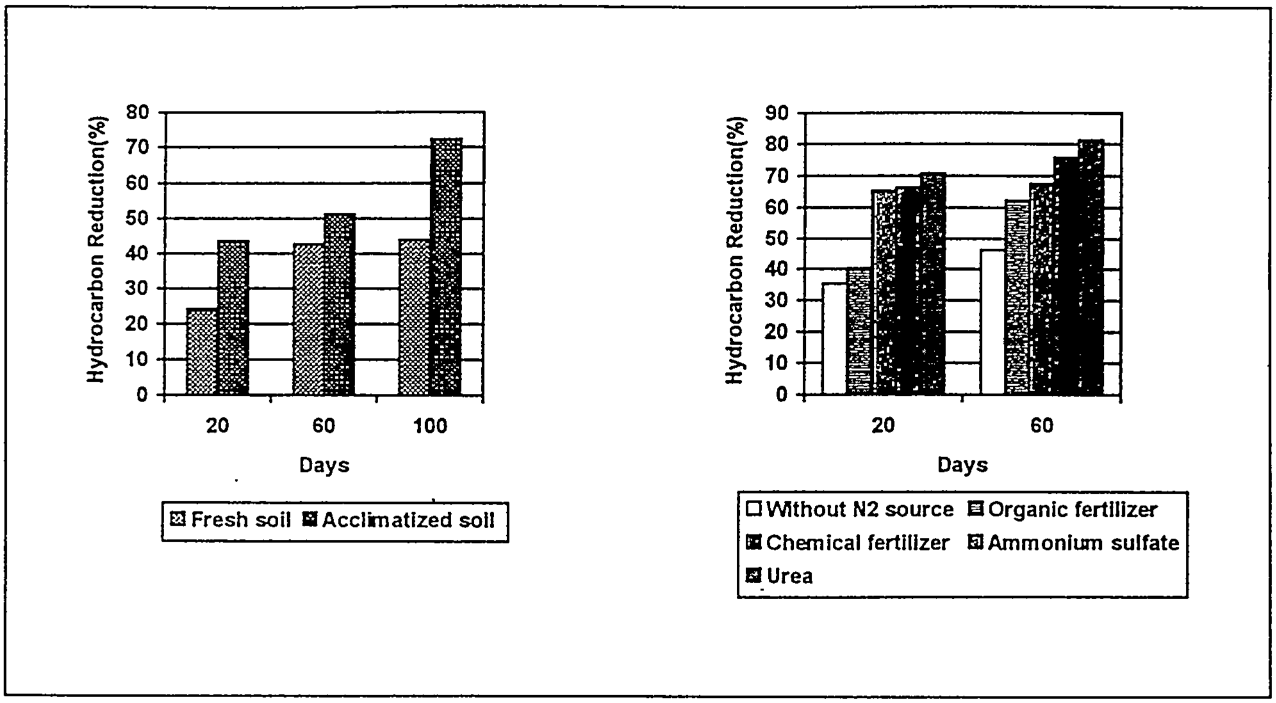
(a) (b)

Fig. 2 Time of the Microorganisms in the Soil Windrow with Various Additions of Nitrogen for (a) Hydrocarbon-Degraded Micros and (b) Total Count

an enhancement of the total count was observed and the efficiency of the hydrocarbon degradation was higher than when other nitrogen sources were added. This means that the high degradation efficiency needs the synergistic action of the HDM and the other common microorganisms. After HDM degraded complex molecules of hydrocarbon, degradation was further accelerated by the action of increasing common microorganisms. It seem that the increment of HDM in the soil windrow does not necessarily correspond to the efficiency of hydrocarbon reduction.

4 CONCLUSIONS

Microbial acclimatized soil, with high HDM, reduced hydrocarbons better than fresh soil. The addition of a nitrogen source helped to shorten the degradation from 100 days to approximately 20 days at the same percentage of hydrocarbon reduction (70%). The addition of urea in the soil windrow illustrated that the high efficiency of cutting oil degradation did not depend solely on the amount of HDM but also required action from HDM and common microbes in the soil.



(a) (b)

Fig. 3 Reduction of Hydrocarbon in the Treated Soil Windrow: (a) Fresh and Acclimatized Soil and (b) after Adding Nitrogen

5 ACKNOWLEDGMENTS

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RISK ASSESSMENT

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INTEGRATED RISK ANALYSIS OF A HEAVY-METAL-CONTAMINATED SITE IN TAIWAN

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ABSTRACT

The Love Canal episode began the long battle on hazardous wastes in the United States. Obviously, the potential danger of hazardous wastes is one of the hottest issues among environmental professionals as well as the public. The problems of hazardous wastes in economically booming Taiwan are also alarming. Several farmlands in northern Taiwan were contaminated heavily by industrial effluents containing heavy metals (cadmium and lead) in the early 1980s. Regardless of the many studies that have been conducted about these polluted farmlands, there has not been any remediation — just a passive abandonment of farming activities with minimal compensation. This paper addresses a heavy-metal-contaminated farming area. A pollution profile across time is delineated using information from the abundance of reports, and the contamination is modeled mathematically. The past, the present, and future exposures are also modeled. The results are presented in terms of societal impacts and health effects. Reasonable soil guidelines for cleanup are estimated, and recommendations for rational mitigation solutions are presented. The current strategies for cleanup actions are also described.

1 HISTORY OF CADMIUM CONTAMINATION

The Love Canal tragedy ignited a war on inactive hazardous waste sites throughout the United States. The impetus for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) in 1980 was the emerging realizations that inactive hazardous waste sites posed great risk to public health and the environment and that existing laws did not address these abandoned contaminated sites. Superfund and SARA (the Superfund Amendments and Reauthorization Act) pump enormous national resources into mitigating the problems. Obviously, the potential danger of hazardous wastes is one of the hottest issues among environmental professionals as well as the public.

The problems of hazardous wastes in economically booming Taiwan are also alarming. Among many heavily polluted lands, several farmlands in northern Taiwan were contaminated by effluents containing heavy metals from chemical plants in the early 1980s.

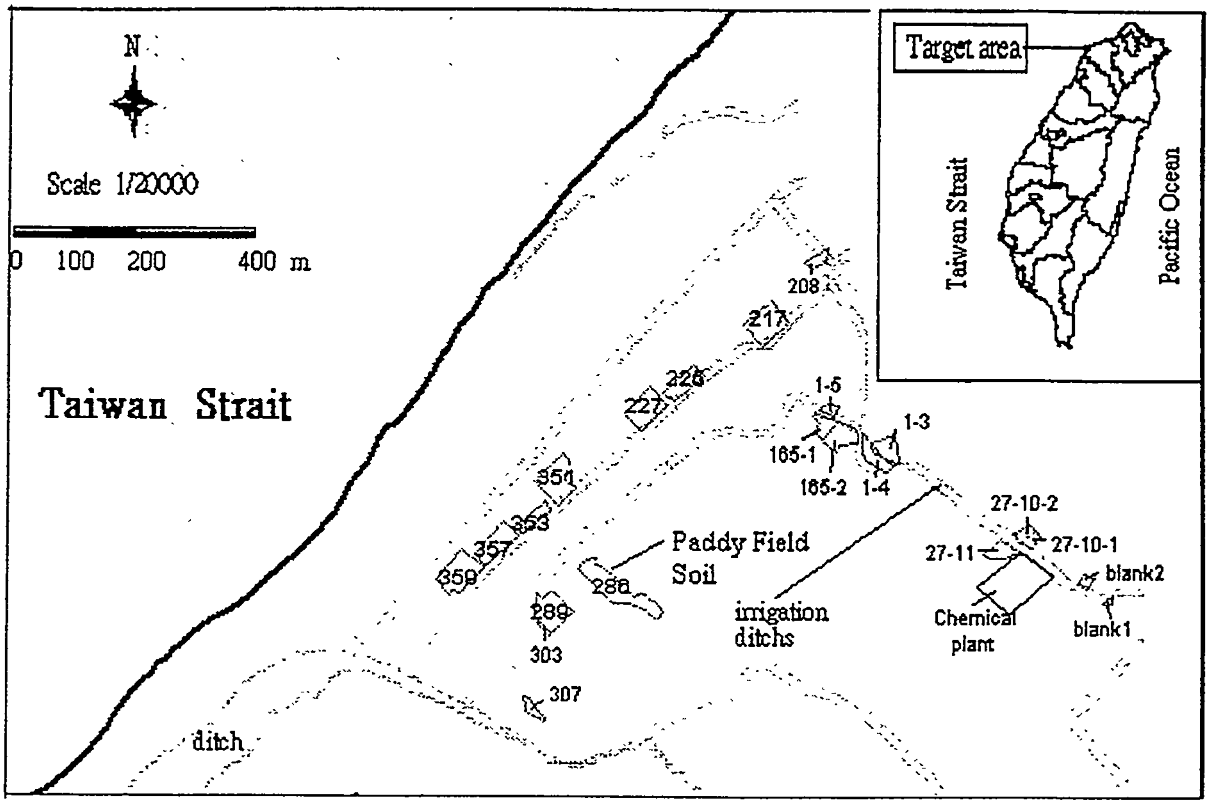


Fig. 1 Area Map of the Ta-Tan Contaminated Site

The main applications of cadmium (Cd) in Taiwan industries are for stearate in the plastic industry and for coating material in the metal-coating industry. Cadmium is imported at an annual average of 120 metric tons. The stearate manufacturing accounts for more than 90% of total consumption. Stearate is one of the major stabilizers for photolysis or thermolysis of plastic products. The waste stream from the final dehydration process of manufacturing stearate can contaminate the environment if the wastewaters are not properly treated. Because heavy metal pollution caused Itai-Itai disease in Japan in the early 1960s, the farmlands within a 1-km radius around three chemical factories in northern Taiwan were studied (Lee et al. 1982).

The contaminated site occupies an area of 17 hectares and formerly housed a chemical plant that manufactured plastic stabilizers. From 1972 to 1984, the chemical plant in Ta-Tan Village discharged wastewater containing heavy metals into irrigation ditches and caused serious pollution in surrounding rice, soil, and groundwater. The government forced the chemical plant to shut down in 1984 because it violated environmental regulations.

Table 1 1982 Measurements of Study Area[a]

Environmental Medium	Cd	Pb	No. of Samples
Ditch water (mg/L)	<0.001-50	0.001-1.31	22
Ditch sediment[b] (mg/kg)	1,306±1,509	10,861±13,940	15
Paddy field soil[c] (mg/kg)	378±216	3,145±3,692	20
Unpolished rice (mg/kg)	2.88±1.01	1.13±0.98	20
Air (μg/m^3)	0.36	N/A	

[a] Lee et al. (1982).

[b] Total sample size is 15. The statistics counted only the top sediments (0-10 cm) because of the significantly lower values (several times to one order of magnitude less) for deeper data (10-20 cm), which are available at some locations.

In 1982, the Taiwan Provincial Institute of Water Pollution Prevention examined sediments from the irrigation canals and soils from 20 lots of a polluted paddy field in Ta-Tan Village (see Fig. 1) (Lee et al. 1992). Up to 4,707 ppm of Cd and 44,427 ppm of lead (Pb) were reported in the sediments of irrigation canals; 1,319 ppm of Cd and 12,742 ppm of Pb were found in the field soil; and 5.3 ppm of Cd and 3.5 ppm of Pb were detected in the rice (Table 1). After a decade, a follow-up report still showed hundreds of parts per million of residual contaminants.

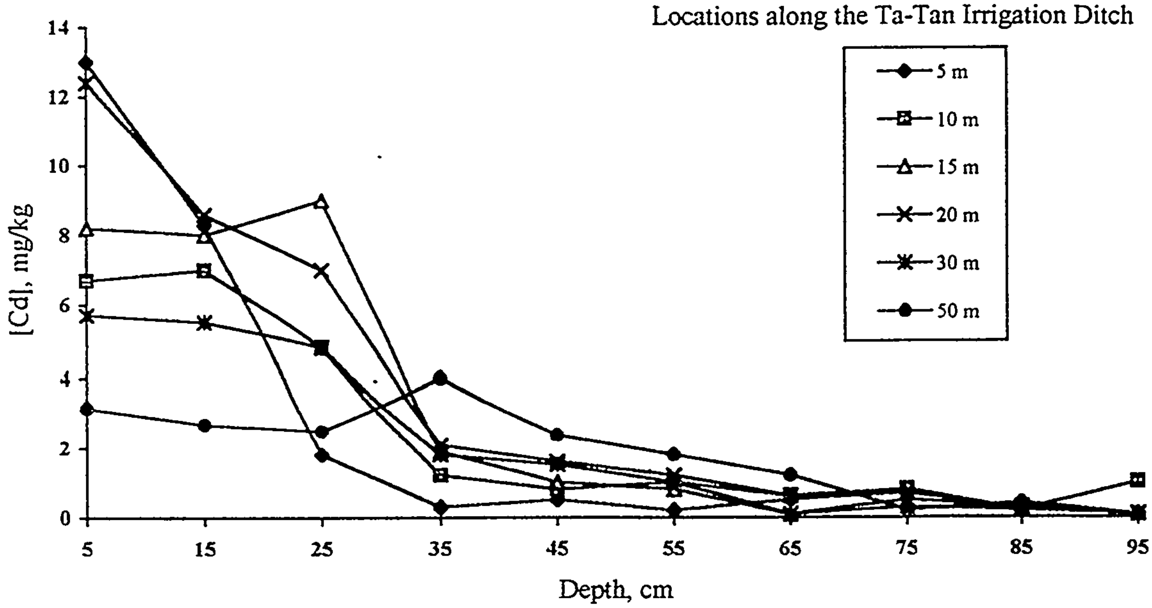
In 1988, concentration depth was profiled along a polluted ditch at paddy field soil No. 27-11. The results are shown in Fig. 2. Although a number of years had passed since the shutdown of the chemical plant, significant amounts of Cd still resided in surface soil. If 1 ppm of Cd is taken as the cutoff point for acceptable soil concentration, the contamination is confined to the top 60 cm. One can reasonably conclude that the downward movement of Cd is much slower than the horizontal spread, which may be caused by severe soil erosion and heavy runoff.

Despite the many studies of these contaminated farmlands, no remedial action has been taken. Though farming activities on these lands have been abandoned, recently approved urban planning in the area will convert the land into residential and business uses.

2 TOXICITY OF CADMIUM AND EPIDEMIOLOGIC DATA

According to the toxicity classification of the World Food and Agriculture Organization, Cd is listed in the first degree of toxicity to the environment, while Pb is listed in the second degree. Although leaching of Cd through soil is limited, plant uptake may translocate Cd into the food chain, and the

Cd may eventually be consumed by humans at the highest trophic level. This process is called bioaccumulation. Chronic poisoning symptoms can occur as a result of human ingestion. The most notorious, Itai-Itai disease, was reported in the 1960s in Japan as a result of ingestion of Cd-contaminated rice irrigated by mining wastewater (Mance 1987). Although Pb contamination in the studied area is even higher, the bioaccumulation effect (via the food chain) and toxicity of Cd are more severe.



[a] **Measurement method: soil was leached with 0.1 M HCl and measured by AAS.**
[b] **Source: Wang and Chen (1989).**

Fig. 2 1988 Soil Depth Profile of Cd along the Ta-Tan Irrigation Ditch

Although the toxic effects of Cd to human beings could affect respiration, blood circulation, and the skeletal, testicular, and nervous systems all over the body, the most critical target organ for chronic long-term exposure is the kidney (Cockerham and Shane 1994). Renal tubular epithelial cells can accumulate high concentrations of Cd (as Cd-metallothionein complexes) without showing signs of injury. The breakdown of the Cd-metallothionein complex within the cell releases Cd to sensitive sites, such as zinc-dependent enzymes, in the cell and triggers cell injury, especially in the proximal tubule cells in the mammalian kidney. The kidney will account for 30 to 50% of the whole-body Cd burden; up to 3,000 ppm of Cd in the renal cortex were reported for some occupational workers. The Itai-Itai disease discovered in Japan is the typical Cd-intoxication symptom of kidney failure.

Acute effects from ingestion of Cd are gastrointestinal effects with diarrhea and vomiting. Acute effects from inhalation are severe chemical pneumonitis. An extended time period of inhalation exposure may lead to chronic obstructive lung disease. Chronic exposure to Cd also inhibits the hydrolysis function of vitamin D, causing calcium imbalance. Due to the loss of calcium from the skeleton, the symptom of osteoporosis will emerge and leads to osteomalacia, also called "Itai-Itai disease."

An epidemiological survey showed that the urine concentration of Cd was 3.5 ± 0.33 ppb in a sample of 80 persons in the polluted area, compared to 1.0 ± 0.13 ppb for a control group of 136 persons. The polluted population also has 7.5% with renal dysfunction, compared to 2.2% in the control group (Chiu et al. 1989).

3 MATERIALS AND METHODS

3.1 Sampling Method

In 1994, samples of ditch water were collected in plastic bottles with concentrated nitric acid as a protectant. Soil samples were taken from the same 20 lots of the paddy field sampled in 1982 (see Fig. 1). Soils were sampled at various depths of 0-15 cm, 15-30 cm, 15-45 cm, and 45-60 cm at each sampling location and were preserved according to the *Methods of Soil Analysis* (Page et al. 1983).

3.2 Analytic Method

3.2.1 Water Quality

Water samples were filtered with a 0.5-µm Millipore filter and tested by atomic absorption spectrophotometry for Pb and Cd. Samples that were too dilute were concentrated first.

3.2.2 Soil Analysis

Since the 1982 study used nitric acid and the 1988 study used 0.1 N hydrochloric acid (HCl), the study in 1994 adopted these two methods to test the soils for Cd, Pb, and salt (mainly Na). For the nitric acid method, soil samples were baked dry at 110°C - 120°C; 1 g was then placed in a test tube with 3-5 mL of nitric acid. After mixing well and sitting for 20-30 min, the mixture was heated to 200°C for 4 hours. To ensure complete digestion, 2 mL of concentrated nitric acid was added drop by drop every hour. The digested solution was then emptied into a 100-mL flask. The glass wall of the test tube was rinsed with 1 N nitric acid to fill the flask up to 100 ml, and the solution was measured by atomic absorption spectrophotometry (Lee et al. 1982). For the HCl method, 10 g of soil was collected and oven-dried for 4 hours at 105°C. The sample was then placed in a 250-mL

Pyrex flask with 100 mL of 0.1 N HCl. After shaking for 1 hour at 180 rpm, the solution was filtered and measured by atomic absorption spectrophotometry (Page et al. 1983).

4 METHODOLOGIES OF RISK ASSESSMENT

4.1 Computer Simulation

RESRAD-CHEM, a version of the RESRAD computer modeling code (RESidual RADioactive material guidelines) developed by Argonne National Laboratory (ANL 1995) for the U.S. Department of Energy, is used for this chemical risk assessment. RESRAD has been applied to establish soil cleanup guidelines for many radioactively contaminated sites. RESRAD-CHEM is a modified version to accommodate the problems of toxic chemical contamination.

To evaluate existing and potential health effects, RESRAD uses two types of health indices. Cancer risks from multiple substances are estimated by direct sum of all individual cancer risks. However, in this case the cancer risk is only applicable to the inhalation pathway because risk factors of Cd for other pathways are unavailable. The inhalation risk factor of 1.8×10^{-3} per $\mu g/m^3$ is used for Cd (IRIS).

To evaluate noncancer risks, the Hazard Index is used. The Hazard Index is defined as Σ (Exposure Level/Reference Dose)$_i$, where index i is for ith toxicant, and reference doses are the lowest experimental dose level adjusted with some safety factors. The ingestion reference dose of 5×10^{-4} mg/kg/day (EPA 1984a) is used for Cd, the inhalation reference dose of 4.3×10^{-4} mg/kg/day is used for Pb (EPA 1984a,b), and the ingestion reference dose of 1.4×10^{-3} mg/kg/day is used for Pb (EPA 1986). Many environmental transport parameters were drawn from previous reports for the modeling (Table 2).

4.2 Scenario Definitions

Two potential exposure scenarios involving peasants and workers are assumed for this site-specific assessment. Several potential and realistic pathways are considered: drinking water from a nearby contaminated well and food ingestion (rice from a contaminated field, fish from a surrounding pond adjacent to and downstream of the contaminated area, and livestock raised in the contaminated area).

Scenario A assumes the presence of a resident farmer in the immediate vicinity of the site, 10% of whose drinking water is obtained from a well located at the downgradient edge of the contaminated area (90% of the water in this area is obtained from a public water supply). He ingests plant foods grown in a garden in the contaminated area and meat from livestock raised in the contaminated area.

It is also assumed that 20% of the fish consumed by the individual are caught from a pond adjacent to and downstream from the contaminated area.

Scenario B assumes industrial use of the site. A hypothetical person works in the area of the site for 8 hours per day (6 hours outdoors and 2 hours indoors), 5 days per week, 50 weeks per year. It is also assumed that the industrial worker does not ingest any drinking water, plants, or fish from the contaminated area. The primary risk to this hypothetical worker is from inhalation of contaminated dust during working hours.

Table 2 Key Environmental Parameters Used in RESRAD-CHEM Analysis

Symbols	Values	Unit	Description
ρ_s	1.6	g/cm^3	Density of saturated zone[a]
ρ_{u1}	1.53	g/cm^3	Density of top unsaturated zone (0.2 m)[a]
ρ_{u2}	1.63	g/cm^3	Density of bottom unsaturated zone (0.8 m)[a]
θ_t	0.4	--	Soil total porosity[b]
θ_e	0.3	--	Soil effective porosity[b]
K_s	5,110	m/yr	Saturated zone hydraulic conductivity[e]
K_{u1}	50.4	m/yr	Top unsaturated zone hydraulic conductivity (0.2 m)[a]
K_{u2}	28.2	m/yr	Bottom unsaturated zone hydraulic conductivity (0.8 m)[a]
S	0.1	--	Saturated zone hydraulic gradient[e]
D_{pump}	10	m	Well pump intake depth (below table)[e]
A	1.7×10^5	m^2	Area of contaminated zone[d]
t	0.1	m	Thickness of original contaminated zone
t_t	0.2	m	Thickness of top unsaturated zone[g,h]
t_b	0.6-1.0	m	Thickness of bottom unsaturated zone[g,h]
Et	0.682	--	Evapotranspiration coefficient[c]
Pr	1.875	m/yr	Precipitation[c]
R	0.3~0.9	--	Runoff coefficient (0.6 ± 50%)
$(R_d)_u$	9.86	cm^3/g	Distribution coefficient of contaminated zone
(Rd)s	25	cm^3/g	Distribution coefficient of saturated zone

[a] Chen et al. (1992).
[b] Clapp and Hornberger (1978).
[c] Central Weather Bureau (1993).
[d] Lee et al. (1982).
[e] CTCI (1989).
[f] McWorter and Sunada (1977).
[g] MOE (1992).
[h] Wu et al. (1992).

5 RESULTS AND ANALYSIS

5.1 Heavy Metal Concentrations in Soil

Due to the highly sandy soil (80%) in this area, the 1994 measurements showed that the extraction power of nitric acid on Cd is 1.38 times that of HCl. Near the seashore, the bottom soil contained 67% of the amount of Cd in the topsoil, whereas in soils away from the seashore, the bottom soil contained 21% of the amount of Cd in the topsoil. The extraction power of nitric acid on Pb is even higher, 1.86 times that of HCl. The difference between near the seashore and away from the seashore on the Pb ratios of bottom soil to top soil is even greater, 67% versus 0.08%. Such a deviation may be due to the effect of salt on the soil absorption power (Kd), because the sodium content in soil near the seashore is 217% of that away from the seashore.

5.2 Model Prediction of Heavy Metal Fate in Soil

The 1982 soil sampling results were used for the initial input into the RESRAD model, and the 1994 levels were used for verification and calibration. There are no reliable data on the runoff coefficient in this area. However, due to the high precipitation intensity in the summer season (especially during the typhoon season) and the poor coverage of the soil surface, the runoff coefficient is expected to be high. By minimizing the system error, a runoff coefficient of 0.65 was obtained for the whole area. Based on this optimum runoff, the values for Kd near the seashore were re-optimized to be 2.95 for Cd and 4.05 for Pb. Such a change in Kd could be due to a strong soil-washing effect of seawater near the seashore. The model predictions based on a runoff coefficient of 0.65 are much closer to the actual 1994 measurements due to the optimization process (see Table 3).

5.3 Risk Assessment

Because of the different Kd values near the seashore (within 300 m, about 9 hectares) and away from the seashore (600-1,000 m away, about 8 hectares), this study considered these areas as two distinct zones for risk assessment; the results are summarized in Table 4 and Fig. 3. The maximum Hazard Index (HI) near the seashore was estimated to be 490, occurring after 16-20 years had elapsed (1998-2002). The maximum HI near the seashore is clearly higher than that away from the seashore (about 100) and will occur sooner. One of the possible explanations is that the groundwater table is shallower near the seashore (0.6 to 0.8 m) than away from the seashore (1 to 1.2 m). Due to sodium's effect on the soil absorption capability, a lower Kd is also expected near the seashore. Both factors do favor Cd migration from soil into groundwater near the seashore. Higher concentrations of Cd and Pb consequently result in higher HIs near the seashore. Faster movement of groundwater (relative to the slow release mechanism for soil-bound heavy metal) near the seashore also predicts an earlier peak hazard impact than away from the seashore. The predicted cancer risks are shown in

Fig. 4; however, the relative importance of inhalation-induced cancer in the overall health effects is considerably less than the HI.

The results also showed that the critical pathway is water dependent, primarily groundwater transport. Blocking the contaminants' pathway into the groundwater is apparently the key mitigation

Table 3 RESRAD-CHEM Prediction for Heavy Metals (mg/kg) in 1994

	Cd				Pb			
	Measurement		Prediction (1994)		Measurement		Prediction (1994)	
			Inland	Seashore			Inland	Seashore
Number	1982	1994	Kd of 6.8	Kd of 2.95	1982	1994	Kd of 8.5	Kd of 4.05
27-10-1	410	45	60		806	238	172	
27-10-2	128	--	19		3,869	352	824	
27-11	93	14	14		11,762	2,157	2,505	
165-1	808	88	119		735	646	157	
165-2	530	78	78		5,176	1,291	1,102	
1-3	130	56	19		2,344	896	499	
1-4	700	158	103		12,742	2,465	2,714	
1-5	275	142	40		357	1,219	76	
286	59	48	9		737	153	157	
289	45	32	7		92	32	20	
307	5	4	1		67	20	14	
Mean(a)	289	66	43		3,517	861	749	
SD(a)	282	51	41		4,624	846	985	
208	331	5		5	4,046	44		173
217	413	5		6	2,442	156		104
303	364	5		5	1,255	55		54
351	148	17		2	2,187	35		93
353	271	15		4	1,274	141		54
357	895	24		13	3,086	191		132
359	1,319	11		19	7,079	306		302
225	44	--		--	79	--		--
227	594	--		--	2,757	--		--
Mean(b)	487	12		8	2,689	133		130
SD(b)	399	7		6	2,014	98		87
Mean(c)	378	42			3,145	578		
SD(c)	345	47			3,625	753		

[a] Average inland Cd/Pb concentration.

[b] Average Cd or Pb concentration near the seashore.

[c] Total average.

measure. Presently the government only controls "plant foods" (e.g., rice); however, the groundwater also poses a potential threat to local residents due to the partial coverage of the modern drinking water supply. Furthermore, there are still some chicken farms on the site. Poultry products are highly water dependent, as are fish from nearby ponds. The bioaccumulation effect on Cd and Pb through the meat food chain may even amplify the groundwater hazard. Although banning fisheries and increasing the supply of public drinking water are immediate actions to take, the most important mitigation is complete cleanup of the heavily contaminated soil in the area. However, because of no action from the government (local or central) since 1982, the migration of contamination continues to spread farther and farther.

Recently, this area was considered for industrial development. Still, no cleanup guideline has been established for Taiwan yet. The cleanup criteria for industrial applications are suggested by RESRAD-CHEM to be 12.5 mg/kg for Cd and 125 mg/kg for Pb (see Table 5). If this area is still confined to agricultural use in the future, the near-seashore criteria should be 1 mg/kg for Cd (3 mg/kg away from the seashore) and 20 mg/kg for Pb (35 mg/kg away from the seashore). However, the environmental report for the new industrial development for this area proposes cleanup to minimum levels of 5 mg/kg for Cd and 250 mg/kg for Pb. Therefore, the proposed soil criteria in the industrial development plan are appropriate for Cd but not for Pb based on RESRAD's recommendations. The rationale used in the development project's report directly borrows from the conclusions of studies of other areas, instead of performing a site-specific investigation. Such nonspecific application could be dangerous to engineering design, especially to the hazardous waste management aspects of the design.

Table 4 Maximum Hazard Index for Scenario A at the Site

	Away from Seashore				Near Seashore			
	Water Independent		Water Dependent		Water Independent		Water Dependent	
Pathway	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Soil	3.7	16.2			5	10.9		
Plant Foods	13.1	2.8	5.5		18.2	1.9	20	
Meat	12.1	0.2			16.9			
Fish			79	71			430	135
Water			8.5	26			40	50
Milk								
After 1982	0 yr	0 yr	45 yr	62 yr	0 yr	0 yr	16 yr	20 yr

Notes:
Water independent: hazard not resulting from groundwater.
Water dependent: hazard resulting from groundwater.

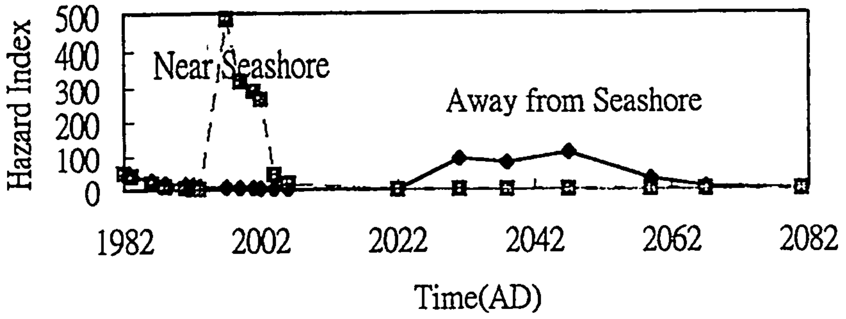


Fig. 3 Hazard Index for Farmer at the Contaminated Site (Cd + Pb)

5.4 Risk and Social Economic Impacts

Presently the only regulation for heavy-metal-contaminated food is the Food Hygiene Management Regulation (promulgated in 1975, amended in 1983). According to this regulation (Section 11), edible foods (including raw materials) containing toxic materials or any substance that could damage human health shall not be manufactured, processed, sold, stored, imported, exported, donated, or displayed publicly. The penalty for violation can be either a fine from $400 to $1,600 or up to 3 years in jail, and the violator's business license or permit will be suspended. In the past, such law enforcement was generally applied to food manufacturers and merchants only. Unfortunately, the penalties are not harsh enough to stop illegal acts among these groups.

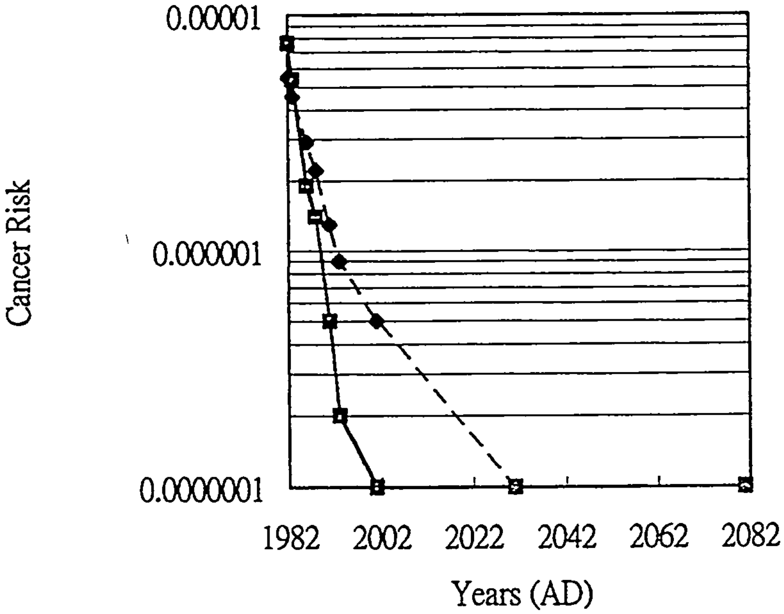


Fig. 4 Cancer Risk from Cd and Pb Contamination (mainly from dust inhalation)

Table 5 Residual Heavy Metal Concentration Guidelines (mg/kg) for the Contaminated Site Suggested by RESRAD-CHEM

Heavy Metal	Soil Location	Scenario A	Scenario B
Cd	Near seashore	1	12.5
	Away from seashore	3	12.5
Pb	Near seashore	20	125
	Away from seashore	35	125

Currently, U.S. federal agencies use a consistent numerical standard to regulate radiation. The risk to the general public is about 2×10^{-5} per year (for the detrimental effects to all generations) if one is exposed at the regulation limit of 100 mrem/yr. To be consistent with the use of HIs, the equivalent for radiation dose can be derived as follows. The no observed adverse effect level for radiation dose is on the order of 10 rem (the occupational limit is set to 5 rem). Using a safety factor of 10 for human variability and another factor of 10, the Reference Dose is the commonly adopted 100 mrem for many regulatory limits. This implies that an HI of 1 will have a risk of 2×10^{-5} if EPA regulates hazardous chemicals similarly. For known or suspected carcinogens, acceptable exposure levels are the concentration levels that represent an excess upper-bound lifetime cancer risk of 10^{-4}~10^{-6} (EPA 1990). It is the position of the U.S. Environmental Protection Agency that risk greater than 10^{-4} may call for remediation or institutional controls to restrict access to the hazardous site. The calculated peak HI then can be converted to a peak risk of 10^{-2} (HI ~ 500) away from the seashore and 2×10^{-3} (HI ~ 100) near the seashore. Compared with these figures, the cancer risks (~10^{-5}) from inhalation are at least one order of magnitude less.

The conversion from impacts to dollar amounts may be more tricky. According to the 1992 data, in United States, the comprehensive cost for one accidental death is $3,000,000 (National Safety Council, 1993). The cost includes not only economic components, but also a measure of the value of lost quality of life associated with the death, that is, what society is willing to pay to prevent it. The value of lost quality of life was obtained through empirical studies of what people actually pay to reduce their safety and health risks. The corresponding maximum cost of about $30,000 per year for the hypothetical peasant is used in modeling. Because the major contributed pathways are foods (fowl, pork, and rice), a family of four will amount to $120,000 annually. This amount is much more than the compensation received from the government or even what an average peasant family can earn in Taiwan. Regardless of whether the comprehensive costs are less than in the United States, the impacts of heavy metal pollution cannot be ignored.

The use of HI is a simplistic approach because the Reference Doses have varying precisions and may not be based on the same toxic effects. Thus, combining hazard quotients to produce an HI is likely combining different effects that have different toxicological significance. The assumption of additivity is valid only if chemicals induce the same toxic effect by the same mechanism. However, the HI approach is reasonably sufficient for screening purposes.

Presently, there is no numerical guideline in Taiwan for soil concentration of Cd (one has been awaiting approval by the Yuan Legislature for years). The current regulations for water pollution are 0.1 mg/L for effluents and 0.01 mg/L for water quality of any water body. If the aqueous concentration of 0.01 mg/L and the distribution coefficients of 10 to 25 cm^3/g are used, the acceptable residual soil concentration should be less than 1 mg/kg. These values are still far below the previous l-mg/kg cutoff point.

To deal with hazardous wastes is now a "cradle-to-grave" proposition. The technologies for hazardous waste management originate from the landfilling of solid wastes in the past. Several remediation technologies are commercially available, such as chemical treatment, soil washing, and nitrification. Their costs may range from $100 to $1,000 per ton of contaminated soil. The limitation of soil washing is that the clay content of the treated soil cannot exceed 30%. This technology apparently is not suitable for the Ta-Tan case because the soil used for rice growing is highly clayey. Vitrification can almost guarantee the effective immobilization of Cd in the soil. However, the cost can be very high, especially because utility costs in Taiwan are several times higher than in the United States. If chemical treatment is applied for the Cd-contaminated soil and the cleanup depth is 1 m, the total cost will be $272,000,000 ($\$100/\text{ton} \times 17\ \text{ha} \times 10{,}000\ \text{m}^2/\text{ha} \times 1\ \text{m} \times 1.6\ \text{tons/m}^3$). However, today's "landfill" is also modernized. Not only must the wastes be capsule sealed, but multi-liners (made of clay, HDPE, etc.) must be in place, leachates must be removed and treated, and a battery of monitoring groundwater well must be in place for compliance with current and future stringent environmental regulations. More appropriate socioeconomic cost and risk factors for Taiwan are needed to evaluate the impacts. Remediation technologies and engineering costs need to be studied for availability and feasibility.

6 SUMMARY AND CONCLUSIONS

The environmental cost accompanying the miraculous growth of Taiwan's economy is rather substantial. Although extensive efforts from academia and government have been spent studying contamination of hazardous wastes, no actual cleanup action has been taken yet. This paper focuses on an integrated approach to assess a Cd-contamination case. Many useful values from numerous previous reports and studies were used for the modeling of the farmland contamination. Exposures from the past, the present, and the future are further evaluated and simulated. Modeling results echo the findings of an epidemiological study for the local residents. Health effects are evaluated in terms of HI and cancer risk. Conversions to monetary equivalents for evaluating social and economic risks are also presented.

While a ban on agricultural activities may stop food-chain contamination, development and use of the contaminated area before proper mitigation will pose significant potential threats to public health. To avoid future exposure from the groundwater pathway, cleanup or immobilization is necessary.

Although an overall picture of heavy contamination can be drawn from this paper, the conclusions are still very preliminary. However, heavy pressure to develop this land may result in disastrous social impacts unless careful mitigation measures are taken. This preliminary site-specific study demonstrates the inappropriateness of using crude cleanup criteria from another irrelevant study area. To further perfect the modeling, time-dependent parameters are necessary for incorporation into the modeling. A detailed numerical model may help to provide better guidance to mitigate this heavily contaminated site. Better local socioeconomic cost estimates for Taiwan are needed to evaluate the impacts. Some ongoing studies are also expected to obtain up-to-date data for verifying the modeling results and completing the previous studies.

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MANAGING RISKS AND HAZARDS IN INDUSTRIAL OPERATIONS

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1 INTRODUCTION

The twentieth century has been a period of phenomenal growth worldwide. In the post-World-War-II decades, a stunning growth in size, complexity, and diversity has been experienced in all industrial manufacturing sectors — petroleum refining and petrochemicals, industrial and specialty chemicals, semiconductors and electronics — as well as in a variety of infrastructural, utility, and support industries. Industrial manufacturing areas are more widely spread, and more and more are colocated with commercial and residential areas. This rapid and complex industrial growth has been accompanied by its share of industrial accidents, which have caused deaths, injuries, property damage, and undesired releases that affect the environment. Communications and media reporting technologies have gone through their own growth and evolution, resulting in deeper and wider coverage of industrial incidents and risks. Managing the risks and hazards of industrial operations is therefore fast becoming an integral part of doing business, not only as a response to growing regulatory and public pressures but also as a means of reducing financial and legal risks.

A clear understanding of what we mean or imply by a hazard and a risk is important. A hazard can be referred to as a condition or activity that has the potential to cause adverse consequences on life, property, and the environment. Risk is the probability of the occurrence of an adverse consequence of a specified nature and magnitude resulting from a potential hazard.

In the last decade, in developing countries in the Pacific Basin, Latin America, East Europe, and other regions, industrial bases have been growing and modernizing more rapidly than what may have been experienced earlier in other nations. In some of the countries experiencing the growth, large populations and special ecosystems are close to industry and therefore vulnerable to undesired releases and accidents. In such situations, the need for effective risk and hazard management is even more crucial.

There exist grim reminders of industrial accidents (such as those in Bhopal, India; Chernobyl, Russia; and many other places) that have resulted in catastrophic proportions of deaths, injuries, property damage, and adverse effects to the environment. The long-term scars on business and society as well as subsequent legal and political impacts cannot be ignored or easily forgotten.

"Post mortems" of hundreds of accidents and analyses of lessons learned have shown that a majority of accidents are preventable and that the risks and hazards of industrial operations can be minimized, if not completely eliminated. Commitment and diligence in executing an effective risk and hazard management plan are essential to achieving risk minimization.

The primary and underlying objective of an industrial operation is to manufacture products that result in profit. Industrial operations basically handle and process raw materials and convert them to saleable products. The processing can involve purely physical or chemical changes, although a majority of operations involve both physical and chemical changes.

Obviously, the hazards and risks associated with any industrial operation depend primarily on the materials being handled or processed, processing technology, design and integrity of the industrial plant, and manner in which the plant is managed and operated. Of course, the consequence and severity of a potential hazard or an undesired incident set the relative level of risk.

For example, we recognize that the inherent risks and hazards associated with operating nuclear, toxic chemical, or liquefied natural gas plants are significantly higher than those associated with operations such as machine shaping/fabricating, material packaging, plastic extrusion/molding, bread baking, or bottling of soft drinks.

It is therefore important to note at the outset that the type and level of risk and hazard management will differ significantly with the diversity and specific nature of the operation.

The main objective of this paper is to demonstrate that it makes good business sense to identify risks and hazards of an operation and take appropriate steps to manage them effectively and meet the business objectives of the operation. Developing and implementing an effective risk and hazard management plan also contribute to other requirements and standards that are practiced by industry (e.g., ISO 14000), country-specific industrial safety and emergency response regulations, and healthy community relations.

2 DEVELOPMENT OF RISK MANAGEMENT SYSTEM

Risk and hazard identification and management are not new to industrial operations. Since the most primitive times of technical discoveries and evolution, mankind has learned to recognize the hazards and dangers of technical operations. Of course, the majority of earlier learning was accomplished as a result of mistakes and lessons learned accompanied by injuries and damage. With the phenomenal technical advances and industrial revolutions of the nineteenth century, the area of operational risk and safety had its own growth and evolution. Occupational health and safety, industrial accidents and releases, environmental impacts, emergency preparedness and response, and similar topics have been studied in great depth, regulated, and organized, and the results from these efforts have been applied extensively. There is an overwhelming amount of information, factual data, and experience available in the area of risk and hazard identification and management. The subject is highly developed, and information can be effectively applied.

The challenge has been in accepting and integrating the discipline of risk and hazard management of industrial operation as a part of good business practice. Items such as operational risks, hazards, safety, environment, etc. have been traditionally considered as purely technical and scientific support disciplines to an operation and a cost burden. The prime objective of making a profit focused on cost and financial management of the basic operation of converting raw materials to products and selling the products at a profit-making price. Risk management focused on financial and commercial aspects. Risks and hazards of the operations resulting in accidents and other consequences were treated as items covered under normal casualty insurance and a cost of doing business.

Recent experience and consequences of accidents and undesired releases and evolving regulations and public pressures are changing the way businesses are managing risks and hazards. Industry is beginning to recognize and accept the idea that the management of business as well as operational risks need to be considered to remain competitive. In addition to their main benefits of minimizing injuries, deaths, and adverse environmental impacts, industry leaders report that effective risk and hazards management plans yield the following side benefits to the operation:

- Improved productivity,
- Improved product quality,
- Improved employee team work and morale, and
- Better company image.

Development of an effective risk and hazard management system begins with fully understanding and addressing the key objectives and features of the industrial operation. The risk management program must provide effective administration and up-to-date and sound technical and business analyses and involve all plant personnel. Most important, the plan must be given priority, have the commitment of the highest level of company management, and involve leadership and stewardship. It must be a part of the company's mission, objective, policy — a way of life.

Almost all industrial operations have a system of documentation that describes the plant and its operation, maintenance, safety, emergency response, and other management and administrative procedures. The organization, format, accessibility, and maintenance vary with individual plant culture and established procedures. Often a single document consolidating the various topics does not exist in a centralized location. The nature, content, and details of the information vary with the nature, type, complexity, and size of the operation as well as company policies. However, the existing system and information are retrievable and useful in developing an effective risk and hazard management program. Experience and knowledge of the plant personnel are an invaluable supplement to the documented information.

3 KEY ELEMENTS OF A RISK MANAGEMENT PLAN

Most of the present day risk and hazard management programs are derived from industry guidelines and practices. In some instances, regulations requiring a risk management plan have adopted industry practice, logic, and experience in setting guidelines and requirements of items to be addressed. An effective program typically addresses the following elements:

- Objective and purpose,
- Employee participation,
- Process and materials safety information,
- Plant/process hazards and risk analysis,
- Operating procedures and practice,
- Employee training,
- Contractors,
- Prestartup safety review,
- Plant mechanical integrity,
- Permits for work on operational/energized systems,
- Management of change,
- Incident investigations,
- Emergency preparedness and response, and
- Self audits of risk management plans.

A useful and successful risk management plan must be:

- Accompanied by clear objectives,
- Credible,
- Simple and easy to understand and implement,
- Thorough and accurate, and
- Well-publicized and accessible.

Preparation of such a plan requires:

- A team of senior, experienced, and qualified individuals who believe in the usefulness of the plan under the leadership of a strong champion committed to the success of the plan;

- Clear and achievable objectives, scope, and budget;

- A definitive and committed schedule; and

- The commitment of resources to achieve the scope, budget, and schedule.

Figure 1 depicts the key activity path for preparing a risk management plan at an existing plant. If the plan is for a new facility, all of the elements would be developed in parallel with the detailed design, engineering, procurement, and construction phases. If the technology is being transferred from another similar plant, useful information on the existing plant can be retrieved and tailored to the needs of the new plant.

Experience in developing risk management plans has shown that the most important activity at the heart of the whole process is a thorough and objective hazard and risk identification and analysis. This element has a relationship with every element of the overall risk management plan, as shown in Figure 2.

4 HAZARDS AND RISK ANALYSIS METHODS

Eleven methods have evolved and developed for performing hazards and risk analysis, as listed below:

1. Process/system checklist (PSCL);
2. Safety review (SR);
3. Relative ranking: Dow and Mond indices (RR);
4. Preliminary hazard analysis (PHA);
5. What if analysis;
6. Hazard and operability study (HAZOP);
7. Failure modes, effects and criticality analysis (FMCA);
8. Fault tree analysis (FTA);
9. Event tree analysis (ETA);
10. Cause-consequence analysis; and
11. Human error analysis (HEA).

Methods 1 through 5 tend to be more experienced-based, qualitative, and limited in forward prediction. Methods 6 through 11 are more advanced and quantitative. The method chosen depends on the nature of the industrial operation, the local plant culture, and the desired level of quantification and prediction of risk.

Typically the petroleum, chemical, and allied industries use methods 1 through 7. The more advanced methods are used by complex operations requiring attention to a number of parallel and sequenced operations (e.g., nuclear plants, large and complicated mechanical and electronic control systems, weapon systems).

Hazard and operability studies (HAZOPs) are popular in petroleum, chemical, and allied process plants and have found increasing application in the last decade.

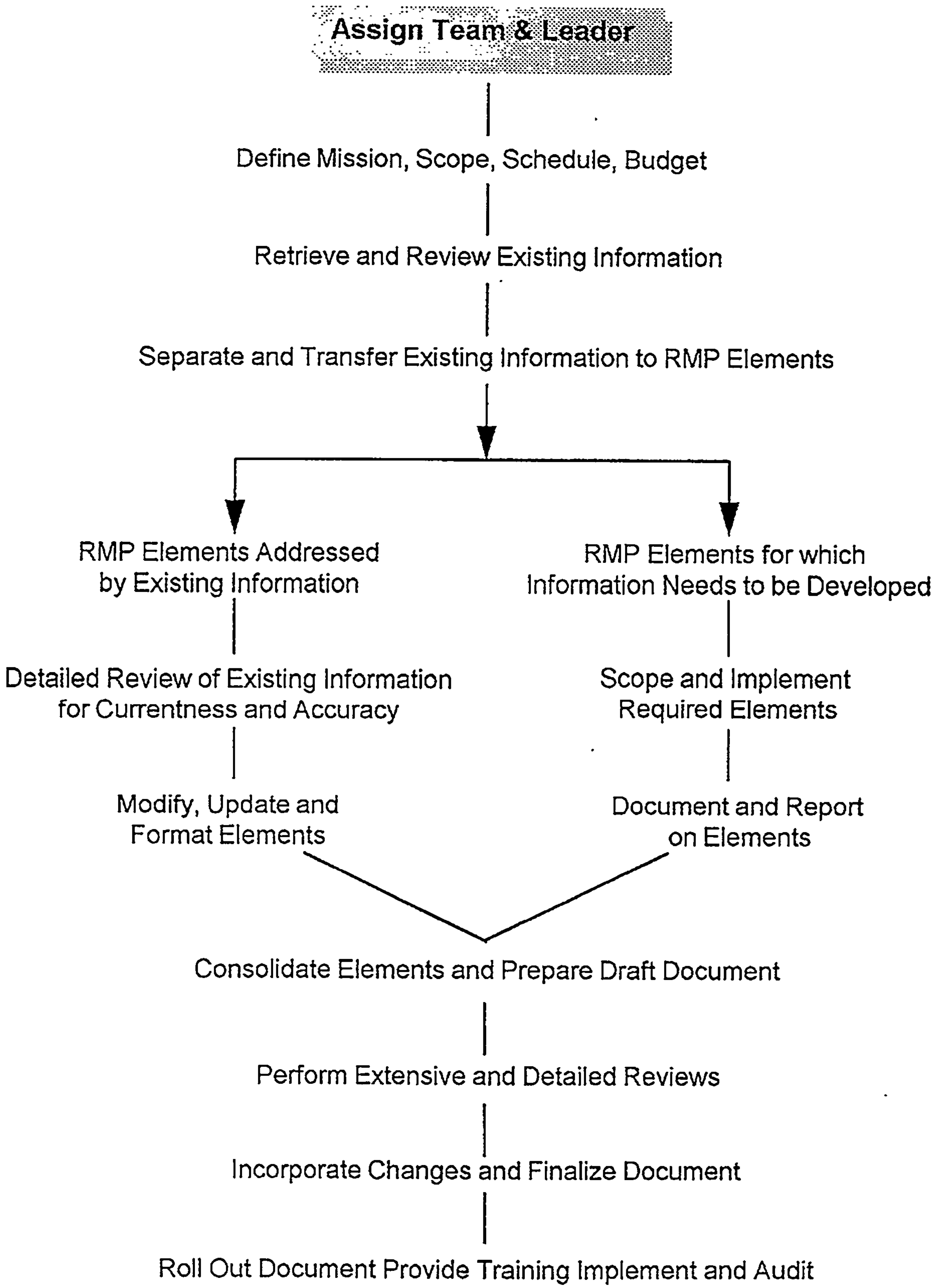

Fig. 1 Key Activity Path for Preparing a Risk Management Plan for an Existing Operation

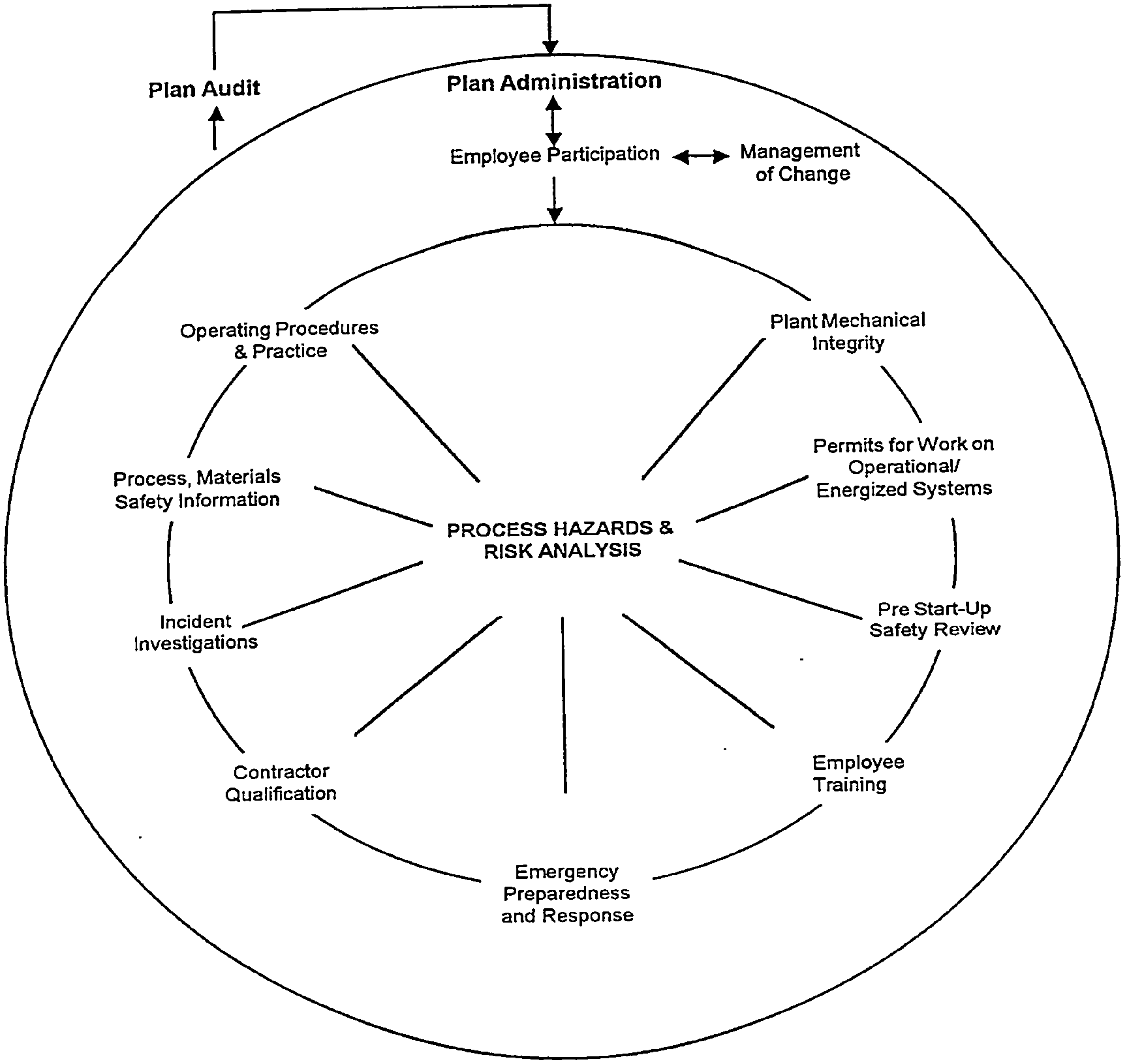

Fig. 2 Relationships of Hazard and Risk Analysis in a Risk Management Plan

Experience shows that the usefulness of a hazard analysis is independent of any of the above methods used. Of greater importance are:

- The experience and in-depth knowledge of the hazard analysis team with regard to the facility and industrial operation;
- The thoroughness used in considering and evaluating every possible deviation leading to a hazard and its cause, consequence, risk, and response/mitigation; and
- The use of a method or combinations of methods that are appropriate for the type, size, and complexity of the operation under study.

It must be emphasized that the quality of the hazard and risk evaluation is not dictated by the method but by the performing teams' depth of experience in the nature of the process, materials, engineering, construction, operations, and maintenance of the plant. Risk and hazard analysis requires experience; a forward-thinking, open mind; the ability to consider all potential hazards and risk situations; and prioritization of most risky situations that require mitigation and/or response training and preparedness.

Finally, the ability to usefully apply the findings in daily and overall business management should be the main focus.

Information from the following elements is necessary for performing a hazard and risk analysis:

- Process and materials safety,
- Operating procedures and practice,
- Plant mechanical integrity and maintenance,
- Incident history and investigation findings,
- Prestartup and safety review,
- Existing level of employee training, and
- Existing emergency preparedness and response.

The findings of the hazard and risk analysis are then useful in enhancing all of the above and developing the following elements:

- Employee participation and training,
- Contractor qualification and training,
- Management of change, and
- Emergency response.

Integration of the upgraded and developed elements provides a complete risk management plan. The next challenge is to roll out and implement the plan. This responsibility lies with the leader and the members of the risk management plan team.

5 POTENTIAL RISK VERSUS COST OF PREVENTION

The usefulness of developing and implementing a risk management plan is best illustrated by examples. Table 1 shows a simple way of examining a potential risk versus the cost of preventive action. Although financial consequences can be weighed against the cost of prevention, a consideration of personnel evacuation, injury, and/or death requires astute judgment and evaluation in determining risks and implementing corrective actions. Low-consequence, high-frequency risks must be weighed against high-consequence, low-frequency risks. An example of the latter would be the incident in Bhopal, India.

The low-probability, high-consequence event did occur only once in the history of similar plants. However, the number of deaths and negative impact on the industry can never be erased from history. In hindsight, no effort should have been spared in evaluating every potential event, however insignificant or infrequent it may have appeared.

6 CONCLUSIONS

The cost of developing and preparing the first risk management plan typically varies from $50,000 to $200,000, depending on the accuracy and level of information available and the size, complexity, consequence, and frequency of potential hazards.

A risk management plan enables the analysis of potential hazards, as shown in Table 1. The next step would be a prioritization of the high-risk situations that can impact the operation of the plant as well as the overall company business. Integrating the financial risks of operations into the overall business risks seems logical and essential in today's management. At the operational level, management can review the benefits of corrective actions against the potential financial and business risks and act to prevent and minimize risks — a form of added insurance.

In almost every case, performing a thorough hazard analysis identifies potential hazards and risks as well as their penalties and adverse impacts. From that knowledge, management can evaluate the integrated business risk of that operation and implement preventive steps for added insurance of safety. It also enables a business to prepare and train for response to unanticipated incidents and accidents.

Table 1 Example Risk Findings — Typical Situations from Different Plants

	Potential Hazard	Consequence or Incident	Potential Financial Loss	Occurrence Probability[a]	Potential Financial Risk	Estimated Cost for Preventive Action
1.	Vessel pressure buildup and safety valve failure in hydrocarbon service	Vessel rupture explosion	$2.0 million	0.082 in two years	$164,000 once every two years	$80,000 (one time)
2.	Breakage of monel metal hose in chlorine unloading	Chlorine release to atmosphere requiring personnel evaluation; loss of production	$80,000	0.05 in 3 years	$4,000 once every 3 years	$10,000 (one time)
3.	Maloperation of toxic chemical system	Spill of toxic chemicals; atmospheric release causing injury/death	$30 million not including legal and compensatory damages	0.01 in 10 years	$300,000 once in 10 years; will be much higher if legal and compensatory damages are included	$100,000 (one time)

[a] Occurrence probabilities are based on nonpublished information on experience.

Developing, implementing, monitoring, and continually upgrading a practical risk management plan are fast becoming a necessary part of running an industrial operation. It is never too late to start.

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A PILOT EXERCISE ON COMPARATIVE RISK ASSESSMENT IN MEXICO

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ABSTRACT

Concern in the Mexican government and academic institutions about human health problems derived from exposure to environmental contaminants has been increasing. This interest prompted us to perform a pilot study to identify and rank potentially problematic environmental situations. We were given access to files from the Instituto Nacional de Ecologia. We screened about 2,500 documents and selected about 200 reports for further analysis. We adapted methodologies developed by the U.S. Environmental Protection Agency (EPA 1993) and ATSDR (1992) to analyze environmental data.

San Luis Potosi City and Region Lagunera were the areas posing greater risks. We chose San Luis Potosi City to perform a more detailed study, since here a smelting complex is located within an urban zone. The high levels of As, Pb, and Cd in environmental media resulted in a higher body burden in exposed children than children living 7 km away. Multiple regression analysis suggested that alterations in sensorial nerve transmission were mainly related to As in urine (AsU), whereas those in motor nerves were mainly related to Pb in blood (PbB). No apparent relationships associated with CdU were found. Slower auditory nerve conduction was associated with both AsU and PbB.

These findings suggest that exposed children are also at high risk of suffering other adverse health effects. This exercise illustrates the need to perform studies aimed at identifying and ranking environmental contamination problems in industrializing countries.

1 INTRODUCTION

Human health risk assessment has been defined as an evaluation of the toxic properties of a chemical and human exposure to (1) ascertain the likelihood that exposed humans will be adversely affected and (2) characterize the nature of the effects they may experience (NAS 1983). Comparative risk analysis involves an additional component to risk assessments; it entails comparing risks across problem areas to arrive at a relative ranking of the human health risks posed by the various problem areas. Comparative risk methodologies are appealing management tools that could help government officials systematically measure, compare, and rank environmental problems, thereby providing important input for the priority-setting process.

There is increasing concern in the Mexican government and academic institutions about human health problems derived from exposure to environmental contaminants. However, experience in applying risk assessment methodologies in Mexico is limited. This interest prompted us to perform a pilot study to identify and rank situations that are, or may become, a threat to human health, with the purpose of planning further studies in selected populations.

2 METHODOLOGY

We were given access to files from the Instituto Nacional de Ecologia to collect and analyze environmental data. The initial screening comprised about 2,500 documents, from which about 200 reports were selected for further analysis. Information chosen included studies performed from 1980 to date containing data on concentrations of environmental contaminants, biological monitoring, or health effects. Information about Mexico City was excluded because authorities considered it to be a zone with special characteristics.

In the first stage of this project, we reviewed methodologies for comparing risks and setting environmental priorities developed by the EPA (1993) and ATSDR (1992). We developed questionnaires to record information on the area's physical, geographical, and operational setting and basic information on contaminants present in the area.

On the basis of information sufficiency, 15 studies were selected to assess exposure and characterize risks. A system based on four ranking indicators was used to assess the severity of the problem:

- The number of people potentially exposed was determined.
- Contamination severity was assessed by dividing the ratio concentration in environmental media by the maximum allowable concentration (contamination/MAC).

- Risks posed by noncarcinogens were characterized by using the individual exposure ratio (IER), that is, the ratio of estimated environmental dose (EED) to reference dose (RfD).

- Individual cancer risk (ICR) was calculated by multiplying the carcinogenic potency of the agent by the dose to the exposed individual (EED).

Other characteristics studied were the main contaminated environmental media, main contaminants in each medium, weight of evidence for carcinogenicity, availability of local information on health effects, and anthropogenic or natural sources of pollution (Table 1). No attempt was made to rank the severity of health effects, since severity scales developed emphasize different factors and there is no universally accepted approach.

3 RESULTS AND DISCUSSION

3.1 Information Quality

There was limited information on the concentrations of environmental contaminants in environmental media. Most of the documents available (about 90%) contained information only about the physicochemical parameters of superficial and deep waters. Of the remaining 10%, only a few have been published in periodic journals and even fewer gave indication of having adhered to quality assurance/quality control (QA/QC) practices. No information pertaining to adverse health effects was available. There is an obvious need for studies offering a broader picture of the status of the environment in Mexico.

3.2 Ranking

According to the number of people potentially exposed, the more serious situations would be in Region Lagunera, San Luis Potosi, Valle de Culiacan, Sin., and Aguascalientes (Table 1). However, small populations (fewer than 1,000 inhabitants) were found to suffer from serious health effects derived from contaminant exposure. Contamination severity (contamination/MAC) was greater in Morales, S.L.P., Tultitlan, San Luis Potosi, and Valle de Culiacan, Sin. The risk of systemic effects (EED/RfD) was greater in San Luis Potosi, El Salvador de Arriba, Coah., Region Lagunera, and Tultitlan. The risk of having cancer (potency × EED) was greater in Region Lagunera, El Salvador de Arriba, Coah., Valle del Guadiana, Dgo, and Morales, S.L.P. The main contaminants found in the 15 locations were arsenic, lead, chromium, endrin, and fluoride. Except by Region Lagunera, where aquifers are naturally contaminated by arsenic, the more problematic environmental situations were of anthropogenic origin.

Table 1 Pilot Exercise on Comparative Risk Assessment in Mexico[a]

			Contamination				System Toxicity		Carcinogenic Effects		
Area	Population	P	MC	CONC/MAC	P	MCM	IER	P	ICR	P	∑ Ranks
San Luis Potosi, S.L.P.	489,238	2	As	64.45	3	Soil	62.6	1	7.7×10^{-4}	5	11
Comarca Lagunera	1,016,000	1	As	8.47	6	DW	30, 42	3	4.7×10^{-2}	1	11
Tultitlan, Edo. de Mex.	246.464	4	Cr	69.05	2	Soil	28.13	4	--	b	16
Valle de Culiacan, Sin.	465,000	3	Endrin	55.15	4	SW	14.66	6	--	b	19
Morales, S.L.P.	25,000	11	As	810.4	1	Soil	13.28	7	7.1×10^{-4}	4	23
El Salvador de Arriba, Coah.	998	15	As	41.00	5	DW	32.8	2	5.7×10^{-2}	2	24
La Piedad, Mich.	34,963	9	F	7.70	7	DW	15.33	5	--	b	27
Valle de Guadiana, Dgo.	15,054	13	F	4.76	9	DW	7.79	8	2.0×10^{-3}	3	33
Aguascalientes, Ags.	181,277	5	F	2.00	12	DW	3.8	11	--	b	34
Lagos de Moreno, Jal.	33,762	10	F	2.53	10	SW	5.06	9	--	b	35
Hidalgo y Zinapecuaro, Mich.	61,878	8	B	6.07	8	DW	3.77	13	--	b	35
Soledad de Diaz Gutierres, S.L.P.	132,979	6	F	1.90	13	DW	3.8	12	--	b	37
Santiago, Ixcuintla, Nay.	17,321	12	F	2.26	11	SW	4.53	10	--	b	39
Ensenada, B.C.N.	77,687	7	F	1.26	15	DW	2.53	15	--	b	43
Rio Grande, Zac.	11,651	14	F	1.30	14	DW	2.66	14	--	b	48

[a] P = priority; MC = main contaminant; MCM = main contaminant media; SW = superficial water; and DW = deep water.

[b] For calculations, six points were added to noncarcinogenic substances.

3.3 Greater Risks for Human Health

The results showed that contamination in San Luis Potosi and Region Lagunera were posing the greater risks for human health. Previous studies have shown that aquifers in Region Lagunera, located in the central part of northern Mexico, have very high concentrations of arsenic and fluoride because of natural contamination, and serious health effects attributed to As exposure have been described. Those effects include cutaneous manifestations (skin pigmentation changes, keratosis, and skin cancer), gastrointestinal disturbances, alterations in the heme metabolism pathway, and genotoxic effects (Cebrian et al. 1994).

3.4 San Luis Potosi

We chose this city, located in the central part of Mexico, to perform a more detailed study, because here a smelting complex consisting of a copper smelter and a zinc electrolytic refinery is located within an urban zone. The metropolitan zone has 600,000 inhabitants. Its main economic activities are related to metallurgy and the smelting industry. The annual capacity (1990) of the complex is about 90,000 tons of copper, 16,800 tons of lead by-products, and 8,500 tons of arsenic trioxide. The zinc refinery and its cadmium-smelting plant have an annual capacity of 90,000 tons of zinc, 600 tons of cadmium, and 140,000 tons of sulfuric acid. The characteristics of contamination produced by smelters suggested that children were at high risk of being exposed. Earlier studies suggested that children in Morales have absorbed considerable quantities of arsenic (Diaz-Barriga et al. 1993).

3.5 Environmental Contamination and Neurological Alterations

In the second stage, we assessed environmental contamination by As, Pb, and Cd; the body burden of these elements; and the presence of neurological alterations in children living in a smelter community. The study was undertaken in two urban zones of San Luis Potosi: Morales, close to the smelter complex, and Gral. I. Martinez, 7 km away from the complex. The As levels in soil (124-5,000 μg/g), house dust (259-9,120 μg/g), and air (0.2-3.9 $\mu g/m^3$) and the Pb levels in soil (106-3,356 μg/g), house dust (255-7,200 μg/g), and air (0.02-3.60 $\mu g/m^3$) were higher in Morales than in the control area. Similar findings were observed regarding Cd. Ingestion of contaminated soil and food and inhalation of contaminated air were considered relevant exposure pathways. The range of As levels (20-272 μg/L) in urine (AsU) and Pb (6-27 μg/dL) in blood (PbB) indicated that environmental exposure increased the body burden of these elements in the exposed children. Multiple regression analysis suggested that alterations in sensorial nerve transmission were mainly related to AsU, whereas those in motor nerves were mainly related to PbB. No apparent relationships were found with CdU. Slowing in auditory nerve conduction was significantly associated with both AsU and PbB. The relative contributions of As, Pb, and other elements to the presence of neurological alterations remain to be ascertained. These findings also suggests that exposed children are at high risk of suffering adverse health effects other than neurological alterations, since the literature suggests that cardiovascular and pulmonary systems are early targets for arsenic toxicity.

The results showed the usefulness of the ranking system described here as a rapid screening method, since it was able to distinguish between a variety of environmental situations. This exercise also illustrates the need to perform studies aimed at identifying and ranking environmental contamination problems in industrializing countries.

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EXPOSURE TO METHYL *TERT*-BUTYL ETHER, BENZENE, AND TOTAL HYDROCARBONS AT THE SINGAPORE-MALAYSIA CAUSEWAY IMMIGRATION CHECKPOINT

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ABSTRACT

The primary aim of this study was to determine the extent and levels of exposure to volatile organic compounds (VOCs) from automobile emissions in a group of immigration officers at a busy cross-border checkpoint. A majority (80%) of the workers monitored were exposed to benzene at levels between 0.01 and 0.5 ppm, with only 1.2% exceeding the current Occupational Safety and Health Administration occupational exposure limit of 1 ppm. The geometric mean (GM) concentrations of 8-hr time-weighted average exposure were 0.03 ppm, 0.9 ppm, and 2.46 ppm for methyl-*tert*-butyl ether (MTBE), benzene, and total hydrocarbons (THC), respectively. The highest time-weighted average concentrations measured were 1.05 ppm for MTBE, 2.01 ppm for benzene, and 34 ppm for THC. It was found that motorbikes emitted a more significant amount of pollutants compared with motor cars. On average, officers at the motorcycle booths were exposed to four to five times higher levels of VOCs (GMs of 0.07 ppm, 0.23 ppm, and 4.7 ppm for MTBE, benzene, and THC) than their counterparts at the motor car booths (GMs of 0.01 ppm, 0.05 ppm, and 1.5 ppm). The airborne concentrations of all three pollutants correlated with the flow of vehicle traffic. Close correlations were also noted for the concentrations in ambient air for the three pollutants measured. Benzene and MTBE had a correlation coefficient of 0.97. The overall findings showed that the concentrations of various VOCs were closely related to the traffic density, suggesting that they were from a common source, such as exhaust emissions from the vehicles. The results also indicated that although benzene, MTBE, and THC are known to be volatile, a significant amount could still be detected in the ambient environment, thus contributing to our exposure to these compounds.

1 INTRODUCTION

As lead is gradually phased out of motor vehicle fuels, methyl-*tert*-butyl ether (MTBE), an oxygenate, is gaining acceptance as an octane booster in gasoline. It is also added in gasoline to promote more complete fuel combustion, thereby reducing tailgate carbon monoxide emissions (EPA, 1993). The exposure to MTBE is widespread; it is estimated that over 100 million people are exposed to MTBE and its combustion products. Although there have been several reports of health complaints among residents in cities where MTBE is used in gasoline, few exposure and toxicological studies have been conducted on this compound (Belpoggi et al., 1995). There is no recommended exposure limit for MTBE by the Occupational Safety and Health Administration and the National Institute of Occupational Safety and Health. The U.S. Environmental Protection Agency has classified MTBE as a "possible carcinogen" (EPA, 1993). Currently, most of the gasoline sold in Singapore and Malaysia contains about 1 to 5% MTBE (v/v). Benzene (BZ) is another component in gasoline, normally at levels between 2 and 5%. The International Agency for Cancer Research has classified BZ as a human leukemic agent (IARC, 1982). Despite numerous epidemiological reports on its health hazards, relatively few studies have been carried out to measure the concentrations of BZ in relation to its emissions from vehicle exhaust. Owing to the toxicological relevance of these two compounds as well as the extensiveness of their use, more information on exposure to these compounds is obviously needed. With the increased use of unleaded petrol due to the engine exhaust requirements of new vehicles, there is also growing concern about the effects of the higher BZ content and the presence of MTBE in unleaded petrol on the environment and human health.

The primary aim of the present study is to determine the extent and levels of exposure to automobile emissions in a group of immigration officers at a busy cross-border checkpoint. Particular attention was paid to the environmental concentrations of MTBE, BZ, and total hydrocarbons (THC). The checkpoint studied is located at the northern part of Singapore. It is a relatively well-ventilated open station with one end facing the sea. On average this checkpoint handles about 60,000 vehicles (about 203,000 passengers) per day, with an estimated inspection time of 1.2 min per vehicle. Due to the high traffic volume, peak-hour traffic jams and long queues are twice-daily occurrences. The large number of stationary and slow-moving vehicles results in poor dispersion of exhaust emissions. Over 80 full-time staff (25% of the total workforce) working on different shifts were selected for this study. Environmental monitoring was carried out from September 1995 to February 1996.

2 MATERIALS AND METHODS

2.1 Sampling

A total of 87 area samples were collected between September 1995 and February 1996 at the Immigration Checkpoint. The samples were collected during both peak and off-peak periods, following the duty and shift roster of a particular team of immigration staff. Area samples were collected from motorcar lanes, motorcycle lanes, and lanes handling both motorcycles and motorcars. Both arrival and departure sides of the checkpoint were monitored. All sampling durations followed the shift durations. The length of the morning and afternoon shifts was 7 hours, while the night shift was 10 hours long.

2.2 Procedure for Area Sampling

Area sampling was performed using personal pumps (MSA C-120 and MSA high-flow pumps) and charcoal absorbent tubes. The pumps were calibrated and set to a suitable flow rate for optimum sampling using the gas bubble flowmeter and the MSA Auto Calibrator. The pump and charcoal tube assembly was placed inside the counter, with the charcoal tube positioned at a small opening on the glass panel. This opening is used by the immigration officers to communicate with the passport holders and is at approximately mouth level of the officer working inside the counter. The time of the sampling was recorded. A new charcoal tube broken at the sampling environment was analyzed as a sample blank to check for background correction.

2.3 Preparation of Charcoal Tube Samples

Due to the large number of samples and long analysis time (25 min), the charcoal in both the front and back sections was analyzed together. The retaining clips and plugs in the charcoal tubes were removed using a puller wire, and the contents of the tube were emptied into a 2-mL vial. One milliliter of chromatographic-grade CS_2 was added to the vial, which was capped immediately and then agitated with a vortex mixer and left to stand for 30 min. Desorbed samples required for repeat analysis were sealed in an airtight container and stored at 4°C for a maximum of 3 days.

2.4 Sample Storage and Analysis

The collected samples were sealed and stored at -20°C until analysis. Samples were analyzed with an HP 5890A gas chromatograph equipped with a FID detector using helium as the carrier gas. The column used for the analysis was WCOT (50 m × 0.26 mm × 0.25 μm) fused silica with stationary phase CP-Select CB for MTBE. The temperature program was set at 35°C for 5 min before heating at a rate of 4°C/min to 130°C and then holding for 1.5 min.

2.5 Detection Limit

The detection limits were 0.75 μg (3 ppb) and 0.22 μg (1 ppb) for MTBE and BZ, respectively.

3 RESULTS AND DISCUSSION

3.1 Comparison between Shifts

The highest MTBE, BZ, and THC exposure levels were recorded during the afternoon shift, whereas the night shift had the lowest levels (Fig. 1). Emissions of MTBE, BZ, and THC were all found to be significantly higher for the motorbike lanes as compared with the motorcar lanes (Fig. 2).

3.2 Comparison between Weekdays and Weekends

Benzene and MTBE exposure levels for motorcar lanes showed no significant differences when weekends and weekdays were compared (Fig. 3). In contrast, the MTBE, BZ, and THC exposure levels for motorcycle lanes were significantly higher on weekdays (Fig. 4).

3.3 Correlations between MTBE and BZ

There is strong correlation between BZ and MTBE levels at the checkpoint for all vehicles (r = 0.977), for cars only (r = 0.956), and for motorcycles only (r = 0.978) (Fig. 5).

3.4 Comparison between Vehicle Types

The frequency curves for BZ, MTBE, and THC show that motorcar lanes have lower levels of airborne unburned hydrocarbons than do motorcycle lanes (Fig. 6). It is also clear from Fig. 1 that the MTBE and BZ emissions levels are significantly higher in motorcycle lanes.

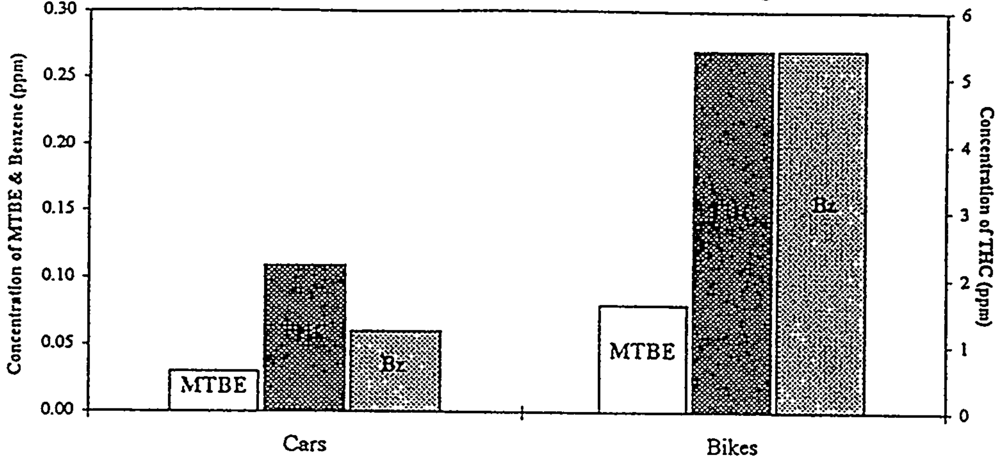


Figure 1a. Concentration of MTBE, Benzene and THC, Morning Shift

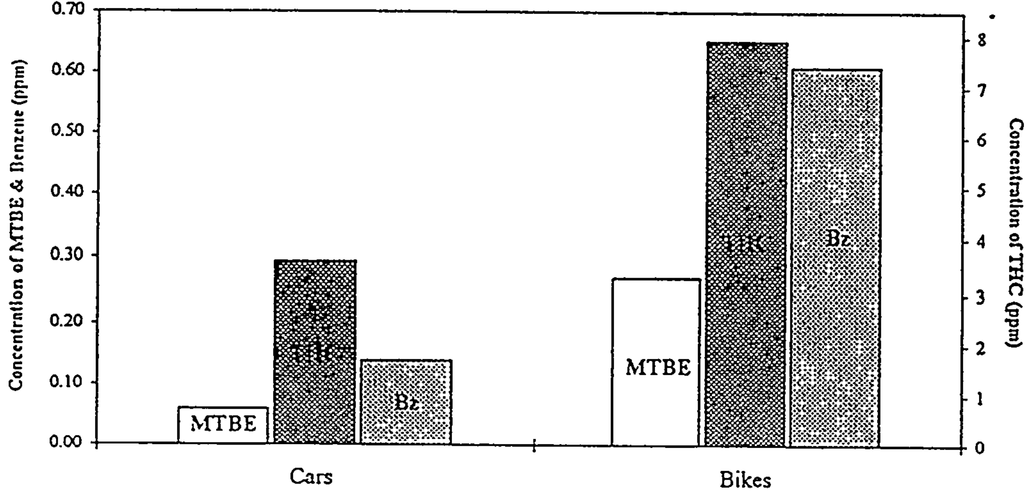


Figure 1b. Concentration of MTBE, Benzene and THC, Afternoon Shift

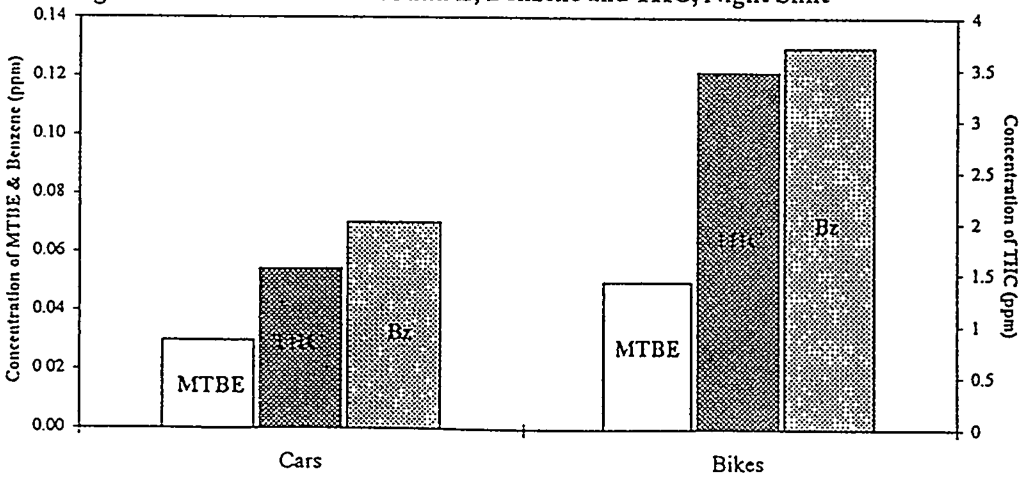


Figure 1c. Concentration of MTBE, Benzene and THC, Night Shift

Figure 2. Concentrations of MTBE and Benzene at Different Workshifts

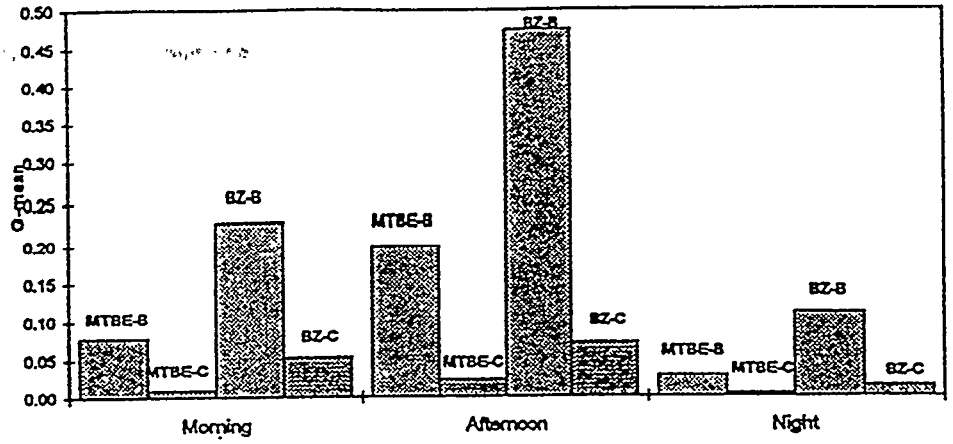


Figure 3. Concentrations of Benzene, MTBE and THC for Cars

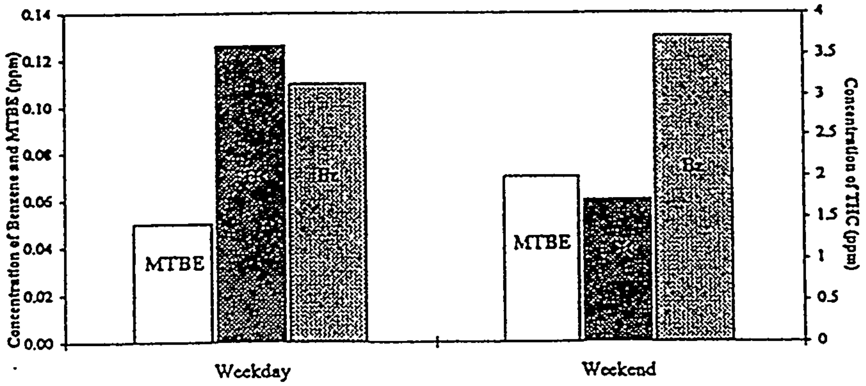


Figure 4. Concentrations of Benzene, MTBE and THC for Bikes

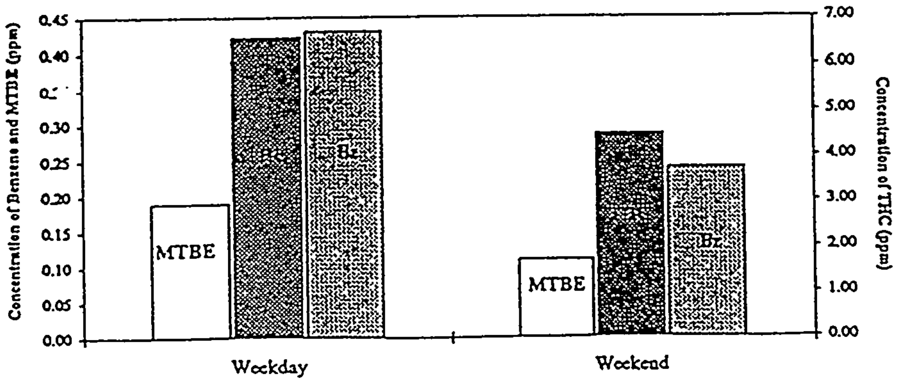


Figure 5a. Correlation Graph of Benzene and MTBE for All Vehicles

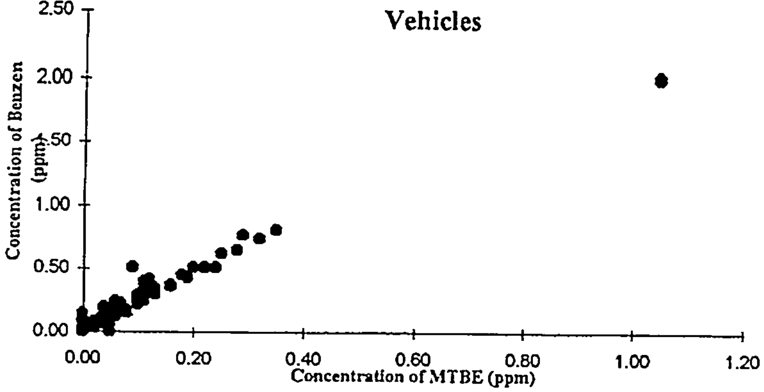


Figure 5b. Correlation Graph of Benzene and MTBE for Cars

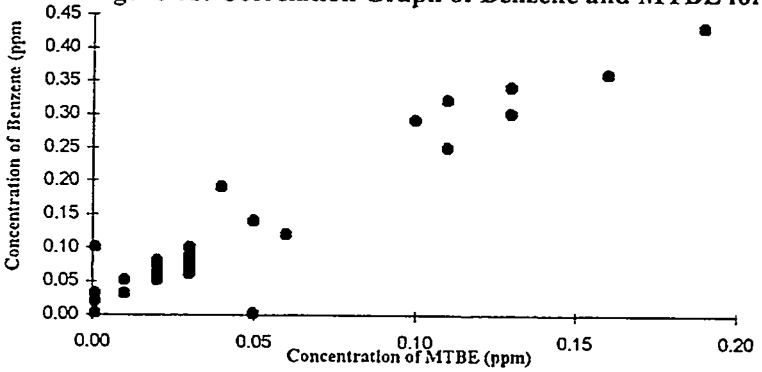


Figure 5c. Correlation Graph of Benzene and MTBE for Bikes

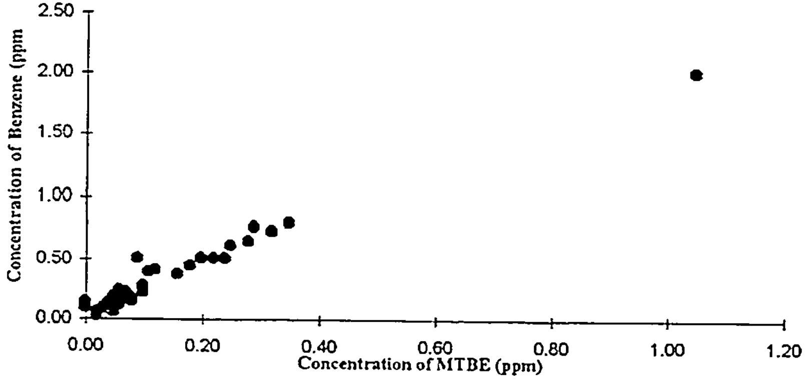


Figure 6a. Cumulative Percentage Curve for MTBE

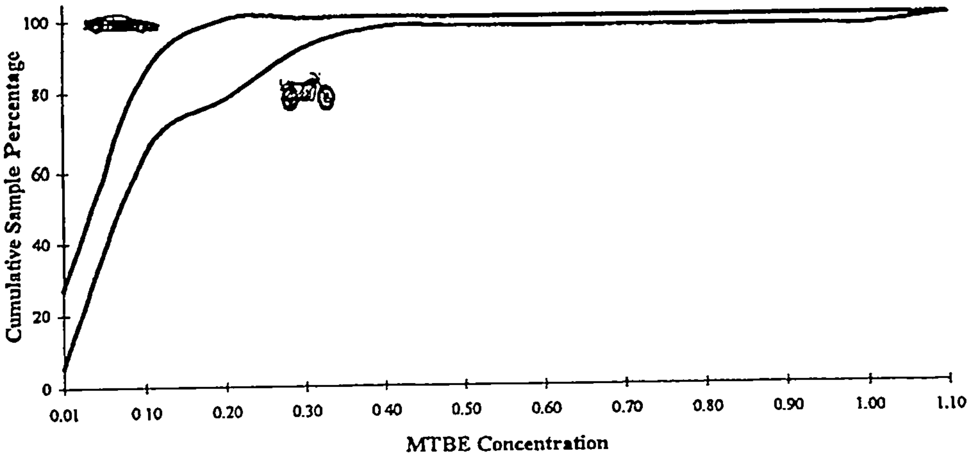


Figure 6b. Cumulative Percentage Curve for Benzene

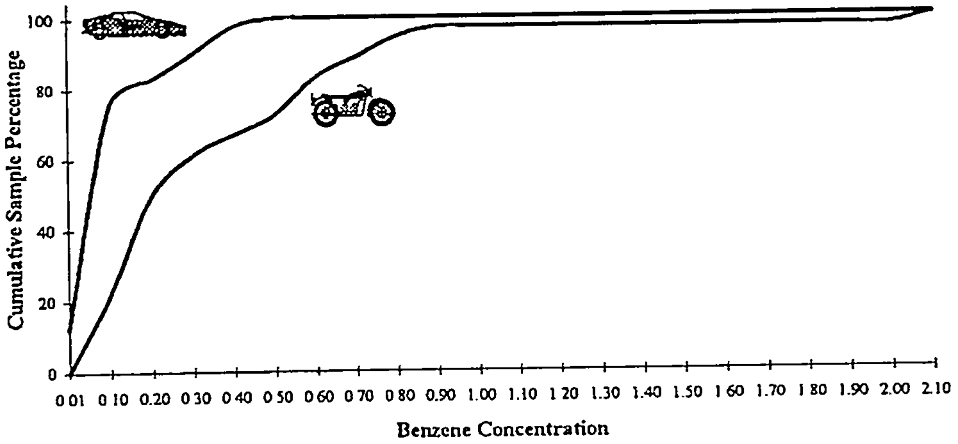
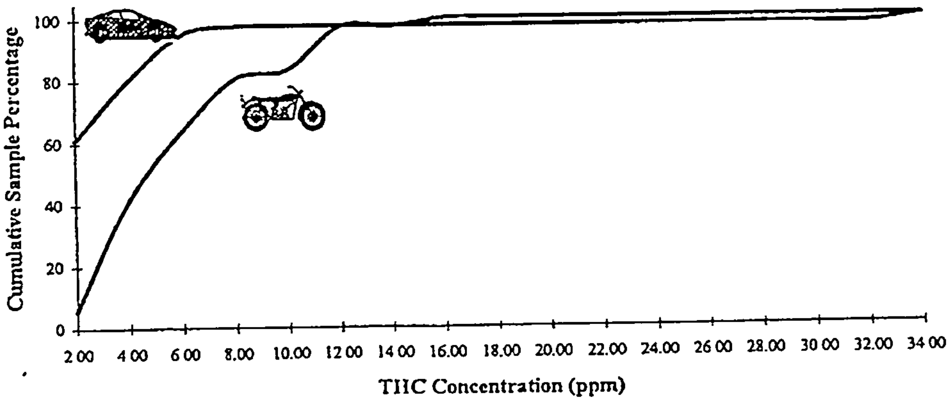


Figure 6c. Cumulative Percentage Curve for THC



Statistics from the Immigration Department put the average daily number of passenger vehicle arrivals at close to 30,000, with half of this number being motorcycles. An equal number of passenger vehicles also depart Singapore daily. Because the bulk of these vehicles belong to Malaysians working in Singapore, many vehicles pass through the checkpoint in the morning (arrival) and evening (departure) peak periods. The morning peak period is from 6 am to 9 am and falls between the night and morning shifts. The evening peak period starts after 5:30 pm, easing only after 8 pm. This coincides solely with the afternoon shift.

To ease the severe congestion during the morning peak hour, a "mini-checkpoint" was built to cater to motorcycle arrivals, thus easing the congestion of motorcycle lanes at the main checkpoint building. However, the same could not be done for the departure section due to land constraints. Because most of the sampling was performed at the main checkpoint building, a lower hydrocarbon pollution level was recorded during the morning peak period (night and morning shifts) compared with the evening peak period (afternoon shift), for motorcycle lanes.

Throughout the morning (8 am - 3 pm) and afternoon shifts (3 pm - 10 pm), there is a constant flow of vehicles in both the arrival and departure sections of the checkpoint. During the night shift (10 pm - 8 am), however, the traffic passing through the arrival and departure sections is relatively light. This, coupled with the fact that the evening peak period lies only within the afternoon shift (unlike the morning peak period, which is shared between the tail end of the night shift and the start of the morning shift), may explain the observation that the airborne hydrocarbon levels are highest during the afternoon shift and lowest during the night shift.

Saturdays and Sundays are considered "weekends," while Mondays to Fridays are considered "weekdays." The vehicles passing through the checkpoint on weekends (especially Sundays) are largely made up of motorcars traveling for leisure purposes, such as family outings to Johore Bahru and Malaysians visiting Singapore. Because these trips are mostly for the weekend only, most of these vehicles will have to make a return trip back to either Singapore or Johore. This accounts for the heavy motorcar traffic throughout the weekend. The results support this assumption, as the MTBE and BZ levels in the motorcar lanes show insignificant changes when comparing weekends and weekdays. Since there are less workers traveling to Singapore on weekends, the number of motorcycles passing through the checkpoint is also lower on weekends compared with weekdays. This is reflected in the significantly lower MTBE, BZ, and THC levels in the motorcycle lanes on weekends.

Area samples collected in motorcycle lanes recorded MTBE, BZ, and THC levels four to five times higher than samples collected in motorcar lanes. This significant difference could be largely due to the poor combustion efficiency of small-capacity (< 150 cc), two-stroke motorcycle engines, which form a large percentage of the motorcycles entering Singapore. Studies on direct exhaust sampling of stationary vehicles have shown that a 125-cc two-stroke motorcycle emits up to 100 times more BZ and other aromatic compounds than a 1600-cc motorcar fitted with a catalytic converter (Ng and

Cheng, 1995). At present, all motorcycle exhaust systems do not have catalytic converters. Newer motorcars, on the other hand, are usually equipped with catalytic converters and exhaust gas recycling systems that reduce emissions of incomplete combustion products like hydrocarbons.

Another reason for the significant difference between motorcycle and motorcar emissions is the present system of allocating lanes designated for handling a particular vehicle type. Immigration Department statistics indicate that the average number of motorcycles passing through the checkpoint daily is roughly equal to the number of motorcars. However, due to the difference in these vehicle sizes, only three to four lanes (excluding the "mini-checkpoint") at both the departure and arrival sections of the checkpoint are allocated for motorcycles, whereas the remaining 20 lanes are allocated for motorcars. This results in a larger number of vehicles per lane in the motorcycle lanes.

4 CONCLUSION

Several trends have been established from the results of our study at the Immigration Checkpoint. Motorcycle lanes were more heavily polluted with airborne hydrocarbons than motorcar lanes. Immigration staff were exposed to the highest levels of hydrocarbons during the afternoon shift, while exposure during the night shift was the lowest. The levels of MTBE and BZ experienced by the immigration staff were well below the exposure limits of 40 ppm for MTBE and 5 ppm for BZ set by the Singapore Ministry of Labour. Because the majority (80%) of the workers were exposed to BZ at levels between 0.01 and 0.5 ppm, with only 1.2% exceeding the occupational limit of 1 ppm set by the Occupational Safety and Health Administration, it is believed that the current exposure levels do not pose any serious acute or chronic health risk to the immigration staff at the checkpoint.

5 ACKNOWLEDGMENTS

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HUMAN HEALTH AND ECOSYSTEM EFFECTS

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MOLECULAR EPIDEMIOLOGY OF CHILDHOOD LEUKEMIA WITH EMPHASIS ON CHEMICAL EXPOSURES

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1 INTRODUCTION

Developing markets in the Pacific Basin depend heavily on the production and export of consumer goods. The generation of hazardous waste as a by-product of industrial production can be linked to adverse health outcomes, such as childhood leukemia, in ways that are presently unknown.

In California, exposures resulting from hazardous waste disposal are of concern in the etiology of childhood cancer. Approximately 63% of the 57 hazardous waste sites that the U.S. Environmental Protection Agency (USEPA) included in the national priority list under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) statute were in the six-county San Francisco Bay area. This area includes California's Silicon Valley, where a disproportionate majority of these sites are located. Although only one study links hazardous waste disposal to childhood leukemia (Lagakos et al., 1986), evidence is accumulating that in utero and maternal pesticide exposures as well as chemical exposures during childhood are important in the etiology of childhood leukemia (Buckley et al., 1989; Shu et al., 1988; Lowengart et al., 1987; Leiss and Savitz, 1995).

With the rapid development of molecular biology techniques and resources available through the California Department of Health Services (CDHS), a laboratory component to this epidemiologic investigation provides the opportunity to link specific genetic changes found in childhood leukemia with chemical exposures.

For these reasons, the University of California, Berkeley (UCB), with support from the National Institute of Environmental Health Sciences, has undertaken this study to investigate whether children with leukemia have common genetic changes, whether children with genetic changes experience common chemical exposures, and whether the occurrences of these genetic changes correspond to the same temporal sequence as exposure. The purpose of this paper is to describe the study design and report on the status of research activity.

2 HYPOTHESIS

This study investigates three primary hypotheses. First, exposures to certain chemicals, prior to or at the time of conception, can damage maternal or paternal germ cells and increase the risk of childhood leukemia. A history of exposures to certain chemicals will correlate with molecular findings. Second, secondary exposures or characteristics are present in parents and/or children that modify effects to primary environmental exposures on disease risk, such as dietary practices, tobacco smoke, and genetic susceptibilities. Finally, a temporal relationship exists between the presence of genetic change and the time at which biologic specimens were obtained, which will make it possible to identify whether genetic changes present in the bone marrow at diagnosis are also present in archived samples of newborn blood.

3 STUDY DESIGN AND STUDY POPULATION

To accomplish these objectives, a fairly elaborate case-control study design was implemented. The basic elements of the study design are as follows and are summarized in Fig. 1.

To be eligible for this study, cases must (1) be under age 15 at the time of diagnosis, without previous treatment or diagnosis for cancer; (2) be a resident of California at the time of diagnosis; and (3) have at least one parent or guardian who speaks English or Spanish. Newly diagnosed cases of leukemia occurring in children between the ages of 0-14 are being identified at four Bay area hospitals that have agreed to participate in this study. The hospitals are (1) Children's Hospital Oakland (CHO); (2) Kaiser-Permanente Hospital, Oakland; (3) University of California, San Francisco, Hospital (UCSF); and (4) Lucille Packard Children's Hospital, Stanford University Medical Center (STAN). It is anticipated that approximately 200 cases of incident cases of childhood leukemia will be obtained over three years. This case series, although it is not population-based, will substantially represent the population-based incidence of this disease in the San Francisco Bay Area. In terms of ethnic distribution of cases, most cases will be white, followed by Hispanic. According to California tumor registry data, approximately 10% of the incident cases of childhood leukemia in California occur among Asian children. Cases were initially enrolled at CHO. Beginning in November 1996, all four hospitals have been reporting cases directly to UCB. Currently, the research team is planning to expand case enrollment to the Central Valley farming region of California, where heavy agricultural pesticide exposure may occur. Twenty-four newly diagnosed cases have been reported to the UCB study center since July 1995. Of these, 21 were eligible, and 3 were ineligible because of the age at diagnosis or place of residence.

Controls: Figure 1 shows two comparison groups included as part of the study design: (1) birth certificate controls (BCCs) and (2) friend controls. The rationale for two control groups emerged because of growing evidence from previous childhood leukemia studies that the use of random-digit dialing to obtain controls may have resulted in a control group biased with respect to socioeconomic

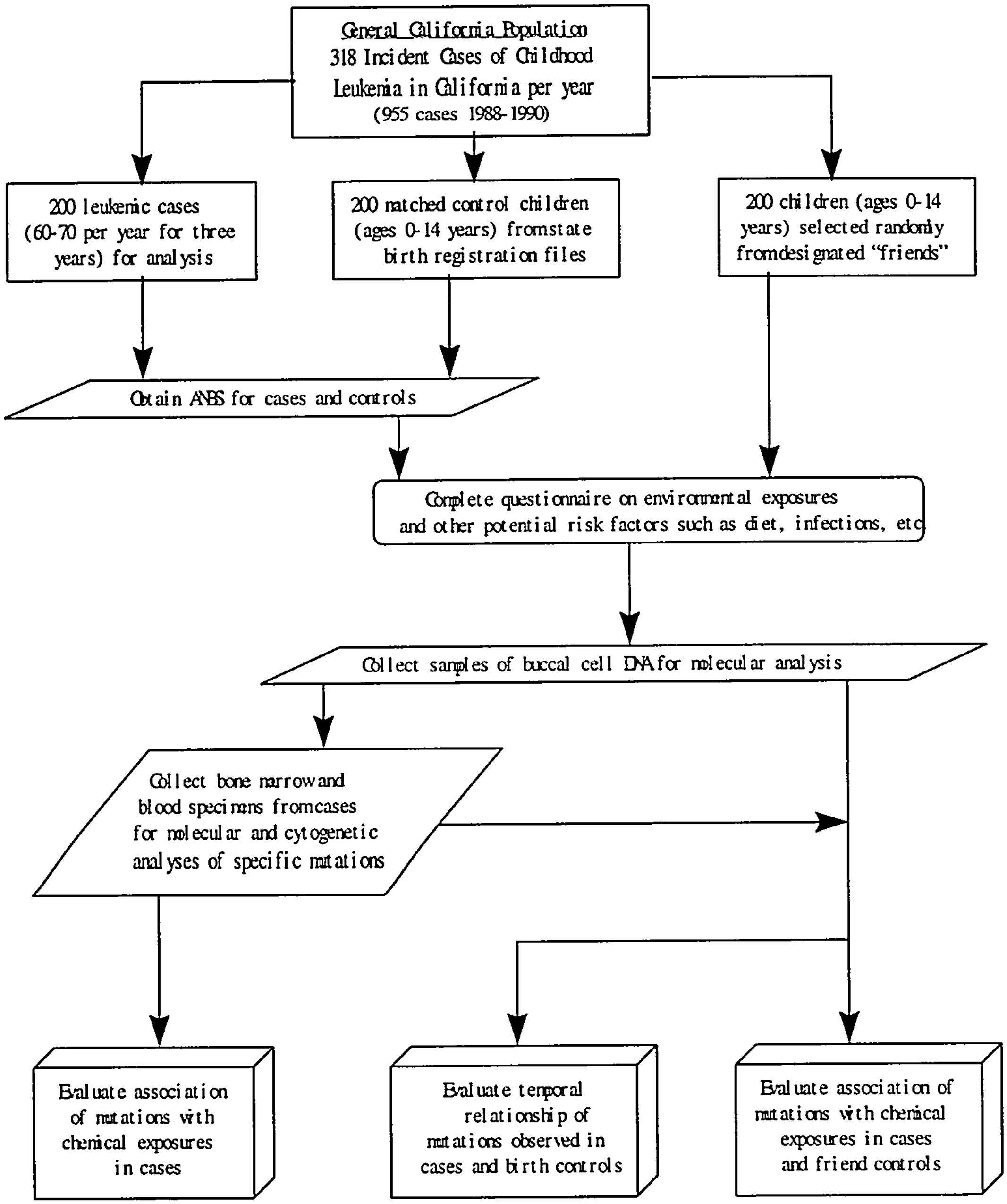

Fig. 1 Overview of Study Design and Hypotheses Related to Leukemia Risk and Environmental Exposures

status and residential stability, factors that may play a role in childhood leukemia (Savitz et al., 1988; London et al., 1991; NRPB, 1991). These two matched control groups are being included to facilitate confounder overlap with respect to variables related to socioeconomic status (friend controls) and to maximize on population-based randomization (BCCs).

The BCCs are selected from the California birth records. To match the BCC to the case, the following criteria are used: (1) date of birth, (2) mother's county of residence at birth, (3) gender of case, (4) mother's race as reported on the birth certificate, and (4) parent's Hispanic status (either mother or father are Hispanic). If no controls fit these criteria, a search for a match born within three months of the case date of birth (either direction) is conducted. If still no match is found, the search can be expanded to include adjacent counties.

With respect to friend controls, the family of the index case is requested to nominate three friends of the child at the time the in-home interview takes place. The friend controls are matched on the following criteria: (1) year of birth, (2) county of residence at diagnosis, (3) gender, (4) race, (5) English or Spanish as primary language, and (6) the control must not be a blood relative. One nominee is randomly selected to participate in the study.

To date, UCB has obtained consent from 9 cases; 2 have refused; and the participation of 10 more is pending. Three BCCs and three friend controls have been identified and agreed to participate. We have been pleased with the success with which birth certificate controls have been located and their willingness to participate. This is also true of the friend controls.

4 DATA COLLECTION

4.1 Biological Samples

One objective of molecular analysis in this study is to explore the relative contributions of pre-existing susceptibilities and molecular lesions induced de novo by exposure. To accomplish this objective, several biological samples are being obtained.

Bone Marrow and Peripheral Blood: When a case presents at any of the four hospitals, a research nurse contacts UCB either by telephone or fax that bone marrow and blood will be obtained. Bone marrow for the definitive diagnosis of leukemia is routinely obtained at the participating hospitals. UCB receives the third or fourth draw of bone marrow aspirate, usually about 0.5-1 mL of aspirate. Pretreatment blood (approximately 5 mL) is also obtained, usually at the same time as the bone marrow.

Two forms are completed by the research nurse to indicate information about a new case: (1) a rapid case ascertainment form and (2) a specimen transmittal form. In practice, the specimen transmittal form is faxed first to the UCB study center, indicating that the specimen is ready to be picked up by courier for delivery to UCB.

Fresh bone marrow and blood are delivered to the UCB study center, inventoried, labeled, and delivered to the UCB laboratory of Dr. Martyn Smith. The fresh samples are processed immediately into separate cell types (white blood cells, red blood cells, plasma) and frozen at −20 to −70°C or cryopreserved at −134°C for future analysis.

4.1.1 Buccal Cells

Buccal cells, which are epithelial in origin, line the inside of the mouth and are exfoliated regularly. Buccal cells are important in this study, since this is the only biological sample being obtained for both cases and controls, as well as the mother of each case and control. Buccal cells will be obtained from the cases by the research nurse at the time of informed consent. Interviewers are trained to obtain buccal cells from control children at the time of personal interview. A variety of approaches are available in the published literature with respect to obtaining buccal cells. After testing several methods, it was determined that the cytobrush technique is the most efficient for epidemiologic field investigations, since the cytobrushes require no mixing, measuring, or refrigeration prior to or within several days after tissue collection (Richards et al., 1993). Buccal cells are collected on a cytobrush by twirling the brush gently along the inside of the mouth for 30 seconds. Three samples are taken, at least one on each side of the mouth.

4.1.2 Archived Newborn Blood Samples

One of the unique advantages of this study design is the ability to identify the temporality of genetic changes. A small blood sample from the heel of newborns is obtained for children born in California to screen for certain genetic diseases. These samples are stored by the CDHS and are retrieved by linkage with the birth certificate file maintained by the state. Eight of the nine participating cases were born in California. Thus, only one case will be excluded from analysis of temporality of genetic change, since no ANBS is available for out-of-state births.

4.1.3 Cytogenetics

Laboratory results from the diagnosis of childhood leukemia, such as cytogenetics and immunophenotyping, are available in the medical record through the participating hospitals. Medical records will be abstracted to obtain information such as specific translocations and cell-surface markers present in the leukemic cells.

4.2 Questionnaire and Interview

Environmental exposure is currently quantified indirectly by means of two questionnaires that serve to collect data about potential environmental exposures: a self-administered questionnaire followed by an in-person interview (and in-home questionnaire) to confirm earlier responses and expand data collection. Both questionnaires are administered in English or Spanish, whichever is the preference of the respondent.

4.2.1 Self-Administered Questionnaire

The self-administered questionnaire is presented to the parents of the case after informed consent is obtained. Because information is requested on residential and occupational histories, vaccination records, and other information from the past, allowing the respondent to review personal records at home was seen as a way to obtain quality data. A reminder postcard is sent to the respondent after 10 days and then a follow-up telephone call is made at a later date, if the questionnaire has not been returned. A stamped envelope is provided for returning the questionnaire.

4.2.2 In-Home Interview

About one month after the case has been enrolled in the study, the interview occurs. Prior to the in-home interview, the interviewer has identified questions for further clarification or confirmation from the self-administered questionnaire and is prepared to administer the in-home questionnaire. The interviewer also obtains buccal cells from the mothers and child control groups at the in-home visit. To date, 16 self-administered questionnaires have been distributed, and 14 have been returned completed. Nine in-home interviews have been completed.

5 DATA ANALYSIS

Data analysis is composed of two parts: (1) laboratory analysis and (2) statistical analysis of all data collected.

5.1 Biological Samples

Table 1 summarizes the sources of data, the endpoint of interest, and the group (case or control) from which data will be derived. Categories 6-16 of Table 1 identify the endpoint of interest by biological specimen that will be analyzed. Categories 1-6 are obtained from the medical record.

Table 1 List of Variable Categories and Sources of Data for Descriptive and Analytic Study of Childhood Leukemia

Category No.	Specimen/Data Source	Data Collection	Endpoint	Example of Outcome	Analysis Groups
1	Patient history	Medical records	Clinical parameters	Age, presence of CNS involvement	Cases
2	Bone marrow	Medical records	FAB morphology	L1 or L2	Cases
3	Bone marrow	Medical records	Immunophenotype	Cytoplasmic immunoglobulin	Cases
4	Bone marrow	Medical records	Cytogenetic	Philadelphia chromosome	Cases
5	Peripheral blood	Medical records	White count	Prediagnostic white count	Cases
6	Buccal cells	Wiencke lab	Genetic polymorphisms in GST-T1 and OST-M1	Deficient vs. nondeficient	Cases & controls
7	Peripheral blood	Wiencke lab	N-ras	Mutation in N-ras or negative	Cases
8	Bone marrow	Wiencke lab	N-ras	N-ras or negative	Cases
9	Bone marrow	Smith lab	Molecular detection of translocations	t(9;22), t(8;21) 11q23 MLL gene disruption	Cases
10	Peripheral blood	Smith lab	Molecular detection of translocations	t(9;22), t(8;21) 11q23 MLL gene disruption	Cases
11	ANB sample	Smith lab Wiencke lab	Chromosome translocation N-ras mutation	t(9;22), 11q23 N-ras mutations	Cases
12	Peripheral blood	Smith lab	V(D)J recombinase	T-cell receptor rearrangement	Cases
13	Bone marrow	Smith lab	V(D)J recombinase	T-cell receptor rearrangement	Cases
14	ANB sample	Smith lab	V(D)J recombinase activity	T-cell receptor rearrangement	Cases & controls
15	ANB sample	Smith lab	FISH detection of chromosome specific aneuploidy	Trisomy of chromosome 8 or 12	Cases
16	ANB sample	Smith lab	FISH detection of chromosome specific aneuploidy	Trisomy of chromosome 8 or 12	Cases
17	Questionnaire	Epidemiology	Numerous	Prenatal maternal exposure	Cases & controls

5.1.1 Bone Marrow and Peripheral Blood

Polymerase chain reaction (PCR) assay will be used to identify the presence of N-ras mutation as well as to detect certain translocations in samples being stored at -70°C. Slides of bone marrow and peripheral blood smears are being stored at -20°C to conduct fluorescence in situ hybridization (FISH) to detect chromosome specific aneuploidy. This will allow cytogenetic data to be obtained on samples that cannot be cultured for conventional cytogenetic analysis. In addition, FISH may be used to further analyze questionable samples.

5.1.2 Buccal Cells

Procedures for removing buccal cells from the cytobrush and then extracting DNA from buccal cells has been successful. DNA extracted from buccal cells is being stored at -70°C for future analysis by using PCR to detect genetic polymorphisms. Genetic polymorphisms will be examined in two glutathione transferase genes (GST): M1 and T1. GST enzymes function to detoxify reactive intermediates produced by Phase I metabolism of numerous compounds. Loss of expression of GST M1 has been linked to increase susceptibility to some cancers (Seidegard et al., 1986).

5.1.3 Archived Newborn Blood

Access to newborn blood samples is a unique design advantage over previous studies of childhood leukemia, since analysis of the samples allows determination of the temporality of genetic change. Archived newborn blood samples have been retrieved from the CDHS. Isolation and amplification of DNA from these samples to detect DNA polymorphisms and mRNA expression have been successfully completed by using PCR and reverse transcriptase PCR (rt-PCR). Test analyses have shown that it is possible to detect translocations if present in the newborn blood samples by long amplification PCR on DNA or rt-PCR on RNA.

5.1.4 Other Analyses of Biological Samples

Blood and bone marrow when available from each case are being cryopreserved at -134°C. As analytic techniques and endpoints of interest change, these samples will be available for future analysis. Test analyses have shown that white blood cells can be recultured once cryopreserved.

5.2 Statistical Analysis

The proposed analysis of the study will incorporate both descriptive and multivariate statistical techniques, consistent with analysis of data from a matched case/control study design.

A unique feature of this study will be the ability to evaluate the presence or absence of molecular changes classified by self-reported exposure status. Table 2 shows molecular changes stratified by self-reported pesticide exposure. Controls will not be included in some comparisons since blood and bone marrow were not obtained from disease-free participants.

The presence (or absence) of the GST polymorphisms will be correlated between the mothers of cases and case children. This same correlation can be established between the mothers of control children and control children, for both birth certificate and friend controls, respectively.

Buccal cells were obtained from both cases and controls. Thus, an association between the polymorphic status of the matched pairs (presence/absence) and case/control status can be determined. Table 3 shows the prevalence of GSTm1 polymorphisms between cases and both sets of controls.

Table 2 Prevalence (%) of Selected Molecular Changes in Case Group Stratified by Self-Reported Exposure

	Exposure to Pesticide		No Exposure to Pesticide	
Percent Present	ANBS Blood[a]	Marrow	ANBS Blood[a]	Marrow
A. Translocations				
t(1;19)				
t(9;22)				
t(4;11)				
t(9;11)				
t(6;11)				
t(11;19)				
B. N-ras Mutation (1p22-32)				
C. Hyperploidy				
Chromosome 8				
Chromosome 12				
Chromosome 21				
X chromosome				

[a] ANBS = archived newborn blood sample.

Table 3 Calculation of Odds and Odds Ratio between GSTmu Status in Buccal Cells at Diagnosis and Childhood Leukemia

GST Status	Case	Control		Total N
		Friend	Birth	
Present				
Absent				

6 CONCLUSIONS

Tremendous advances have been made in the treatment and survival of children who develop leukemia, yet for 90% of these leukemias, the cause(s) of this disease remain largely unknown. While molecular biology has aided in the identification of genetic changes to characterize childhood leukemia, advances to better understand how environmental exposures, such as hazardous waste, influence the disease process have not kept pace with changes in the clinical characterization of leukemia. This study may help to reduce the percentage of leukemias for which etiology is not well-understood.

7 ACKNOWLEDGMENTS

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MULTIPLE MECHANISMS OF PCB NEUROTOXICITY

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ABSTRACT

Polychlorinated biphenyls (PCBs) have been implicated in cancer, but many of the symptoms in humans exposed to PCBs are related to the nervous system and behavior. We demonstrated three different direct mechanisms whereby PCBs are neurotoxic in rats. By using flow cytometry, we demonstrated that the *ortho*-substituted PCB congener 2,4,4', but neither TCDD nor the coplanar PCB congener 3,4,5,3',4', causes rapid death of cerebellar granule cells. The *ortho*-substituted congener 2,4,4' reduced long-term potentiation, an indicator of cognitive potential, in hippocampal brain slices, but a similar effect was observed for the coplanar congener 3,4,3',4', indicating that this effect may be caused by both *ortho*- and coplanar congeners by mechanisms presumably not mediated via the Ah receptor. It was previously shown that some *ortho*-substituted PCB congeners cause a reduction in levels of the neurotransmitter dopamine, and we present *in vitro* and *in vivo* evidence that this is due to reduction of synthesis of dopamine via inhibition of the enzyme tyrosine hydroxylase. Thus, PCBs have a variety of mechanisms of primary neurotoxicity, and neurotoxicity is a characteristic of *ortho*-substituted, non-dioxin-like congeners as well as some coplanar congeners. The relative contribution of each of these mechanisms to the loss of cognitive function in humans exposed to PCBs remains to be determined.

1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of 209 individual chemical compounds that differ in the position and the number of chlorines on the biphenyl rings. PCBs are persistent in the environment and bioaccumulate in the food chain. While a primary source of human exposure to PCBs is from fish taken from contaminated water, other food sources are also important sources of exposure.

In humans, PCBs accumulate in body fat (Tuefel et al. 1990), and the body burden can be approximated through an analysis of serum (Bush et al. 1984). Since fat is excreted during lactation, breast milk is a major source of exposure to infants (Yakushiji et al. 1984). While there is some metabolism of PCBs (Birnbaum 1985; McFarland and Clarke 1989), the body's ability to rid itself of these compounds is limited. The individual congeners of PCBs differ in their susceptibility to degradation and in their water solubility (Birnbaum 1985), but all are persistent both in the environment and in living organisms.

Until relatively recently, human health concerns regarding PCBs were limited to considerations of their dioxin-like actions mediated through activation of the Ah receptor. Some PCB congeners, those with chlorines in the *meta* and *para* positions on the biphenyl rings, assume a coplanar configuration similar to that of 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) and can activate the Ah receptor (Kafafi et al. 1993). Safe (1990) has determined toxic equivalents for a variety of PCB congeners, and has found some to be up to one-tenth as toxic as TCDD. Because TCDD and some PCBs are carcinogenic and immunosuppressive in animals (Silberhorn et al. 1990), most human concerns regarding PCBs have focused on cancer. However, to date there has not been direct evidence for this relationship in human populations (Silberhorn et al. 1990). The World Health Organization and the International Programme on Chemical Safety have adopted the concept of PCB toxic equivalent factors based on the ability of various congeners to activate Ah receptors (Ahlborg et al. 1994). Although this approach is not inappropriate with regard to dioxin-like Ah receptor activity, it has led both to a general assumption that it is only the dioxin-like activity of PCBs that is of concern with regard to the health of the public, and to an underestimation of the potential health risks due to exposure to non-dioxin-like PCB congeners and possible effects of both *ortho*-and non-*ortho* congeners that may not depend on Ah receptor activation.

Two episodes of mass poisoning with PCBs and their degradation products have occurred in Japan and in Taiwan. Both episodes resulted from contamination of cooking oils with PCBs, and the exposure was much greater than experienced through consumption of contaminated fish. A variety of effects were observed in adults, but the most dramatic effects were found in children born to mothers who consumed the contaminated oil. These children showed impaired growth, delay of developmental milestones, deficits on formal developmental testing, and abnormalities on behavioral assessment (Chen et al. 1992; Guo et al. 1994; Lai et al. 1994; Rogan et al. 1988; Yu et al. 1991; Yu et al. 1994). Other studies of occupationally exposed mothers have shown a lower birth weight of infants (Taylor et al. 1989). Two groups have reported developmental abnormalities of U.S. children exposed to PCBs in their environment. Gladen et al. (1988) showed that U.S. children exposed transplacentally to PCBs had lower psychomotor scores than control children. Jacobson et al. (1990) investigated children exposed to PCBs from contaminated Great Lakes fish and found poorer short-term memory function on both verbal and quantitative tests when tested at 4 years of age. In a recent report, Jacobson and Jacobson (1996) have reinvestigated some of these children at the age of 11 years and found that the most highly exposed children suffered an IQ deficit of 6.2 IQ points and a shortened attention span. The IQ deficit correlated significantly with prenatal exposure but not postnatal. In sum, these observations suggest that PCB exposure during development may cause an irreversible decrement in IQ and attention span.

We have performed studies to determine how these compounds affect the nervous system of animals and have found several different actions. Of particular importance is our finding that the lower chlorinated, *ortho*-substituted congeners of PCBs potently affect the nervous system, at least in the assay systems that we have investigated. These congeners are often implied to be "non-toxic," since they are poor activators of the Ah receptor (Kafafi et al. 1993; Safe 1990). Our observations suggest that, insofar as neurotoxicity is concerned, activation of the Ah receptor is not required, and provide an experimental basis for understanding at least some of the cognitive and behavioral effects of PCBs reported in exposed human populations.

2 METHODS

2.1 Flow Cytometry Studies

Cerebellar granule cells were isolated from 7-14 day old Wistar rat pups as described by Oyama et al. (1992a,b) and were suspended at 1×10^6 cell/mL in Tyrode's plus 0.25% fetal bovine serum. The cells were stained with 7-aminoactinomycin-D (7AAD, 5 μg/mL), a DNA binding dye excluded from living cells (Haugland 1992). A Becton-Dickinson FACScan flow cytometer exciting at 488 nm and measuring emission at 680 nm was used to collect data at 30 s and 1, 3, 5, 10, and 45 min after the addition of test compounds. Single congeners (AccuStandards, New Haven, CT) were dissolved in dimethylsulfoxide (DMSO, final concentration 0.2%). Data were analyzed using the Lysis II program, and statistical significance was determined using Anova and Duncan's *t*-test.

2.2 Long-term Potentiation Studies

Hippocampal brain slices were prepared from young male Wistar rats (150–200 g) as previously described (Hori et al. 1993). After preincubation in oxygenated (95% O_2/5% CO_2) Krebs-Ringer solution for at least 2 h, the slices were submerged under a nylon net in the recording chamber and a stimulating electrode placed on the Schaffer collateral tract. The monosynaptic population response was recorded in the dendritic area of CA1 upon a submaximal (about 50%) stimulation of the Schaffer collaterals at a frequency of 0.05 Hz. After a stable response was achieved, two tetanic stimulations (100 Hz, 1 s each separated by 5 s) were given to initiate long-term potentiation (LTP). LTP was assessed by measuring the change in amplitude and slope of the CA1 dendritic synaptic field response, which persisted after a period of at least 60 min. Slices exposed to PCBs (Aroclor 1254, congeners 2,4,4' trichlorobiphenyl or 3,4,3',4' tetrachlorobiphenyl) were prepared as above and further incubated in 0.1% DMSO Kreb's Ringer containing 1 to 10 μM PCB. The solutions were continuously agitated by bubbling 95% O_2/5% CO_2, and slices were maintained in this solution for between 1 and 5 h. Following this incubation, the slices were mounted in the submersion chamber and perfused with normal Krebs-Ringer solution.

2.3 Tyrosine Hydroxylase Studies

2.3.1 In vitro Studies

Pheochromocytoma (PC12) cells were grown as previously described (Seegal et al. 1989). Crude cell homogenates were prepared, and dopamine synthesis was estimated by monitoring *de novo* synthesis in the presence of excess tyrosine and added tetrahydrobiopterin, the cofactor required for synthesis of dopamine. Dopamine concentrations in the media from both PCB and DMSO exposed cell preparations were determined using high-performance liquid chromatographic (HPLC) procedures described by Seegal et al. (1986).

2.3.2 In vivo Studies

Adult male rats were exposed to either Aroclor 1254 (1,000 ppm in chow) or control chow for 60 days and euthanized 30 min after receiving intraperitoneal injections of either 100 mg/kg 3-hydroxybenzylhydrazine (NSD-1015), an inhibitor of aromatic amino acid decarboxylase, or saline. Dopamine, L-DOPA, 3,4-dihydroxypheny-lacetic acid (DOPAC), and homovanillic acid (HVA) concentrations were determined in the striatum and nucleus accumbens by previously described HPLC procedures. Single PCB congeners and Aroclor 1254 were obtained from AccuStandard, New Haven, Connecticut, USA.

3 RESULTS

Figure 1 shows results obtained from flow cytometric studies of cerebellar granule neuron viability after acute exposure to TCDD, a coplanar PCB (3,4,5,3',4' pentachlorobiphenyl), or a mono-*ortho* PCB (2,4,4' trichlorobiophenyl). The neurons were incubated with 7AAD, a dye impermeant to viable cells. Neither the DMSO controls nor the coplanar PCBs significantly affected the cell viability (7AAD uptake) over the 45-min exposure period. However, the mono-*ortho* congener caused a dose-dependent reduction in viability, which increased over time. At 100 μM, 80% of cells died within 45 min. The threshold concentration of 2,4,4' for cell death was about 10 μM. These observations are similar to those reported by Kodavanti et al. (1993), which showed that 2,2' dichlorobiphenyl was cytotoxic while 3,4,5,3',4' was not when the same neuronal cells were used in a somewhat different assay system.

Long-term potentiation is a sustained change in synaptic efficacy, measured with electrophysiological techniques, that can be induced at certain central synapses by application of

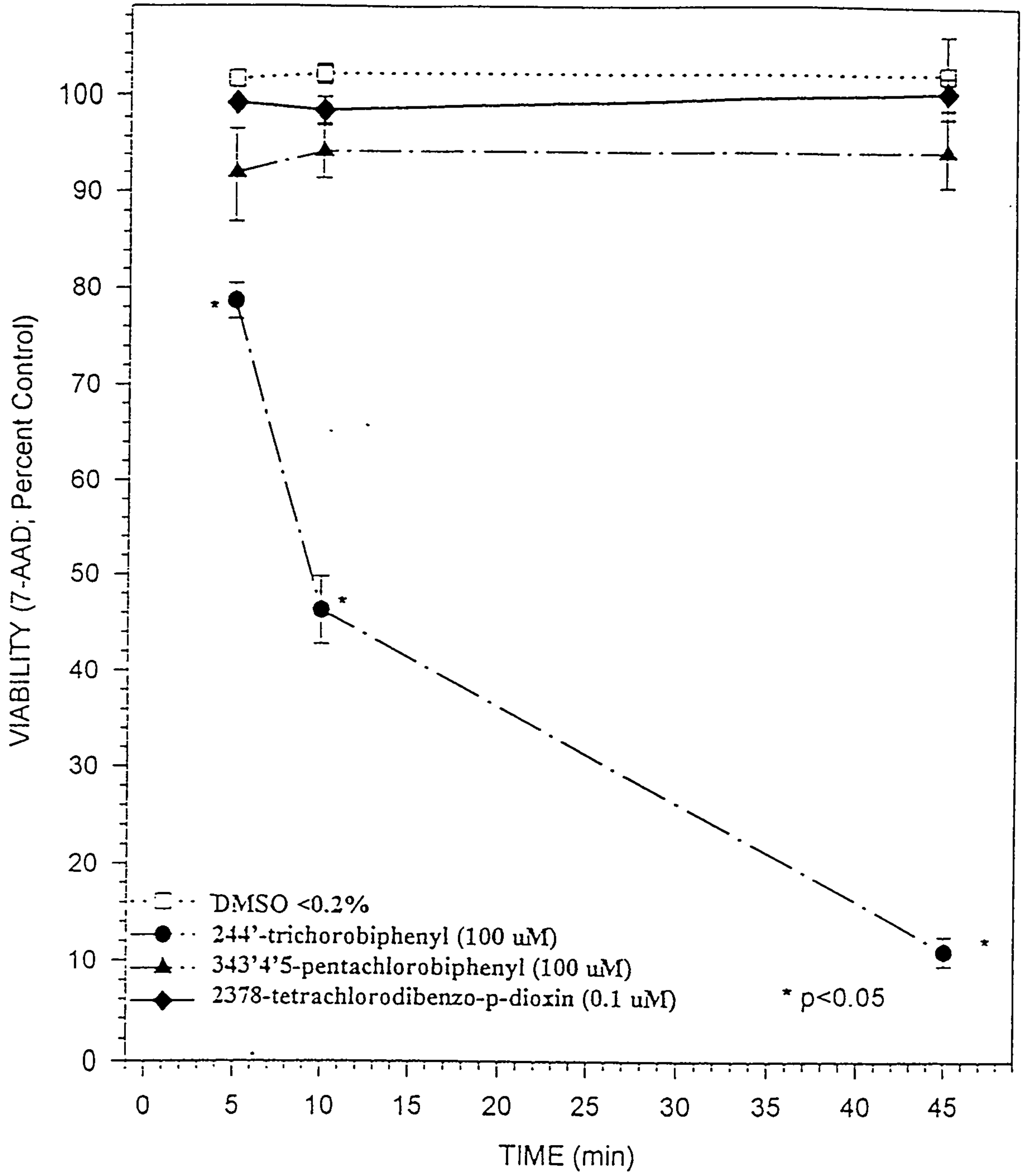

Fig. 1 Viability of Cerebellar Granule Cell Neurons with Time, Measured by Uptake of 7-AAD and a Flow Cytometer (There was no significant effect on viability of 0.2% DMSO, 100 μM of 3,4,5,3',4' pentachlorobiphenyl, or 0.1 μM of TCDD. However, 2,4,4' trichlorobiphenyl caused a time-dependent reduction of viability.)

particular patterns of stimulation or a brief tetanic activation. Figure 2 shows the field EPSP responses recorded in a control slice from the CA1 region of rat brain hippocampus before and after tetanus (A), and similar recordings from a slice incubated for 5 h with 50 μM of Aroclor 1254 (B). After the tetanic stimulation, which is the induction stimulus for LTP, the response in the control slice increased to a sustained elevation in responsiveness that lasted for more than 1 h. The slice incubated with 50 μM of Aroclor 1254 had a normal initial amplitude, but there was no LTP after tetanus. Figure 3 shows the average effects of 2,4,4' trichlorobiphenyl and 3,4,3',4' tetrachlorobiphenyl on LTP from six experiments, where the ordinate is the field EPSP amplitude after tetanus divided by the amplitude prior to tetanus. Both congeners significantly reduced LTP at the hippocampal Schaffer collateral-CA1 synapses. A ratio of 1.0 indicates total blockade of LTP.

Previous results of Seegal et al. (1989) have demonstrated that PCBs reduce the concentration of dopamine in PC12 cells maintained in culture, and a further study by Shain et al. (1991) demonstrated that *ortho*-substituted or *ortho-para*-substituted congeners were the most potent in mediating this action. The reductions in cellular dopamine may be due to a PCB-induced inhibition of dopamine synthesis, since the reductions in cellular dopamine occur in the absence of either increased release of dopamine into the media or enhanced metabolism of dopamine to either HVA or DOPAC. Additional *in vitro* and *in vivo* experiments were performed to obtain convincing evidence that the PCB effect on dopamine content is through inhibition of the rate-limiting synthetic enzyme, tyrosine hydroxylase.

In the first series of experiments, we determined the rate of *de novo* synthesis of dopamine in crude homogenates of PC12 cells, exposed to either 2,2' dichlorobiphenyl or DMSO, and observed a decrease in the rate of synthesis of dopamine in the presence of 2,2' as compared to the DMSO control. In the control, the synthesis rate was 143 ± 8.1 pmole/min/mg protein. When the same assay was done in the presence of 65 μM of 2,2' dichlorobiphenyl, the rate of dopamine synthesis was reduced to 70.7 ± 14.1 pmole/min/mg protein.

To determine (1) whether the decreases in dopamine synthesis observed *in vitro* also occur *in vivo* and (2) the biochemical site(s) for this decrease in dopamine synthesis, we exposed adult rats to Aroclor 1254 for 60 days and measured striatal concentrations of L-DOPA, DOPAC, and HVA in animals injected intraperitoneally with either an inhibitor of aromatic amino acid decarboxylase (NSD-1015) or saline 30 min prior to euthanasia. As shown in Table 1, PCBs significantly reduced dopamine, DOPAC, and HVA concentrations in striatum. More important, treatment with NSD-1015 resulted in highly significant decreases in DOPAC and HVA concentrations in PCB-exposed animals, but not controls, and these decreases were exacerbated by co-treatment with PCBs. In addition, L-DOPA concentrations, which were detectable only in NSD-1015 animals, were significantly reduced in PCB-exposed animals relative to control.

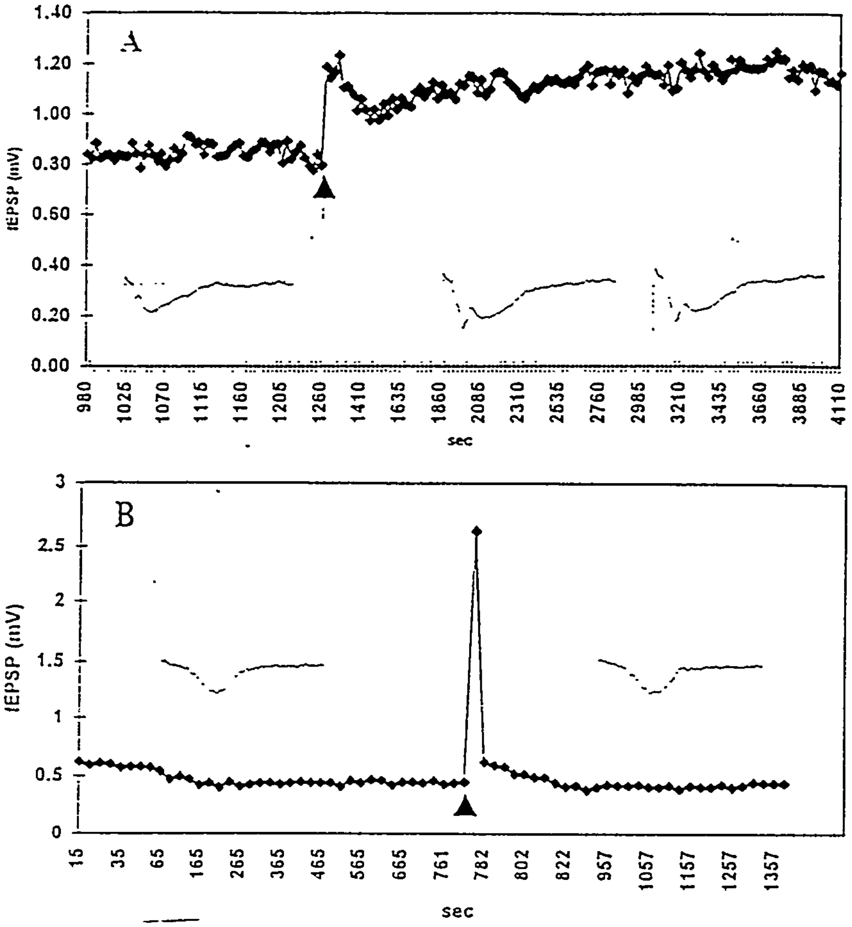

Fig. 2 LTP in CA1 Neurons of Rat Hippocampal Slices after 5 h of Incubation in 50 ppm of Aroclor 1254 (Graph A is a control slice exposed for the same period to 0.1% DMSO. Tetanic stimulation of the Schaffer collaterals was applied at the arrow. Graph B is from a slice incubated in Aroclor 1254. No LTP is seen in the latter.)

4 DISCUSSION

These observations demonstrate that both *ortho*-substituted and coplanar PCBs affect nervous system function, and the *ortho*-substituted PCBs may do so in at least three different ways. Some ortho-substituted PCB congeners cause neuronal cell death. The second action is a selective blockade of LTP without obvious alteration of other indicators of electrical excitability. LTP is generally accepted as a model system for study of learning and memory, since it occurs primarily in limbic, cortical, and subcortical brain regions known to be involved in cognitive functions (Baundry and Massicotte 1992). It is reduced or absent in animals with deficits in learning ability (Grant et al. 1992; Ramakers et al. 1993; Silva et al. 1992) and is blocked by exposures such as lead (Altmann et al. 1991; Hori et al. 1993; Lasley et al. 1993), known to reduce cognitive function. The third

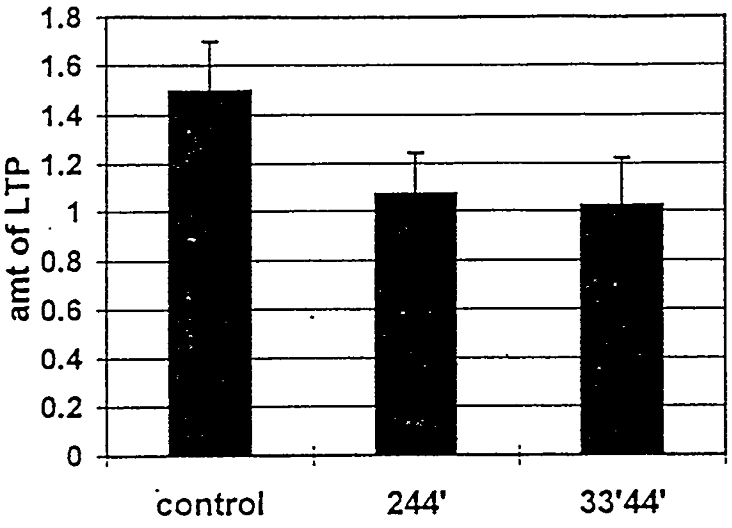

Fig. 3 Results from Experiments in Adult Rats Showing the Expression of CA1-LTP in 12 Control Slices, 5 Slices from 3 Rats Treated *in vitro* with 10 µM of 2,4,4' and 7 Slices from 3 Rats Treated with 10 µM of 3,4,3',4' PCB for 1 to 5 h (The amplitude of the population synaptic response prior to tetanus is taken as 1.0, so LTP is the response amplitude above 1.0 measured 1 h after tetanic stimulation.)

Table 1 Striatal Concentrations of L-DOPA, Dopamine, DOPAC, and HVA in Adult Male Rats Following 60-day Exposure to a Diet Containing 1,000 ppm of Aroclor 1254[a]

Striatal Concentration	Saline		NSD-1015	
	Control	PCB	Control	PCB
L-DOPA	n.d.[b]	n.d.	17.7 ± 0.8	14.3 ± 0.6[c]*
Dopamine	229 ± 5	211 ± 4*	221 ± 5	213 ± 4
DOPAC	26.8 ± 1.0	20.8 ± 0.5**	11.0 ± 1.3	6.5 ± 0.7*
HVA	12.7 ± 0.4	8.9 ± 0.22***	10.5 ± 0.5	7.0 ± 0.3***

[a] Tyrosine hydroxylase activity was assessed through the use of NSD-1015, an inhibitor of aromatic amino acid decarboxylase (100 mg/kg, i.p., 30 min prior to sacrifice).

[b] n.d. = Not detected without the use of NSD-1015.

[c] *p ≤ 0.05. ***p ≤ 0.01, ***p ≤ 0.001, pairwise *t*-tests comparing each PCB-treated group with the respective control group.

action is a reduction in dopamine levels. While the exact mechanisms whereby a congener like 2,4,4' kills cerebellar granule cells and blocks LTP are not known at present, our results indicate that dopamine synthesis is most likely blocked by a direct inhibition of tyrosine hydroxylase. It is likely that these three actions are distinct. Neither the reduction in tyrosine hydroxylase activity nor the reduction of cellular dopamine concentration is known to have any role in the development of CA1 LTP. None of the CA1 cells in the hippocampus make dopamine, and dopamine has not been implicated as having any role in the development of LTP. Cerebellar granule neurons are also not dopaminergic. The effects of PCBs in intact slices do not result in cell death, as indicated by the fact that the neuronal population response is not significantly altered by PCB exposures, which reduce and, in some cases, totally block LTP. Thus, we have demonstrated three apparently different forms of neurotoxicity of PCBs, each of which has the potential to adversely affect human health. The demonstration that both *ortho-* and coplanar PCBs block LTP is at least suggestive evidence that the action is mediated by a mechanism independent of Ah receptor activation, since 2,4,4' is known not to be a potent activator of this receptor.

It is somewhat difficult to determine exactly what the concentration of PCBs is in the tissues used in these experiments. In all three *in vitro* preparations, we have applied aqueous solutions of PCBs and DMSO of defined concentrations, but we have found that the PCBs will concentrate in the biological tissues (unpublished observations). The fact, however, is that these several effects on nervous tissue were all specific to particular congeners and biological indicators. Thus, these are clearly not nonspecific actions.

It is particularly noteworthy that all of the three actions on the nervous system occurred with *ortho-*substituted congeners. While the exact mechanisms of action of these effects are uncertain, clearly they are not mediated via Ah receptors. Some (Abramowicz 1990) have argued that the lower chlorinated, *ortho*-substituted congeners are, in general, much less toxic than more highly chlorinated congeners and are relatively innocuous products of anaerobic biodegradation. Our observations suggest that the process of biodegradation, which results in removal of chlorines in the *meta* and *para* positions, may actually result in the generation of more neurotoxic congeners.

While there has been no demonstration of neuronal cell death in either whole animals or in human exposure to PCBs, the children of Yushu and Yu Cheng demonstrated movement disorders, and movement is controlled by the cerebellum. Our observations and those of Kodavanti et al. (1993) strongly suggest that further studies should investigate neuronal cell loss in some areas, including the cerebellum.

Dopamine is a critical neurotransmitter in the brain. Dysfunction of dopaminergic systems is implicated in a variety of human neurologic diseases, including Parkinson's disease, where dopaminergic neurons are lost, and in some forms of mental illness. Most drugs used for treatment of depression and schizophrenia are active at dopamine receptors, implicating these receptors in the neuronal circuits responsible for mood and mental health. Substances, like *ortho*-substituted PCBs, that interfere with dopamine synthesis would be reasonably expected to result in abnormalities of mental state.

Our studies on PC12 cells show conclusively that 2,2' dichlorobiphenyl causes a reduction in dopamine synthesis. Dopamine is synthesized from tyrosine in a two-step process. Tyrosine is converted to L-DOPA through action of tyrosine hydroxylase, and L-DOPA is then converted to dopamine through the action of L-aromatic amino acid decarboxylase. By blocking the conversion of L-DOPA to dopamine, one can begin to determine which of these enzymatic pathways is blocked by PCBs. Even in the absence of treatment with NSD-1015, PCBs significantly decreased striatal DOPAC concentrations. Alterations in DOPAC concentrations have recently been shown to reflect the rate of newly synthesized dopamine (Soares-da-Silva and Garrett 1990; Zetterstrom et al. 1988). Thus, PCBs appear to selectively reduce newly synthesized dopamine. NSD-1015, which prevents the conversion of the intermediate product, L-DOPA, to dopamine, and which has been widely used to estimate the activity of the rate-limiting synthetic enzyme, tyrosine hydroxylase (Westerink and Van Putten 1987), also significantly decreases striatal concentrations of DOPAC and, to a lesser extent, striatal concentrations of HVA. This observation provides further evidence that inhibition of dopamine synthesis results in decreases in dopamine metabolite concentrations. Furthermore, co-treatment of animals with PCBs and NSD-1015 significantly decreased striatal L-DOPA concentrations when compared to NSD-1015 treatment only, suggesting that these two agents act in concert to reduce the activity of tyrosine hydroxylase.

This conclusion is contrary to that of Angus and Contreras (1995) who used [H3]tyrosine in PC12 cells. They report that PCBs inhibit dopamine synthesis at the level of aromatic amino acid decarboxylase, the enzyme that converts L-DOPA to dopamine. The discrepancy with our conclusion may relate to the *in vitro* versus *in vivo* systems, as well as in the use of NSD-1015 versus labeled precursor. Further investigation of this important question is warranted.

Examination of the changes in striatal dopamine concentration following exposure to PCBs demonstrates only an 8% decrease in content. Changes of this magnitude would be expected to have little if any effect on normal behavior of the animal. However, HPLC analyses of brain punches to not allow resolution of the small, readily releasable pool of dopamine, that is presumed to be the functional pool, from its larger, nonphysiological storage pool. On the basis of the significant decreases in striatal DOPAC content, we suggest that PCB exposure results in very significant changes in concentrations of the physiologically more important readily releasable vesicular pool of dopamine. We are currently developing use of brain microdialysis, which should allow us to more rigorously determine how PCBs affect these two pools of cellular dopamine.

Perhaps the most significant finding in these studies is the blockade of LTP by PCBs, since LTP is a measure for cognitive potential and memory. It is now widely known that lead exposure in children results in a loss of cognitive potential (McMichael et al. 1994; Schwartz 1994). While the exact mechanism whereby lead causes these actions is still a subject of research, we do know that lead also blocks LTP (Altmann et al. 1991; Hori et al. 1993; Lasley et al. 1993). Further study of exactly how PCBs alter LTP is important. The recent demonstration that *in utero* exposure to phenobarbital causes a decrement in IQ of adult men (Reinisch et al. 1995) is further evidence that cognitive ability can be permanently disrupted by exposure to chemicals in the perinatal period.

Children born to mothers who consumed contaminated rice oil in the Yushu and YuCheng incidents showed not only reduced physical growth (Guo et al. 1994) but also disordered behavior (Chen et al. 1994; Yu et al. 1994) and reduced cognitive functioning, which persisted to the age of at least 12 years following congenital exposure (Lai et al. 1994). In these children, it is not possible to determine precisely which of the various PCB congeners or which of the PCDFs, that were formed when the PCBs were heated, are responsible for the CNS symptoms. The recent study of Jacobson and Jacobson (1996) has provided the most definitive evidence to date that children exposed to PCBs *in utero* suffer from an IQ deficit, but this study also cannot distinguish which PCB congeners are significant. Our animal results provide suggestive reasons to believe that both lightly chlorinated, *ortho*-substituted PCB congeners and coplanars may be to blame, although clearly further study is needed. Since our investigations to date have been of acute exposure of brain slices from young adult rats to the PCB mixtures, clearly further investigation must be done in which animals are exposed *in utero*.

In the past, much of the attention to the effects of hazardous chemicals in our environment has focused on cancer as an endpoint. While clearly cancer is an important public health problem, inadequate attention has been directed to the neurobehavioral effects of pollutants. Cancer is usually a disease of adults who have at least lived a major portion of their lives. It is difficult to compare morbidity and mortality from cancer to the demonstration that children exposed to agents, such as lead and PCBs, will suffer from a reduced cognitive potential and probably a shortened attention span that may permanently reduce their intellectual potential. Death is not the only important endpoint, and in some ways these nonfatal and more subtle effects on the nervous system may be of much greater societal importance. *Science* recently published an editorial entitled "Excessive Fear of PCBs" (Abelson 1991), which considered only carcinogenesis as a concern. Kimbrough (1993), in an article in a book entitled *Phantom Risk*, does not even mention neurobehavioral effects of PCBs in discounting any effect on human health. Our results, in concert with the human studies done to date, are consistent with the conclusion that PCBs are like lead in having significant effects on brain function, reflected in reduction of cognitive ability and altered behavior. It is likely that, as in the case of lead, it is the developing nervous system that is most vulnerable to these actions. Furthermore, the above discussion has not considered indirect effects on the nervous system mediated through the immune system via the neuroendocrine immune circuit, or through endocrine disruption via effects on either thyroid or sex steroid hormones (McKinney and Waller 1994; Seegal and Schantz 1994), although the immune system and both hormonal systems clearly affect the brain. Effects on the nervous system are difficult to determine in human populations but deserve much more attention than has been given to date. Furthermore, these subtle effects may occur at low levels of exposure and may be long-lasting or permanent. These considerations suggest that the significance of PCB neurotoxicity may have been grossly underestimated to date.

5 ACKNOWLEDGMENT

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THE APPLICATION OF COMPUTER MODELING
TO HEALTH EFFECT RESEARCH

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ABSTRACT

In the United States, estimates show that more than 30,000 hazardous waste disposal sites exist, not including military installations, U.S. Department of Energy nuclear facilities, and hundreds and thousands of underground fuel storage tanks; these sites undoubtedly have their own respective hazardous waste chemical problems. When so many sites contain hazardous chemicals, how does one study the health effects of the chemicals at these sites? There could be many different answers, but none would be perfect. For an area as complex and difficult as the study of chemical mixtures associated with hazardous waste disposal sites, there are no perfect approaches and protocols.

Human exposure to chemicals, be it environmental or occupational, is rarely, if ever, limited to a single chemical. Therefore, it is essential that we consider multiple chemical effects and interactions in our risk assessment process. Systematic toxicity testing of chemical mixtures in the environment or workplace that uses conventional toxicology methodologies is highly impractical because of the immense numbers of mixtures involved. For example, about 600,000 chemicals are being used in our society. Just considering binary chemical mixtures, this means that there could be 600,000 × 599,999/2 = 359,999,400,000 pairs of chemicals. Assuming that only one in a million of these pairs of chemicals acts synergistically or has other toxicologic interactions, there would still be 359,999 binary chemical mixtures possessing toxicologic interactions. Moreover, toxicologic interactions undoubtedly exist among chemical mixtures with three or more component chemicals; the number of possible combinations for these latter mixtures is almost infinite. These are astronomically large numbers with respect to systematic toxicity testing.

Therefore, the development of predictive and alternative toxicology method is imperative. To have a reasonable chance to deal with the complex issue of toxicology of chemical mixtures, we believe that the following concepts must be

considered: (1) exploitation of recent advances in computational technology; (2) use of mathematical/statistical modeling; and (3) coupling of computer modeling with very focused, mechanistically based, short-term toxicology studies. Our approach uses physiologically based pharmacokinetics/pharmacodynamics (PBPK/PD) modeling coupled with very focused, model-directed toxicology experiments as well as other statistical/mathematical modeling such as isobolographic analysis and response surface methodology. Because the toxicity produced by xenobiotics in the body is mediated by interactions between the chemicals and their metabolites and biological molecules or structures, understanding the PBPK/PD of xenobiotics is a necessity in toxicology. With the advent of PBPK/PD and computer modeling, the correlation of quantitative and temporal descriptions of xenobiotic concentrations at target tissues or organs with specific toxicities becomes attainable. By linking the interactive chemical components in a chemical mixture at the level of PBPK/PD modeling, we believe that it is possible to deal with the health effects, collectively, of the chemical mixture of interest. We propose using the "bottom-up" and "top-down" approaches for reaching the ultimate goal of predictive and alternative toxicology for chemical mixtures. The bottom-up approach refers to systematic toxicologic interaction studies starting with binary chemical mixtures based on toxic mechanism(s). We use PBPK/PD modeling as a guide and then add a third, fourth, ... etc., chemical on the basis of mechanistic considerations. In this way, we build up the chemical mixture as well as the interlinkage of PBPK/PD modeling of all the components of the chemical mixture. Ultimately, the integrated PBPK/PD model would encompass all the toxicologic interactions in the chemical mixture and be able to predict toxicities for the entire mixture. The top-down approach, as the name implies, starts out with a more complex chemical mixture of several to many component chemicals. By using a particular toxicologic endpoint for the entire chemical mixture as a guide, we can study that toxicologic endpoint on some of its submixtures and components on the basis of our knowledge of the individual chemicals. In so doing, we base our selection of the submixtures on an educated guess rather than working through all the possible combinations. In this manner, we conduct experiments more efficiently on finer and finer submixtures until we work with individual chemicals. Of course, the integration of PBPK/PD modeling and other statistical/mathematical modeling with top-down experimentation is also an essential feature of this approach. The ultimate goal again is to predict toxicities for the entire mixture.

This paper describes a number of our specific research projects. These examples partially illustrate the ongoing research at Colorado State University and also illustrate related ideas with respect to possibly using novel applications for risk assessments of chemical mixtures.

1 INTRODUCTION

This paper is related to the application of computer modeling to health effect research. At the outset, one might ask, "Why computer modeling?" Without some of us ever realizing it, computer modeling is all around us. For instance, weather forecasting, stock market predictions, airline reservations, and even the traffic light signals at busy intersections are examples of the widespread applications of computer modeling. In biomedical engineering, the development of the heart-lung machine, kidney dialysis instruments, the artificial heart, etc., is also based on computer modeling. Computer modeling is very much an integral part of our daily life. Thus, it is not surprising that computer modeling has slowly but surely been used in health effect research.

To experience health effects from chemicals, one must first be exposed to chemicals. If we consider the food and drinks we ingest, the indoor and outdoor air pollutants we inhale, the cosmetics, toiletries, and medicine we use, there is really no such thing as a single chemical exposure. Systematic toxicity testing of chemical mixtures in the environment or workplace that uses conventional toxicology methodologies is highly impractical because of the immense numbers of mixtures involved. For example, a chemical mixture with 25 components has $2^{[25]}$ -1 or 33,554,431 combinations (i.e., one chemical at a time, any two chemicals in combination, any three in combination, etc.) (Yang, 1994; Yang et al. 1995a). Furthermore, this huge number of combinations is just for one concentration per chemical. From a different perspective, about 600,000 chemicals are being used in our society (NTP, 1994). Just considering binary chemical mixtures, this means that there could be 600,000 × 599,999/2 = 359,999,400,000 pairs of chemicals. Of course, there are also chemical mixtures with three or more component chemicals; the number of possible combinations for these latter mixtures is almost infinite.

Given the above discussion, it is obviously impossible to rely on conventional toxicity testing methodologies to deal with chemical mixtures. Thus, we must utilize and integrate (1) computational technology; (2) focused, mechanistically based, short-term toxicology studies; and (3) mathematical/statistical modeling.

Can "predictive and alternative toxicology" be developed for chemical mixtures by using physiologically based pharmacokinetics/pharmacodynamics (PBPK/PD) coupled with statistical/mathematical modeling? In our opinion, the answer to this question is yes. Because the toxicity produced by xenobiotics in the body is mediated by interactions between the chemicals and their metabolites and biological molecules or structures (DHHS, 1986), understanding the PBPK/PD of xenobiotics is a necessity in toxicology. With the advent of PBPK/PD and computer modeling, the correlation of quantitative and temporal descriptions of xenobiotic concentrations at target tissues or organs with specific toxicities becomes attainable. By linking the interactive chemical components in a chemical mixture at the level of PBPK/PD modeling, we believe that it is possible to deal with the health effects, collectively, of the chemical mixture of interest. We propose the "bottom-up" and "top-down" approaches for reaching the ultimate goal of predictive and alternative toxicology for chemical mixtures. Examples are used to briefly explain these two approaches.

1.1 Bottom-Up Approach

The bottom-up approach refers to systematic toxicologic interaction studies starting with binary chemical mixtures based on toxic mechanism(s). We use PBPK/PD modeling as a guide, then add a third, fourth, ... etc., chemical into the modeling and experimental work on the basis of mechanistic considerations. In this way, we build up the chemical mixture as well as the interlinkage of PBPK/PD modeling of all the components of the chemical mixture. Ultimately, the integrated PBPK/PD model would encompass all the toxicologic interactions in the chemical mixture, and it would be able to predict toxicities for the entire mixture. For instance, we have already studied the toxicologic interactions with respect to impairment of liver regeneration by Kepone in the hepatotoxicity of CCl_4 by coupling experimental toxicology, PBPK/PD modeling, and Monte Carlo simulation (El-Masri et al. 1995, 1996). Since Kepone pretreatment is a prerequisite for this toxicologic interaction, we must hold Kepone as a constant component in all mixtures. Thus, with the addition of two new, known hepatotoxins, 1,1,2,2-tetrachloroethane (1,1,2,2-TE) and hexachloro-1,3-butadiene (HCBD), two new binary chemical mixtures are formed (i.e., Kepone + 1,1,2,2-TE; Kepone + HCBD). Modeling and experimental toxicology results can be obtained for these binary chemical mixtures. Subsequently, we can form the three-component chemical mixtures (i.e., Kepone + CCl_4 + 1,1,2,2-TE; Kepone + CCl_4 + HCBD; Kepone + 1,1,2,2-TE + HCBD) and the four-component chemical mixture (i.e., Kepone + CCl_4 + 1,1,2,2-TE + HCBD). Of course, modeling and experimental toxicology results will be obtained for these chemical mixtures as well. In this manner, more and more complicated chemical mixtures are built up on the basis of mechanisms of toxicity.

As a glimpse of the possible utility of this type of approach, we discuss the findings of PBPK/PD modeling of a binary chemical mixture (Kepone and CCl_4) on the basis of mechanisms of toxicity of interactions and the application of the computer in acute toxicity studies.

The order of the discussion is (1) background toxicology information on Kepone and CCl_4, singly and in combination; (2) our effort on PBPK/PD modeling and model validation by using published data; (3) the coupling of the PBPK/PD model with Monte Carlo simulation and the prediction of acute toxicity (i.e., mortality), based on pharmacodynamics of hepatotoxicity, in CCl_4-dosed rats with or without pretreatment of dietary Kepone; and (4) comparison of computer-predicted results with observed data from experiments conducted in our laboratory.

CCl_4 is a well-known hepatotoxin (Plaa, 1991). Following free radical formation through the P450 enzyme system, the toxicity of CCl_4 can be an accumulation of lipids (steatosis, fatty liver) and degenerative processes leading to cell death (necrosis) (Plaa, 1991). Kepone (also known as chlordecone) is found in the environment as a result of photolytic oxidation of Mirex, a pesticide used for the control of fire ants, or as a pollutant from careless and irresponsible discharge (Menzer, 1991). At relatively low levels (e.g., 10 ppm in the diet), even repeated dosing of Kepone in the diet up to 15 days caused no apparent toxicity to the liver (Lockard et al. 1983a).

The toxicologic interaction between Kepone and CCl_4 was reported by Curtis et al. (1979). They illustrated that a 15-day dietary exposure of male rats to Kepone at 10 ppm, an environmentally realistic level of contamination, markedly enhanced liver toxicity produced by an intraperitoneal (i.p.) injection of a marginally toxic dose of CCl_4 (100 μL/kg). This toxicologic interaction is unique for three reasons: (1) unlike many other toxicologic interaction studies that usually deal with acute toxicity at very high doses, in this instance, Kepone is administered at a very low environmental level; (2) CCl_4 is also dosed at a marginally toxic level; (3) the magnitude of toxicologic interaction is very large. On the basis of the administered dose, the enhancement of CCl_4 lethality is about 67-fold. The mechanism of this toxicologic interaction was elucidated to be the obstruction by Kepone of the liver's regeneration process (Mehendale, 1984, 1991, 1994).

We chose this binary interaction as a model system to develop our bottom-up approach for chemical mixtures. As shown in Fig. 1,[c] the pharmacokinetic portion of the PBPK/PD model was an adaptation of the PBPK model of Paustenbach et al. (1988). Initial verification of this PBPK model was carried out by using data from exhaled breath analyses from CCl_4-treated rats in our laboratory (El-Masri et al. 1996). This PBPK model was then linked with a PBPD model (Fig. 2) developed in our laboratory on the basis of the reported mechanism of toxicologic interaction between Kepone and CCl_4. By incorporating cell birth/death processes into the PBPK/PD model, time course computer simulations of mitotic, injured, and pyknotic cells after treatment with CCl_4 alone or in combination with Kepone (10 ppm in the diet for 15-day pretreatment) were carried out. Verification of the PBPK/PD model was carried out by comparing simulation results with existing time course data in the literature (Lockard et al. 1983b), as shown in Fig. 3.

To work toward the goal of predictive and alternative toxicology, this PBPK/PD model was coupled with Monte Carlo simulation to predict the acute lethality of CCl_4 alone and in combination with Kepone (10 ppm in the diet for 15-day pretreatment). In so doing, we were able to conduct acute toxicity studies of a very large sample (i.e., 1,000 rats/dose) on the computer (El-Masri et al. 1996). As shown in Table 1, these a priori predictions of lethality were in very good agreement with experimentally derived values except at very high CCl_4 dose levels. In this latter case, the under-prediction of lethality resulted from toxicity other than the liver. It was most likely a neurotoxic effect on the central nervous system. Histomorphometric analyses of the liver supported this explanation (El-Masri et al. 1995, 1996). The extent and prevalence of hepatocellular necrosis at 6,000 μL/kg was disproportionally small because some of the rats died of CNS effects of CCl_4 before hepatotoxicity could be developed.

Figures and table appear at the end of this paper.

1.2 Top-Down Approach

The top-down approach, as the name implies, begins with a more complex chemical mixture of several to many component chemicals. Here we use a chemical mixture of seven groundwater contaminants (arsenic, benzene, chloroform, chromium, lead, phenol, and trichloroethylene) to illustrate the essence of the top-down approach. From earlier studies (Constan et al. 1994, 1995), we have already obtained interesting preliminary findings on the complete mixture and some of its submixtures. Because there are $2^{[7]} - 1 = 127$ combinations for seven chemicals at only one concentration, systematic toxicity testing on all the combinations is prohibitively expensive. Thus, we tried to minimize experimentation by using educated guesses to set study priorities for the submixtures to be tested. For instance, the initial fractionation into a metal submixture and organic chemical submixture appeared to be a reasonable first step. Because we were interested in finding out the potential promoter activities of this chemical mixture, its submixtures, and components, further subfractionations according to the known carcinogenicity of these chemicals seemed to be a reasonable approach as well. In this manner, we can conduct experiments on finer and finer submixtures until we work with individual chemicals. As a representative scenario, Fig. 4 illustrates this approach graphically.

Although the overall number of combinations for seven chemicals is 127, by using the top-down approach, we would study only a total of five chemical mixtures and seven individual chemicals. On the basis of our knowledge and experience with the seven chemicals, we believe that this simplified top-down scheme (Fig. 4) would be sufficient to "tease out" the chemicals responsible for the findings (i.e., increased liver cell proliferation around the hepatic vein, pharmacokinetic and enzyme kinetic changes) from our earlier studies (Constan et al. 1994, 1995).

PBPK/PD modeling of chemical mixtures beyond two components is at an embryonic stage. Therefore, our discussion here is largely conceptual. The simplest and most primitive way is to consider the whole mixture as a single entity. Depending on the endpoint(s) chosen, such as liver cell proliferation or enzyme or pharmacokinetic parameter changes, we may consider, in the modeling process, the effects of this entire chemical mixture on that specific endpoint. There are some concerns about this approach; they are discussed elsewhere (Krishnan et al. 1994; El-Masri et al., 1997). The most complicated and thus the most refined way is to have a PBPK/PD model for each of the chemical components in the chemical mixture. These models are then linked at pharmacokinetic and/or pharmacodynamic level(s) to include all known toxicologic interactions. Even though this way may require very complex modeling and computer simulation, the current capability of computational technology should permit us to do so. Between the above two ways is a compromise approach. In this approach, the chemical engineering concept of "lumping analysis" (Sapre and Krambeck, 1991) may be applied to "lump" certain chemicals into a group as an entity. Considering how successful the application of this technique is in chemical engineering processes, it is reasonable to assume that the application of lumping analysis for PBPK/PD modeling of chemical mixture toxicology is possible. Recently, we developed a theoretical approach toward the top-down evaluation of complex chemical mixtures such as JP-5 or other petroleum products (Verhaar et al. 1997); this approach involves the integration of QSAR, lumping analysis, and PBPK/PD modeling.

2 DISCUSSION AND PERSPECTIVES

Our research effort on PBPK/PD modeling with chemical mixtures aims at developing predictive and alternative toxicology. By "predictive toxicology," we are referring to tissue dosimetry at the pharmacokinetic and pharmacodynamic levels. By "alternative toxicology," we are working toward minimizing animal experimentation, as illustrated in the example given for Monte Carlo simulation coupled with PBPK/PD modeling of Kepone/CCl_4 interactions. The application of PBPK/PD to the risk assessment of chemical mixtures may have several advantages: (1) the incorporation of mechanistic information on toxicologic interactions; (2) the conservation of resources and reduction in animal killing and suffering in the hazard identification step; and (3) a decrease in the necessity for using large uncertainty factors. Thus, PBPK/PD modeling will provide more realism into the risk assessment process. Of course, one must be aware of the fact that PBPK/PD modeling has its own intrinsic "uncertainties"; therefore, as much as practicable, any PBPK/PD model must be rigorously validated with experimental results before the "predictive toxicology" so derived becomes meaningful.

The linkage of two of the most challenging areas in toxicology today — PBPK/PD 12 and statistical/mathematical modeling linked with the experimental toxicology of chemical mixtures — will have immense potential for application to risk assessments of chemical mixtures. Figure 5 is our strategy for predictive and alternative toxicology for chemical mixtures and the development of innovative risk assessment methodologies for chemical mixtures. We are attempting to couple PBPK/PD and other experimental toxicology with isobolographic analysis and/or response surface methodology for the modeling and analysis of toxicologic interactions. With the aid of techniques such as Monte Carlo simulation, we may better predict tissue dosimetry at the pharmacokinetic and pharmacodynamic levels. By using such values as benchmark doses, the human risk assessment of chemical mixtures may be carried out with less uncertainty.

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Table 1 Kepone/Carbon Tetrachloride Mortality by PBPK/PD Modeling Coupled with Monte Carlo Simulation vs. Experimental Observations (after El-Masri et al. 1995)

Dose Given		Model Predictions[a]		Observed[b]	
Kepone (ppm)	CCl_4 ($\mu L/kg^{-1}$)	No. of Dead Rats	% Dead	No. of Dead Rats	% Dead
0	100	0	0.0	0	0.0
0	1000	1-2	13.2	1	11.1
0	3000	3	32.8	4	44.4
0	6000	4-5	47.8	8	88.8
10	10	0	0.0	0	0.0
10	50	4-5	47.5	4	44.4
10	100	8-9	84.0	8	88.8

[a] Mortalities in 48 hours, *n* = 9; Monte Carlo simulation, *n* = 1,000.

[b] Actual lethality studies, *n* = 9.

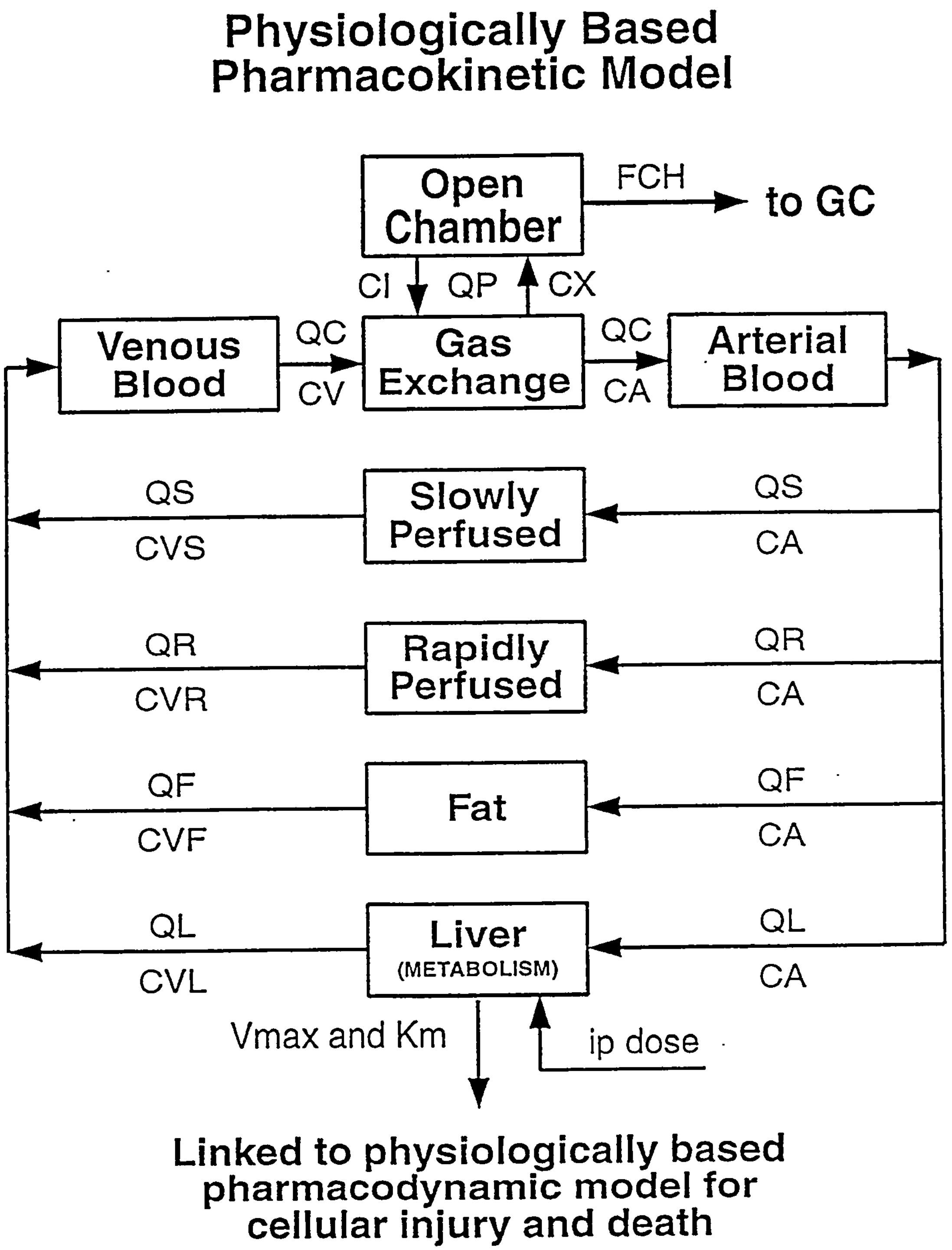

Fig. 1 PBPK Model for CCl_4 Adapted from Paustenbach et al. (1988) (CI and CX are concentrations of CCl_4 in the inhaled [thus chamber concentration] and exhaled breath. CV and CA represent venous and arterial blood concentrations of CCl_4. Q depicts blood flow rate. S, R, F, L refer to slowly perfused, rapidly perfused, fat, and liver compartments, respectively. Vmax and Km are in vivo hybrid constants representing maximal velocity and affinity constants for enzyme systems involved in the metabolism of CCl_4 [after El-Masri et al., 1995].)

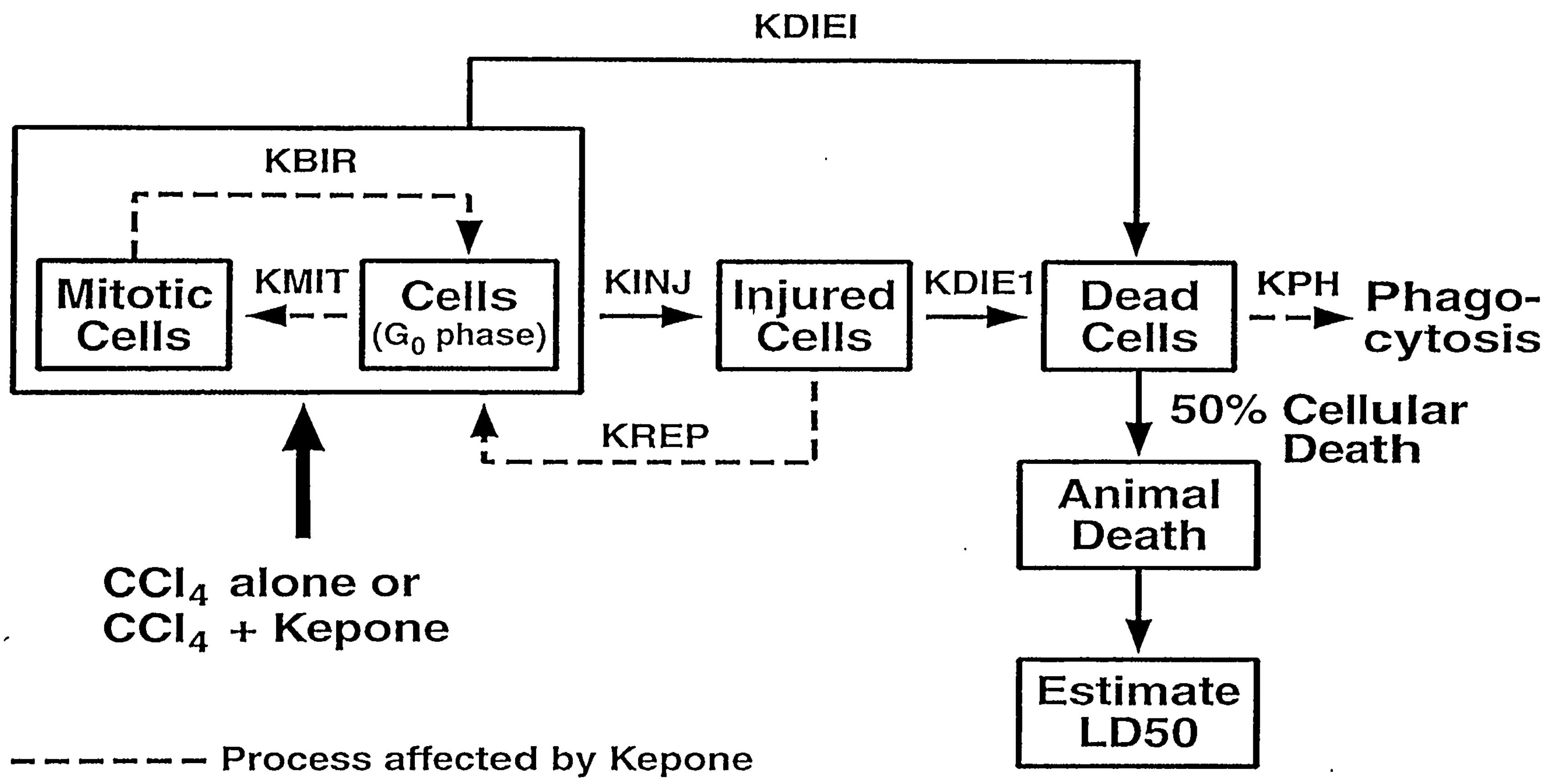

Fig. 2 PBPD Model for Toxicologic Interactions between Kepone and CCl_4 (This depicts the schematic of pharmacodynamic effects of CCl_4 on the cellular injury and death. The dashed lines depict the processes that are affected by the presence of Kepone. When cells are exposed to the reactive metabolites of CCl_4, their inherent death rate is influenced by two mechanisms. A major mechanism of cellular injury leading to death is lipid accumulation, which is illustrated here as the formation of injured cells and dead cells via two rate constants, KINJ and KDIE1. For simplicity, all other causes of cell death, including natural cell death and other CCl_4-related toxicities, are lumped together into a hybrid constant, KDIEI, as a second mechanism. The injured cells can either be repaired to become viable cells again or continue to die. All dead cells, whether induced to die or injured to death, are removed from the liver by phagocytosis. Additionally, the PBPD model considers the effects of CCl_4, alone or in combination with Kepone, on cellular mitotic and birth rates [after El-Masri et al. 1995].)

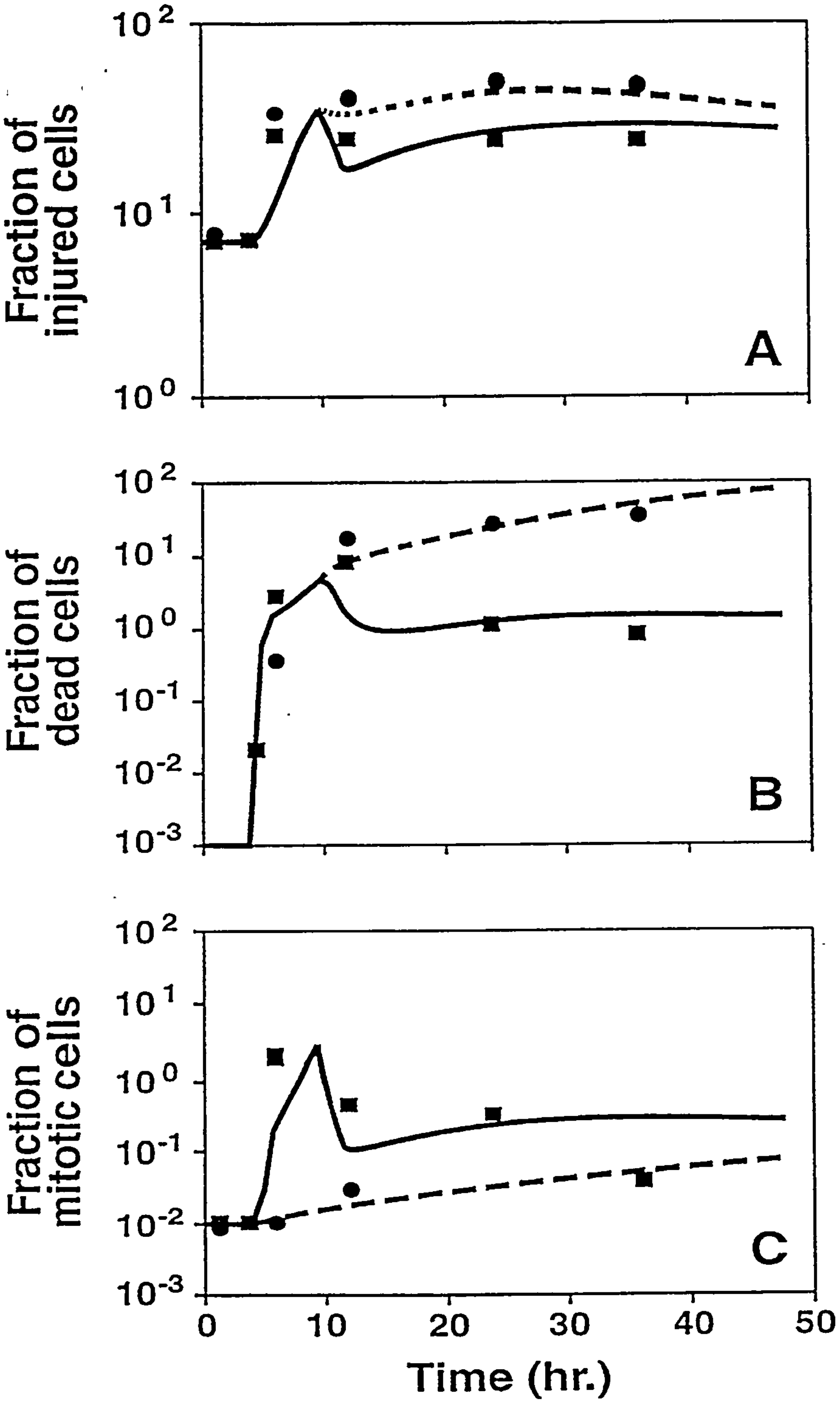

Fig. 3 PBPK/PD Model Predictions of the Pyknotic, Injured, and Mitotic Cells from Rats Exposed to CCl_4 Only (squares and solid lines) or CCl_4 with Kepone Pretreatment (circles and dashed lines) (The experimental data were obtained from Lockard et al. [1983 a, b]. The model predictions are shown by the lines [after El-Masri et al. 1996].)

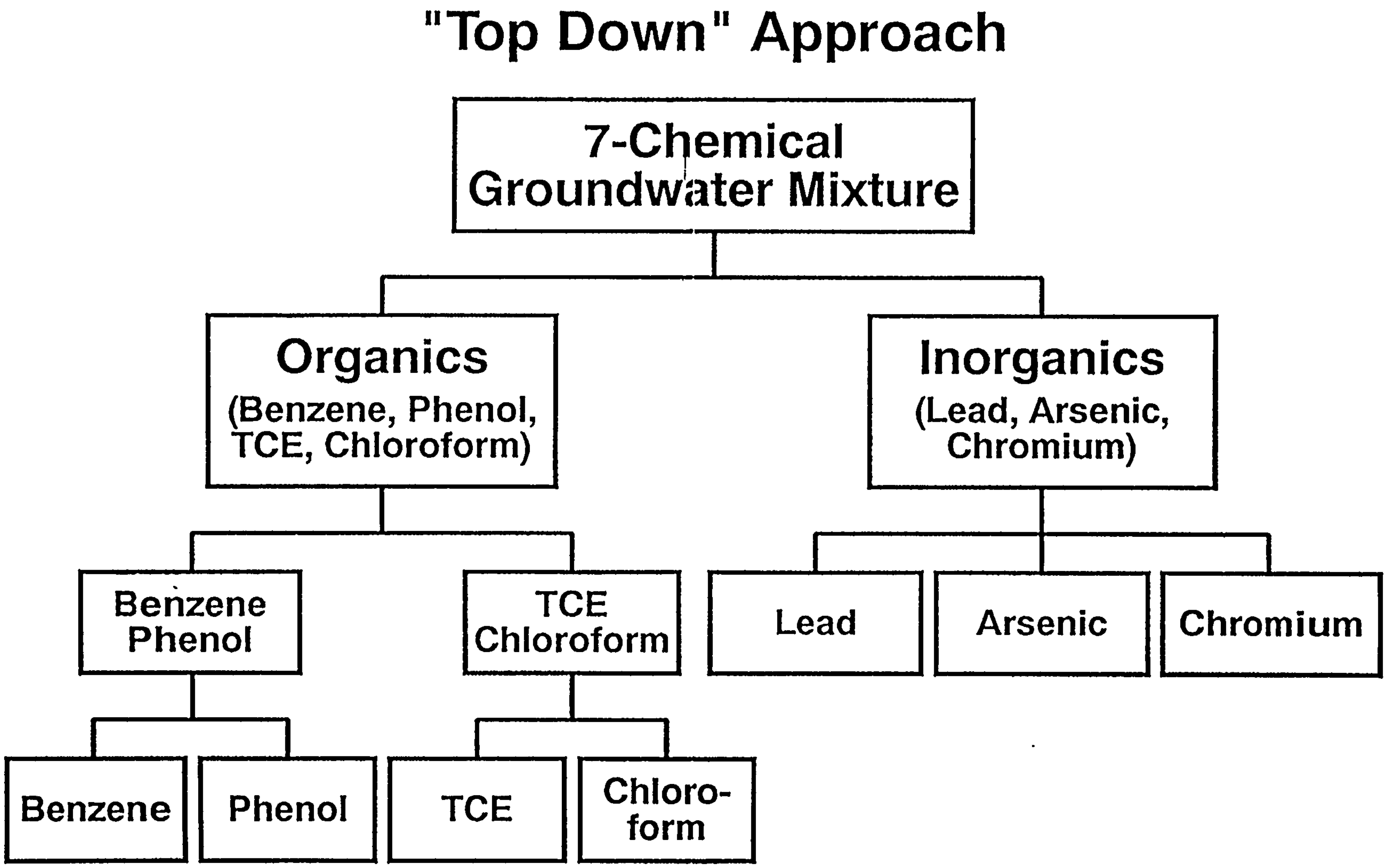

Fig. 4 Top-down Approach to the Evaluation of Chemical Interactions in Chemical Mixtures of Groundwater Contaminants from Superfund Hazardous Waste Disposal Sites (after Yang et al. 1995b)

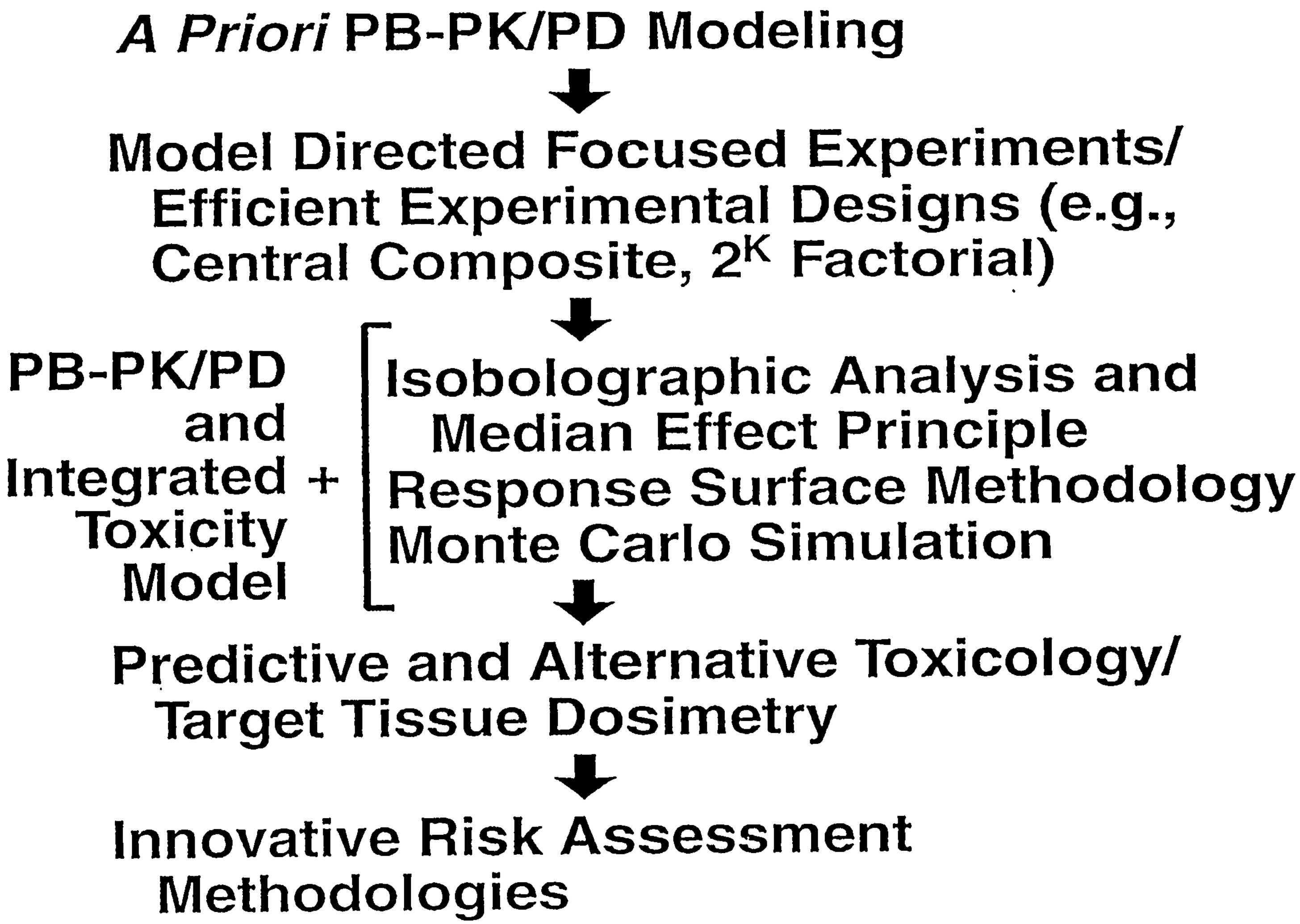

Fig. 5 Our Proposed Strategy/Approach to Develop "Predictive and Alternative Toxicology" and Formulate an "Innovative Risk Assessment Methodology" for Chemical Mixtures (modified from El-Masri et al. 1995)

CYTOTOXIC AND DNA-DAMAGING EFFECTS OF METHYL *TERT*-BUTYL ETHER AND ITS METABOLITES ON HL-60 CELLS *IN VITRO*

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ABSTRACT

Methyl *tert*-butyl ether (MTBE) is a widely used oxygenate in unleaded gasoline; however, few studies have been conducted on the toxicity of this compound. This study evaluates the cytotoxic and DNA-damaging effects of MTBE and its metabolites in a human haemopoietic cell line, HL-60. The metabolites of MTBE studied include tertiary butyl alcohol (TBA), α-hydroxyisobutyric acid (HIBA), and formaldehyde. Comet assay is used to assess DNA damage, and the cytotoxicity is investigated by lactate dehydrogenease (LDH) release. The results show no significant cytotoxic effects of MTBE, TBA, and HIBA over a concentration ranging from 1 to 30 mM. Formaldehyde, in contrast, causes a substantial LDH release at a concentration of 5 μM. Hydrogen peroxide, a known oxidative agent, at concentrations ranging from 10 to 100 μM, produces a significant dose-related increase in DNA damage, whereas a much higher concentration of MTBE (1 to 30 mM) is required to produce a similar observation. The genotoxic effects of TBA and HIBA appear to be identical to that of MTBE. Conversely, DNA damage is observed for formaldehyde at a relatively low concentration range (5 to 100 μM). These findings suggest that MTBE and its metabolites, except formaldehyde, have relatively low cytotoxic and genotoxic effects.

1 INTRODUCTION

For the last 10 to 15 years, methyl *tert*-butyl ether (MTBE) has been widely used as an oxygenated additive in gasoline, mainly to improve the combustion process and reduce emissions of carbon monoxide. Exposure to MTBE is widespread: it is estimated that more than 100 million people are exposed to MTBE and its combustion products in the United States alone (U.S. Environmental

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Protection Agency 1993). In addition, there is a potential risk for contamination of drinking water due to spills and leakage from underground gasoline storage tanks.

During the last few years, some preliminary studies have been conducted on the carcinogenicity of MTBE. According to the U.S. National Toxicology Program, some evidence of carcinogenicity of MTBE has been found in rodents. For instance, Burleigh-Flayer et al. (1992) found increased incidence of liver tumors in mice that had inhaled MTBE. In another chronic inhalation study, a significant increase in kidney and testicular tumors was identified in male rats (Chun et al. 1992). Similar results were also observed in rats by Belpoggi et al. (1995). Based on the overall evidence, MTBE has been classified as a Group B2 carcinogen, i.e., probable human carcinogen with sufficient evidence from animal experiments and inadequate data from human epidemiological studies (Rudo 1995).

However, some of the carcinogenic results from animal studies have been disputed. For instance, Mennear (1995) believed that the higher incidence of testicular tumor (Leydig cell tumor) in MTBE-treated rats found by Belpoggi et al. (1995) was most probably attributed to the differential survival rate, rather than to MTBE exposure. At present, no published data are available on the genotoxicity or mutagenicity of MTBE, although some privately communicated results showed that MTBE is not mutagenic in activated *S. typhimurium* and does not increase the incidence of chromosomal aberrations in mammalian cells under *in vitro* conditions (Wibowo 1994). Therefore, studies on the cytotoxicity and genotoxicity of MTBE and its metabolites will help to gain a better understanding of the possible health effects of MTBE.

The primary purpose of the present study is to determine whether, and in what concentration range, MTBE and its metabolites cause cytotoxic and DNA-damaging effects in a human haemopoietic cell line, HL-60. This cell line has been demonstrated to be particularly useful as a model to characterize the myelotoxic effect of certain carcinogens and to study the mechanisms involved (Sharma et al. 1994; Shen et al. 1996). The MTBE metabolites studied include tertiary butyl alcohol (TBA), α-hydroxyisobutyric acid (HIBA), and formaldehyde. The cytotoxic and DNA-damaging effects of a known oxidative agent, hydrogen peroxide (H_2O_2) are also investigated as a positive control.

2 MATERIALS AND METHODS

2.1 Chemicals

Methyl *tert*-butyl ether, TBA, formaldehyde, and H_2O_2 were obtained from E. Merck (Germany). HIBA, penicillin, streptomyčin, and ethidium bromide (EtBr) were provided by Sigma Chemicals Company (United States). Normal melting agarose (NMA), low-melting-point agarose (LMA), and RPMI 1640 medium were purchased from Gibco (United States). Fetal bovine serum (FBS) was purchased from Cytosystems (Australia). Reagents for lactate dehydrogenase (LDH) measurements were from Abbott Laboratories (United States).

2.2 Cell Culture

HL-60 cells were cultured in RPMI 1640 medium, supplemented with 10% FBS, 50 units/mL penicillin, and 50 μg/mL streptomycin. Cells were grown at 37 °C in a 5% carbon dioxide, 95% air incubator. HL-60 cells were harvested by centrifugation (1,000 rpm × 5 min). The final concentration of cells was 5×10^6 cell/mL in RPMI 1640 medium without FBS before treatment.

2.3 Treatment

MTBE and its metabolites (TBA, HIBA, and formaldehyde) were diluted to the required concentrations in deionized-distilled water. Cells were incubated with different doses of these chemicals for 1 h. For comparison, H_2O_2 was used as a positive control in the experiments.

2.4 Measurement of DNA Damage by Comet Assay

The Comet assay was conducted according to the method described by Zhuang et al. (1996). Briefly, it includes four steps: slide preparation, electrophoresis, staining, and evaluation of DNA damage.

2.4.1 Slide Preparation

Fully frosted microscopic slides were covered with 80 μL of 0.7% NMA at 50°C in Ca^{2+} and Mg^{2+} free PBS (pH 7.4). They were immediately covered with a slide and kept at room temperature for about 5 min to allow the agarose gel to solidify. Then 10 μL of a freshly prepared cell suspension was mixed with 75 μL of 0.65% LMA at 37 °C, and the mixture was rapidly pipetted onto the first agarose layer and spread with another cover slide. The slide was kept on ice for 5 min to let the gel solidify. After removing the cover slide, 80 μL 0.65% LMA was added as the third layer and again covered with a slide. After removing the last cover slide, the slide was immersed in a freshly prepared cold lysing solution containing 100 mM N_2 EDTA, 2.5 M NaCl, and 10 mM Tris (pH 10), with 1% Triton X-100 and 10% DMSO for 1 h at 4 °C to lyse the cells and permit DNA unfolding.

2.4.2 Electrophoresis

The slides were removed from the lysing solution, drained, and placed in a gel electrophoresis tank side by side, avoiding spaces and with the agarose ends facing each other, nearest the anode. The tank was filled with fresh electrophoresis buffer (1 mM Na_2 EDTA and 300 mM NaOH, pH 13.0) to a level approximately 0.25 cm above the slides. The slides were put in the buffer for 20 min to allow the unwinding of DNA and expression of alkali labile damage before electrophoreses. Electrophoresis was conducted at 4°C for 20 min at 25 V (Bio-Rad, power supply 200/2.0) and adjusting the current to 300 mA by increasing or decreasing the buffer level. After electrophoresis, the slides were gently neutralized in 0.4 M Tris-HCl buffer (pH 7.5) for 5 min. This procedure was repeated twice before DNA staining.

2.4.3 Staining

For staining, 50 μL EtBr (20 μg/mL) was added to each slide and covered with a slide. The slides were placed in a humidified airtight container to prevent drying of the gel and examined by using a fluorescence microscope within 2 days after completion of staining.

2.4.4 Evaluation of DNA Damage

In this study, the extent of DNA damage was evaluated by measuring DNA migration in the field of electrophoresis, and the distance of DNA migration from the body of the nuclear core to the end of the tail (tail length) was used as an index of DNA damage (Singh et al. 1988; Tice et al. 1990). Slides were examined at 400 X magnification by using a fluorescence microscope (Nikon, Japan), equipped with an excitation filter of BP 546/10 nm and a barrier filter of 590 nm. Images of 100 randomly selected cells (50 cells from each of 2 replicate slides) were analyzed for each sample.

2.5 Determination of Cytotoxicity

From each flask, 100 μL aliquot of medium was collected for determining LDH activity in the medium. Total LDH activity in cells was determined after thorough breakdown of HL-60 cells using ultrasonication. The ratio of LDH release (%) of the treated group to the control was used as an index of cell injury. The percentage of LDH release in each group was obtained according to the following formula:

$$\text{LDH release (\%)} = \text{(LDH activity present in the medium after incubation)/} \\ \text{(total LDH activity)} \times 100.$$

2.6 Statistical Analysis

All data are from three (Comet assay) or four (LDH release) independent experiments and presented as mean ± SE. The difference between the treated and control group was analyzed using the student's *t* test. A p value less than 0.05 was considered statistically significant.

3 RESULTS

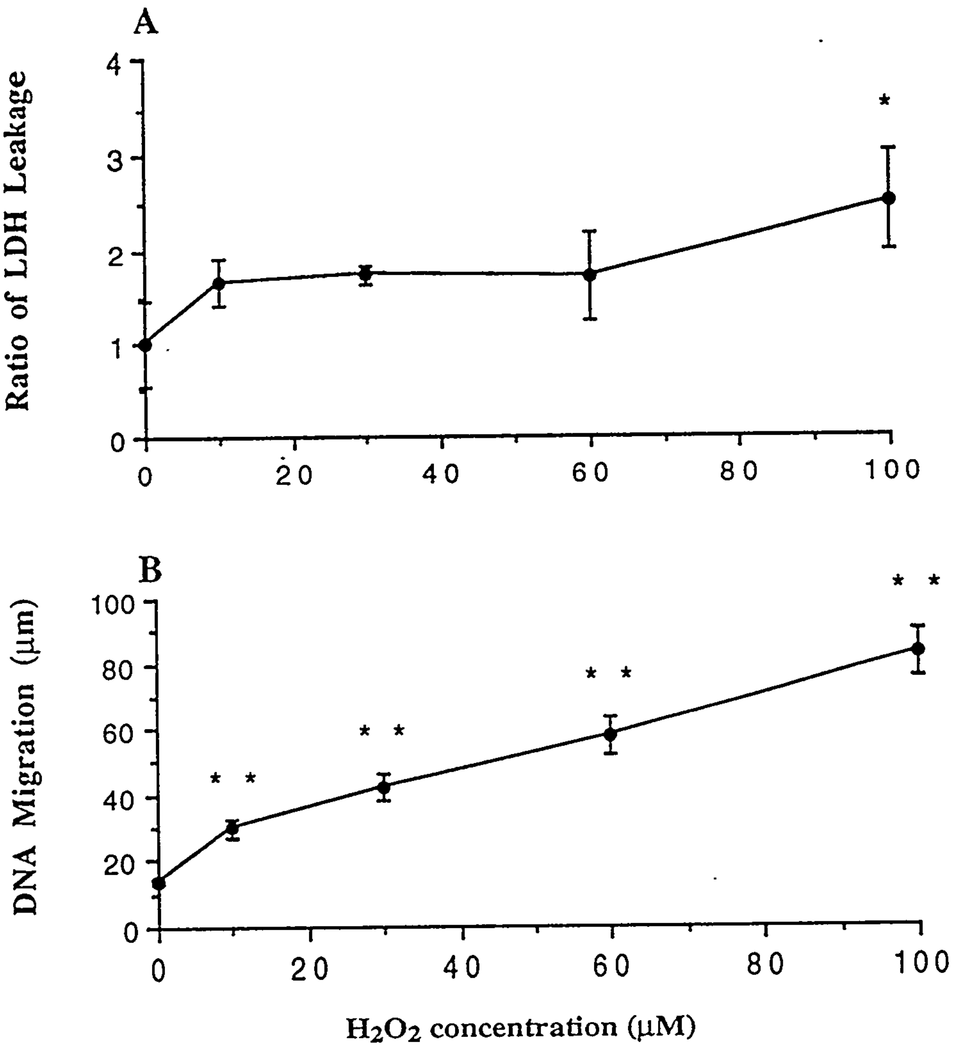
3.1 Cytotoxicity of MTBE and Its Metabolites

In this set of experiments, the cytotoxic effects of MTBE and its metabolites were evaluated by determining the LDH release. HL-60 cells were treated with H_2O_2, MTBE, or its metabolites (TBA, HIBA, and formaldehyde) for 1 h. Figure 1A shows that significant LDH release from HL-60 cells was only observed when cells were treated with 100 μM of H_2O_2, and no evident changes were noted in other concentration groups. On the other hand, MTBE and its two metabolites (TBA and HIBA), over a much higher concentration range of 1 to 30 mM, all failed to induce any marked changes in LDH release (Fig. 2A). Formaldehyde, in contrast, caused a significant cytotoxic effect, as a substantial amount of LDH was released at a relatively low concentration of 5 μM with 1 h incubation (Fig. 3A). However, the extent of LDH release caused by formaldehyde gradually plateaued from 10 μM onward.

3.2 DNA Damage Caused by MTBE and Its Metabolites

In this part of the experiments, the DNA-damaging effects of MTBE and its metabolites were determined by using Comet assay, as shown in Picture 1. No tail was observed in the control cells (Picture 1A), and obvious tails were formed in both H_2O_2- and MTBE-treated HL-60 cells (Pictures 1B and 1C). Figure 1B shows that H_2O_2 ranging from 10 to 100 μM produced a significant dose-related increase in the length of DNA migration, reflecting a dose-dependent pattern of DNA-damage caused by H_2O_2. Results from Fig. 2B show that a much higher concentration range of MTBE (1 to 30 mM) was required to produce a similar effect. It was also found that the DNA-damaging effect of two MTBE metabolites, TBA and HIBA, appeared to be similar to that of MTBE (Fig. 2B).

In contrast, HL-60 cells were rather sensitive to the DNA-damaging effect of formaldehyde, as significant changes were observed when the HL-60 cells were treated with a much lower concentration range (5 to 100 μM) (Fig. 3B). Similar to the changes of LDH release induced by formaldehyde (Fig. 3A), a gradual decrease in DNA damage was also observed with increasing formaldehyde concentration. When HL-60 cells were incubated with 500 μM of formaldehyde for

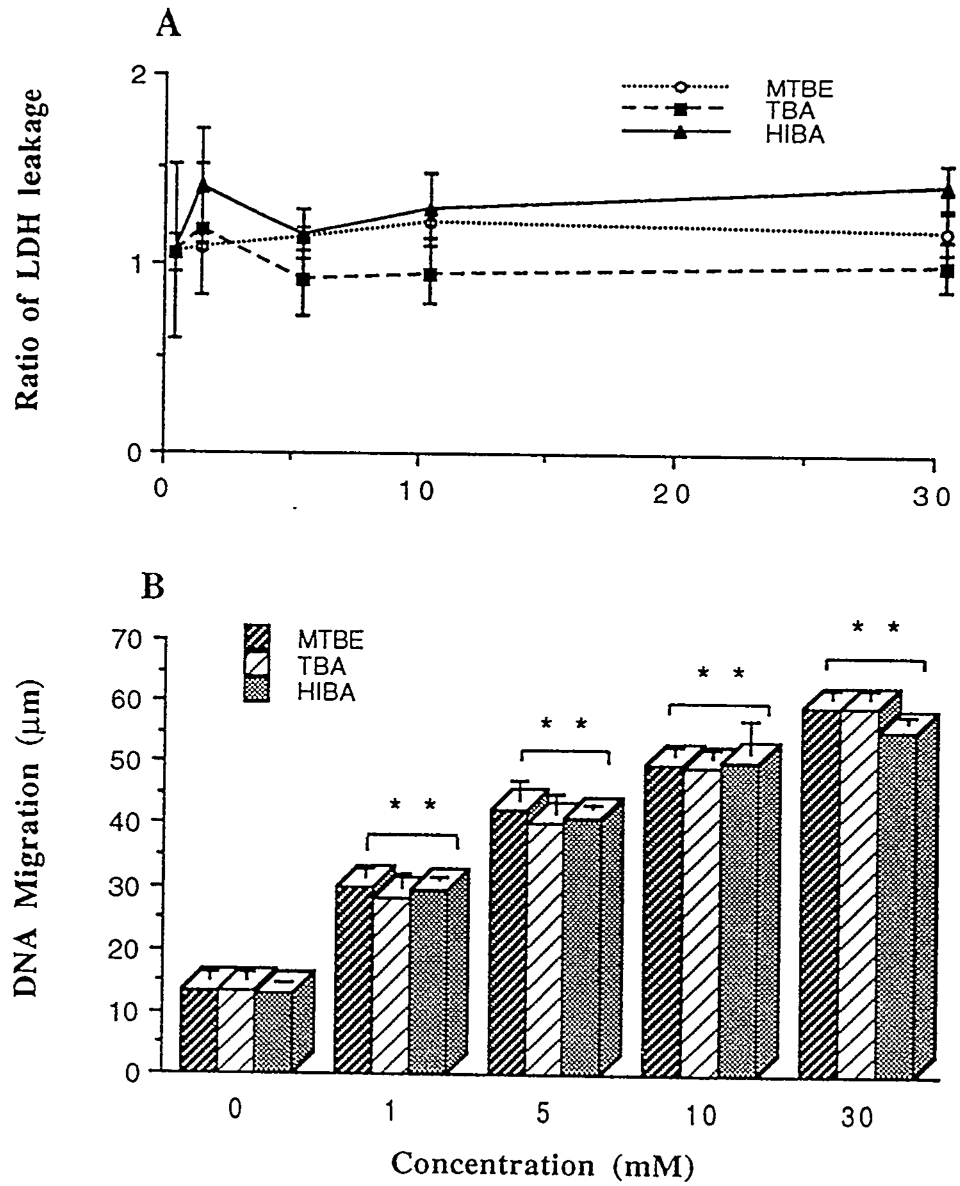


Figs. 1A and 1B H_2O_2-induced Cytotoxicity Determined by the Ratio of LDH Release (1A) and DNA Damage Determined by Comet Assay (1B) (Data are expressed as mean ± SE. * $p < 0.05$ ** $p < 0.01$ compared to the control group [0 concentration]; student's *t* test.)

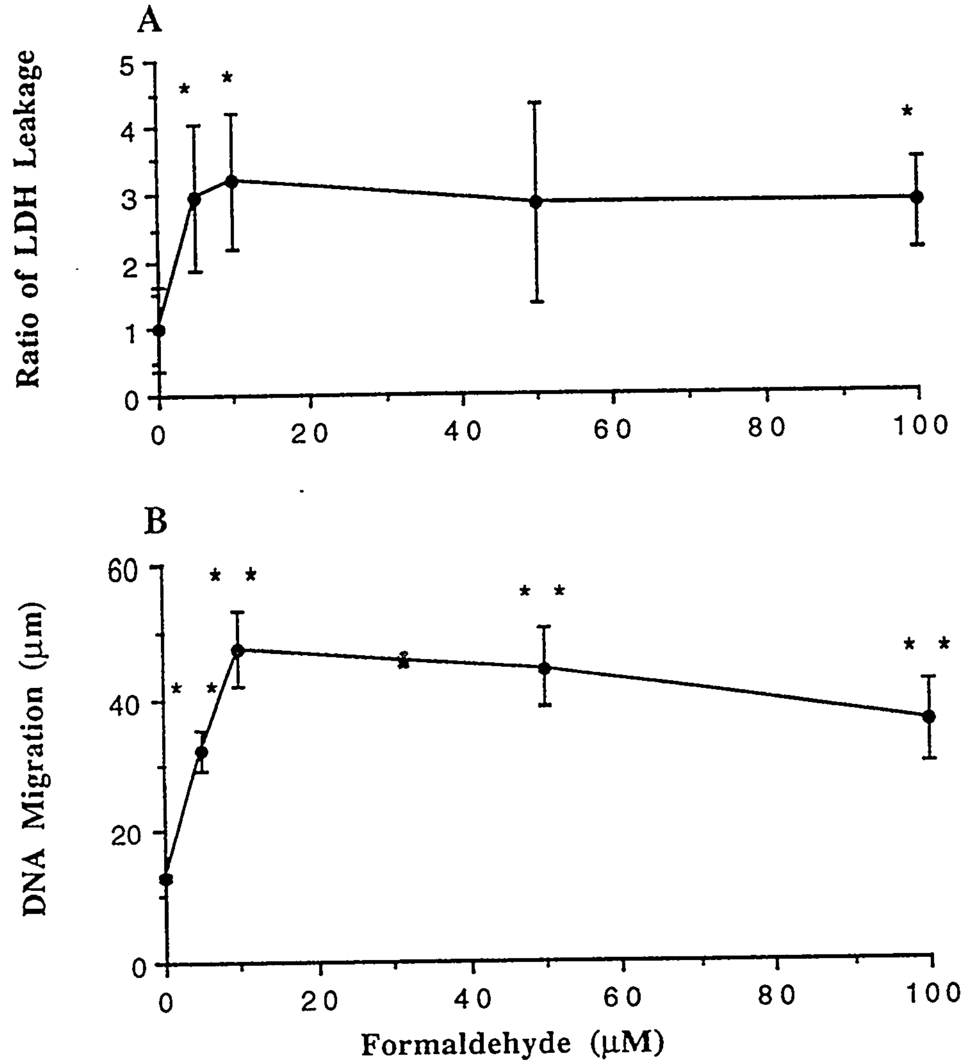
1 h, almost all cells were fixed, and no DNA migration (Comet tail formation) was found, as shown in Picture 1D.

4 DISCUSSION

MTBE has become a public health concern in recent years because of its extensive use as an oxygenated additive in gasoline and its widespread environmental and occupational exposure. In

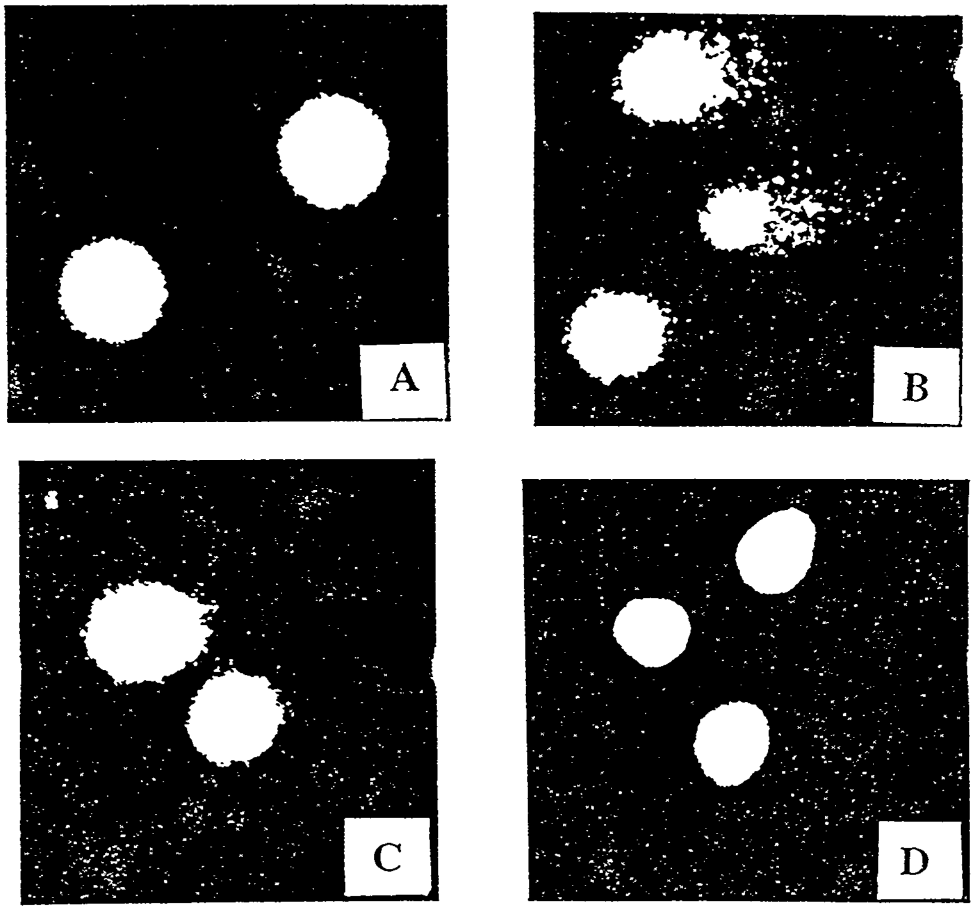


Figs. 2A and 2B MTBE and Its Metabolites (TBA and HIBA)-Induced Cytotoxicity Determined by the Ratio of LDH Release (2A) and DNA Damage Determined by Comet Assay (2B). (Data are expressed as mean ± SE. ** $p < 0.01$ compared to their respective control group [0 concentration; student's t test].)



Figs. 3A and 3B Formaldehyde-Induced Cytotoxicity Determined by the Ratio of LDH Release (3A) and DNA Damage Determined by Comet Assay (3B). (Data are expressed as mean ± SE. * $p < 0.05$ ** $p < 0.01$ compared to the control group [0 concentration; student's *t* test].)

contrast to its extensive usage, only a limited number of studies report the hazardous effects of this compound. Results from this study demonstrate that MTBE causes significant DNA damage in a dose-dependent manner over the range from 5 to 30 mM in a human cell line (HL-60) determined by Comet assay (Fig. 2B). However, no evident cytotoxicity was observed under the same concentrations measured by LDH release (Fig. 2A). Compared to the results in Fig. 1B, the genotoxic effect of MTBE (Fig. 2B) is found to be lower than that of H_2O_2, a known oxidant causing oxidative DNA damage.



Picture 1. Comet Images of HL-60 Cells Incubated for 1 h with (A) Control, (B) 30 μM of H_2O_2, (C) 10 mM of MTBE, and (D) 500 μM of Formaldehyde

It is well elucidated that MTBE is metabolized by the cytochrome P450 system to various metabolites, including TBA, HIBA, and formaldehyde (Cedebaum and Cohen 1980; Brady et al. 1990), as illustrated in Fig. 4. In the present study, the cytotoxicity and genotoxicity of these three metabolites were also investigated. It was noted that both TBA and HIBA exert similar toxic effects to their parental compound, MTBE (Figs. 2A and 2B). This finding is reminiscent of the results from the acute toxicity study. The acute oral LD_{50} of MTBE and TBA in rats is 3.9 and 3.5 g/kg, respectively (Wibowo 1994).

Unlike the other two metabolites, formaldehyde has been well studied as a potent human carcinogen (Feron et al. 1991; McLaughlin 1994). In the present study, results showed significant changes of

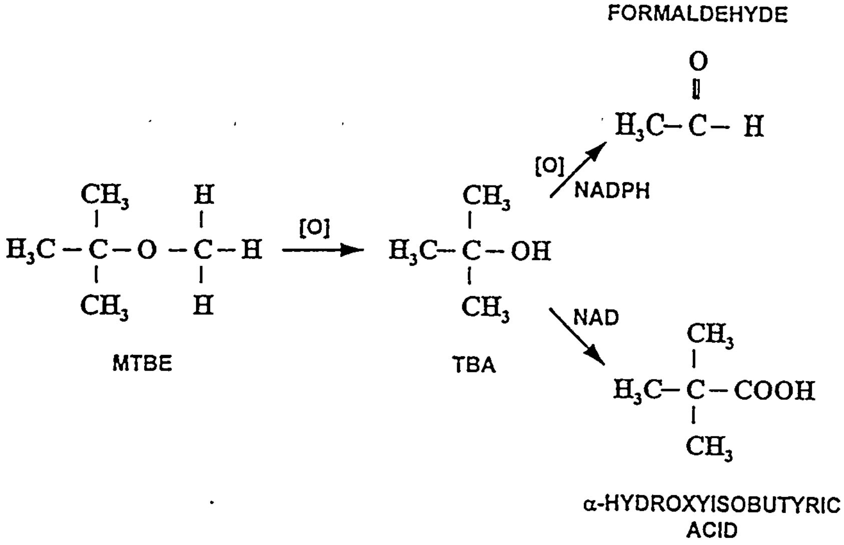


Fig. 4 Pathways of MTBE Metabolism by Microsomal Cytochrome P450 and the Formation of Its Three Main Metabolites: TBA, HIBA, and Formaldehyde

LDH release and DNA migration in HL-60 cells exposed to formaldehyde at 5 μM for 1 h, indicating that formaldehyde possesses higher potency of cytotoxicity and genotoxicity than other MTBE metabolites. It is thus believed that formaldehyde may contribute to the carcinogenicity of MTBE found in animal studies. Results from Figs. 3A and 3B also show that with the further increase of formaldehyde concentration, the extents of LDH release and DNA migration decreased. This may be explained by the fact that formaldehyde fixes the cellular components (proteins or DNA) at higher concentrations, preventing LDH release and DNA migration (Picture 1D).

At present, the carcinogenicity of MTBE has been demonstrated by a few animal studies. Burleigh-Flayer et al. (1992) found the increased incidence of liver tumors in mice after exposing to 400, 3,000, or 8,000 parts per million MTBE for 18 months. Using the same exposure concentration, Chun et al. (1992) demonstrated a significant and dose-dependent increase of testicular tumors in male F344 rats. In addition, an increase of kidney tumors was also identified (Chun et al. 1992). A recent animal study revealed similar results in Sprague-Dawley rats administrated by gavage (Belpoggi et al. 1995).

The results of these chronic animal studies may imply a cancer risk for humans. Nevertheless, from what we have known about the mechanisms that cause tumors (in laboratory animals), there is always a large margin of safety for humans. While opinions on MTBE's carcinogenicity may vary among scientists associated with this issue, most agree that further study is necessary, especially on the potential hazards related to environmental and occupational exposure of MTBE. In the present study, the DNA-damaging effect of MTBE in human HL-60 cells under *in vitro* conditions, although at a relatively higher concentration compared to H_2O_2, supports its carcinogenic findings in animal studies.

In summary, the cytotoxic and genotoxic effects of MTBE and its metabolites (TBA, HIBA, and formaldehyde) on HL-60 cells were studied under *in vitro* conditions. A dose-dependent pattern was observed for MTBE, TBA, and HIBA, causing DNA damage at concentrations of 1 mM and above. However, these compounds did not possess evident cytotoxic effects on HL-60 cells under the same concentrations. On the other hand, significant changes of DNA damage and LDH release in formaldehyde-treated cells were noted with a lower concentration range (10 to 100 μM). These findings suggest that MTBE and its metabolites, except formaldehyde, have a relative low cytotoxic and genotoxic effect. It is believed that the carcinogenicity of MTBE observed in animal studies could mainly be due to the motabolic transformation from MTBE to formaldehyde.

5 ACKNOWLEDGMENTS

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POSSIBLE MECHANISMS FOR ARSENIC-INDUCED PROLIFERATIVE DISEASES

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ABSTRACT

The possible mechanisms for the cardiovascular diseases and cancers which have been observed upon chronic exposure to arsenic have been investigated. We tested the hypothesis that nonlethal levels of arsenic are mitogenic, cause oxidative stress, increase nuclear translocation of *trans*-acting factors, and increase expression of genes involved in proliferation. Cultured porcine vascular (from aorta) endothelial cells were used as a model cell system to study the effects of arsenic on the target cells for cardiovascular diseases. Treatment of postconfluent cell cultures with nonovertly toxic concentrations of arsenite increased DNA synthesis, similar to the mitogenic response previously observed with hydrogen peroxide. Within 1 hour of adding noncytotoxic concentrations of arsenite, cellular levels of oxidants increased relative to control levels, indicating that arsenite promotes cellular oxidations. Arsenite treatment also increased nuclear translocation of NF-κB, an oxidative stress-responsive transcription factor, in a manner similar to that observed with hydrogen peroxide. Pretreatment of intact cells with the antioxidants *N*-acetylcysteine and dimethylfumarate prevented the arsenite-induced increases in both cellular oxidant formation and NF-κB translocation. Arsenite had little or no effect on binding of NF-κB to its DNA recognition sequence in vitro, indicating that it is unlikely that arsenite directly affects NF-κB. The steady-state mRNA levels of intracellular adhesion molecule and urokinase-like plasminogen activator, genes associated with the active endothelial phenotype in arteriosclerosis and cancer metastasis, were also increased by nontoxic concentrations of arsenite. These data suggest that arsenite promotes proliferative diseases such as heart disease and cancer by activating oxidant-sensitive endothelial cell signaling and gene expression. It is possible that appropriate antioxidant therapy would be useful in prevention of arsenic-induced cardiovascular disease and cancer.

1 INTRODUCTION

Chronic exposures to low levels of environmentally derived arsenic are associated with proliferative diseases such as cardiovascular diseases and cancer. Many people in many countries, including Japan, China, Taiwan, Thailand, Singapore, India, Australia, United States, Argentina, Chile, Mexico and Zimbabwe, have been exposed to arsenic through contaminated drinking water, from mining and smelting operations, and from agricultural uses of arsenical pesticides. Increased incidence of skin, lung, bladder, liver, and kidney cancer (1), as well as ischemic heart disease, hypertension, "Blackfoot" peripheral vascular disease, arteriosclerosis, and aortic aneurysm and other diseases of arteries, arterioles, and capillaries have been observed in people chronically exposed to arsenic (2). It has been suggested that arsenic-induced cancer and cardiovascular disease may share common risk factors, an indication of similar modes of action in these pathologies (3). However, the exact cellular and molecular mechanisms for these cardiovascular diseases and cancers in response to arsenic are presently not known.

2 TOXICITY OF ARSENIC

Arsenate $[(HO)_2As^VO_{2-}]$ is the most common form of arsenic found in the environment. Because of its similar coordination to oxygen and overall geometry, arsenate readily acts as a phosphate mimic (Fig. 1) and has been shown to selectively inhibit mitochondrial oxidative phosphorylation. The toxicity associated with arsenate is known to occur through the uncoupling of oxidation from substrate phosphorylation by arsenate substitution of 3-phosphoglyceroyl phosphate with a corresponding decrease in ATP production.

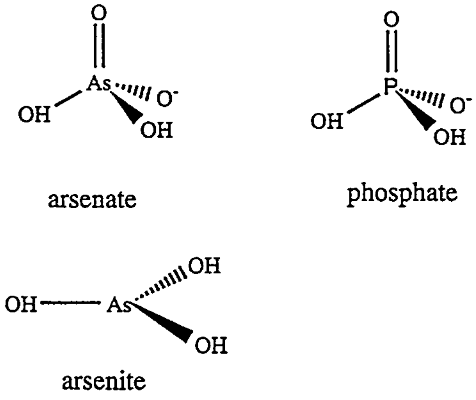

Fig. 1 Structures of Arsenate, Inorganic Phosphate, and Arsenite at pH 7

Arsenite [$As^{III}(OH)_3$], the more toxic of the two valence states, enters the cell through simple diffusion and is extremely thiol-reactive, preferentially binding to vicinal thiols and dithiols (4). This thiol-reactivity is believed to be associated with much of the toxicity observed with arsenite exposure. Arsenite can directly target sulfhydryl groups located within a critical protein molecule, thus denaturing the protein and/or altering its function. Protein denaturation can lead to autophagic degradation and increases in reactive oxygen species (ROS). For proteins that contain iron (Fe) atoms, autophagic degradation results in the release of Fe, which can then go on to perform Fenton chemistry, thus generating hydroxyl radicals that can damage DNA (5). Upon internalization of exogenous arsenic, the metalloid undergoes metabolism and exists in both valence states, arsenite [As(III)] and arsenate [As(V)], inside cells.

Fenton Reaction

$$Fe^{3+} + \text{reductant} \text{ ----> } Fe^{2+}$$

$$Fe^{2+} + H_2O_2 \text{ -----> } Fe^{3+} + OH^- + OH^\cdot$$

An indirect mechanism by which arsenite elicits its toxic effects is by binding and inhibiting those enzymes that are necessary for removal of ROS, namely catalase (removal of hydrogen peroxide, H_2O_2) and superoxide dismutase (removal of superoxide, $O_2^{\cdot -}$). Also, mitochondria are continuously producing ROS because of cellular respiration and readily produce such reactive species as H_2O_2, superoxide anion, and peroxynitrite (6). Since arsenate is known to directly uncouple oxidation from substrate phosphorylation, it is not surprising that mitochondrial ROS are increased directly by arsenic exposure. The cellular damage that is typically produced by ROS is believed to occur through an imbalance between the concentration of ROS present within cells and the ability of cells to scavenge or detoxify ROS. This imbalance produces what has been termed intracellular oxidative stress. Intracellular ROS, including hydrogen peroxide, hydroxyl radical, singlet oxygen, and superoxide anion, have all been shown to directly or indirectly damage critical molecules such as membrane-associated lipids, protein, and DNA (7).

Although arsenic compounds are considered to be relatively nongenotoxic, they are believed to act as co-carcinogens by inhibiting specific DNA repair processes, thus enhancing the carcinogenic effects of other known carcinogens that damage DNA (8–12). Figure 2 depicts the multistage model of carcinogenesis and the probable effect that arsenic has on enhancing this process at the initiation and promotion stages. Immediately after DNA damage occurs in a cell, a variety of cellular repair processes are activated to repair the specific damage that occurred and to allow the cell to progress unimpeded through the cell cycle. As depicted in Fig. 2, DNA damage that is not adequately repaired results in an overall increase in initiation events that overburden the repair process and that may enhance the carcinogenic phenotype. Also shown in Fig. 2 is the potential for arsenic compounds to contribute to carcinogenesis by acting at the promotion stage of this complex process. Promotion of carcinogenesis is generally considered to involve altered gene expression that is associated with informational changes in various intracellular and intercellular signaling pathways that produce an

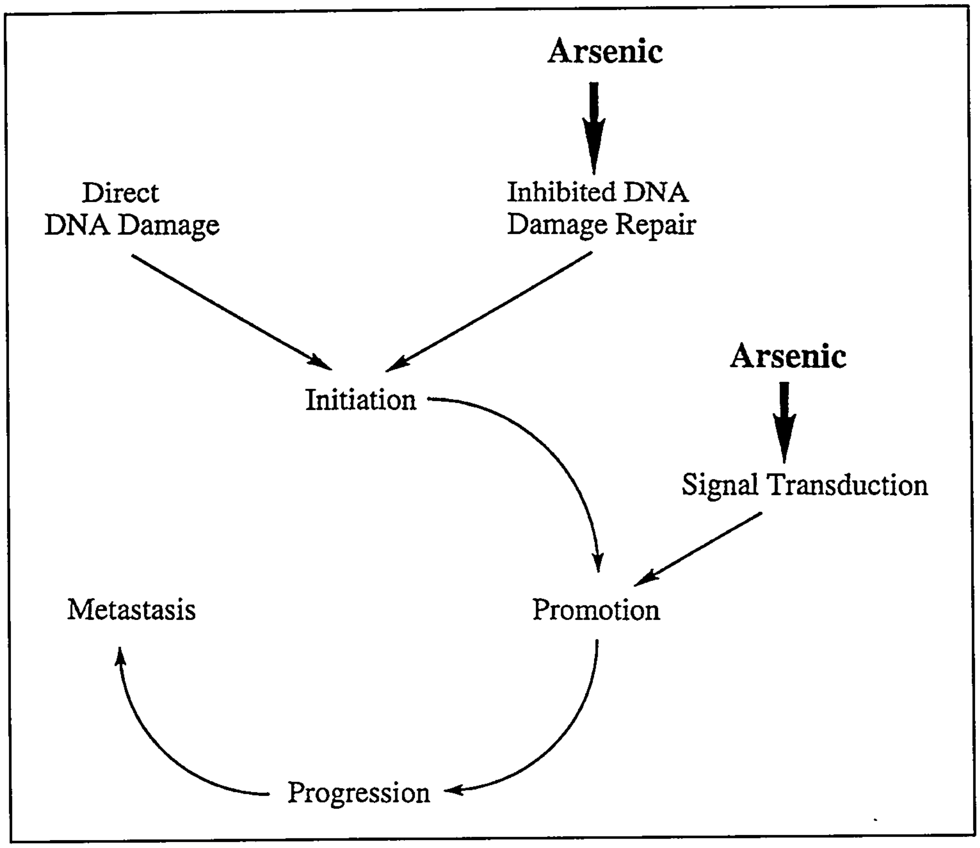

Fig. 2 Multistage Model of Carcinogenesis and the Proposed Mechanism for Arsenic Compounds Acting as Co-Carcinogens

altered phenotype. There is now sufficient evidence that arsenite is able to directly affect these signaling pathways by either activating intracellular kinases, inhibiting thiol-dependent phosphatases, or affecting phosphotransferase reactions (13–15). The high thiol-reactivity of arsenite is believed to be responsible for these effects through direct interaction or indirect oxidation of critical protein sulfhydryls in regulatory components of these pathways.

The extreme and diverse reactive nature of intracellular arsenic leads to the variety of biological effects observed upon increased exposure to environmental arsenic compounds. Table 1 summarizes many of the biological effects of arsenic that have been observed in mammalian systems. The intracellular effects of arsenic include increases in gene expression, inhibition of specific enzyme activities, decreased ATP production, protein phosphorylation, and the generation of oxidative stress.

TABLE 1 Intracellular Effects of Arsenic Compounds in Mammalian Systems

Effect	Reference
Induced gene products	
Heme oxygenase	(16)
Ornithine decarboxylase	(17)
Macrophage stress protein 23	(18)
Heat shock proteins (Hsp 107, 89, 70, 68, 27)	(19,20)
c-Fos	(20)
Enzyme/metabolic inhibition	
DNA ligase I & II	(10,11)
Thymine dimer excision activity	(12)
Hsp27 serine/threonine phosphatase	(14)
Mitochondrial oxidative phosphorylation	(21)
Protein phosphorylation	
Hsp27	(13,19)
Oxidative stress	
Arsenic-peroxyl radical formation	(22)
Cellular oxidative damage	(22,23)
Oxidant formation	(24,25)

3 DETOXIFICATION OF ARSENIC

Both prokaryotes and eukaryotes have defense mechanisms that have been shown to protect against arsenic toxicity. In *E. coli*, the *ars* operon codes for four proteins (ArsA, ArsB, ArsC, and ArsR) whose activities together help to reduce arsenate to arsenite and remove arsenite from the cell (26) (Fig. 3). ArsA is an ATPase that resides in the cytoplasm in the form of a dimer bound to ArsB, a transmembrane protein containing 12 helices. ArsA contains two glycine residues that are thought to be directly involved with the conversion of ATP to ADP and inorganic phosphate. Together, ArsA and ArsB confer resistance to arsenite by exporting arsenite through the ArsB channel with energy provided directly by ArsA. In addition to ArsA and ArsB, ArsC is an arsenate reductase that requires glutathione and glutaredoxin to reduce arsenate to arsenite, thereby conferring resistance to arsenate. Transcription of the *ars* operon is regulated by ArsR, a negative regulatory protein that remains bound to the operon in the absence of arsenite, thus preventing transcription of *arsA*, *arsB*, and *arsC* genes under normal nontoxic conditions.

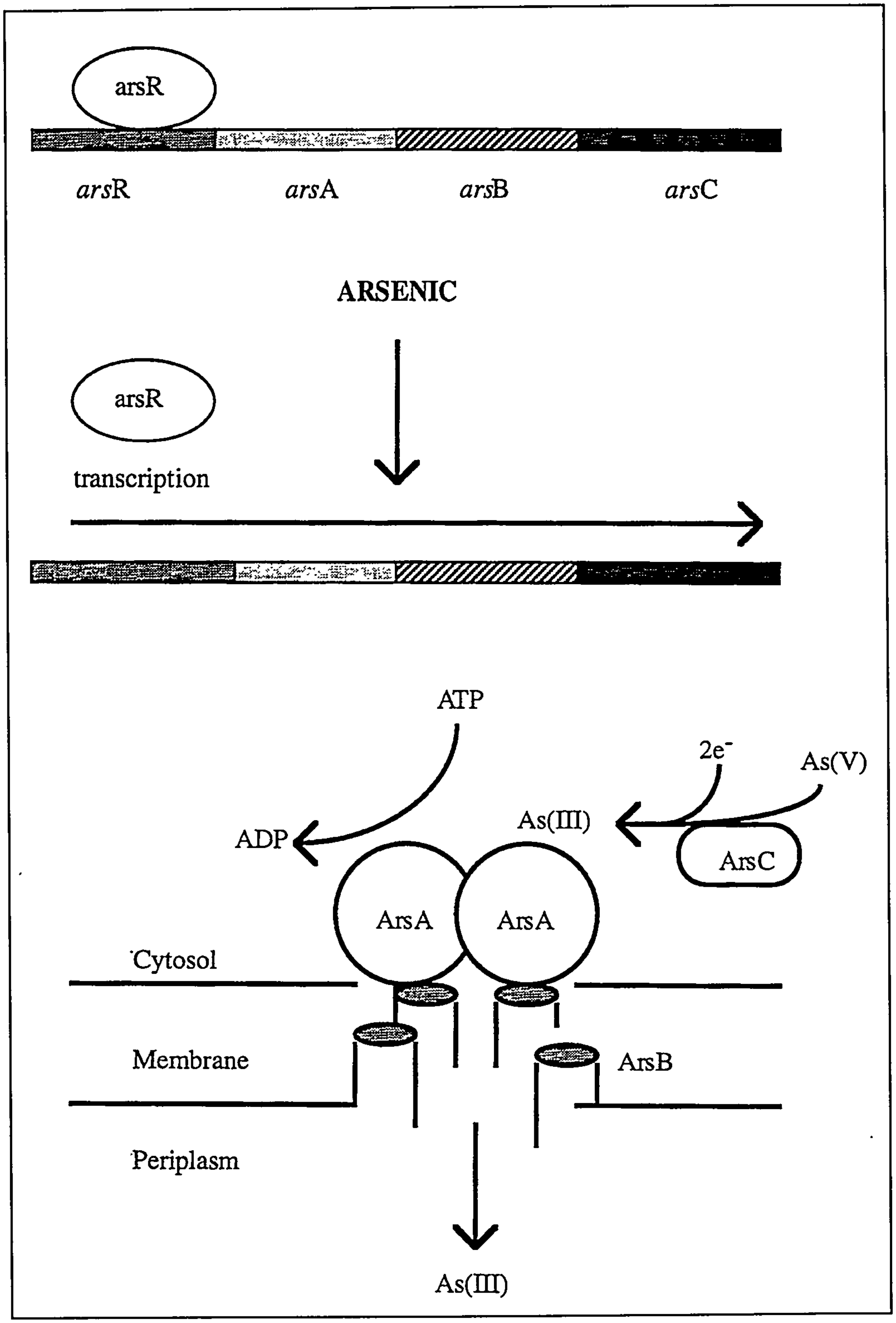

Fig. 3 Regulation of the *Ars* Operon and Detoxification of As(v) and As(III) (Adapted from Ref. 26.)

In eukaryotes, the primary means of detoxifying arsenite is proposed to occur through arsenite methylation (27). Arsenite methyltransferases are enzymes responsible for converting arsenite to monomethylarsonate (MMA) and dimethylarsinate (DMA) through the following proposed mechanism:

$$\mathrm{H_2As^{V}O_4^{-}} + 2e^{-} \rightarrow \mathrm{As^{III}(OH)_3} + \mathrm{CH_3^{+}} \rightarrow \overset{\mathrm{MMA}}{\mathrm{CH_3As^{V}O_3^{2-}}} \quad ,$$

and

$$\mathrm{CH_3As^{V}O_3^{2-}} + 2e^{-} \rightarrow \mathrm{CH_3As^{III}(OH)_2} + \mathrm{CH_3^{+}} \rightarrow \overset{\mathrm{DMA}}{\mathrm{(CH_3)_2As^{V}O_2^{-}}} \quad .$$

and Dimethylated arsenicals have the least affinity for sulfhydryl groups thus rendering this mechanism a possible means for arsenite detoxification. Another potential mechanism for arsenite detoxification is by direct cellular removal via glutathione S-transferase π (GSTπ), a phase II detoxifying enzyme for electrophiles. GSTπ is known to be overexpressed in arsenic-resistant SA7 Chinese hamster ovary cells and is thought to facilitate arsenic excretion (28). Resistance to arsenite and arsenate has also been observed in cells transfected with the multidrug resistance-associated protein (MRP), which exports glutathione-conjugates out of cells (29). It has been proposed that glutathione-As(III) complexes such as $\mathrm{As(GS)_3}$ may be exported by the MRP/glutathione S-conjugate export carrier (GS-X pump) (30). In addition to methylation, GSTπ, and the MRP/GS-X pump, mammals may detoxify arsenite through the induction of heat shock proteins. Heat shock proteins bind denatured proteins under stress, as for example increased temperature conditions, in order to prevent their degradation. In step-down arsenite treatment, it was shown that Reuber H35 rat hepatoma cells treated with 100 μM arsenite for 1 hour followed by 10 μM arsenite for 2 hours showed resistance to 300 μM treatment by means of a prolonged induction of heat shock proteins in comparison to cells only treated with 300 μM arsenite (31). In a similar manner to arsenic resistance mediated by heat shock protein binding, three cytosolic proteins (MW = 100, 450, and >2000 kDa) isolated from rabbit liver have been shown to bind arsenite strongly, and it has been suggested that these may play an intermediary role in maintaining arsenite in a nontoxic bound state until it can be methylated (32).

4 GENERATION OF INTRACELLULAR OXIDATIVE STRESS BY ARSENIC

There is now sufficient evidence that suggests that arsenic compounds are able to produce elevated levels of intracellular ROS and free radicals during cellular metabolism that can lead to oxidative stress and cellular damage. Genomic DNA isolated from L-132 cells treated with dimethylarsine, a metabolite of inorganic arsenic, demonstrated single-strand DNA breaks while electron spin resonance spectroscopy in vitro identified both superoxide anion and arsenic-peroxyl radical formation (22). The authors concluded that it was the arsenic-peroxyl radical that was mainly responsible for the observed DNA damage since the detoxifying enzymes superoxide dismutase and catalase had no significant effect on inhibiting the damage. Other evidence has been reported that found severe oxidative damage to red blood cells isolated from mice treated with arsine gas by examining hemoglobin denaturation and hemolysis (23).

Recently, an oxidant-sensitive fluorescent probe has been utilized to characterize and quantitate increased cytosolic oxidation within cells treated with arsenite (24, 25). The oxidant probe utilized in these studies, 2',7'-dichlorofluorescin diacetate, is a nonpolar, nonfluorescent molecule that easily crosses the cytoplasmic membrane and accumulates within the cytosol after rapid deacetylation by intracellular esterase activity. The deacetylated and polar, nonfluorescent molecule is easily oxidized and becomes fluorescent after oxidation, producing 2',7'-dichlorofluorescein (DCF). The resulting fluorescence can easily be quantitated using fluorescence spectroscopy and is a direct measure of the intracellular oxidant concentration, with an increase in fluorescence being an indicator of oxidative stress. Figure 4 illustrates the DCF fluorescence that was observed in endothelial cells treated with 5 μM arsenite over a 2 h time course and demonstrates an immediate increase in the intracellular oxidant concentration, which peaked at 30 min and declined to baseline level by 2 h. This arsenite-mediated oxidative stress may produce cellular oxidative damage and may also be involved in affecting oxidant-sensitive signaling pathways, causing changes in gene expression and alteration of phenotype.

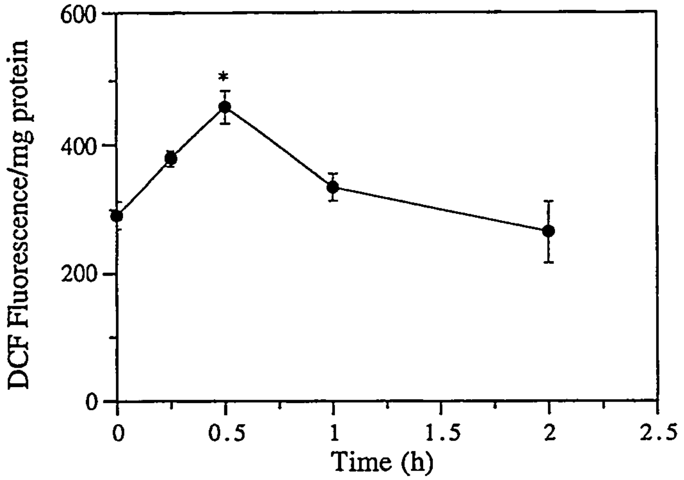

Fig. 4 Arsenite Increases Oxidant Formation in Endothelial Cells (DCF fluorescence, an indicator of cytosolic oxidation, is rapidly increased and of limited duration in cells treated with 5 μM arsenite: *P <0.001. Adapted from Ref. 25.)

It is now well established that intracellular thiol status is important in both oxidant formation and activation of oxidant sensitive transcription factors, such as NF-κB (see below). Intracellular free thiols are known to act as antioxidants, rapidly reducing reactive oxidized molecules, while reversible reaction of protein sulfhydryls located in signaling proteins with free thiols is believed to be a common mediator in activation pathways of NF-κB (33). To examine the effect of intracellular thiol status on oxidant formation by arsenite, endothelial cell cultures were pretreated with 10 μM dimethylfumarate (DMF) or 10 mM *N*-acetylcysteine (NAC), two known cellular antioxidants, for 24 h. NAC and DMF pretreatment resulted in a two- to three-fold increase in intracellular nonprotein thiols (data not shown). Under these antioxidant conditions there was a complete inhibition of cellular oxidant formation mediated by 5 μM arsenite (Fig. 5). The induction of cellular oxidants by arsenite and inhibition by antioxidants makes it likely that oxidant stress-responsive factors will be activated by arsenite in endothelial cells.

5 ACTIVATION OF NF-κB BY ARSENIC

While arsenite has been shown to induce stress-response proteins (Table 1), it may also be involved in the induction of other stress-related proteins, such as transcription factors. NF-κB is a family of mammalian transcription activator proteins that reside in the cytoplasm of unstimulated cells, typically in the form of p50-p65 heterodimers bound to the inhibitory subunit IκB. The p50-p65 heterodimers translocate to the nucleus and bind DNA following cellular activation by various stimuli including tumor necrosis factor-α, UV light, interleukins 1 and 2, bacterial and viral pathogens, and oxidants (34–37). The protein dimers bind DNA consensus sequences in the promoter region of genes and activate transcription. Endothelial cell genes that are known to contain NF-κB consensus sequences in their promoter region include interleukins (38–40), adhesion molecules (40), nitric oxide synthase (41), *c-myc* (42), and urokinase-like plasminogen activator (uPA) (43). Thus, increased nuclear translocation of NF-κB may play a key role in gene expression induced by arsenite.

Translocation of NF-κB can be measured by preparing nuclear protein extracts from control or arsenite-treated tissues or cultured cells. These extracts are then incubated for 20 minutes with a radiolabeled double-stranded DNA probe that contains the consensus NF-κB binding site. After incubation, the protein/DNA mixture is separated and resolved on a polyacrylamide gel. Protein bound to radiolabeled DNA causes the DNA to migrate more slowly than unbound DNA, producing a shift in mobility. Autoradiography can then be used to identify and quantify the radiolabeled DNA and NF-κB activation. The data in Fig. 6 demonstrate that adding increasing amounts of arsenite to intact endothelial cells causes a rapid increase in the amount of NF-κB in the nucleus of the cell. This effect is maximal by 30 to 60 minutes and is sustained for at least 4 hours.

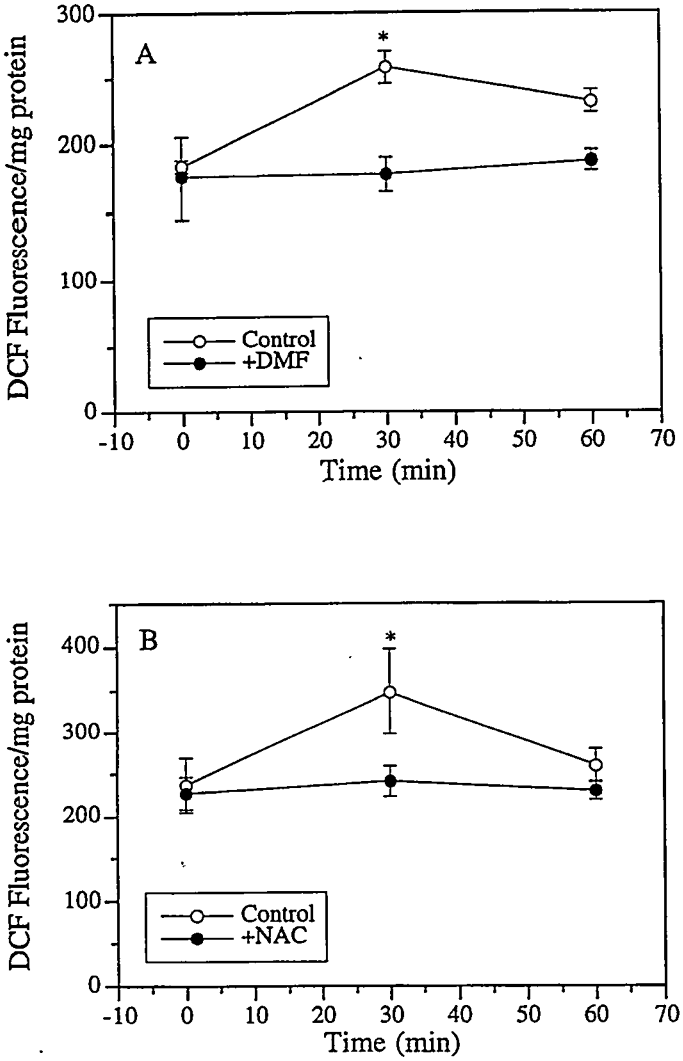

Fig. 5 Antioxidants Dimethylfumarate (DMF) and *N*-acetylcysteine (NAC) Inhibit Arsenite-Induced Oxidant Formation (Endothelial cell cultures pretreated with 10 μM DMF [A] or 10 mM NAC [B] for 24 hours were treated with 5 μM arsenite and examined for oxidant formation. The 30-minute peak of oxidant formation is completely abolished by both DMF and NAC; *P <0.01. From Ref. 25.)

5.1 Inhibition of Arsenic-induced NF-κB Activation by Antioxidants

Thiol-containing compounds are known antidotes for arsenite-induced injury. The protective effects of free thiols, such as glutathione and cysteine, against the toxic effects of arsenite suggest that arsenic toxicity results from forming reversible bonds with the thiol groups of specific regulatory proteins (33). Low concentrations of arsenite induce increased glutathione levels in vascular

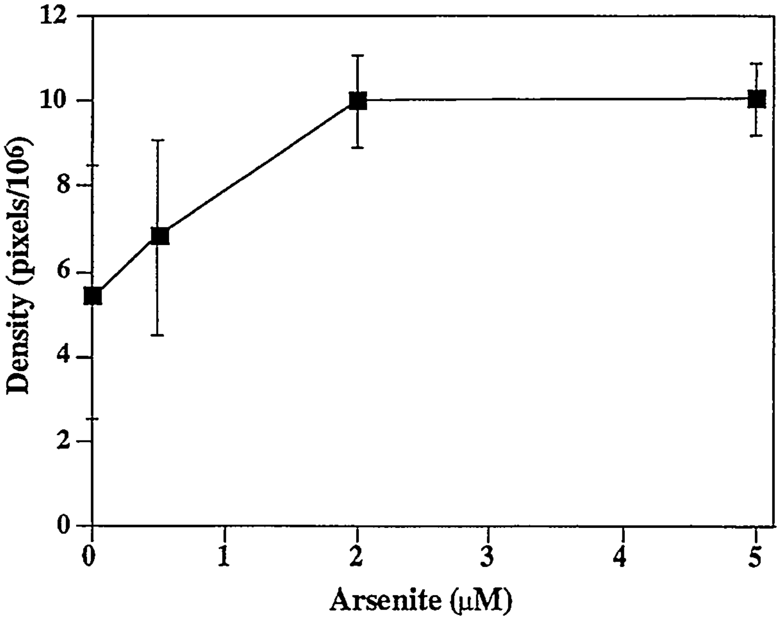

Fig. 6 Dose Response Relationship for NF-κB Translocation after Arsenite Treatment (Endothelial cells were incubated with increasing concentrations of arsenite for 1 h. Nuclear proteins were then extracted and equal amounts were analyzed by electrophoretic mobility shift assays. The data in the graph are the means ± s.d. of relative densities of κB bands retarded by nuclear extracts from duplicate cultures at each concentration of arsenite. From Ref. 15.)

endothelial cells (44), and this enhancement in glutathione levels protects the endothelium against injury from higher amounts of arsenic (45, 46). Reversible oxidation of protein sulfhydryls appears to be a common mediator for the ability of many stimuli to activate NF-κB translocation. Figure 7 illustrates the effect of incubating endothelial cells with NAC or DMF to elevate thiol levels prior to examining arsenite-medicated activation of NF-κB. Pretreatment with these compounds for 24 h increases the thiol content of the cells by two- to three-fold (see above) and completely inhibits the ability of arsenite to stimulate NF-κB translocation. This is consistent with the ability of NAC and DMF to completely block arsenite-induced oxidants in these cells.

5.2 Arsenic Inhibition of NF-κB Binding to Its DNA Consensus Sequence

NF-κB binds in the major groove of DNA both to functional groups on the bases and to the sugar-phosphate backbone via peptide loops connecting β-strands (47). Both the p50 and p65 subunits contain redox-sensitive cysteine residues, Cys59 for p50 and Cys120 for p65, which are required for DNA binding and therefore cause NF-κB activity to be sensitive to the overall redox status of the cell (47, 48). NF-κB is believed to be under redox control at least at two defined levels. While

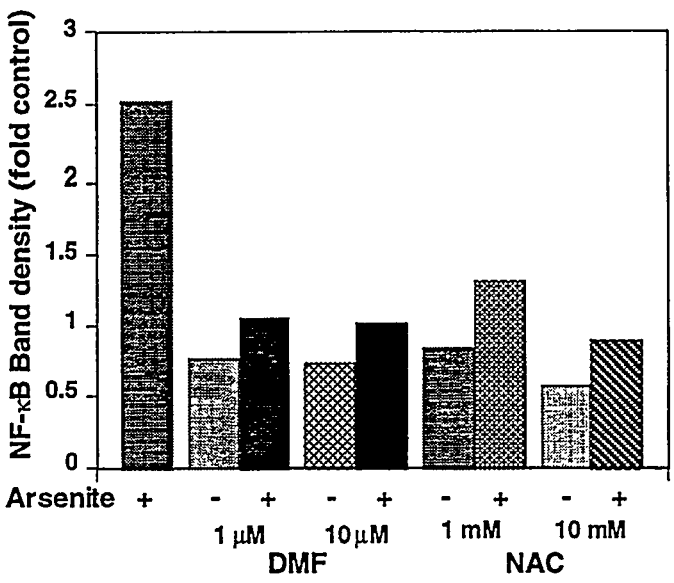

Fig. 7 Antioxidant Inhibition of Arsenite-Induced NF-κB Activation (Endothelial cell cultures were incubated for 18-24 h in complete medium containing either no additives, DMF, or NAC. The cells were then treated with 2.5 μM arsenite for 1 h. Nuclear proteins were extracted and equal amounts were analyzed by electrophoretic mobility shift assays. The densities of κB bands retarded by nuclear extracts from duplicate cultures were determined and the fold differences from control [31.6 ± 4 pixel/cm^2] were calculated. Adapted from Ref. 25.)

activation and nuclear translocation of NF-κB are dependent upon reactive oxygen intermediates and phosphorylation events that are inhibited by reducing agents, NF-κB-DNA binding in the nucleus is facilitated by free thiols (49). Since arsenite is capable of generating intracellular ROS, activation of NF-κB would be expected. However, activation of NF-κB-dependent genes may be inhibited if oxidizing conditions are present within the nucleus which are known to prevent NF-κB binding to DNA. In vitro studies focusing on the latter form of redox control have examined the effects of arsenite on binding of NF-κB to its DNA consensus sequence.

Since arsenite has been shown to preferentially bind preformed dithiols and vicinal thiols, it was questioned as to whether arsenite would bind to those protein thiols necessary for NF-κB-DNA interaction or to dithiothreitol (DTT), a dithiol used in the protein incubation buffer to maintain protein thiol groups in the reduced state for optimal binding activity. If either event occurred, it might prevent binding of a transcription factor such as NF-κB to an oligodeoxyribonucleotide probe containing the consensus sequence. Total nuclear proteins isolated from human lung A549 cells preincubated in the presence of 0.5, 1, 2, or 5 mM arsenite for 15 minutes prior to incubation with a radiolabeled DNA probe elicited a strong inhibition of NF-κB-DNA binding at the higher concentrations, as shown by electrophoretic mobility shift assay and densitometry analysis (Fig. 8).

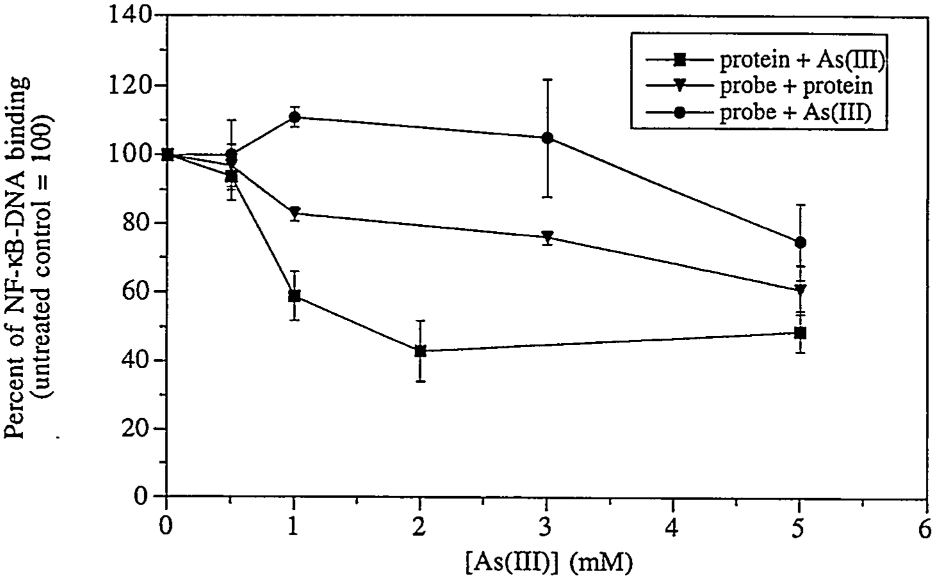

Fig. 8 Pretreatment of Total Nuclear Proteins or DNA Probe Containing the NF-κB Consensus Sequence with Arsenite Decrease NF-κB-DNA Binding (Electrophoretic mobility shift bands were quantitated by phosphorimaging or densitometry. Each data point represents mean ± s.d. (n=3).)

As shown in Fig. 8, no significant decrease in NF-κB-DNA binding was observed between 0 and 0.5 mM arsenite. However, between 2 and 5 mM, binding decreased to levels about 40-50% that of the untreated control. Similarly, preincubation of the DNA probe with total nuclear proteins prior to addition of arsenite decreased NF-κB-DNA binding, although the extent of decrease was less than that observed for protein-arsenite preincubation. At the highest arsenite concentration, binding was reduced to 60% of the control. When the DNA probe was preincubated with varying concentrations of arsenite, no decrease in binding was observed up to 3 mM arsenite, and only a slight decrease occurred at the 5 mM treatment. That arsenite preincubation with total nuclear proteins elicited the strongest inhibition, and that little or no inhibition was observed when arsenite was preincubated with the DNA probe, suggests that arsenite interacts primarily with proteins rather than with DNA. Nevertheless, arsenite was able to have an inhibitory effect on binding even when protein was preincubated with the DNA probe, thus showing that a decrease in reducing conditions can reverse NF-κB-DNA binding. It cannot be overlooked that higher concentrations of arsenite or longer incubation times may be required to reduce binding to levels observed when arsenite was preincubated with protein. Regardless of pretreatment conditions, in no instance did arsenite completely inhibit NF-κB-DNA binding over the course of the incubation time (20-35 minutes). In a thiol binding study comparing Cd(II), Zn(II), and As(III), As(III) was shown to bind dithiols tightly but at a slower rate than observed for either cadmium or zinc, two metals capable of rearranging and binding monothiols and binding dithiols (4). It therefore seems likely that longer incubation times with arsenite may be required to attain complete inhibition of binding.

In order to confirm the role of free thiols in NF-κB-DNA binding, nuclear extracts were preincubated with various concentrations of DTT for 30 minutes prior to the addition of arsenite and DNA probe. At 0.6 mM DTT, NF-κB binding was inhibited by arsenite to levels 50% of the untreated control, which was also examined at 0.6 mM DTT (Fig. 9). As the concentration of DTT was increased, a gradual recovery of NF-κB-DNA binding was observed until at 1.6 mM DTT, binding was at 80% of control levels. Complete recovery of binding may not have been achieved because of residual arsenite-protein binding or some other form of arsenite complexation.

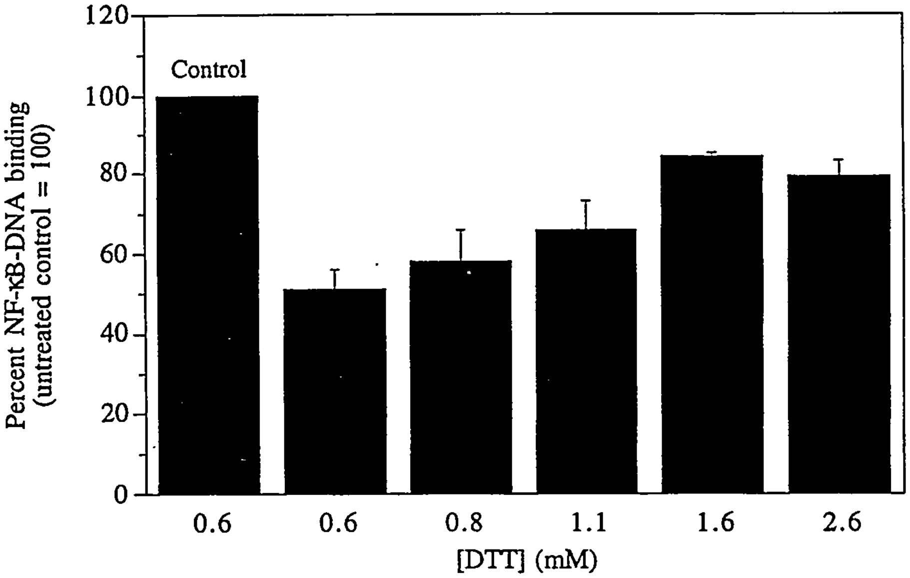

Fig. 9 Inhibition of NF-κB-DNA Binding by Arsenite can be Partially Recovered by Increasing the Concentration of Dithiothreitol (DTT) (Total nuclear proteins were incubated with varying concentrations of DTT for 30 minutes prior to addition of 1 mM arsenite [5 minute incubation] and finally DNA probe [20-minute incubation].)

Arsenite can bind to or cause oxidation of critical sulfhydryl groups required for protein-DNA binding. In the cytoplasm, activation of NF-κB by oxidative mechanisms results in nuclear translocation and subsequent gene induction. This research addressed the question of what concentration of arsenite would be required to inhibit NFκB-DNA binding in the nucleus and the mechanism of inhibition. From these data, it can be inferred that over a short period of time

(20-35 minutes) only high arsenite concentrations (1-5 mM) will reduce binding of NF-κB to its DNA consensus sequence in vitro, and that NF-κB protein is the primary target of arsenite. Given that arsenite reacts slowly with thiols, lower concentrations may be able to inhibit binding, although longer incubation times may be required to see such an effect. In summary, any inhibition of NF-κB-DNA binding most likely occurs through a direct thiol-related mechanism; however, the importance of this interaction in vivo is unclear.

6 ARSENITE INDUCTION OF ENDOTHELIAL CELL GENE EXPRESSION

Vascular disease that is produced in response to environmental toxins has been associated with an activated endothelial cell phenotype. This phenotype has altered expression of fibrinolytic proteins such as urokinase-like plasminogen activator (uPA) and increased expression of adhesion molecules for circulating cells. Arsenite levels are also known to be highly correlated with the incidence of Blackfoot disease (50). However, little is known of the direct effects of relevant concentrations of arsenite on uPA or adhesion molecule expression in endothelial cells. Hence, two genes with NF-κB elements in their promoters, intracellular adhesion molecule (ICAM) and uPA, were chosen to investigate these direct effects. Solution hybridization analysis for ICAM mRNA from porcine aortic endothelial cells demonstrated that arsenite caused a 2–2.3-fold increase relative to control in steady-state levels over a 6 h period of exposure (Fig. 10[A]). Quantitative RT-PCR for uPA levels in pulmonary microvascular endothelial cells also demonstrated that arsenic induces the expression of this gene several hours after exposure of the cells to either arsenite or the inflammatory cytokine, tumor necrosis factor-α (Figure 10[B]). Further work will be required to demonstrate how arsenite affects expression of the other components of the fibrinolytic system and how these changes relate to the progression of arsenite-induced peripheral vascular diseases. In addition, the direct effects of arsenite on expression of fibrinolytic proteins in exposed populations may be complicated by known effects of other components of arsenic-contaminated drinking water, such as high levels of humic acid (51, 52).

7 CONCLUSIONS

Chronic exposure to arsenic may result in cellular changes leading to proliferative diseases such as cancer and cardiovascular diseases. Our studies have shown that arsenite induces oxidant formation in porcine aortic endothelial cells and that the antioxidants NAC and DMF completely block arsenite-induced cellular oxidant formation. An oxidant-sensitive transcription factor, NF-κB, is activated by arsenite, but this arsenite-induced activation of NF-κB is blocked by these antioxidants. Expression of ICAM and uPA genes, which have NF-κB elements in their promoter regions, was shown to be increased by arsenite. Thus, a model emerges (Fig. 11) whereby arsenic, through effects on signal transduction pathways, results in phenotypic changes in a critical target cell that enhance the proliferation of that cell. These changes appear to be sensitive to antioxidants, and therefore it

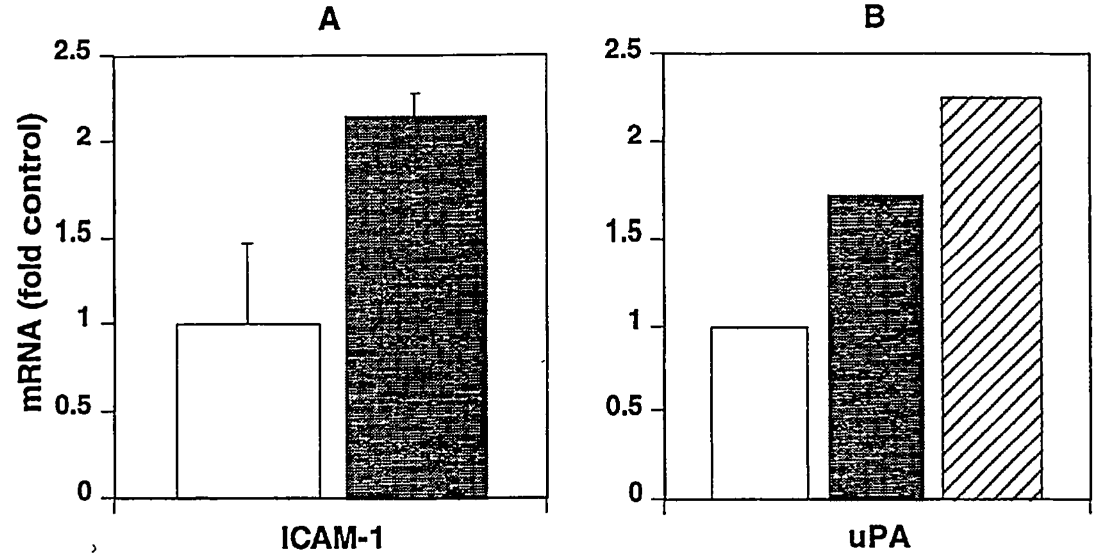

Fig. 10 Steady-state mRNA Levels in Arsenite-Treated Cells ([A] Porcine endothelial cells were incubated for 6 h in the absence [open bar] or presence [shaded bar] of 2.5 μM arsenite. Total RNA was extracted and analyzed for levels of ICAM-1 mRNA by solution hybridization. [B] Human microvascular endothelial cells were incubated for 8 h in the absence [open bar] or presence of either 2.5 μM arsenite [shaded bar] or 10 ng/mL of tumor necrosis factor-α [striped bar].)

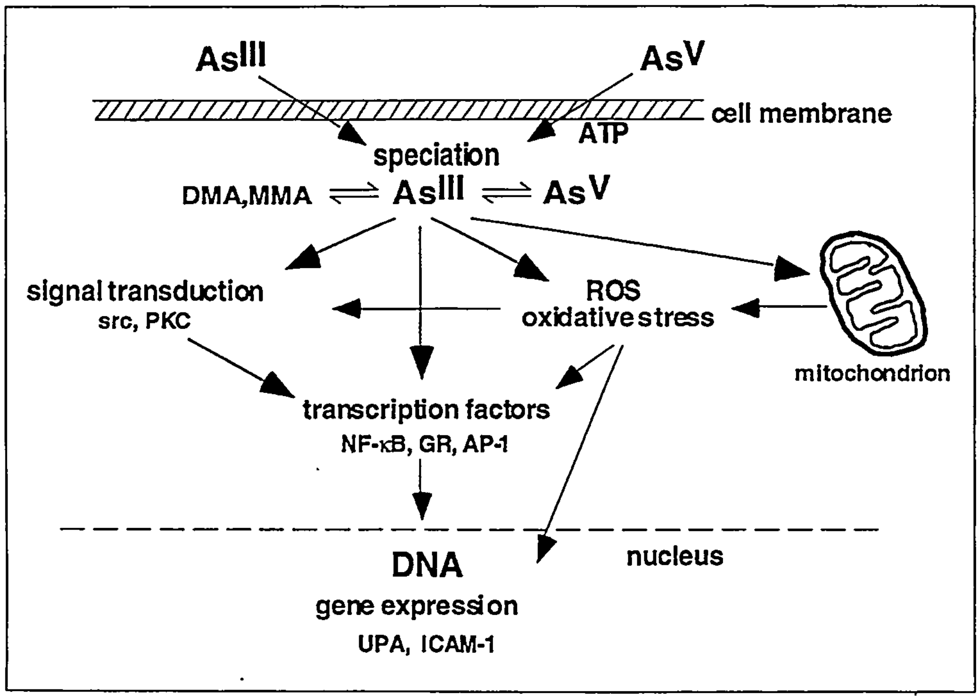

Fig. 11 Model for the Mechanism of Arsenite-Induced Proliferative Diseases

is possible that antioxidant therapy may be useful in the prevention of arsenic-induced proliferative diseases.

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DMPS (DIMAVAL) AS A CHALLENGE TEST TO ASSESS THE MERCURY AND ARSENIC BODY/KIDNEY LOAD IN HUMANS AND AS A TREATMENT OF MERCURY TOXICITY

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ABSTRACT

Mercury is an element which, with its compounds, is hazardous and is found in hazardous wastes. In order to develop suitable diagnostic and therapeutic agents for mercury exposure, we have sought alternative test systems. We have used the chelating agent 2,3-dimercaptopropane-1-sulfonate (DMPS, DIMAVAL®) for estimating the body burden of mercury in normal humans and in dental personnel in a developing country, and for detoxifying humans with mercurous chloride exposure. Use of the DMPS-mercury challenge test has shown that two-thirds of the mercury excreted in the urine of volunteers with dental amalgams appears to be derived from the mercury vapor released from their amalgams. The DMPS challenge test (300 mg, by mouth, after an 11 hr fast) was useful for monitoring dental personnel for mercury vapor exposure. The DMPS challenge test was given to 11 factory workers who make a skin lotion that contains mercurous chloride, 8 users of the skin lotion, and 9 controls. The increases in urinary Hg resulting from the DMPS challenge were 45, 87, and 38-fold, respectively. The results demonstrate that in humans exposed to mercurous chloride, the DMPS-mercury challenge test is of value for a more realistic estimation of mobilizable Hg. DMPS should be considered for use to determine mercury body burdens and to treat humans exposed to mercury and its compounds via exposure to hazardous wastes.

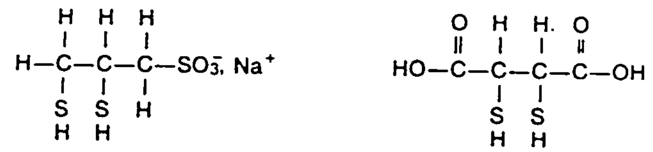
1 INTRODUCTION

For a number of years, our laboratory has studied the use of metal mobilizing agents, sometimes called chelating agents, for the diagnosis and treatment of heavy metal intoxication (Aposhian, 1983; Aposhian and Aposhian, 1990; Aposhian et al., 1995). One of our primary interests has been mercury poisoning. Mercury is a hazardous element that exists in many forms and is found in hazardous wastes. It is a therapist's nightmare. Why? First, unless there is severe intoxication, the signs and symptoms of mercury poisoning are very nonspecific. Second, once mercury is present in the body it may be very difficult and sometimes impossible to remove, especially from the brain. In addition, next to lead, mercury poisoning is the most common of the heavy metal poisonings. But since it does not occur that frequently or severely, the opportunity to test chelating agents for their therapeutic effectiveness in humans with mercury poisoning has been relatively rare. In the last few years, however, we have been presented with a number of unusual opportunities for such testing of therapeutic efficacy.

The first opportunity presented itself when we were asked to investigate whether DMPS (DIMAVAL®) was useful in measuring the body burden of mercury. The second opportunity dealt with dental personnel with occupational exposure to elemental mercury. The third dealt with mercurous chloride.

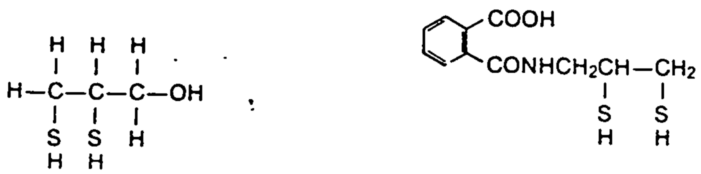
The major interest of our laboratory during the last 11 years has been the study of the therapeutically useful, orally effective, water-soluble dimercapto chelating agents. Examples of these chelating agents are the sodium salt of 2,3-dimercaptopropane-1-sulfonic acid (DMPS) and 2,3-meso-dimercaptosuccinic acid (DMSA) (Fig. 1). DMPS was developed in the former Soviet Union, where it has been an official drug since the late 1950s (Klimova, 1958). In the United States, it has been used successfully to treat humans intoxicated by mercury vapor (Campbell et al., 1986).

DMPS as DIMAVAL capsules is approved by the German FDA as a mercury antidote, and DMPS preparations for parenteral use are available in Germany. Therapeutically useful chelating agents



DMPS
(2,3-DIMERCAPTO-1-PROPANE-SULFONIC ACID, Na SALT)
UNITHIOL, DIMAVAL

DMSA
(MESO-DIMERCAPTO SUCCINIC ACID)
SUCCIMER



DIMERCAPROL
(BRITISH ANTILEWISITE, BAL)

DMPA
N-(2,3-DIMERCAPTOPROPYL)
PHTHALAMIDIC ACID

Fig. 1 Chemical Formulas for Chelating Agents Used for Treating Heavy Metal Poisoning of Humans

(Table 1) are used to increase the excretion of a number of heavy metals. A chelating agent, for example, competes with endogenous ligands in the body for the mercury. Once chelation takes place, the mercury chelate is more soluble in water than the mercury in the body before chelation. A number of reviews of these chelating agent are available (Ding and Liang, 1991; Angle, 1993; Jones, 1994; Aaseth et al., 1995; Aposhian et al., 1995).

Table 1 Chelating or Metal-Binding Agents That Have Been Effective in Humans for the Treatment of Heavy Metal or Metalloid Poisoning

Metal-Binding Agent	Metal Ion
$CaNa_2EDTA$	Pb^{+2}
BAL (DIMERCAPROL)	As^{+3}, Hg^{+2}
meso-DMSA (CHEMET)	Pb^{+2}, Hg^{+2}, As^{+3}
DMPS (DIMAVAL)	Hg^{+2}, Cu^{+2}, As^{+3}
D-penicillamine	Cu^{+2}
Desferroxamine	Fe^{+3}, Al^{+3}
Dithiocarbamates	possible Pt^{+4}, Cd^{+2}

It has become apparent during the last 10 years that many individuals in the population have had a chronic, low-level exposure to elemental mercury. Clarkson et al. (1988a) stated that "the release of mercury from dental amalgams makes the predominant contribution to human exposure to inorganic mercury including mercury vapor in the general population." In addition, dental personnel have occupational exposure. Thus, it occurred to our group that dental personnel might be very suitable for the use of chelating agents to determine the body/kidney burden of mercury.

"Silver" dental amalgams are complex metal alloys. For example, one of the most frequently used dental amalgams in the Tucson, Arizona, area consists of 47.3% metallic mercury and 52.7% alloy powder. The alloy powder contains 49.5% Ag, 20.0% Cu, 30.0% Sn, and 0.5% Pd. Other formulations are available throughout the world. About 3% of the world's yearly production of mercury is used to make dental amalgam (Berlin, 1979; WHO, 1991), and 160 million restorations are done each year in the United States alone (Moen and Poetsche, 1970). Mercury dental amalgams appear to have been first employed in 1826 (Bremner, 1954). Since then, controversies as to their safety have arisen again and again. Stock (1926) indicated that dental amalgams might be a source of mercury, sufficient to cause toxicity. Evidence for his claims was not convincing and was contested by Borinski (1931).

The evidence that mercury vapor is released from amalgams is formidable (for reviews see Eley, 1987; Clarkson et al., 1988a; Enwonwu, 1987). This has been supported by experiments in which amalgams containing radioactive metallic ^{203}Hg were placed in the teeth of sheep (Hahn et al., 1989). Criticisms (Wallis et al., 1986; Larsson and Sagulin, 1990; Dodes, 1990) of the latter experiments (Hahn et al., 1989) have been lessened to some extent after the experiments were repeated in a monkey with essentially the same results (Hahn et al., 1990). Calculations based on experimental determinations of the intraoral air of humans indicate that mercury vapor is not only released from dental amalgams, but is also absorbed (Eley, 1987; Clarkson et al., 1988a; Hahn et al., 1990). Mercury vaporization at the surfaces of amalgam fillings appears to be generated mainly by the friction caused by occlusion and by the contact of food with amalgam surfaces. The release of mercury vapor from dental amalgams under various conditions such as brushing, chewing, and drinking is now generally accepted.

Excellent reviews of elemental, inorganic, and organic mercury toxicity are available (Clarkson et al., 1988b). Amalgams liberate elemental mercury, Hg^0, in vapor form. The vapor is rapidly absorbed by the lungs (about 80%) and enters the blood where within 1 minute it is transported to and crosses the blood-brain barrier. It also enters other organs. In the brain, it is quickly oxidized to mercuric mercury that remains there and is toxic.

2 USE OF DMPS TO STUDY THE BODY BURDEN OF MERCURY

2.1 Methods

2.1.1 Subjects

Fourteen normal, healthy male and five female undergraduate and graduate students between 18 and 29 years old were recruited from the University of Arizona. In addition, one male research associate, age 49, was a subject. During the week prior to administration of the chelating agent, a dentist examined each subject and gave him or her an amalgam score (Aposhian et al., 1992), which was calculated as follows: A tooth was considered to be a five-sided cube (the sixth side being under the gums and invisible). If an amalgam surface had a diameter of 1 mm or less, it was given a score of 1; a diameter of more than 1 up to 2 mm, a score of 2; and a diameter of above 2 mm or more, a score of 3. Such a score was given to each amalgam surface on a tooth. The *amalgam score* is a summation of the score of all the amalgam surfaces on all the teeth in the subject's mouth. A large enough group was initially recruited to allow 10 subjects with no amalgams and 10 subjects with amalgams to make up the study group.

2.1.2 Protocol

The subjects were asked not to consume seafood for 30 days prior to administration of the chelating agent. They were made to fast from 11 h prior to DMPS to 4 h after DMPS administration. Urine was collected at –11 to 0 h and at 1, 2, 4, and 9 h after administration of the chelating agent. The dose of 300 mg DMPS was chosen on the basis of previous clinical reports (Aposhian et al., 1992; Maiorino et al., 1991; Kemper el al., 1990). This dose was given to each subject independent of body weight because the regimen was being developed as a diagnostic test. For this and the other studies of this paper, urine was collected in acid-washed graduated cylinders with ground glass stoppers. Hydrochloric acid was added to the urine immediately after collection, to give a final concentration of 1%. All glassware was washed with 2% nitric acid. All urine samples were processed in duplicate, at least.

2.1.3 Analytical Procedures

Urinary mercury values were determined by cold vapor generation as described in previous publications. Validation of the analytical method for determining total urinary mercury has been reported elsewhere (Aposhian et al., 1992).

2.2 Results

DMPS administration increased the urinary excretion of mercury in normal humans. Even before administration of the chelating agent (–9 to 0 h), the 10 normal volunteers with amalgam fillings in their mouths excreted almost 3 times more mercury in their urine than did the no amalgam group, $p < 0.002$ (Table 2). After DMPS administration to individuals of the no amalgam group, the mean

Table 2 Urinary Mercury Excretion before and after the Oral Administration of 300 mg DMPS to Normal Individuals with and without Dental Mercury Amalgams[a]

	Group		
Item	No Amalgam (μg Hg ± SE)	Amalgam (μg Hg ± SE)	p
–9 to 0 h	0.27 ± 0.04	0.70 ± 0.11	<0.002
0 to 9 h	5.10 ± 1.11	17.16 ± 3.32	<0.003
p	<0.001	<0.001	

[a] N = 10 for each group. DMPS was given at zero time. SE = standard error.

urinary excretion of mercury increased 19 times. For the amalgam group, it was 25 times greater after DMPS administration. In individual cases, increases as much as 70-fold and as little as 12-fold after DMPS administration were noted at various collection times. By 9 h after DMPS administration, urinary excretion of mercury by the amalgam filling group was 3.4 times greater than that of the group without amalgam fillings (Table 2).

2.2.1 Amalgam Score and Urinary Mercury Excretion after DMPS

Is there a positive linear relationship between the amalgam score and urinary excretion of mercury after DMPS administration? Linear regression analysis of the mercury excreted after DMPS administration indicated a highly significant positive linear correlation with the amalgam score. Two hours after DMPS administration there was a definite positive linear relationship ($r = 0.95$) between amalgam score and the urinary mercury after DMPS administration. The correlation coefficients for 1, 4, or 9 h after DMPS administration decreased slightly with time at the 0-4 and 0-9 h periods but they were still highly significant (Aposhian et al., 1992).

2.3 Discussion

The results of the present experiments show that there is a pool of inorganic mercury in the human body that can be mobilized by administering the chelating agent DMPS, and that more mercury is excreted by the individuals with amalgams than those without (Table 2). A linear relationship exists between the amalgam score and the urinary mercury after DMPS administration. Those subjects with amalgams had an average urinary mercury excretion before and after DMPS administration that was approximately 3 times that found for those without amalgams (Table 2). Therefore, if would appear that two-thirds of the mercury in the urine of students with amalgams originated from mercury vapor that was released originally from the amalgams in their mouths, oxidized to mercuric mercury, and excreted in the urine.

3 ARE URINARY MERCURY LEVELS OF DENTAL WORKERS IN A DEVELOPING COUNTRY WITHIN A NORMAL RANGE?

With this previous work in mind, our group was very receptive to any opportunity to do a diagnostic study using DMPS to estimate the body/kidney burden of mercury. Thus, when we were approached to do a study in Monterrey, Mexico, we quickly agreed. The purpose of the research was to determine whether urinary mercury levels of dental workers in a developing country were within a normal range. Urines of dental workers employed in a modern new hospital/clinic in Monterrey, Mexico, and those of a nondental control group were collected under standardized conditions before and up to 6 h after DMPS administration and analyzed for total mercury.

3.1 Methods

3.1.1 Subjects

The subjects were 5 dentists (1 female and 4 males, ages 26-34 yr, mean 30.2); 10 female dental technicians (ages 17-27 yr, mean 20.2 yr) whose duties include formulation of amalgam; and 13 nondental personnel (5 females and 8 males, ages 23-51 yr, mean 36.4 yr). All dental personnel were employed in a dental clinic in Monterrey, Mexico, and routinely work with amalgam. The dental clinic is part of a hospital built by a progressive company to provide improved medical and dental care for its employees. The building was less than 5 years old at the time this study began, and had excellent modern medical and dental facilities. The dental clinic had four examining rooms and one very small windowless preparation room. It is in the latter that a dental technician prepared dental amalgam as needed. To do this, the technician removed metallic mercury from a bottle, placed it on a small piece of white filter paper, and then added to it a portion of alloy powder. She than carried this to the dentist in the examining room who with his hands squeezed the excess mercury through the filter paper, and then used the amalgam to complete the restoration. This method of amalgam preparation was used in the United States about 20 years ago. It has been replaced in the United States by capsules containing amalgam.

The control, nondental subjects were employed at the Centro de Investigacion Biomedica del Noreste, Instituto Mexicano del Seguro Social (IMSS), in Monterrey. Dentistry is not practiced at this IMSS facility and research using mercury is nil. The alcohol consumption of these populations was small; more than 65% of the subjects drank alcohol less than once per month.

3.1.2 Protocol

For the DMPS-mercury challenge test, the subjects were made to fast overnight beginning 11 h before DMPS administration to 4 h after DMPS administration, at which time they ate a turkey sandwich (Table 3). Urine was collected from –11 to 0 h and from 0-6 h after administration of the chelating agent. (The mercury content of the 11 h urine was determined and then divided by 11 and multiplied by 6 to obtain the –6 h or pre-DMPS urinary Hg value.) Molin et al. (1991) have reported a close correlation ($r = 0.99$) between urinary mercury excretion during the first 6 h after DMPS and that during the 24-h period after DMPS. DMPS, 300 mg, was given by mouth and subjects were encouraged to drink sufficient mercury-free water to maintain a urine output of approximately 500 mL per collection period. The DMPS dose was given to each subject independent of body weight because the regimen is a diagnostic test.

Table 3 DMPS Challenge Test Protocol

1. Fast 11 h overnight and collect urine during this time.
2. Next morning at 0 h give 300 mg DMPS by mouth.
3. At 0 h begin collecting urine for next 6 h.
4. Eat chicken or turkey sandwich at +4 h.
5. At +6 h, empty bladder and end urine collection.
6. Acidify urine and freeze until analyzed.
7. Analyze for Hg by cold vapor AA

3.2 Results: Urinary Excretion of Mercury

The administration of the DMPS challenge to dental technicians, dentists, and nondental personnel resulted in an 88-fold (range = 11-335), 49-fold (range = 45-76), and 35-fold (range = 14-132) increase, respectively, in the mean 6 h urinary excretion of mercury as compared with that during the 6-h period before administration of this chelating agent (Table 4). These increases are statistically highly significant (Table 4). The mean urinary mercury excretion before DMPS administration for the dental technician group and dentists was 6 and 4 times greater, respectively, than that of the nondental controls. After DMPS administration, however, the mean urinary mercury for the dental technician group and dentists was 15 and 6 times greater, respectively, than that of the nondental controls.

Since toxicologists are usually more concerned with concentrations, the μg Hg/L of urine also was determined (Table 4). The urinary mercury concentration also showed a substantial (at least 12-fold) increase after DMPS administration. In addition, such data indicate that the difference in urinary concentrations of mercury is not as marked as the difference in absolute amounts being excreted during the 6-h period after DMPS.

It is particularly satisfying to us that when the director of this clinic was shown these results, remedial steps were taken to decrease the exposure to mercury of these very young dental technicians.

4 DMPS CHALLENGE TEST AND MERCUROUS CHLORIDE EXPOSURE

A number of people in Mexico and the United States use a cosmetic to bleach or lighten their skin. The most important ingredient of the cosmetic lotion is, according to the manufacturer, mercurous chloride. When asked by the company's owner to assess their factory and workers, we were able to

Table 4 Urinary Hg before and after DMPS Challenge Test

		μg Hg ± SE		μg Hg ± SE	
Group	*n*	−6 to 0 h (before)	0 to +6 h (after)	−6 to 0 h (before)	0 to +6 h (after)
Dental technicians	10	4.84 ± 0.742	424. ± 84.9	29.7 ± 6.73	481 ± 121
Dentists	5	3.28 ± 1.11	162. ± 51.2	19.8 ± 7.19	275 ± 107
Nondental	13	0.783 ± 0.189	27.3 ± 3.19	3.00 ± 0.620	37.2 ± 15.1

Notes:

p values determined by single-factor ANOVA.

For urinary Hg before and after treatment $p < 0.001$ for the dental technicians, $p < 0.015$ for the dentists, and $p < 0.001$ for the nondental personnel.

For −6 to 0 h: dental technicians vs. nondentals, $p < 0.001$; dentists vs. nondentals, $p < 0.005$; dental technicians vs. dentists, $p = 0.252$.

For 0 to +6 h: dental technicians vs. nondentals, $p < 0.001$; dentists vs. nondentals, $p < 0.001$; dental technicians vs. dentists, $p = 0.0597$.

SE = standard error.

expand the study to determine the urinary mercury levels of not only the factory workers involved in the production of the lotion but also of users of the cosmetic. Urines of the skin lotion makers, skin lotion users, and those of a nonexposed control group were collected under standardized conditions before and for 6 h after DMPS administration and analyzed for total mercury.

The DMPS challenge test had not been used previously in humans exposed to mercurous mercury (Hg^{2++}). Calomel (mercurous chloride) is less poisonous than mercuric (Hg^{++}) chloride because of its insolubility in water and poor absorption from the gastrointestinal tract (Clarkson et al., 1988b). In the intestine, small amounts are converted to the more soluble mercuric ions which are absorbed, expressing mercury's characteristic toxic effects (Fingl, 1970). Of all the tissues, the kidney had the highest accumulation of inorganic mercury (Clarkson et al., 1988b). In the 1940s, calomel was added to teething powders because of its bactericidal quality; it caused numerous cases of acrodynia, known as pink disease, in children (Warkany and Hubbard, 1951). After considerable controversy, in 1955 products containing calomel were withdrawn from sale in the United Kingdom and Australia. Pink disease then disappeared, apart from a few isolated cases. This disease, however, has been shown to be linked to Young's syndrome, which is found in men who developed obstructive azoospermia, resulting in reduced fertility (Hendry et al., 1993). Young's syndrome and pink disease appear to share a common etiology. Other sources of exposure to calomel are the many Chinese patent medicines used both in China and in the United States (Kang-Yum and Oransky, 1992). Renal failure and ultimately death have been reported among Chinese who have used these calomel-containing medicines chronically (Kang-Yum and Oransky, 1992). Numerous calomel-containing products are now manufactured in the United States. They are readily available without prescription and are not regulated by the FDA. In London, ethnic remedies (Kew et al., 1993) and skin lighteners (Godlee, 1992) containing calomel have been reported to be available for purchase.

4.1 Methods

Subjects fasted for 11 hours and then were given 300 mg of DMPS administered orally with two 8 ounce glasses of water (Table 3). All subjects consumed a standard meal (turkey sandwich and fruit) 4 hours after drug administration (Table 3). DIMAVAL, 100 mg DMPS capsules of the same lot number were used in this study and were obtained from Heyl, Berlin. In Germany, DIMAVAL is registered with the German FDA. To minimize the contribution of other sources to the urinary mercury levels, subjects were asked to refrain from eating seafood for 15 days prior to enrollment in the study. Subjects who used the skin cream were asked not to apply the cream the morning of the study and to shower well that morning. Subjects who were employed in the factory were asked to shower well and change into clean clothing prior to arrival at the study site, and were provided housing in a hotel beginning the day prior to drug administration.

4.1.1 Urinary Mercury Analysis

Total mercury in urine was determined by cold vapor generation/atomic absorption after acid digestion of the samples as previously described (Aposhian et al., 1992). Mercury content of urines was analyzed at the University of Arizona. Validation of mercury assays from our laboratory has been published previously (Aposhian et al., 1992; Gonzalez-Ramirez et al., 1995).

4.1.2 Analysis of Skin Lotion

Calomel in the skin-lightening lotion was isolated and purified by successive extractions with chloroform, ethyl acetate, water, and ethanol. The dried residue was analyzed for mercurous mercury by the mercaptoacetate test (Hand et al., 1943). The amount of mercurous mercury in the residue was determined by cold vapor generation/atomic absorption after acid/hydrogen peroxide digestion.

4.1.3 Urinary Lead Analysis

Total lead in urine was determined at the Instituto Mexicano del Seguro Social (IMSS), Monterrey, N.L., Mexico, by flame atomic absorption after extraction of the samples using the method of

Zinterhofer et al. (1971). The laboratory participates in the Blood Lead Proficiency Testing Program from the Wisconsin State Laboratory of Hygiene.

4.2 Results

4.2.1 Study Population

The subjects were skin lotion makers (4 females and 7 males, ages 19-57 yr); users of the skin lotion for skin-lightening purposes (6 females and 2 males, ages 21-78 yr); and controls (2 females and 7 males, ages 18-39 yr). The lotion makers were employed in various stages of producing a lotion or cream suspension that contains calomel (mercurous chloride). The years of employment of the lotion makers with the firm ranged from 1.5 to 15 yr (mean 6.2 yr). Nine subjects (controls) who had no known exposure to mercury were recruited from the same city. All subjects were recruited by the factory management.

4.2.2 Clinical Findings

One of the factory employees had gingival lines on physical examination and demonstrated slight past pointing on finger-to-nose testing and slowed rapid alternating movements. Another factory employee had gingival lines and distal nail lines on physical examination. The latter subject was difficult to assess for neurologic impairment because of a severe closed head injury he had sustained as a child with residual neurologic impairment. A third employee had gingival lines only and a fourth demonstrated some slowing with finger-to-nose testing. These four subjects had been employed in the factory for 2.5 to 11 yr. No subject had clinical evidence of tremor, peripheral neuropathy, Parkinsonian effects, dysarthria, or emotional lability. None of the subjects in the control or cosmetic-using groups had similar findings.

4.2.3 Calomel in the Skin Lotion

To be certain the skin lotion at the time of sale contained mercurous mercury, a residue was isolated from it and shown to contain mercurous mercury as determined by the mercaptoacetate test. The residue turned dark gray after the addition of mercaptoacetate. Mercaptoacetate reduces mercurous to elemental mercury but forms a pale yellow complex with mercuric mercury. The residue was shown to be pure mercurous chloride (101%) as determined by cold vapor AAS and comparison with a mercurous chloride standard. These results were verified by testing mercurous chloride and mercuric chloride standards. All skin lotion users applied the same brand.

4.2.4 Urinary Excretion of Mercury

When the lotion makers, users, and controls were challenged with DMPS, the mean 6 h urinary excretion of mercury (μg) increased 45-fold (range 26-249), 87-fold (range 39-169), and 38-fold (range 12-77), respectively (Table 5). These increases were highly significant statistically for the lotion makers and users (Table 5). The mean urinary mercury (μg) excretion for the makers and users before DMPS administration was 231 times and 33 times greater, respectively, than the controls (Table 5). After DMPS administration, however, the mean urinary mercury (μg) excretion for the makers and users was 274 times and 77 times greater, respectively, than that of the controls. Because toxicologists are usually more concerned with concentrations, the μg Hg/L in urine was also calculated (Table 5) and showed a substantial increase after DMPS administration.

4.2.5 Urinary Excretion of Lead

DMPS given to lotion makers, users, and controls resulted in a 4.7-fold (range 3.0-11.4), 5.3-fold (range 2.3-13.7), and 7.6-fold (range 3.2-16.5) increase, respectively, in the mean 6 h urinary excretion of lead (Fig. 2). These increases are highly significant (Fig. 2). The mean urinary lead (μg) excretion before DMPS was essentially the same for all groups. The mean urinary lead (μg) excretion for the lotion makers or lotion users after DMPS was essentially the same and significantly less than that of the controls.

4.3 Discussion

Calomel is a white, odorless, tasteless, heavy powder that is very insoluble in water and is poorly absorbed from the gastrointestinal tract (Clarkson et al., 1988b). Very little data on the toxicology and pharmacokinetics of calomel are available. Tissue levels of mercury were very high (527 μg/g in the kidney) in one individual who used calomel as a laxative over a long period of time (Weiss et al., 1973). When calomel was given intravenously to rats, rabbits, and guinea pigs, mercuric ions (Hg^{++}) accumulated in the kidney and red blood cells (Hand et al., 1944). In another report mercuric sulfide crystals were found at autopsy in cells of the kidney, liver, and intestinal tissues of an individual who had chronically ingested calomel (Weiss et al., 1973). The biochemical mechanism for the conversion of mercurous to mercuric mercury in mammalian tissues is unknown.

The body burdens of mercury in factory workers who manufacture a skin lotion containing mercurous chloride (calomel) were larger than in users of the lotion and in controls who had not been occupationally exposed to mercury (Table 5). Mercurous mercury (Hg^{2++}) was the main form of mercury exposure. Lotion makers were exposed to calomel powder via inhalation during the production of this cosmetic. The lotion users were exposed topically since the lotion is sold as a cosmetic for topical application to lighten or bleach skin color. The DMPS-mercury challenge test indicated that the body burden of mercury in all these groups of subjects was much larger than indicated before DMPS administration (Table 5). The mean mercury excretion after DMPS for the lotion users, however, was considerably less than that of the lotion makers (Table 5). This might be because the users had used the cosmetic for many years (some as long as 25 years), whereas the workers had been exposed for a shorter period of time. Molin et al. (1991) suggested that DMPS mobilizes kidney mercury from recent exposures.

Table 5 Urinary Mercury before and after DMPS Challenge Test

	µg Hg ± SE	
Group	−6 to 0 h (before)	0 to +6 h (after)
Skin lotion makers	113.± 26. (11)	5037. ± 682. (11)
Range	16.0 to 314	1728 to 10307
Skin lotion users	16.2 ± 3.4 (8)	1410. ± 346. (8)
Range	1.84 to 35.3	71.8 to 3075
Controls	0.49 ± 0.11 (8)	18.4 ± 7.1 (8)
Range	0.07 to 0.98	3.17 to 54.2

Notes:

For urinary Hg before vs. after DMPS treatment; $p < 0.001$ for lotion makers, $p < 0.002$ for lotion users, and $p < 0.05$ for controls. For -6 to 0 h: makers vs. controls, $p < 0.002$; users vs. controls, $p < 0.001$; makers vs. users, $p < 0.01$. For +6 to 0 h: makers vs. controls, $p < 0.001$; users vs. controls, $p < 0.001$; makers vs. users, $p < 0.001$. The number in parentheses is the number of subjects included in the mean. Outlying values were rejected by the Q test. Outlying values: Skin lotion users 0 to +6 h: 7,321 µg/L; Controls -6 h to 0 h: 5.86 µg, 17.0 µg/L; 0 to +6 h:111 µg.

SE = standard error.

The differences between the urinary mercury of the control group and the lotion makers or users before DMPS were highly significant (Table 5). The difference between the -6 to 0 h urinary mercury content (before DMPS) of the lotion makers and the lotion users was moderately significant ($p < 0.01$). But after DMPS administration, the difference between the lotion makers and the lotion users became highly significant ($p < 0.001$). The differences between the 0 to +6 h urinary mercury content (after DMPS administration) of the control group and the lotion makers or lotion users were also highly significant. In fact, these differences in the urinary mercury excretions after the DMPS

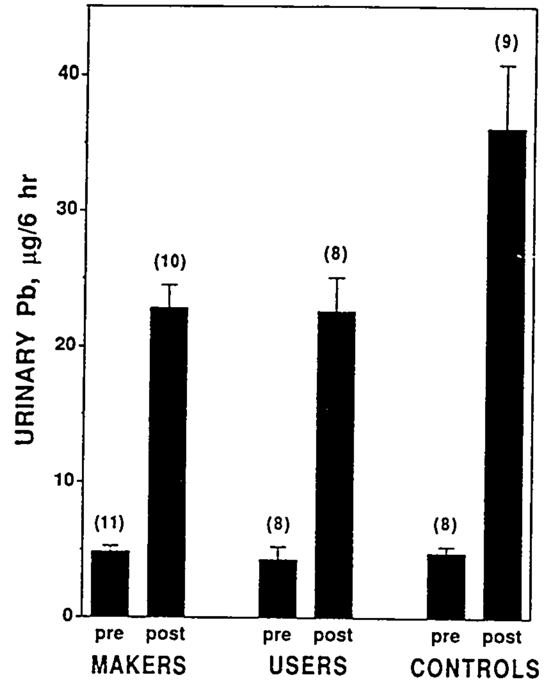


Fig. 2 The DMPS Challenge Test and Urinary Lead (Pb) Excretion (Values are the mean ± S.E.M. Pre, -6 to 0 h before DMPS administration; post, 0 to +6 h after DMPS. For urinary Pb before vs. after DMPS, p <0.001 for each group. For 0 to +6 h, lotion makers vs. controls, p<0.02; lotion users vs. controls, p <0.05.)

challenge were more statistically significant than the differences found before the DMPS challenge (Table 5), indicating that one of the benefits of the use of the DMPS challenge test is a greater sensitivity and utility when comparing different groups having different exposures to mercury.

The magnitude of the increased urinary excretion of mercury after DMPS was greatest in the case of the lotion users, 87-fold (Table 5). The greatest increase in the lotion maker group and conrol group after the DMPS challenge was of the individual of each group who had the greatest urinary mercury excretion before DMPS administration. This particular lotion maker excreted 10 mg Hg during the 6 h after DMPS administration. However, the individual in the lotion user group who had the greatest urinary mercury excretion after DMPS had the third highest urinary mercury excretion before DMPS. Most of the lotion makers had contact with the calomel during their duties at the factory. The lotion maker with the greatest amount of mercury in his urine both before and after the

DMPS challenge adds the calomel to a large open vat containing water, mixes it, filters the calomel solution, and then pours it into an agitator tank. His gums had a gray line. Another lotion maker, who is in charge of maintenance and cleans the bottle-filling equipment, had the second greatest amount of urinary mercury after the DMPS challenge. Shortly before the study, he had dismantled older equipment that had been used previously to make calomel from elemental mercury (Hg^0). At the time of our studies, mercurous chloride was being purchased for use. Another lotion maker, who had the third greatest amount of urinary mercury after the DMPS challenge, collected samples for analysis. If the analysis was poor, he emptied the production tank, discarded the suspension, and began the process over again. These 3 lotion makers had the greatest exposure to calomel among the 11 lotion makers in the study. They also had the highest urinary mercury values before the DMPS challenge. Corrective measures have been taken in this factory including better training in the handling of calomel and in the use of dust masks to prevent inhalation of calomel powder. In addition, the workers have been given three courses of DMPS treatment to decrease their body levels of mercury (Gonzalez-Ramirez, personal communication).

It should not be overlooked that (1) the DMPS challenge test increased the mean urinary mercury excretion 45-, 87-, and 38-fold in the respective study groups (Table 5); (2) DMPS has a tremendous capacity to increase urinary mercury; the mean urinary mercury concentration was as high as 4,282 μg Hg/L after DMPS. The normal level is <5 μg Hg/L.

In the present study there was not a linear positive correlation between the urinary mercury, either before or after DMPS, and the number of amalgams or the amalgam score. Amalgam restorations in Mexico appear to be very large in diameter, precluding any correlation between diameter and urinary mercury excretion. The control group did not have any amalgams (probably because they could not afford them). Exposure to mercurous chloride appeared to overwhelm any contribution of mercury from the amalgams in the lotion makers or users.

The mean urinary lead excretion in all three study groups was significantly increased by the DMPS challenge (Fig. 2), suggesting that the DMPS challenge test may be of use for determining the body burden of lead. The mean urinary lead excretions before and after DMPS administration, however, were in the normal range for adults. The person with the highest urinary mercury also had the highest urinary lead.

It is obvious from the results of the present study that DMPS will mobilize both mercury and lead during the same course of treatment (Table 5 and Fig. 2). This is not surprising since DMPS has been used for the treatment of mercury or lead intoxication (Chisolm and Thomas, 1985). Whether mercury or lead ions have a greater affinity for DMPS, however, is not known. Information as to affinity constants of these metal ions for DMPS would be helpful. Interestingly, the increase in urinary lead excretion after DMPS was greatest for the control group. Obviously, their exposure to lead had been greater than the other two groups studied. We do not know the source of this exposure.

The results of this study of humans exposed to mercurous chloride demonstrate the usefulness of the DMPS-mercury challenge test for gaining a more realistic estimation of the body burden of mercury in humans. In retrospect, however, the concentration of mercury in the urine before DMPS administration was sufficient to have been indicative of the need for DMPS treatment for the lotion makers and users.

5 CONCLUSIONS

The overall value of all these experiments that we have reported in this paper is that the DMPS-mercury challenge test can be used to better evaluate exposure to mercury of humans. The usefulness of this procedure for evaluating human exposure in the environment produced by hazardous waste sites should be determined.

6 ACKNOWLEDGMENTS

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THE RELATIONSHIP OF BONE AND BLOOD LEAD TO HYPERTENSION: FURTHER ANSLYSES OF THE NORMATIVE AGING STUDY DATA

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ABSTRACT

In an earlier report based on participants in the Veterans Administration Normative Aging Study, we found a significant association between the risk of hypertension and lead levels in tibia. To examine the possible confounding effects of education and occupation, we considered in this study five levels of education and three levels of occupation as independent variables in the statistical model. Of 1,171 active subjects seen between August 1991 and December 1994, 563 provided complete data for this analysis. In the initial logistic regression model, age and body mass index, family history of hypertension, and dietary sodium intake, but neither cumulative smoking nor alcohol ingestion, conferred increased odds ratios for being hypertensive that were statistically significant. When the lead biomarkers were added separately to this initial logistic model, tibia lead and patella lead levels were associated with significantly elevated odds ratios for hypertension. In the final backward elimination logistic regression model that included categorical variables for education and occupation, the only variables retained were body mass index, family history of hypertension, and tibia lead level. We conclude that education and occupation variables were not confounding the association between the lead biomarkers and hypertension that we reported previously.

1 INTRODUCTION

Lead is one of the most toxic hazards, and it is commonly found in hazardous waste. In the United States, the Agency for Toxic Substances and Disease Registry lists lead as the number one ranked hazard present in declared Superfund sites, a ranking that reflects the combined consideration of a hazard's toxicity as well as its prevalence.

Exposure to lead can occur through both ingestion and inhalation and through a variety of vectors. The multiplicity of possible exposure vectors has made it imperative to measure an individual's dose through the use of biological markers.

Measurement of lead in blood has become one of the most widely employed biological markers used in environmental surveillance. Indeed, the U.S. Centers for Disease Control (CDC) maintains a standard for childhood lead exposure that is expressed as the maximal tolerable level of lead in a child's blood (currently listed at 10 μg/dL). This level has been set after reviewing an extensive body of epidemiologic literature relating blood lead levels to neurotoxic effects.

In an effort to understand the full toxicologic implications of lead exposure, however, a further consideration must be that the level of lead in blood is not the correct biological marker (i.e., blood lead level poorly represents the internal dose of lead that has the most biological relevance with respect to some forms of toxicity).[1] Instead, there is mounting evidence that the biological marker of choice for some forms of toxicity may be provided by measurement of lead in bone.

Lead is known to accumulate in the skeleton, with a half-life of years to decades.[2,3] Bone serves as a long-lived repository of 75% and 90-95% of lead in children and adults, respectively.[4,5,6] Many studies have demonstrated that bone lead levels remain elevated despite declines in blood lead, thus raising the issue of whether bone lead may be a better biological marker of chronic toxicity. Indirect evidence shows that lead is released from these bone stores, particularly during times of increased bone turnover.[7,8]

With the recent development of in vivo x-ray fluorescence (XRF) for making rapid and safe measurements of bone lead, it is now possible to conduct epidemiologic studies by using the bone lead level as a measure of cumulative lead exposure.[9] In 1994, an epidemiologic investigation of construction workers with moderate exposures to lead in the past reported that bone (but not blood) lead levels were associated with lower hemoglobin and hematocrit values.[10]

More recently, an investigation of middle-aged to elderly men found that bone (but not blood) lead levels were associated with increased odds of developing hypertension.[11] The link between low-level lead exposure and blood pressure is of significant concern, given the role of hypertension as a leading risk factor for cardiovascular disease morbidity and mortality.[12,13] In this paper, we follow up on this investigation, describing analyses that build on those just reported. Specifically, we examine the role of education and occupation as possible confounders to the link between lead burden and hypertension. All research performed herein was approved by the human research committees of the Brigham and Women's Hospital and the Department of Veterans Affairs outpatient clinic.

2 METHODS

2.1 Study Subjects

Study subjects were participants in the Normative Aging Study (NAS), a longitudinal study of aging established by the Veterans Administration (now Department of Veterans Affairs) in 1961.[14] The study cohort consists of 2,280 community-dwelling men from the greater Boston area who were 21 to 80 years of age upon enrollment in the study. Volunteers who had a history of treatment for hypertension or had other chronic conditions such as heart disease, diabetes, cancer, peptic ulcer, gout, recurrent asthma, bronchitis, or sinusitis were not admitted to the study. Also disqualified were those with either systolic blood pressure >140 mm Hg or diastolic blood pressure >90 mm Hg. Biochemical characteristics were not considered as eligibility criteria. Study subjects have subsequently returned for examinations every 3 to 5 years over the follow-up period, with an attrition rate of roughly 1% per year over the life of the study. At each visit, extensive physical examination, laboratory, anthropometric, and questionnaire data have been collected. Measurement of blood lead levels began in 1988. Beginning in 1991, permission was sought from each subject to take KXRF bone lead measurements. Consenting individuals reported to the Ambulatory Clinical Research Center of the Brigham and Women's Hospital.

2.2 History and Physical Parameters

At the start of each participant's core NAS examination, his height and weight were measured as he wore only stockings and undershorts. A complete medical history was taken while the subject was seated, and each subject filled out a questionnaire and was interviewed to confirm the identity and purpose of medications taken daily. Medications were considered as antihypertensive if they included a beta blocker, calcium channel blocker, diuretic, or other vascular agent prescribed by the subject's physician for hypertension. Information on current and past history of smoking was gathered by questions developed for the American Thoracic Society.[15] Each subject was asked if his mother or father had been told by a physician that either one has hypertension. Subjects were queried as to whether they drank, on average, two or more alcoholic drinks per day, and they filled out a validated semiquantitative food frequency questionnaire (FFQ).[16,17] The FFQ lists food items and serving sizes and elicits information on frequency of intake during the past year. Nutrient scores are computed by multiplying the frequency of intake by the nutrient content of the food items.

Micronutrients examined in the present analyses were sodium and calcium, which were adjusted for total caloric intake.

In addition to the data collected that were reported earlier,[11] data were also collected on years of education and occupation. The five levels of education at each subject's most recent visit were used for this analysis: drop out of high school, finished high school, finished some technical education after high school, finished college, and finished graduate education. Occupations were categorized as either white collar or blue collar, and subjects were categorized as either white collar or blue collar for their working lifetimes. A third category was created for subjects who had been observed to change from white collar to blue collar categories or visa-versa.

Immediately after the history review, while the subject remained seated, systolic blood pressure and fifth-phase diastolic blood pressure were measured to the nearest 2 mm Hg in the left arm and then in the right arm with a standard sphygmomanometer. For this study, the means of the left and right arm measurements were used as each participant's systolic and diastolic blood pressures.

2.3 KXRF Bone Lead Measurements

Bone lead was measured in each subject's mid-tibial shaft and patella with an ABIOMED K x-ray fluorescence (KXRF) instrument (ABIOMED, Inc., Danvers, Mass.). KXRF devices are currently limited to research and are available at a handful of institutions worldwide. The physical principles, technical specifications, validation, and quality control procedures of this [18,19,20] and other KXRF instruments[21,22] have been described in detail elsewhere. Since the instrument provides a continuous unbiased point estimate that oscillates around the true bone lead value, negative point estimates are sometimes produced when the true bone lead value is close to zero. The instrument also provides an estimate of the uncertainty associated with each measurement, which is derived from a goodness-of-fit calculation of the spectrum curves and is equivalent to a single standard deviation. Although a minimal detectable limit calculation of twice this value has been proposed for interpreting an individual's bone lead estimate,[23] statistical experiments have shown that retention of all point estimates makes better use of the data in epidemiologic studies.[24] For the present study, 30-minute measurements were taken at the mid-shaft of the left tibia and at the left patella after each region had been washed with a 50% solution of isopropyl alcohol. The KXRF beam collimator was sited perpendicular to the bone surface for the tibia and at 30° in the lateral direction for the patella.

2.4 Blood Lead Measurements

Each blood sample for lead measurement was taken in a trace metal-free tube containing EDTA and sent to ESA Laboratories, Inc. (Bedford, Mass.) for analysis. After room temperature digestion with nitric acid, the sample solution was centrifuged, and the supernatant was poured into a sample cup and analyzed by Zeeman background-corrected flameless atomic absorption (graphite furnace). The instrument is calibrated after every 21 samples with National Bureau of Standard blood lead standards materials. Ten percent of samples were run in duplicate;[3] 10% of the analyses were controls, and 10% were blanks. In tests on reference samples from the CDC, the coefficient of variation ranged from 8% for concentrations below 1.44 mmol/L (30 mg/dL) to 1% for higher concentrations. In comparison with a National Bureau of Standards target of 0.27 mmol/L (5.7 mg/dL), 24 measurements by this method gave a mean of 0.25 mmol/L (5.3 mg/dL) with a standard deviation of 0.059 mmol/L (1.23 mg/dL).

2.5 Statistical Analyses

Statistical outliers were identified for all continuous variables (on the basis of their univariate distributions determined by using the extreme Studentized deviate procedure[25]). As a check on the quality of the KXRF measurements, tibia and patella bone lead measurements were identified that had associated measurement uncertainty estimates of >10 and >15 mg/g bone mineral, respectively. For each individual, weight and height were used to calculate body mass index (kg/m^2), and cumulative smoking and alcohol ingestion were estimated as pack-years of cigarettes at the time of KXRF examination and the proportion of all visits (dating back to the beginning of the study) in which the individual reported drinking two or more alcoholic drinks per day, respectively. A subject was considered to have a family history of hypertension if either parent had hypertension.

We chose hypertension as the outcome because it is of more clinical relevance than blood pressure per se, and space does not permit a discussion of both subjects (a separate analysis of lead and blood pressure will be reported elsewhere). "Hypertension" was defined as taking daily medication for the treatment of hypertension, or, during the time of examination, systolic blood pressure >160 mm Hg or diastolic blood pressure of 96.[3] These relatively high cut-off points for blood pressure were selected to maintain a high degree of specificity among those subjects designated as hypertensive.

The odds ratio for the occurrence of hypertension was assessed by logistic regression models. An initial model was fitted that included age, race, body mass index, family history of hypertension, cumulative smoking, cumulative alcohol ingestion, sodium intake, calcium intake, levels of education, and occupation. Each of the lead biomarkers (i.e., blood lead, tibia bone lead, and patella bone lead) was then added separately to this model. A final model was then selected by using a backward elimination procedure that began with all of the covariates and lead biomarkers and then incrementally discarded terms with the highest P-values and terminated when all remaining variables were significant at the $P < 0.05$ level.

3 RESULTS

During the period from June 1991 through December 1994, a total of 1,171 NAS subjects were seen for their regularly scheduled visits. Of these, 563 (48%) participated in the KXRF bone lead study and had data on all covariates of interest. The major reason given for nonparticipation in the bone lead study was the inconvenience involved in making a separate visit to our bone lead test facility. Participants had a mean age of 66.7 years. A comparison of participants with nonparticipants in the KXRF bone lead study revealed no significant differences with respect to age, body mass index, pack-years of smoking, average alcohol ingestion history, and proportion of individuals who fulfilled the criteria for hypertension. Mean blood lead of the nonparticipants was slightly but significantly higher than mean blood lead of participants.

Levels of lead in the blood, tibia, and patella of participants in this study ranged from <1 to 27.9 μg/dL, <1 to 96 μg/g, and <1 to 142 μg/g, respectively. Both measures of bone lead rose with increasing age in a fairly linear fashion.

The hypertensives had significantly higher levels of body mass index, blood lead, tibia lead, and patella lead levels (Table 1) than the nonhypertensives.

In the initial logistic regression model, age, body mass index, family history of hypertension, and dietary sodium intake, but neither cumulative smoking nor alcohol ingestion, conferred increased odds ratios for being hypertensive that were statistically significant ($P < 0.05$; Model A, Table 2). When the lead biomarkers (i.e., blood lead, tibia lead, and patella lead) were added separately to this initial logistic model, tibia lead and patella lead levels were associated with significantly elevated odds ratios for hypertension (Models C and D, Table 2). Of note is that the addition of either bone lead biomarker was associated with a diminution of the parameter estimate for age, and the confidence intervals no longer excluded zero.

In the final backward elimination logistic regression model that included categorical variables for education and occupation, the only variables retained were body mass index, family history of hypertension, dietary sodium intake, and tibia lead level (Table 3).

4 DISCUSSION

In our earlier report, we examined levels of lead in bone and blood, as individual biomarkers of lead dose, in relation to hypertension.[11] Our findings indicated that in this population, the most significant factors related to the occurrence of hypertension were body mass index, blood lead level, and patella lead level. Chronic alcohol ingestion and smoking, dietary calcium and sodium, and age were not significant factors in the final regression model in this study.

Table 1 Characteristics of Hypertensives and Nonhypertensives in the Normative Aging Bone Lead Study

	Hypertensives (N = 142)		Nonhypertensives (N = 421)	
Characteristic	Mean (SD)	Median	Mean (SD)	Median
Age (yr)	67.1 (6.6)	67.4	66.5 (7.3)	66.4
Body mass index (kg/m^2)	29.1 (4.2)	28.3	27.4 (3.7)[a]	26.9
Dietary sodium (mg/d)	3,574 (1,507)	3,316	3,834 (1,789)	3,487
Dietary calcium (mg/d)	830 (426)	758	832 (386)	745
Blood lead (μg/dL)	7.0 (4.3)	6	6.1 (4.0)[a]	5
Tibia bone lead (μg/g)	24.0 (14.1)	22	20.9 (11.4)[a]	19
Patella bone lead (μg/g)	35.3 (19.7)	31.5	30.1 (18.3)[a]	27
Characteristic	n	n		
Average alcohol consumption[b]				
0-10	86 (61%)	266 (63%)		
10-50	33 (23%)	86 (20%)		
>50	24 (17%)	69 (16%)		
Education				
Beyond college[d]	22 (15%)	47 (11%)		
College level	21 (15%)	72 (17%)		
Technical school	31 (22%)	111 (26%)		
High school	52 (37%)	148 (35%)		
High school dropout	16 (11%)	43 (10%)		
Occupational history				
Blue collar	50 (35%)	156 (37%)		
White collar	64 (45%)	209 (50%)		
Mixed blue and white collar	28 (20%)	56 (13%)		
Family history of hypertension[c]				
Yes	59 (42%)	93 (22%)		
No	83 (58%)	328 (78%)[a]		

Table 1 (Cont.)

Characteristic	n	n
Pack-years of smoking		
0	37 (26%)	139 (33%)
1-20	44 (31%)	116 (28%)
21-40	27 (19%)	77 (18%)
>40	34 (24%)	89 (21%)
Race		
White	137 (96%)	416 (99%)
African-American	5 (4%)	5 (1%)

[a] P is <0.05 in either t-test or chi-square test.

[b] Proportion of all study visits (dating to the inception of the study) in which the subject reported drinking two or more alcoholic drinks per day.

[c] History of physician-diagnosed hypertension in the subject's father or mother.

[d] Reference group.

Table 2 **Results of Logistic Regression Models of Hypertensive Status in Relation to Lead Biomarkers, Age, Race, Body Mass Index, Pack-Years of Cumulative Smoking, Cumulative Alcohol Ingestion, Dietary Sodium, and Dietary Calcium**

			A			B			C			D
Characteristic	β	SE	P-value	β	SE	P-value	β	SE	P-value	β	SE	P-value
Age	0.0313	0.0152	0.04	0.0303	0.0153	0.05	0.0185	0.0166	0.26	0.0195	0.0163	0.23
Race	0.5125	0.4068	0.20	0.4254	0.4097	0.30	0.3439	0.4200	0.42	0.3686	0.4197	0.3798
BMI	0.1076	0.0271	<0.001	0.1096	0.0272	<0.001	0.1048	0.0273	<0.001	0.1050	0.0272	<0.001
Family history	0.8709	0.2202	<0.001	0.8411	0.2215	<0.001	0.8761	0.2208	<0.001	0.8828	0.2209	<0.001
Pack-years of smoking	0.0036	0.0040	0.38	0.0032	0.0040	0.43	0.0023	0.0040	0.47	0.0025	0.0041	0.55
Alcohol ingestion	0.2401	0.3291	0.47	0.2285	0.3295	0.49	0.1935	0.3316	0.56	0.1987	0.3314	0.55
Dietary sodium	-.0002	0.0001	0.03	-.0002	0.0000	0.03	-.0002	0.0001	0.027	-.0002	0.0001	0.03
Dietary calcium	0.0000	0.0003	0.99	0.0000	0.0003	0.90	0.0000	0.0003	0.92	0.0001	0.0003	0.86
Education (yr)												
Beyond college[a]	.	.	.	.	.	.	.	.	.	.	.	.
College level	-0.5581	0.3768	0.14	-0.5774	0.3771	0.13	-0.6022	0.3786	0.11	-0.5838	0.3776	0.12
Technical school	-0.6425	0.3688	0.08	-0.6451	0.3691	0.08	-0.7132	0.3717	0.06	-0.7053	0.3709	0.06
High school	-0.5223	0.3718	0.16	-0.5130	0.3721	0.17	-0.6332	0.3780	0.09	-0.6354	0.3779	0.09
High school drop-out	-0.4338	0.4817	0.37	-0.4828	0.4853	0.32	-0.6202	0.4934	0.21	-0.5970	0.4924	0.23
Occupation												
White collar*	.	.	.	.	.	.	.	.	.	.	.	.
Mixed	0.4250	0.3205	0.18	0.3992	0.3223	0.22	0.3886	0.3235	0.23	0.4241	0.3213	0.19
Blue collar	0.1060	0.2894	0.71	0.0486	0.2928	0.87	0.0201	0.2943	0.95	0.0257	0.2949	0.93
Blood lead (mg/dL)				0.0392	0.0245	0.11						
Tibia lead (μg/g)							0.0190	0.0093	0.04			
Patella lead										0.0122	0.0056	0.04

[a] Reference group.

Table 3 Final Logistic Regression Model of Hypertensive Status after Backward Elimination

Variable	Parameter Estimate	Standard Error	P-value	Odds Ratio (95% CI)
Intercept	-3.8932	0.8049	<0.001	
Body mass index (kg/m^2)	0.0977	0.0261	0.002	1.103 (1.048, 1.161)
Family history (hypertension)	0.8677	0.2155	<0.001	2.381 (1.561, 3.633)
Dietary sodium (mg/d)	-0.0002	0.0000	0.025	1.000 (1.000, 1.000)
Tibia bone lead (mg/g)	0.0215	0.0079	0.007	1.022 (1.006, 1.038)

In further analyses conducted for this paper, we examined the possible confounding effects of education and occupation. We considered the years of education and the three levels of occupation as independent variables in the statistical model. It turned out that those variables were not confounding the association between the lead biomarkers and hypertension.

Since tibia lead is an indicator of long-term lead absorption and stores in trabecular bone, these findings suggest that chronic lead absorption may be a major risk factor for the development of hypertension. Given the cross-sectional nature of this investigation, we could not specifically evaluate the temporality of this relationship, making premature any inference on causality. Nevertheless, our conclusion is supported by a study by Batuman et al.[26] (who found that subjects with hypertension and mild kidney disease had elevated chelatable lead burdens but not blood lead levels in comparison to controls) as well as by animal studies of blood pressure in rats chronically fed low levels of lead.[27] Furthermore, in contrast to Batuman et al., the paucity of subjects in our population with serum creatinines greater than 2.0 mg/dL (6 [0.9%]) suggests that the mechanism of this effect does not require clinically apparent renal failure.

In conclusion, our study suggests that chronic accumulation of lead in bone and mobilization of bone lead may be significant risk factors for the development of hypertension. Further research is needed in the form of prospective epidemiological studies of bone lead and cardiovascular health and basic science studies of chronic lead toxicity to ascertain the causality of this relationship and bone lead's potential mechanism of action.

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HEAVY METALS IN SEMARANG'S URBAN STREAMS: SPATIAL DISTRIBUTION AND BIOINDICATION USING THE GUPPY (*Lebistes reticulatus*)

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ABSTRACT

A field survey on cadmium, lead, copper, and zinc was performed in Semarang, the fifth largest city in Indonesia. Water, sediment, and fish samples were collected from 101 grids of 2 × 2 km. The objectives of the study were (1) to identify the spatial distribution of metals in the sediments of the greater Semarang area, (2) to estimate the background concentrations of the metals present in Semarang, (3) to provide a simple tool for deriving standards for metals in the sediment, and (4) to explore the potential use of the guppy (*Lebistes reticulatus*) as a bioindicator of urban metal pollution. To map the spatial distribution of the metals, concentrations of each metal in sediment were plotted against the corresponding city coordinate. On the basis of these plots, background concentrations of the metals were estimated. A combined pollution index can be derived thereafter by calculating the difference between metals concentrations from a particular grid and their respective background concentrations. Potential use of the guppy as a bioindicator is assessed, based on a comparison on several demographic parameters (i.e., size structure, sex ratio, reproductive success and energetic status) between unpolluted and heavily polluted populations.

1 INTRODUCTION

Urbanization can be defined as aggregation of human population in an area with a subsequent perturbation of the environment (Pizl and Josens 1995). This process usually has serious impacts on soil, as well as on water resources. Heavy metals, such as lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn), are usually associated with the impact of urbanization. Therefore, it is common to use concentrations of heavy metals as indicators of urbanization.

Urban metals pollution has become a subject of increasing interest in human medicine, ecology, and ecotoxicology (Dallinger et al. 1992 after Seinfield 1989). Several authors have reported evidence of the accumulation and effects of heavy metals emitted from urban activities on animals and plants

(Berger and Dallinger 1993; Depledge et al. 1993; Cotrufo et al. 1995; Mackey and Hodgkinson 1995; Pizl and Josens 1995).

In addition to sewage effluent, untreated fecal matter, industrial effluent, untreated industrial wastes, domestic and industrial garbage, one of the major sources of water pollution in Southeast Asian cities is sediments (Low and Balamurugan 1991). Sediments are repositories for physical debris and sinks for a wide variety of chemicals, including heavy metals. The concern associated with the metals contamination in the sediments is that many commercial species and food chain organisms spend a major portion of their life cycle in or on aquatic sediments. This provides a pathway for these metals to be consumed by higher organisms. Direct transfer of chemicals from sediments to organisms is now considered to be a major route of exposure for many species (Adams et al. 1992). Furthermore, information on the status of trace metal pollution in the sediment of coastal areas is of considerable importance in the interest of public health, when seafood from this area is available for consumption (Mat and Maah 1994).

Although studies on heavy metals in several cities in Indonesia, including Semarang, have been carried out for years (Darmojo et al. 1985; Supriharyono et al. 1989; Astuti et al. 1991; Anonymous 1993a, 1994a), the available data and publications are very limited. Similar conditions have been reported in other parts of southeast Asia (Din 1995). The present study is the first that maps a spatial distribution of metals in an entire part of a city; other studies have used a limited set of sampling sites, as demonstrated by most metals studies conducted in the region.

Information on metals spatial distributions at a full-scale provides a full picture of the extent of the city's metals contamination. Furthermore, with regard to the absence of sediments quality standards for metals, which are needed for the assessment and monitoring of urban metal pollution in Indonesia, a reference value of each metal and an index indicating the degree of combined metals contamination in the sediment can be derived based on the above information.

Along with a chemical approach, the decline of environmental quality should be identified through its ecological receptors, i.e., organisms living in the ecosystems (Van Straalen 1992). The chemical approach relies on measurement of the concentration of toxic substances in physical components of the environment. It often provides unrealistic results, since it does not address the interaction between toxicants and organisms (Widianarko et al. 1994). An advantage of an ecological approach is that it makes it possible to demonstrate the actual damages from pollution.

Unlike industrial pollution, urban pollution tends to be chronic in nature. The escalation of the concentration of toxic substances on various components of the urban ecosystem takes place slowly. This chronic exposure might be closely associated with long-term toxicity effects (Dallinger et al. 1992). To evaluate this chronic risk, directly monitoring the emission source is not useful. Vahter et al. (1991) stated that to monitor urban pollution, a simple and reliable bioindicator system should be developed.

The "wild" guppy (*Lebistes reticulatus*), which is easy to find in southeast Asian urban streams, is a prospective candidate for a bioindicator and a species for laboratory toxicity testing. *L. reticulatus* is one of exotic species that has adapted very well to the southeast Asian urban streams, after its introduction in the 1930s for mosquito control (Chou and Lam 1989). Although this fish has shown its persistence in streams contaminated with a wide range of urban wastes, so far almost no ecotoxicological studies have used this species (note: not including the commercially cultured guppy).

The objectives of the present study are (1) to identify the spatial distribution of metals in the sediments of the greater Semarang area, (2) to estimate the background concentrations of the metals present in Semarang, (3) to provide a simple tool for deriving standards for metals in the sediment, and (4) to explore the potential use of the guppy (*Lebistes reticulatus*) as a bioindicator of urban metal pollution.

2 MATERIALS AND METHODS

2.1 Study Area

Semarang has a population of 1.2 million and showed an average annual growth of 1.1% from 1989 to 1993 (Anonymous 1993b). The main activities of this capital city of the Central Java Province are trading and industry. Semarang occupies an area of 373.668 km^2 and is situated in the northern coast of Java. Due to Semarang's topographical characteristics (i.e., a descending altitude toward the coast), hundreds of watercourses, from river to small streams, are subjected to continuous sedimentation. Higher altitude areas in southern parts of the city have regularly sent run-off and sediment to inner-city areas. These flows, combined with seawater from the leveling of coastal land to reclaim the coastal area, results in frequent flooding in the city.

2.2 Sampling

Sampling was conducted from 21 April to 19 August 1995. Based on the topographical map of Semarang, the entire city was subdivided into 101 grids of 2 × 2 km. In each grid, sediment, water, and fish (the guppy) samples were collected from the largest stream (if guppies are present).

A systematic sampling program was performed from west to east, starting from the coast. To reduce the systematic error due to the difference in sampling time, sampling moves from one grid to the next grid, skipping the closest grid, which is then sampled in the next round of sampling, from east to west.

In this study, only sediment samples are considered. Sediment samples were taken from the 5-cm upper layer of surface sediment. Each sample was approximately 1 kg and was transported to the laboratory in a plastic bag. At the laboratory, the pH of fresh sediment samples was measured. The dry matter content of each sample was determined gravimetrically, based on the weight reduction of 20 g of fresh sample to the weight of oven-dried sample (105°C, 18 h).

Prior to the metal analyses, 10 g of oven-dried sediment of each sample was prepared, ground, and passed through a 1-mm mesh sieve. The sediment powder was then stored and transported to Amsterdam in a polyethylene bag.

For the bioindication study, two streams in southwestern Semarang (i.e., Purwosari [C_1] and Kreo [C_2]), were selected to represent the unpolluted site. However, the polluted site was represented by streams from an industrial area, LIK-Bugangan Baru (D_1) in East-Semarang, and from a business district, Jalan Jendral Sudirman (D_2), in West-Semarang. From each stream, 100 fish were randomly collected. The fishes were then quickly transported live to the laboratory and readied for further observation.

2.3 Metal Analyses

Metal analyses were carried out in 1995 October at the laboratory of the Department of Ecology and Ecotoxicology, Vrije Universiteit Amsterdam. A portion of 1-g oven-dried sediment was digested using 6 mL of a mixture of nitric acid, chloric acid, and demineralized water (4:1:1 v/v) in a microwave furnace (CEM MDS 81D). Following the digestion, 10 mL of demineralized water was added to rinse the digestion tube. All of the solution was then collected in a perspex tube and readied for metal analyses. Concentrations of Pb, Zn, and Cu were determined by using the flame Atomic Absorption Spectrophotometer (AAS). An attempt to detect Cd concentration was done by using a graphite furnace AAS. Determination of the metal body burden of the fish was also done by means of a graphite furnace AAS. Oven-dried fish samples were digested in a mixture of HNO_3 and $HClO_4$ (7:1). The digestion was done by placing the glass tubes in a destruction block until dry. Prior to the measurement, 1 mL of HNO_3 (ultrex grade) was added to each tube.

2.4 Measurement of Demographic Parameters

Upon arrival at the laboratory, the sex ratio, number of pregnant females, fresh weight, and body length were determined from the sample of each location (C_1, C_2, D_1, and D_2). For pregnant females, the fresh weight of reproductive tissues (eggs and juveniles) was separated from the fresh weight of somatic tissues. After the weighing, the number of eggs and juveniles in each individual pregnant female was recorded.

All fish samples were then stored in the oven (60°C , 18 h), and the dry weights were identified. The energy content of the fish was calculated based on the concentrations of protein and ether extract, which were determined gravimetrically (Reznick 1983). Only male fishes were used in this measurement. Oven-dried fish tissue was extracted individually in a Soxhlett extraction apparatus using anhydrous ether. The extraction lasted for 6 hours until a constant weight was reached. After the extraction, the sample was ashed in a muffle furnace at 550°C for 6 h. The difference between dry weight and weight after extraction is the fat content (ether extract) in the tissue, which is then multiplied by a factor of 9.5 to arrive at the calorie value. The difference between weight after extraction and after ashing is the protein content of the tissue, which is then multiplied by 5.7 to arrive at the calorie value. The carbohydrate content of the fish is omitted. The energy content in Joules can be derived by multiplying the sum of calories from fat and protein by a factor of 4.184.

2.5 Data Analysis

Data on the concentrations of Zn, Pb, and Cu in the sediment were evaluated by using STATISTICA for Windows, Release 4.5, StatSoft, Inc. (1993). Data sets of each metal were normalized by using a logarithmic transformation. This transformation was carried out to satisfy the assumption of constant variance and normality. The Kolmogorov-Smirnov test for normality was used to detect the normality of each data set (Sokal and Rohlf 1981; Zar 1984). The distribution of normalized data of each metal was then presented in a frequency table. Furthermore, the central tendency statistics, including the 95th percentile were determined for each data set.

A new distribution composed of observation values less than the 95th percentile was constructed to derive the background concentration or the reference value of each metal. The mean of this new distribution is used as an estimate of the reference value.

The information from all three metals was combined into one pollution index. The metal concentration from each site is divided by the corresponding background concentration (derived from the previous analysis). This gives a number that indicates by which factor the background concentration is exceeded at a certain site. The factors for each of these metals were then multiplied, and the logarithm of the product was taken. The same result will be obtained if the logarithm of each metal concentration is taken, subtracted by the logarithm of the background concentration, and the results added for the three metals. We call this index W (Eq. 1).

$$W = \log \left(\prod_{i=1}^{n} C_i / C_{0i} \right) , \tag{1}$$

where:

C_i = concentration of metal i;
C_{0i} = background concentration of metal i; and
n = number of metal.

Spatial distribution of metals (Zn, Pb, and Cu) and W-values are presented in a three-dimensional scatterplot. The X and Y axes represent the distance (in kilometers) to the city's center from west to east and from north to south, respectively. The Z axis represents the corresponding concentration of each metal and the W-value.

Most of data on the demographic parameters were analyzed descriptively and presented graphically. The size structure of the fish population was set up based on a table of frequency distribution of body length. Body lengths of the guppy from four locations were tested by using one-way anova, followed by an LSD posterior test (Zar 1984). Computations used Systat version 2.6. All graphical presentations were done by using Harvard Graphics version 3.0 (for Windows).

3 RESULTS AND DISCUSSION

Cadmium was not detected at all sites, whereas concentrations of Pb, Zn, and Cu were widely spread. Some sites had extremely high metal concentrations (i.e., Zn up to 1,257.1 mg/g, Pb up to 2,665.5 mg/g, and Cu up to 448.2 mg/g). Figures 1, 2, and 3 show that spatial distribution. Figure 1 shows that the highest Zn concentration is in the coastal grids, possibly because of the effect of sedimentation. In Fig. 2, the highest Pb concentrations are clustered in the center of the city, possibly due to the effects of traffic. Figure 3 shows two hot spots. One site in the northeast has extremely high Cu (but normal Zn and Pb), and one site in the southeast has high Zn and Pb (but normal Cu). These hot spots are probably due to localized industrial contamination.

Based on the calculated 75th percentile value, 75% of the sites have low metal concentrations (i.e., Pb < 30.2 mg/g, Zn < 173.8 mg/g, and Cu < 49.0 mg/g). These concentrations are not extreme compared to metals concentrations in sediment of other parts of southeast Asia. Prudente et al. (1994) reported the ranges of metals concentrations in surface sediments from three inflowing rivers of Manila Bay (Table 1). A study on total leachable trace metals concentration in surface sediments of the Kuala Juru and Kuala Muda Rivers on the western coast of Peninsular Malaysia revealed concentration ranges of 4.5 ± 0.5 and 4.2 ± 0.8 µg/g for Cd; 36.8 ± 12.1 and 10.8 ± 3.3 µg/g for Cu; 64.2 ± 11.5 and 46.7 ± 2.8 µg/g for Pb; and 233 ± 63 and 39.4 ± 2.2 µg/g for Zn, respectively (Mat and Maah 1994).

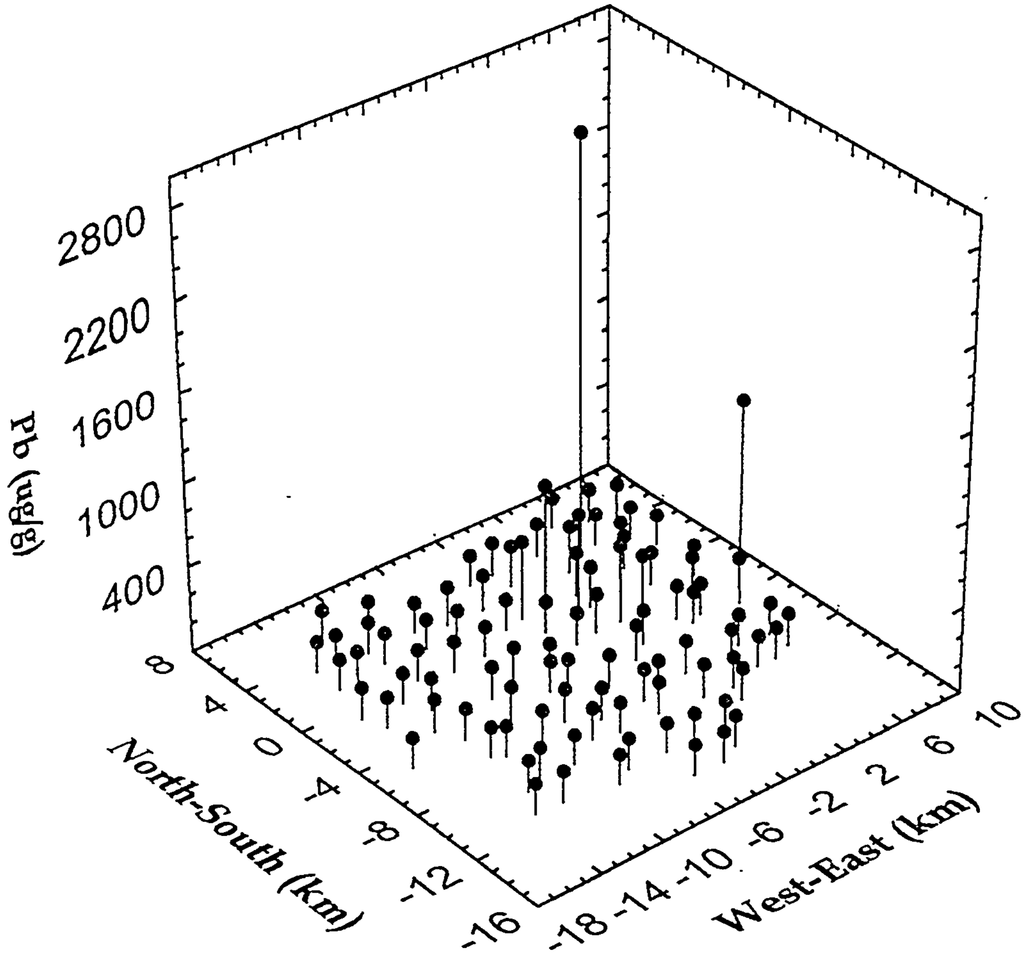


Fig. 1 Spatial Distribution of Lead

Therefore, it seems justifiable to derive the average background concentrations of Cu, Zn, and Pb. The mean value of a new distribution composed of observations at less than the 95th percentile was taken as the estimate of the reference value of each metal. The proposed reference values are 25.64, 143.37 and 40.67 μg/g respectively, for Pb, Zn, and Cu. Except for Pb, these values are slightly higher than target values according to the Environmental Quality Objectives in the Netherlands (Anonymous 1994b), provided sediment that meets this quality can generally be considered to be multifunctional and can be spread on land as dredging sludge without restrictions.

The degree of metal contamination of individual sites can be classified according to the calculated value of the combined contamination index, W (Eq. 1). The degree of metal contamination can be classified into four categories: unpolluted, slightly polluted, polluted, and heavily polluted. A site is classified as unpolluted if its combined contamination index is ≤ 0. A site is classified as slightly polluted if its combined contamination index is $0 < W \leq 1$. A site is classified as polluted if its

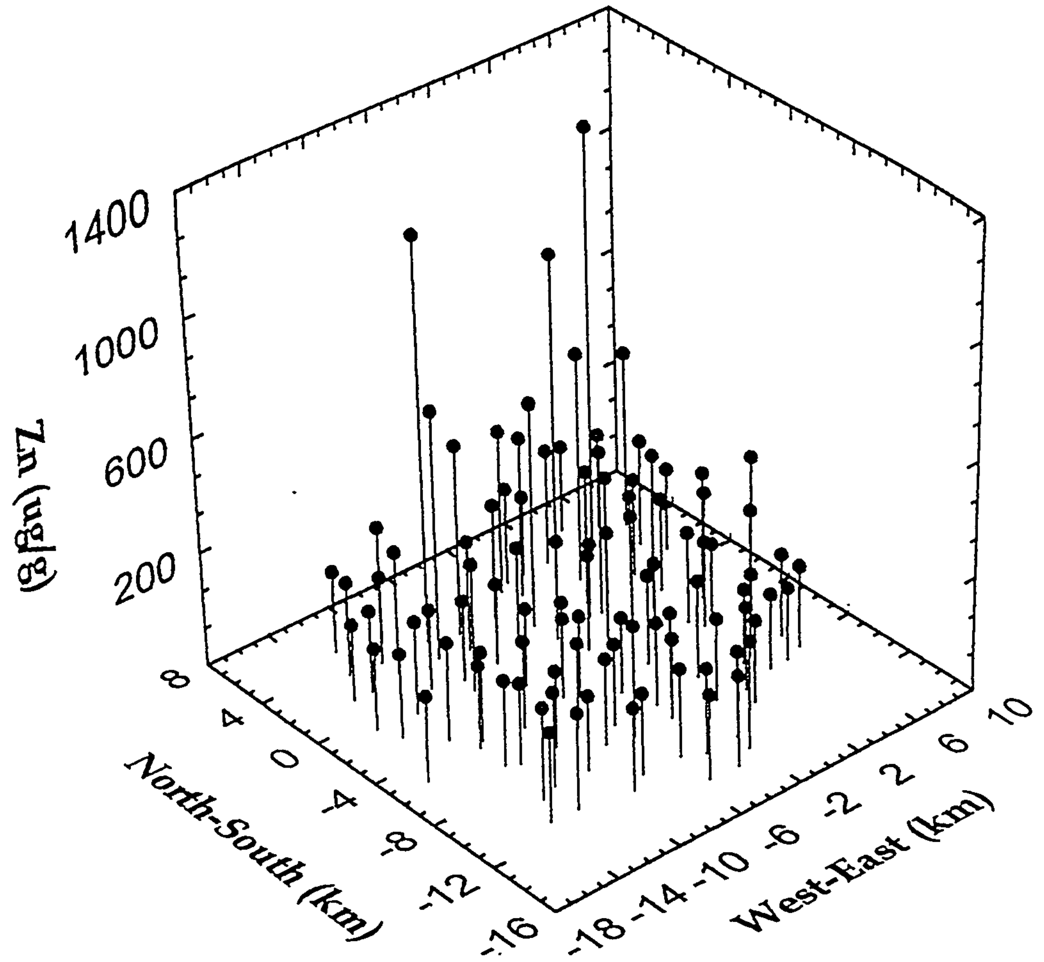


Fig. 2 Spatial Distribution of Zinc

combined contamination index is 1 < W≤2. A site is classified as heavily polluted if its combined contamination index is >2.

Since the antilog of W indicates by which factor the background concentration is exceeded, it implies that metal contamination at unpolluted sites is less than or equal to background concentration, whereas at slightly polluted and polluted sites, metal contamination is greater than 1 to 10 and greater than 10 to 100 times of background concentration, respectively. At heavily polluted sites, metal contamination is more than 100 times of background concentration. Based on this classification, from 101 sites in the greater Semarang area, 51 sites are unpolluted; 36 sites are slightly polluted; 9 sites are polluted; and 5 sites are heavily polluted (Fig. 4).

The approach developed in this study is prospective in the light of the need to define sediment quality standards for the region. It will be useful for the future monitoring of urban metal pollution in Semarang, as well as other cities in southeast Asia, where anthropogenic influences and continuous discharges of municipal and industrial effluents into the urban streams are expected to increase.

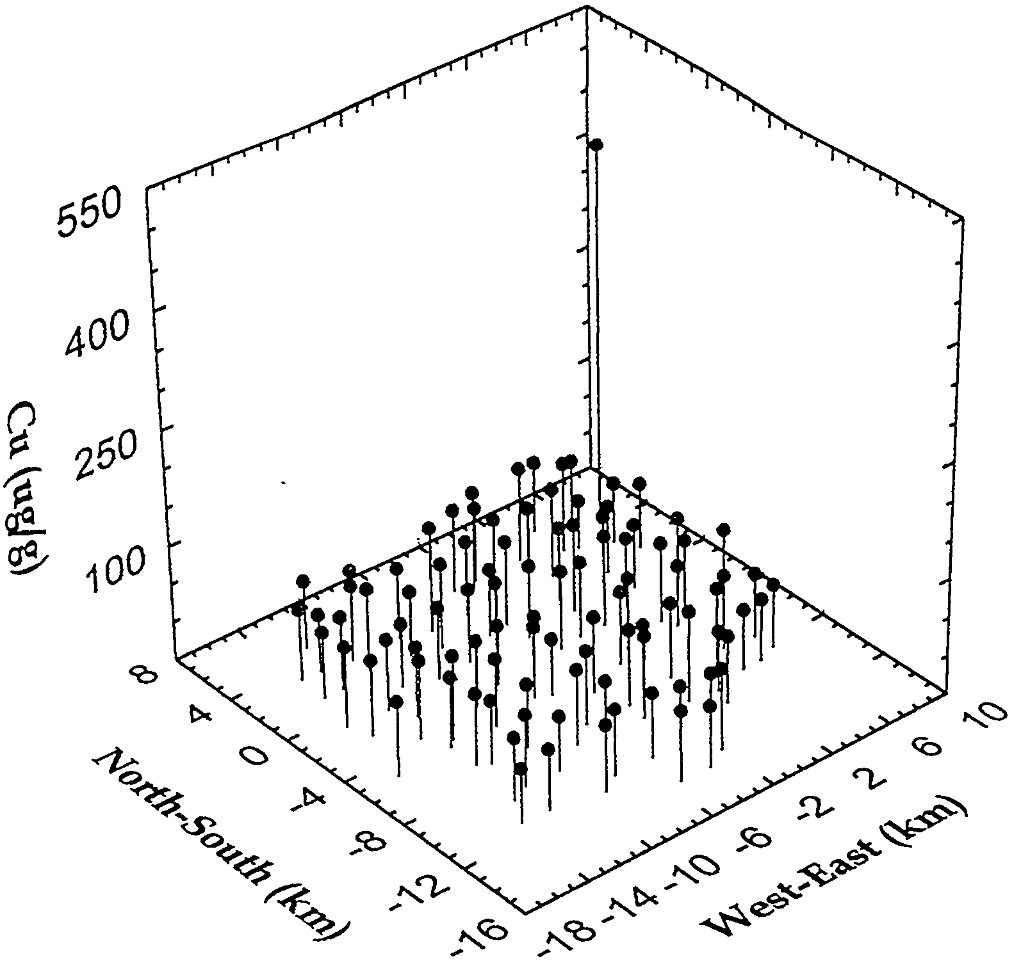


Fig. 3 Spatial Distribution of Copper

Table 1 Range of Metal Concentrations in Surface Sediments[a]

Metal	Marikina River	Pasig River	Rivers of Bulacan
Lead	18-31	66-137	36-198
Zinc	74-169	236-1,560	95-313
Copper	28-79	110-189	36-98

[a] Measurements in micrograms per gram dry weight.

Source: Prudente et al. (1994).

The present approach, however, cannot distinguish the anthropogenic contribution of metals as separated from their natural occurrences. Another approach that can be considered with this study is the determination of anthropogenic input of the metals, either using a separation of mobile fraction of metals (e.g., Fernandes et al. 1994) or a normalization procedure. Din (1992, 1995) applied a normalization procedure for heavy-metal data, using aluminum as the reference material. Regression analysis was used to relate the concentration of each metal with the concentration of aluminum. This procedure seems to be possible for estimating the natural and anthropogenic input of these metals in a particular area.

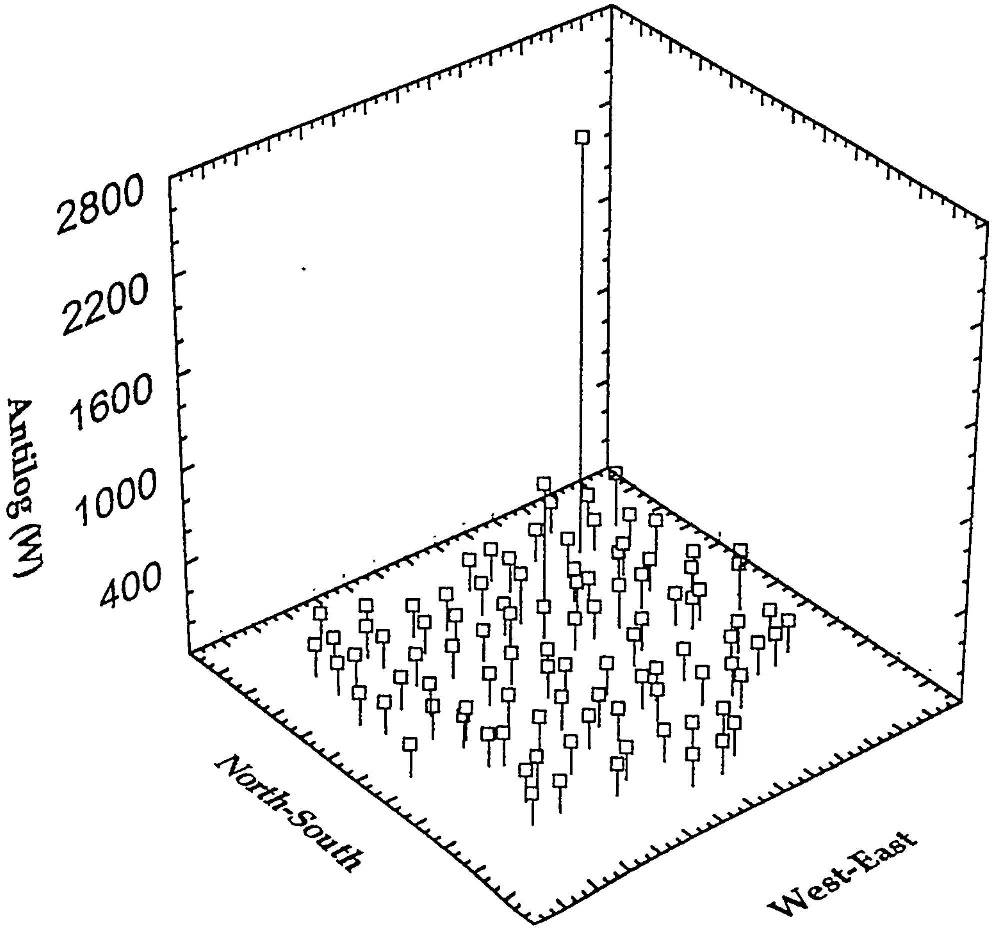


Fig. 4 Spatial Distribution of Metals Contamination

Concentrations of Pb, Cu, Zn, and the W value of the four streams selected for comparison of the guppy population are depicted in Fig. 5. Clearly, the selected sites represent very well the unpolluted and heavily polluted sites, as reflected by the negative W values in C_1 and C_2, and W values of higher than 2 in D_1 and D_2. Data on the metals burden of the fish showed that a difference between unpolluted and heavily polluted sites was only observed on Pb. One implication of this finding is that the future monitoring in Semarang should focus on lead (Fig. 6).

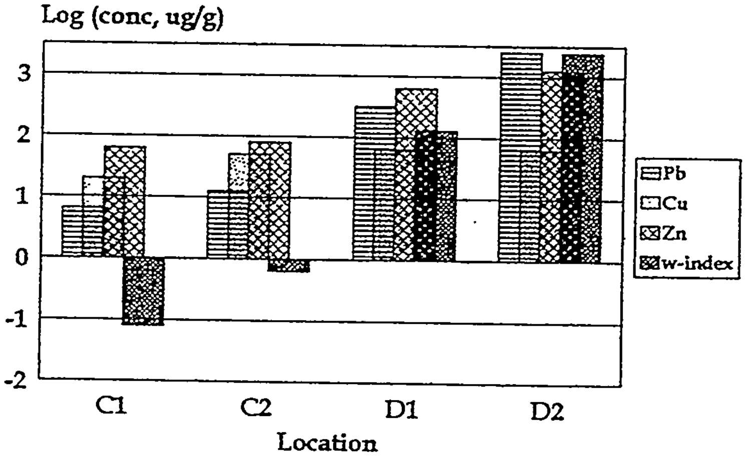


Fig. 5 Metals in Sediment

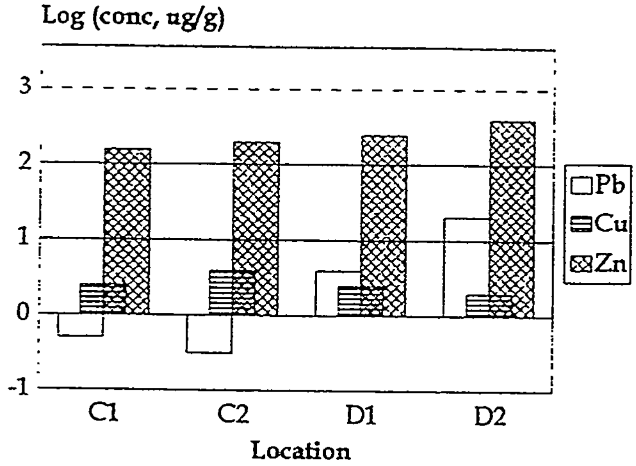


Fig. 6 Metals in Fish

Size structure based on body-length data was set up using five intervals, i.e., 0.5 – 1 cm, 1 – 1.5 cm, 1.5 – 2 cm, 2 – 2.5 cm, and 2.5 – 3 cm. Figure 7 shows that the difference in size structure between unpolluted and polluted sites is inconclusive. No trend shows an association between metal pollution and the distribution of fish body lengths. However, in terms of the average of body sex ratio is a prospective parameter for bioindication (Fig. 8). In unpolluted streams the ratio of females to males is about 3:1, whereas in polluted streams this ratio is 1:1. The ratio of total females to pregnant females also shows a potential for bioindication (Fig. 9). The value of this ratio indicates the proportion of pregnant females among all females. This ratio is a measure of reproductive success. In unpolluted streams, the total/pregnant female ratio is about 5:1, whereas in polluted streams the value is lower. Combining this result with the sex ratios, it can be inferred that the guppy population in a polluted ecosystem tends to have fewer females, but has a higher rate of reproduction than those in unpolluted ecosystems.

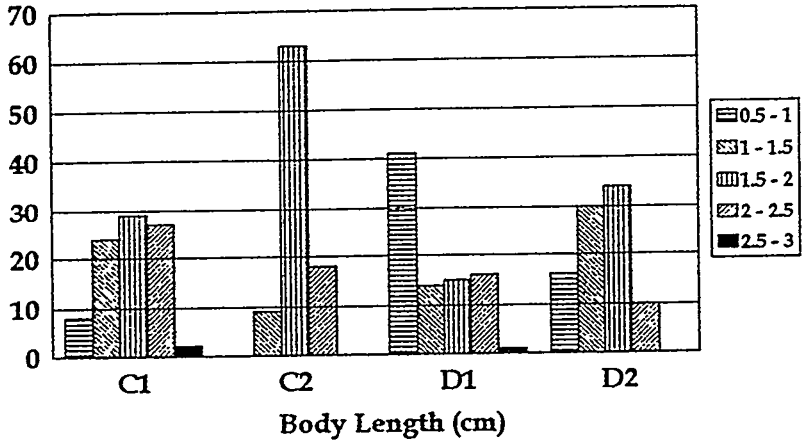


Fig. 7 Size Structure of the Guppy

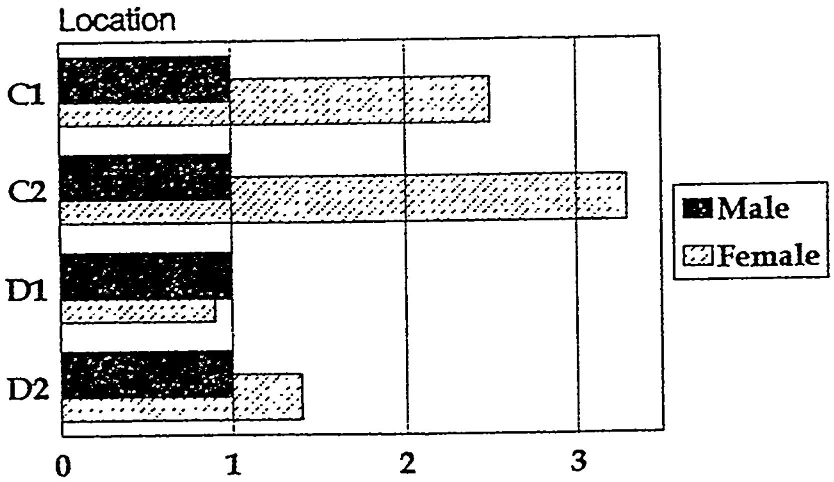


Fig. 8 Sex Ratio of the Guppy

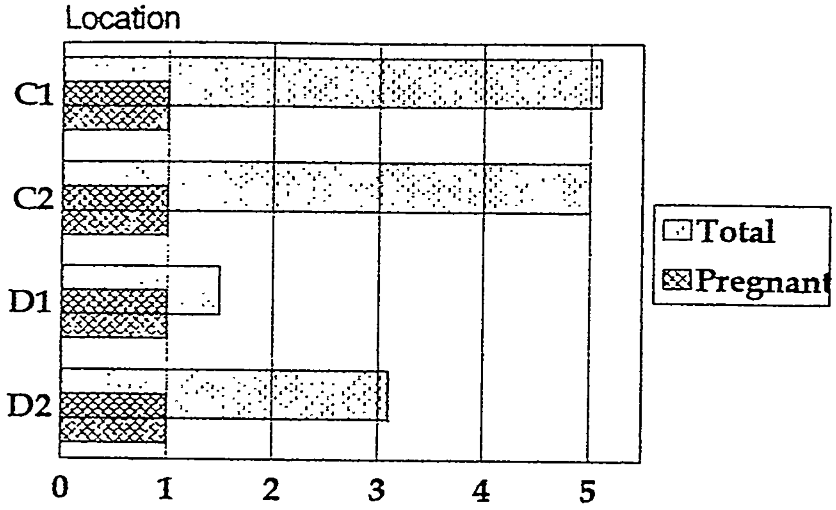


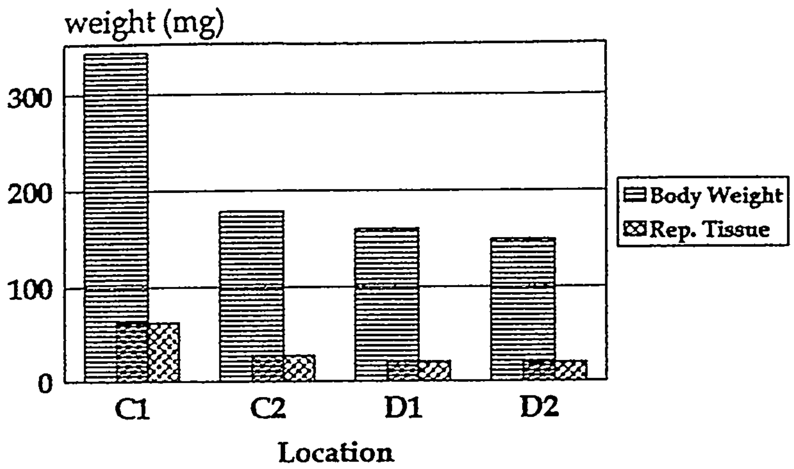
Fig. 9 Total/Pregnant Female Ratio

Other reproductive success parameters include the number of eggs and juveniles per pregnant female and the reproductive allocation expressed as the ratio of weight of reproductive tissues to body weight of each pregnant female (Fig. 10). These parameters do not show any differences between populations and are not suitable for bioindication of metals pollution. Polluted and unpolluted streams show no difference in the energetic status parameter (Fig. 11).

The above findings show that demographic parameters used in this study provide a different level of expression toward metals pollution. For the body size parameter, the average body length has shown a significant difference. The same does not hold for the size structure, although study on other species suggested that this parameter is sensitive to metals pollution (e.g., Van Capelleveen 1987; Hopkin 1989).

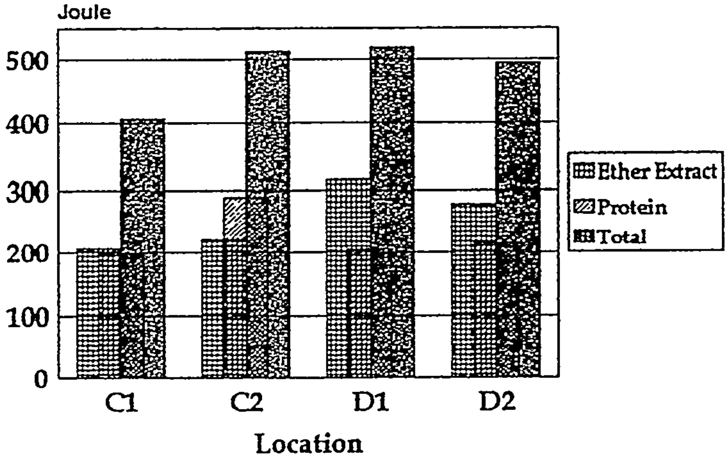
To represent the reproductive success, a parameter suitable for evaluation of urban metal pollution can be identified from this study (i.e., the ratio of total to pregnant females). This parameter is simple to measure. Another simple parameter that seems sensitive to the metals pollution is the sex ratio, which has a direct effect on the reproduction capacity of a population. The use of reproductive parameters is common in ecotoxicology. These parameters are suitable for evaluating chronic pollution using fish as biomonitor organisms (Barnthouse et al. 1987). Ecologically, the role reproductive parameters are very crucial, since reproductive success is a key of existence of the population (Donaldson 1990).

Insensitivity of several parameters used in this study, such as reproductive allocation and energetic status, toward metal pollution should be confirmed further in laboratory ecotoxicity experiments.



*) average body weight of pregnant female & average weight of reproductive tissues

Fig. 10 Reproductive Allocation*)



*) only male individuals

Fig. 11 Energetic Status of the Guppy

In such experiments, factors other than metal contamination can be controlled, so the typical response of each parameter toward elevated metal concentration can be isolated.

4 ACKNOWLEDGMENTS

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USE OF PASSIVE SAMPLING DEVICES TO DETERMINE SOIL CONTAMINANT CONCENTRATIONS

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ABSTRACT

The effective remediation of contaminated sites requires accurate identification of chemical distributions. A rapid sampling method using passive sampling devices (PSDs) can provide a thorough site assessment. We have been pursuing their application in terrestrial systems and have found that they increase the ease and speed of analysis, decrease solvent usage and overall cost, and minimize the transport of contaminated soils. Time and cost savings allow a higher sampling frequency than is generally the case using traditional methods. PSDs have been used in the field in soils of varying physical properties and have been successful in estimating soil concentrations ranging from 1 μg/kg (parts per billion) to greater than 200 mg/kg (parts per million). They were also helpful in identifying hot spots within the sites. Passive sampling devices show extreme promise as an analytical tool to rapidly characterize contaminant distributions in soil. There are substantial time and cost savings in laboratory personnel and supplies. By selectively excluding common interferences that require sample cleanup, PSDs can be retrieved from the field and processed rapidly (one technician can process approximately 90 PSDs in an 8-h work day). The results of our studies indicate that PSDs can be used to accurately estimate soil contaminant concentrations and provide lower detection limits. Further, time and cost savings will allow a more thorough and detailed characterization of contaminant distributions.

1 INTRODUCTION

The potential risk to humans and wildlife from exposure to contaminants at hazardous waste sites continues to be a major environmental issue and is liable to remain so through the end of the century. The United States currently has approximately 1,300 sites proposed or on the U.S. Environmental Protection Agency's National Priorities List (NPL). To date, only approximately 300 sites have been cleaned up. Effective remediation of these sites requires accurate identification of chemical distributions.

Conventional determination of soil contamination typically involves lengthy solvent extractions and sample cleanup procedures followed by chromatographic analysis. This process is usually time consuming and costly. A sampling method that uses passive sampling devices (PSDs) for characterizing soil contaminants could be extremely beneficial. Because of their simplicity and convenience, PSDs have been used for air sampling in industrial hygiene monitoring programs for decades. More recently, PSDs or semipermeable membrane devices have been used in aquatic systems to monitor nonpolar organic contaminants present in water (Södergren 1987; Huckins et al. 1990a,b; 1993; and Johnson 1991). Little work has been conducted to evaluate their effectiveness in soil systems (Brenniman et al. 1992; Zabik et al. 1992).

We have conducted several field trials in which PSDs accurately estimated soil contaminant concentrations. For the same costs, PSDs provide far better resolution in contaminant distributions than do traditional methods because of the increased sampling afforded by PSDs. We provide an overview of PSD use for accurate estimation of soil contaminant concentrations. We discuss field methods, PSD calibration, and estimation of soil contaminant concentrations from PSD levels, using one dieldrin assessment as an example of the technique.

2 THEORETICAL BASIS FOR SAMPLING

To be sampled by the PSD, an analyte must be small enough to permeate the membrane's transient corridors, which are theoretically <10 Å (Fig. 1). Conveniently, most organic contaminants of interest at hazardous waste sites have cross-sectional diameters <10 Å. Analytes reach the PSD membrane surface via aqueous or vapor phase diffusion (volatilization); the latter process is predominant in terrestrial passive sampling.

Volatilization rates of chemicals from soil systems are affected by a number of factors related to soil and chemical properties. The potential volatility of a chemical is directly related to its vapor pressure, although actual volatilization rates depend on environmental conditions and factors affecting chemical behavior at the solid-air-water interface (Spencer et al. 1982). Predictions of volatilization rates from within a soil system can be difficult due to adsorption, desorption, and diffusion. Chemical properties affecting these rates include vapor pressure, water solubility, and structural features. Soil properties that affect volatilization include soil moisture content, airflow, and organic carbon content (Spencer et al. 1973, 1988; Glotfelty and Schomburg 1989; Thomas 1990).

Soil volatilization rates are concentration dependent. As contaminant concentrations in soil increase, volatilization increases proportionately until the soil system is saturated. At saturation, any further increase in concentration will not significantly affect volatilization. Thus, below saturation, increases in soil contaminant concentration should be proportional to increasing PSD concentrations, a relationship supported by our research. PSD uptake in our studies was concentration dependent, increasing with increasing soil concentration (Johnson et al. 1995).

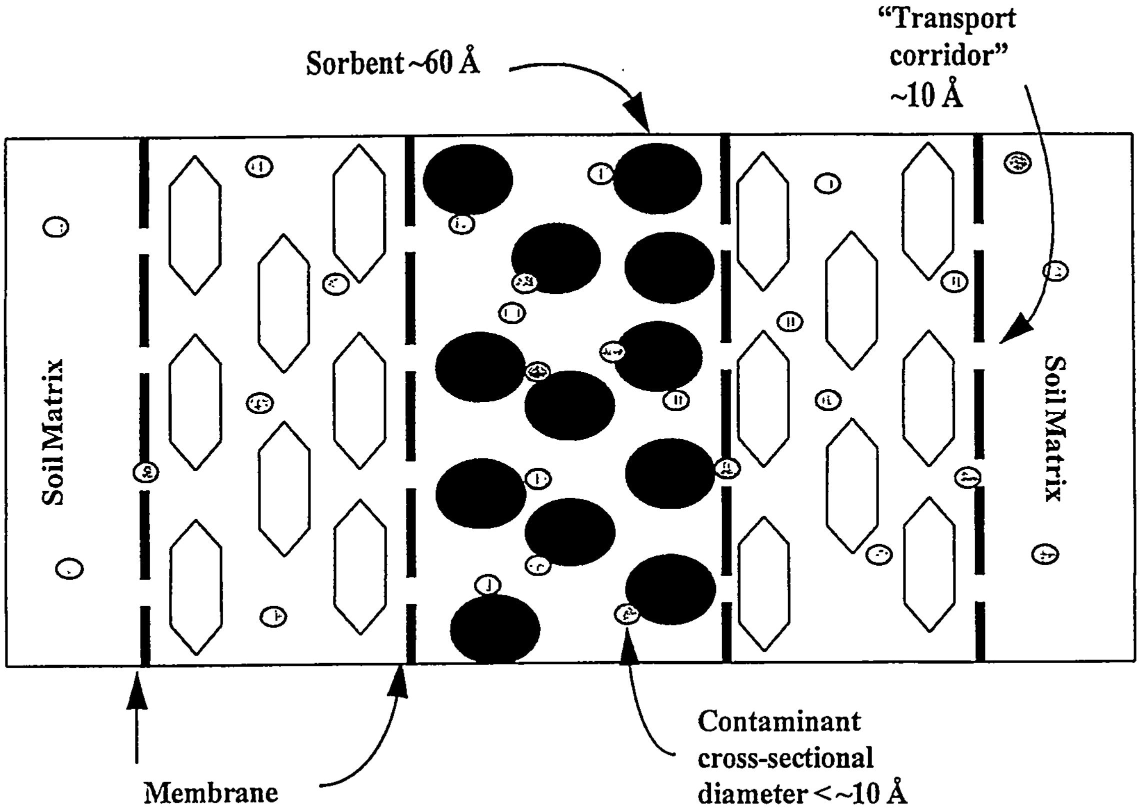

Fig. 1 Cross-sectional Representation of the PSD

3 MATERIALS AND METHODS

3.1 Passive Sampler Construction, Deployment, and Elution

Standard PSDs were constructed using 1-oz (5.5 × 11.5 cm) low-density polyethylene sampling bags (Whirl-Pak® bags; Nasco, Fort Atkinson, WI). The bags were cut to approximately 5.5 × 6.5 cm and filled with 1 g ^{18}C-based solid-phase extraction (SPE) sorbent similar to the construction of Zabik et al. (1992). The final surface area of the PSD was approximately 72 cm^2; wall thickness ranged from 63.5 to 71.1 µm. The sorbent was washed (1 g sorbent: 4 mL solvent), weighed (1 g), and placed into the polymeric bag. Air was removed from the samplers, and they were heat sealed.

At the time of deployment, a small horizontal cut (~40° to the horizon) was made in the soil, and PSDs were placed 7–10 cm below the soil surface. Approximately 50 g of soil was collected from the cut surface, both above and below the location at which each sampler was placed. The soils were stored frozen (-20 ± 1 °C) until extraction. The site was flagged, and PSDs were then left in the field for a specified time (usually one to two weeks), after which they were collected and brought back to the laboratory.

Once retrieved from the field, PSDs were extracted in a manner analogous to that used in SPE. The samplers were opened and the sorbent emptied into fritted glass syringe barrels. Once the barrels were uniformly packed, each PSD was eluted by rinsing the membrane/bag with two 2-mL portions of solvent (hexane followed by acetone). The rinsates were then poured through syringe barrels containing the sorbent. The combined eluates were reduced to a final volume of 2.0 mL.

3.2 Soil Extraction and Cleanup

Once it was determined which soils were to be extracted (see below), a subsample of approximately 11 g (wet weight) was Soxhlet® extracted for 20 h with 250 mL of 1:1 acetone:hexane, and the extracts concentrated to near dryness by vacuum rotary evaporation at 40°C. The samples were quantitatively transferred to 10-mL volumetrics and brought to volume in hexane. Extracts were then subjected a Florisil® column cleanup. Florisil was activated by oven drying at 131 ± 1 °C for 24 h and then stored in a desiccator for no longer than one week prior to use. The columns were constructed of 50-mL burets fitted with a plug of Soxhlet-extracted glass wool and packed uniformly with 18 g of Florisil followed by 5 g of anhydrous sodium sulfate. The Florisil was cleaned and wetted with 50 mL of hexane, and soil sample extracts were then poured onto the column. Dieldrin was eluted from the Florisil with 25 mL of hexane followed by 200 mL of 15% ethyl ether in hexane. Samples were reduced to near dryness using rotary evaporation and then brought to a final volume of 5 mL.

3.3 Instrumental Analysis

Samples quantitated for dieldrin were analyzed on a Hewlett-Packard Model 5890 Series II gas chromatograph (GC) equipped with a ^{63}Ni electron capture detector. The GC was operated with a 1:5 split injection and a purge time of 0.75 min. The column (J&W Scientific; Rancho Cordova, CA) was a 60 m × 0.25 mm i.d. fused-silica capillary coated with a DB-5 stationary phase (film thickness of 0.25 μm). The oven was programmed from 140°C (1 min hold) to 200°C at 2°C/min (1 min hold), to 204°C at 0.5°C/min, and then ramped to 280°C at 60°C/min with a final hold time of 20 min. The instrumental detection limit was 0.005 ng/μL.

3.4 PSD Calibration

After the PSDs were analyzed, six PSDs of low, medium, and high contaminant concentration were selected. Soils collected from the locations at which the PSDs were placed were extracted and analyzed. PSDs were then calibrated to soil concentrations by performing linear regression analysis on concurrent soil (independent variable) and PSD (dependent variable) concentrations. Because the data varied by more than four orders of magnitude, it was log transformed prior to linear regression.

4 RESULTS AND DISCUSSION

In the laboratory, PSDs have been used in studies with 5 OCs (two PCB congeners, 52 and 153, dieldrin, p,p'-DDT, and methoxychlor), three organophosphate pesticides (chlorpyrifos, diazinon, and terbufos), and three herbicides (alachlor, atrazine, and metolachlor). PSDs have been field-tested and proved effective to accurately estimate chemical concentrations in soils contaminated with PCBs (two studies) and dieldrin (four studies). They have been used successfully in soils with organic carbon contents ranging from 0% to 3% (organic matter 0% to 5%), moisture contents ranging from 1% to 26%, and bulk densities ranging from 0.9 to 1.6 g/cm^3.

In the described dieldrin study, PSD uptake ranged from 0.28 to 85 µg dieldrin/sampler. Concurrent soils used for calibration ranged from 0.17 to 180 µg dieldrin/g soil (Table 1). These concurrent PSD and soil samples were used to calibrate the PSDs by the development of a linear regression equation (Fig. 2). From this calibration equation, all of the soil concentrations can be estimated from their respective PSD contaminant levels. The data can then be used to graphically represent contaminant distributions (Fig. 3). On this site, soil concentrations estimated from 42 PSDs ranged from 0.2 to 230 µg dieldrin/g soil.

Table 1 Concentrations of Concurrent PSD and Soil Samples Used to Calibrate the PSDs

Sample Pair	PSD Mass (µg dieldrin/ sampler)	Soil Concentration (µg dieldrin/g soil)	Sample Pair	PSD Mass (µg dieldrin/ sampler)	Soil Concentration (µg dieldrin/g soil)
1	0.28	0.17	4	4.16	7.1
2	0.59	0.41	5	5.3	7.6
3	1.9	2.1	6	85	180

Because of the lower costs associated with passive sampling methods (Table 2), a higher number of samples can be deployed and extracted. Using the values in Table 2, it would cost approximately $450 to extract either 8 soils or to extract 42 PSDs plus 6 soils (for calibration). For visual comparison of the enhanced resolution gained using PSDs, we randomly selected and graphed 8 samples from the site (Fig. 4). Thus, for a similar cost, the use of PSDs provides a higher certainty of soil contaminant concentrations, as they vary over a site. Previously, 4 samples had been collected from within our sampling area; their dieldrin concentrations ranged from 0.3 to 0.9 μg/g soil. Due to the decreased sampling effort, the previous characterization missed major hot spots.

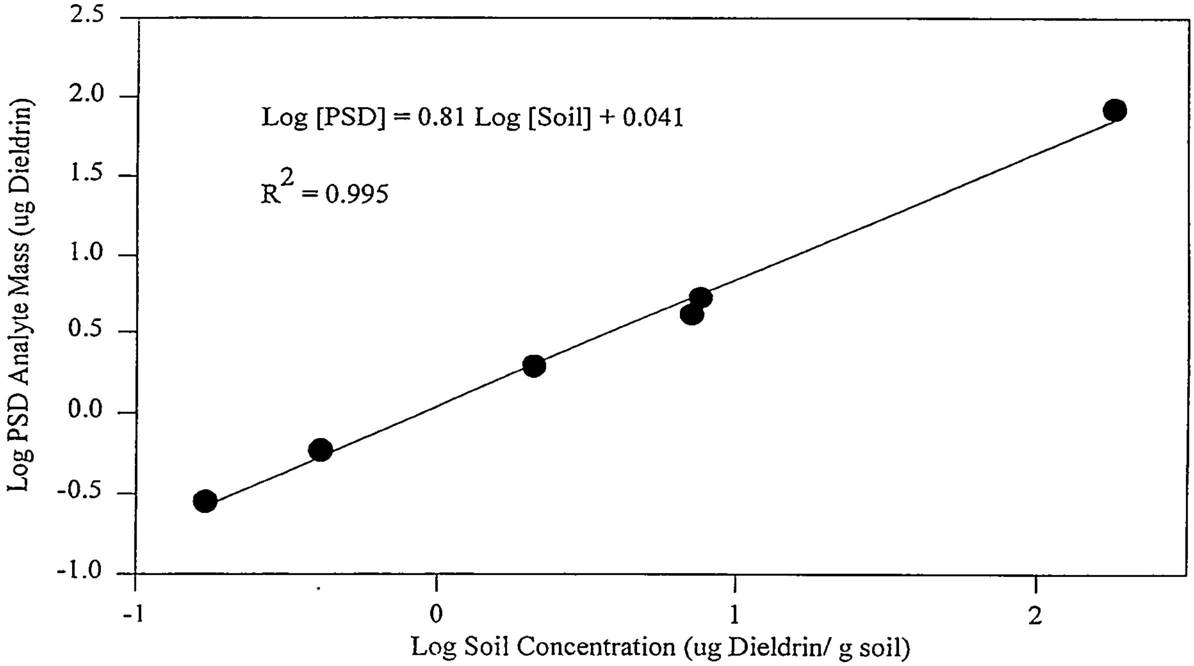

Fig. 2 PSD Field Calibration Curve

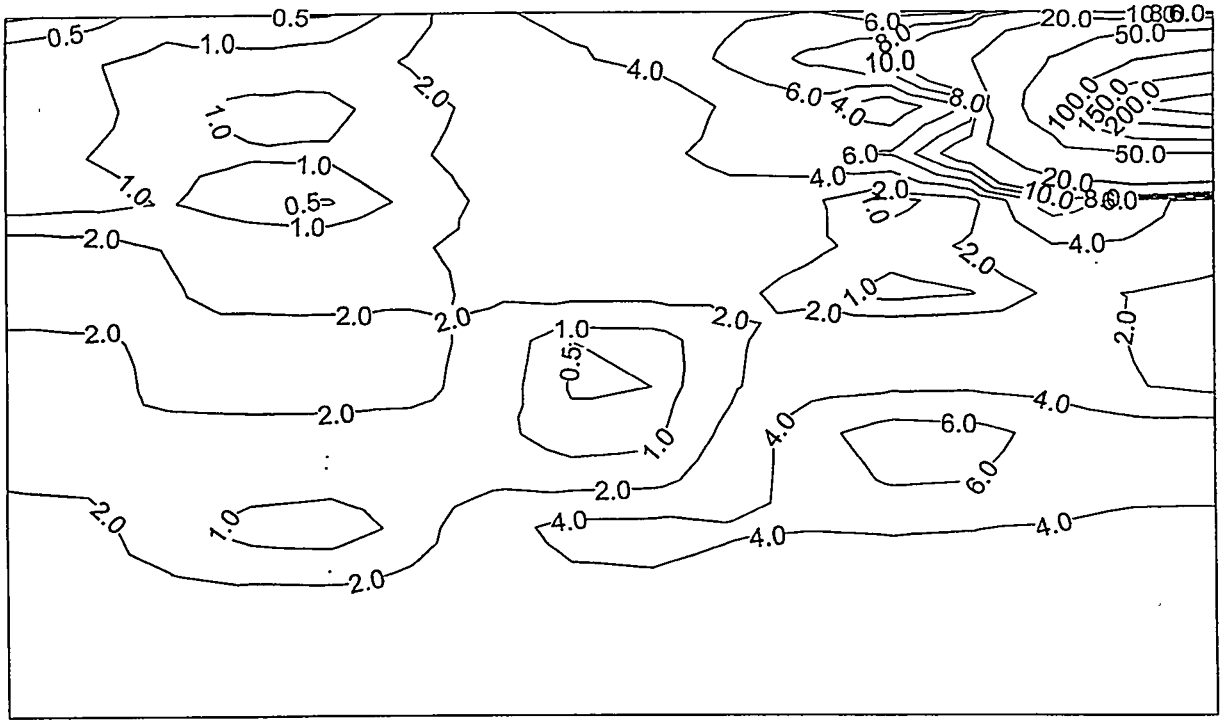

Fig. 3 Estimated Dieldrin Soil Concentrations (μg dieldrin/g soil) from 42 PSDs

Table 2 Comparison of Sampling Methods

Method Parameter	Traditional Method per Sample	PSD Method per Sample
Laboratory time	26 h	10 min
Laboratory prep time	4 h	10 min
Personnel cost	\$40	\$1.70
Solvent volume	~ 400 mL	<10 mL
Supply cost	\$15	\$1.25
Overall cost	\$55	\$2.95
Method recoveries	>80%	>90%

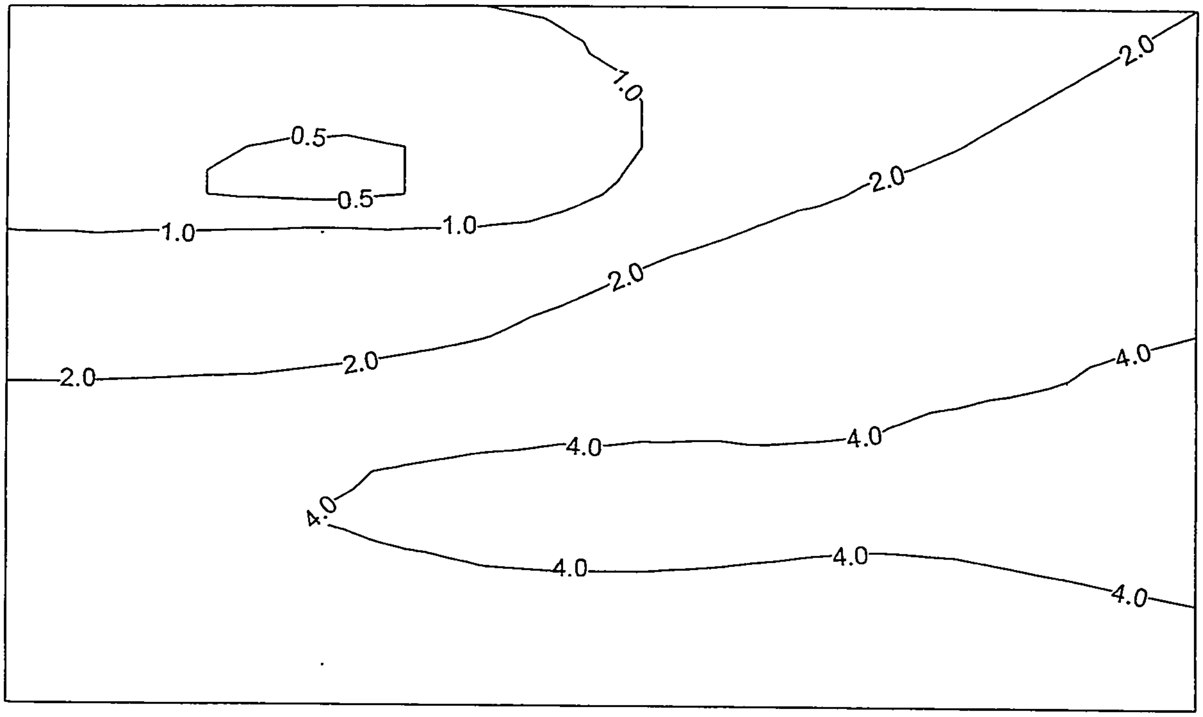

Fig. 4 Estimated Dieldrin Soil Concentrations (μg dieldrin/g soil) from 8 PSDs

5 CONCLUSIONS

PSDs allow for increased sampling frequency, leading to higher resolution of contaminant distributions with less financial costs than traditional soil sampling methods. They have provided accurate contaminant distributions in the field for analytes with a range of physical-chemical properties (dieldrin and 22 PCB congeners). Laboratory studies have shown PSDs to be effective for a number of contaminants (OCs, OPs, and herbicides) with a wide range in physical-chemical properties. We expect that PSDs will be effective for all semivolatile and volatile chemicals in soils. We have shown PSDs to be useful in estimating soil contaminant concentrations ranging from 1 part per billion to 230 parts per million.

While the primary use of PSDs will most likely be in the assessment of persistent contaminants at hazardous waste sites, they should also work effectively for chemicals in soils at industrial, agricultural, and residential sites. Thus far, there are no known soil-related limitations to chemical detectability with PSDs. They should work in virtually all soil types, although in cases where soil conditions are markedly different than those tested (e.g., bogs), the calibration method will have to be evaluated.

6 ACKNOWLEDGMENTS

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INFORMATION MANAGEMENT

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LINKING EMERGING HAZARDOUS WASTE TECHNOLOGIES WITH THE ELECTRONIC INFORMATION ERA

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ABSTRACT

In looking to the future and the development of new approaches or strategies for managing hazardous waste, it is important to understand and appreciate the factors that have contributed to current successful approaches. In the United States, several events in the last two decades have had a significant impact in advancing remediation of hazardous waste, including environmental legislation, legislative reforms on licensing federally funded research, and electronic transfer of information. Similar activities also have occurred on a global level. While each of these areas is significant, the electronic exchange of information has no national boundaries and has become an active part of major hazardous waste research and management programs. It is important to realize that any group or society that is developing a comprehensive program in hazardous waste management should be able to take advantage of this advanced approach in the dissemination of information.

1 INTRODUCTION

Hazardous waste is a topic for the present and the future. Issues involved are diverse, ranging from health effects; to minimization, remediation, or containment techniques; to policy and political implications; and to financial considerations. Environmental awareness has been on the rise since the 1960s. In the United States, environmental legislation has been passed that not only promotes minimizing exposure to hazardous waste by cleaning up air, water, and land, but also supports research to develop new environmental and assessment technologies. As these substances know no borders, the issue is international. In the last 25 years, more than 170 international environmental treaties have been signed; major ones, such as the Basel Convention, have focused specifically on hazardous waste. Advances are occurring on many fronts, and free and open communication of information in these areas must be optimized.

Concurrent with advances in hazardous waste awareness and management, there is a revolution occurring with electronic information systems. In the 1960s, the advent of the information highway was visible to a select few; however, easy and convenient access to databases and other information resources is now available electronically. Electronic information systems have already been introduced in the area of hazardous waste technologies, and the future holds great opportunity for advancing the practice and principles of hazardous waste management through this mechanism.

It is interesting to reflect on how issues, such as environmental legislation, legislative reforms (in the United States) for licensing federally funded research, and the emergence of electronic information, have developed within the same time frame. These three components have, in a synergistic manner, advanced the knowledge of hazardous waste management.

2 ENVIRONMENTAL LEGISLATION

In the United States, publication of *Silent Spring* in 1962 by Rachel Carson brought the topic of toxic waste in the environment to the attention of the American public. Later in the 1960s, the U.S. Congress began to establish environmentally oriented laws. In 1969, the United States passed the National Environmental Policy Act, which required federal agencies assess the impact of their actions on the environment. A year later, the U.S. Environmental Protection Agency (USEPA) was established to improve environmental quality and protect human health. In 1980, Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which mandates the cleanup of abandoned hazardous waste sites. At the same time, the Agency for Toxic Substances and Disease Registry (ATSDR) was established with the public health goal of assessing, preventing, or reducing exposure from Superfund hazardous waste sites. In 1986, under the Superfund Amendments and Reauthorization Act (SARA), the Superfund Hazardous Substances Basic Research Program (SBRP) was established. The SBRP is a multidisciplinary program for advancing the state of the science of hazardous waste identification and remediation, reduction of the amount and toxicity of hazardous substances, and, ultimately, the prevention of adverse human health effects.

Toxic substances and other contaminants cross borders freely, and the issue has taken a presence in international forums. In 1972, 70 governments met in Sweden for the United Nations (U.N.) Conference on the Human Environment. This conference brought environmental issues to an international level. One significant result of this conference was the establishment of the United Nations Environmental Program (UNEP), which was created for the comprehensive consideration and coordination of actions within the United Nations on the problem of the human environment. Since the 1972 U.N. conference, over 170 international environmental treaties have been signed (Brown et al. 1995), which demonstrates the global commitment to the issue. In 1976, UNEP established the International Register of Potentially Toxic Chemicals. This registry collects information on hazardous waste and distributes it to anyone who requests it. The Basel Convention in 1989 established the Control of Transboundary Movement of Hazardous Wastes and their Dispersal. With over 100 signatories on this treaty, the movement of wastes is now managed throughout much of the world. The 1992 U.N. Conference on Environment and Development held in Rio de Janeiro was a pivotal conference that focused on the issues of biodiversity and sustainable development. The report from this meeting included a chapter on both toxic waste and hazardous waste, thus demonstrating the priority of the effective control and management of such releases into the environment.

The last 25 years have witnessed changes in attitudes and policy regarding the care and maintenance of the environment. Included are the issues of the production and release of hazardous waste. Now, on an international level, protection of the environment and protection from hazardous substances in the environment are considered in conjunction with economic development. Any proposal that supports future global welfare must adequately address these issues. Legislation, treaties, and other agreements demonstrate the widespread commitment to the safe management of hazardous waste.

3 U.S. LEGISLATIVE REFORMS

With the enactment of environmental legislation, the cleanup of existing waste sites and the improved management of hazardous waste began. Within a short time, it was obvious that more efficient and cost-effective technologies would be needed. Expertise from a broad range of scientific disciplines is required to address the complex issues of hazardous waste management. While the federal government had been funding research in a wide range of disciplines for many years, much of what was being developed was not being utilized. Beginning in 1980, the United States began a series of legislative reforms that would allow for the transfer of federally funded ideas and technologies from basic research to commercial use. These reforms would foster the exchange of ideas and innovation by allowing the government and private industry to cooperate in the development of technologies. Environmental engineering contractors could now utilize the large base of research and development (R&D) knowledge that had remained unused behind the walls of academia and within federal laboratories.

Before 1980, the policy of the United States was to patent technologies invented within the federal laboratory structure and license these patents to anyone, while the government retained the rights to the patent. The idea behind this policy was that the public had financed the research, so the public should keep the rights to the research (Soderstrom 1988). This policy led to the development of many government-owned, but unlicensed patents, that were not being used. Failure to transfer significant amounts of technology from basic research to commercial uses was mainly due to the lack of incentives to private industry for collaborating with government in the licensure of new technologies. Policymakers began to realize that the resources being spent on R&D were not being returned to society in an effective manner and was hurting the country's productivity.

The first legislative attempt to deal with domestic technology transfer was the Stevenson-Wydler Technology Innovation Act of 1980. The purpose of this act was to "improve the economic, environmental, and social well-being of the United States" by establishing technology transfer as a mission of the federal laboratories and fostering cooperation among federal agencies. Later the same year, Congress passed the Bayh-Dole Act of 1980 "to use the patent system to promote the utilization of inventions arising from federally supported research or development." Specifically, the Bayh-Dole Act enabled small businesses and nonprofit organizations to patent and retain rights to inventions resulting from federally funded R&D. This gave the much-needed incentive for commercial and nonprofit organizations to develop and commercialize their inventions.

Many problems still remained. The Stevenson-Wydler Act addressed existing technologies but had no provisions for the innovation of new technologies. The Bayh-Dole Act provided the commercial incentives, but the remaining patent processes were cumbersome and inconsistent among agencies. Later, Congress amended the Stevenson-Wydler Act of 1980 by passing the Federal Technology Transfer Act of 1986. This Act facilitated technology transfer by allowing government agencies to enter into cooperative research and development agreements (CRADAs). CRADAs are agreements by which government and other organizations can collaborate to research and develop precommercial inventions and ideas where the expense and risk would be too great for either to research and develop on their own. Division of intellectual property rights is established upon entering into the agreement, and profits/royalties are shared among the sponsoring agency, the collaborating organization, and the inventor(s). Subsequent legislation expanded the eligibility for opportunities of entering into CRADAs (the National Competitiveness Technology Transfer Act of 1989) and adjusted the rights of title to intellectual property rights, confidentiality of information, government rights to licenses, and income distribution to inventors (the National Technology Transfer and Advancement Act of 1995).

This series of reforms made technology transfer a mission of the federal government. Where once the government held tightly to its intellectual property, it was now seeking collaborative "investors" to develop commercially viable methods and technologies for private economic growth. Under current law, innovative technologies and other scientific advances supported by the federal government can be readily moved into the private sector. Arguably, the most significant transfer of technology from the U.S. government to the world has recently occurred: the Internet.

4 ELECTRONIC TRANSFER OF INFORMATION

A key component in the promotion of the field of hazardous waste management is the communication of advances. Communities, policymakers, and industrial leaders must be knowledgeable of the state-of-the-art conditions regarding hazardous waste in order to make informed decisions. Their resources must be timely and available in a useable and understandable format. As computers were coming into use in the workplace in the 1960s and 1970s, the framework for networking this 'tool' was developing. In the early 1970s, the U.S. Department of Defense (DoD) developed an experimental network to support military research (ARPAnet). The concept was that the system should be decentralized so as to be able to withstand partial outages. As this system was being developed, local area networks (LANs) were being established within the commercial sector. The next obvious step was for LANs to be linked with each other. The DoD was not the appropriate resource to handle this demand, so in the early 1980s the National Science Foundation (NSF) built a network using the same conventions as used by DoD. The intent of the NSF network was that this system would allow access to everyone. This network, in combination with other networks that have been developed via other resources, has been linked and is what is considered to be the Internet (Krol 1992).

From the beginning, the growth of the Internet has been enormous; however, finding information and making the appropriate connections was a daunting task. Several services, such as Gopher, were developed over the years to facilitate the organization and exchange of information. Most recently (early 1990s), the World Wide Web (Web) came into the Internet marketplace and has rapidly become the service of choice. The Web uses a technology called hypertext that allows one document to be connected to any other document. Typically, documents are created in Hypertext Markup Language (HTML), which is a standardized tagging system used for presenting information in a document on the Web (i.e., on a Web page). Navigating the Internet with hypertext documents makes the Web a very powerful and flexible approach. One Web page can point to any other Web page, which can in turn link to any other page. Unlike some of its predecessors, possibilities on the Web are limitless and open ended.

A key feature of the Web is that anyone who has access to a server on the Internet and the ability to create a hypertext document can develop a Web page. The technology is not difficult to master and, accordingly, the Web has experienced tremendous growth in less than five years. Although the Web went 'on-line' in 1991, it was not until late 1993 with the release of the Windows version of Mosaic (a graphical Web browser) that the Web became commonplace. Between January 1994 and January 1995, the Web went from over 800 sites to over 11,000 sites. It is estimated that by mid-1996 to the number of sites approximated 115,000 (Rickard 1996). Studies conducted to estimate the use of the Web have demonstrated a very broad spectrum of users. Of the estimated 13+ million current users of the Internet, 73.4% are from the United States and 68.5% are male. The average age of users is 33.0 years old, with 17.5% coming from the most represented age group of 25–30. Additionally, 56.5% of Internet users have completed college or some advanced degree (Georgia Tech Research Corporation 1996).

As mentioned before, when the NSF assumed the role of 'overseer' for the Internet, the goal was to provide a system accessible by everyone. This feature has remained a basis for the systems in use today and helps explain why Internet services, such as electronic mail and the Web, are powerful and popular tools. Virtually every segment of society, including those involved in hazardous waste management, has made use of the these technological advances. A cursory survey of the Web, indicates that over 90 sites address various hazardous waste issues; over 507 sites on environmental engineering; 20 on bioremediation; 27 on pollution prevention; and 281 on environmental health (Yahoo 1996). Such searches identify sites originating from academia, government, commerce, community organizations, and individuals.

With this level of interest, universal access, and acceptance, it is not surprising that many federal agencies and international organizations have chosen this medium for information dissemination. On an international level, the UNEP has developed a number of sites reporting on its varied activities. There is access to reports on the various conventions in which UNEP has participated over the years. Other sites include information on the databases that UNEP has established, such as those developed for the International Register of Potentially Toxic Chemicals.

Within the United States, key federal environmental agencies have developed Web pages. The USEPA has established a page that allows the user access to the USEPA sites based on the expertise/interest of the user or by directly accessing any of the USEPA's many resources. For instance, students and teachers can conveniently access educational information, scientists can access information on research opportunities or test methods and guidelines, and business and industry can access information about doing business with USEPA. Other resources available include databases and software, the *EPA Journal*, various newsletters, environmental regulations, contract and grant opportunities, and a host of other information on USEPA activities. Of particular interest are the CERCLIS database, the Toxic Release Inventory, and the fact sheets on the individual sites included on the National Priority List. These sites provide the user with information, such as the official reports on hazardous waste site assessments and remediation, information on the transfer and release of over 300 chemicals into the environment, and extensive information on individual hazardous waste sites.

The ATSDR has been a leader in the environmental health arena in establishing their Web site. The site presents a wide variety of ATSDR's activities. Through this medium, the public can access reports, newsletters, toxicological profiles, public health statements, and other useful information on hazardous substances exposure. In addition, ATSDR supports and maintains the very exhaustive HazDat database, which provides access to information on the release of hazardous substances from Superfund sites. It addition to including site characteristics, impact on populations, exposure routes, and community health concerns, HazDat includes many health effect parameters on specific hazardous substances. HazDat also contains much of the USEPA's CERCLIS data. The HazDat database is now available through the ATSDR Web page.

The final Web page addressed was developed for the SBRP. This program was established at the National Institute of Environmental Health Sciences as a grants program focused on basic research on the identification, remediation, and reduction of risk from hazardous waste. It supports 17 grants, including 134 research projects. Historically, research accomplishments from this program have been reported in the peer-reviewed literature. While this is still the major method of data dissemination, the program has chosen to organize, track, and make available to the public, information being generated by the program through the Web.

The Web page has been organized to allow easy and logical access to the program's entire data set. Each of the 134 projects is represented with a summary of its goals and periodic progress updates. Publication lists are included for each senior investigator and presented by year. One section is devoted to the most significant research advances made during the past year. To facilitate access, the advances are sorted by research discipline (i.e., engineering, bioremediation, human health effects, site assessment, etc.). Another section is devoted to issues, such as outreach, women, children, and underserved populations. Of particular interest to the members of the Pacific Basin Consortium for Hazardous Waste Research and Management is the Tech Focus section of the site. This section provides information on new and innovative technologies developed by the program. A dynamic section of the page focuses on current events of the program. Included are upcoming conference announcements, in-depth reviews of individual research projects, and newsworthy activities taken on by the program. Another very useful feature of this Web page is that it includes a search mechanism, thus allowing topic-oriented access throughout the site.

The SBRP's Web page has been on line for nearly two years and serves as a major component of the program's information and technology transfer strategy. Complete information on all components of the program is accessible to anyone on a timely basis. While the main goal of the program is to support basic research, there is a strong demand to make research advances available to other investigators, risk assessors, regulators, commercial investors, and the educated lay public. The Web has very effectively addressed this requirement. Current use is estimated at 1,000–1,500 users per month, with approximately 22% of the users originating from government, 18% from education centers, 15% from commercial addresses, and <1% from military addresses. Users can access research findings, follow up with a review of appropriate publications, and ultimately contact the investigator for potential application of the research. The site also serves as a resource for other federal agencies focused on environmental health who have need of cutting-edge research findings. Furthermore, the Web page has encouraged intra-program communication; grantees are using this data set to become familiar with other components of this expansive program.

Clearly, the few Web pages discussed (and presented with Web site addresses in Table 1) serve only to demonstrate some of the capabilities and current uses of this technology in the field of hazardous waste. While using the Web is easy and readily accessible, maintaining and updating large Web sites, such as described here, are not insignificant or trivial. The level of commitment made by each of these organizations demonstrates the vitality and validity of this method of data dissemination. In looking to the future, it must be recognized that developments of electronic technology are expanding rapidly, and the utility of this resource for the field of hazardous waste will only increase.

TABLE 1 Web Page Sites: Addresses and Descriptions

Organization	Address (http://)	Web Site Description
UNEP	www.unep.no/	Organizational information, access to products and services, information exchange
UNEP	www.unep.ch/	Access to UNEP convention document (Basel, Rio, Montreal, etc.) and Earth Watch
UNEP - Int. Register of Potentially Toxic Chemicals	irptc.unep.ch/	Access to various IRPTC databases
USEPA	www.epa.gov/	Agency description and list of offices, news and events, contract and grant activities, rules and regulations, and USEPA publications
USEPA	www.epa.gov/epahome.data.html	Access to database systems, including CERCLIS and the Toxic Release Inventory System and to software for monitoring the environment
U.S. EPA Superfund	www.epa.gov.superfund/	Access to Superfund reports, legislation, fact sheets, hotline
ATSDR	atsdr1.atsdr.cdc.gov:8080/ atsdrhome.html	Access to all of ATSDR's Web sites, description of ATSDR's mission, list of office locations
ATSDR - HazDat Database	atsdr1.atsdr.cdc.gov:8080/hazdat. html#A3.1.2a	Access to information on the release of hazardous substances from Superfund sites or from emergency events and on the effects of hazardous substances on the health of human populations
National Institute of Environmental Health Science	www.niehs.nih.gov/	Access to summaries of research being conducted by NIEHS; the journal *Environmental Health Perspective*; the Environmental Health Clearinghouse; and contact and grant opportunities
Superfund Basic Research Program	www.niehs.nih.gov/sbrp/home.htm	Access to the 17 grant programs and descriptions of the 134 research projects, conference announcements, programs highlights, innovative technology descriptions, publication listings
National Toxicology Program	ntp-server.niehs.nih.gov/	Access to *Annual Report on Carcinogens*, results and status of chemicals tested by the NTP, health and safety data on approximately 2,000 NTP chemicals

5 CONCLUSIONS

The many issues regarding hazardous waste and hazardous waste exposure must continue to be addressed. Environmental legislation and international treaties have set the stage for making this issue a priority concern. Revisions on licensing have promoted new partnerships and opened the opportunities to more freely apply basic research findings to commercial applications. Vast amounts of information are now available regarding the many different facets of hazardous waste management. Recent electronic developments have enhanced the ability to communicate this information. It is reasonable to conclude that the field of hazardous waste management has much of the infrastructure it needs to keep up with the demands of an expanding world market. It is now imperative that there be a commitment to the exchange of resources throughout the world. Furthermore, Pacific Basin countries must be a part of this advanced technology in developing electronic database systems for the timely transfer and full dissemination of information.

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NATIONAL INFORMATION NETWORK AND DATABASE SYSTEM OF HAZARDOUS WASTE MANAGEMENT IN CHINA

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ABSTRACT

Industries in China generate large volumes of hazardous waste, which makes it essential for the nation to pay more attention to hazardous waste management. National laws and regulations, waste surveys, and manifest tracking and permission systems have been initiated. Some centralized hazardous waste disposal facilities are under construction. China's National Environmental Protection Agency (NEPA) has also obtained valuable information on hazardous waste management from developed countries. To effectively share this information with local environmental protection bureaus, NEPA developed a national information network and database system for hazardous waste management. This information network will have such functions as information collection, inquiry, and connection. The long-term objective is to establish and develop a national and local hazardous waste management information network. This network will significantly help decision makers and researchers because it will be easy to obtain information (e.g., experiences of developed countries in hazardous waste management) to enhance hazardous waste management in China. The information network consists of five parts: technology consulting, import-export management, regulation inquiry, waste survey, and literature inquiry.

1 INTRODUCTION

Because industries are generating increasing volumes of solid and hazardous waste, China is paying more attention to hazardous waste management. The government has enacted a number of acts and regulations for hazardous waste management and has established laws for pollution prevention and control of solid waste. Research projects on hazardous waste treatment and disposal technology are included in the National Eighth Five-Year Science and Technology Plan and national key research projects. Some regional centralized disposal facilities for hazardous waste are under construction or in the planning stages.

Training is necessary for managers to improve their understanding of new technology and to enhance the development and popularity of treatment and disposal technologies. To effectively analyze and make timely decisions, an extensive network of all related information, documents, and current situations at home and abroad is also required. As a result of an interchange of information with other countries, China's National Environmental Protection Agency (NEPA) and local EPBs have obtained valuable information about the management, treatment, and disposal of hazardous waste. To effectively use and share this information in developing priority research projects, China needs to establish a hazardous waste management information network. Such a system is a powerful tool because it collects, transfers, stores, processes, and maintains large amounts of data and information. The establishment of such a system is an important step in modernizing the management of hazardous waste.

The main objective of this study is to facilitate the sharing of information (by decision makers and researchers) relative to hazardous waste management legislation, laws and regulations, pollution control, waste disposal, and treatment technology. The first step is to set up a network and to analyze the feasibility of expanding the network to serve the entire country and also international information centers.

The resource center for hazardous waste management information will have such functions as information collection, inquiry, and connection. It will be designed as an open system that can be expanded as hazardous waste management develops in China. The long-term objective of the system is to further the research and development of a national and local hazardous waste management information network, which will include such functions as information management, technology consulting, and decision-making support (Fig. 1).

The information national resource center will make it easy for decision makers and researchers to obtain information and relevant experiences regarding hazardous waste management in developed countries. It also will help in making timely and effective policy decisions and in responding to the problems of hazardous waste management in China. In addition, there will be less waste in funding and labor resources in the administration, research, and training techniques for hazardous waste management in China. Several key technical factors are involved in the establishment of a network for hazardous waste information management.

1.1 Information Standardization

As stated, current information in the area of hazardous waste management lacks unified standards. Thus, one of the major problems is to standardize the information, deal with data redundancy and inconsistency, and improve the ability to share information.

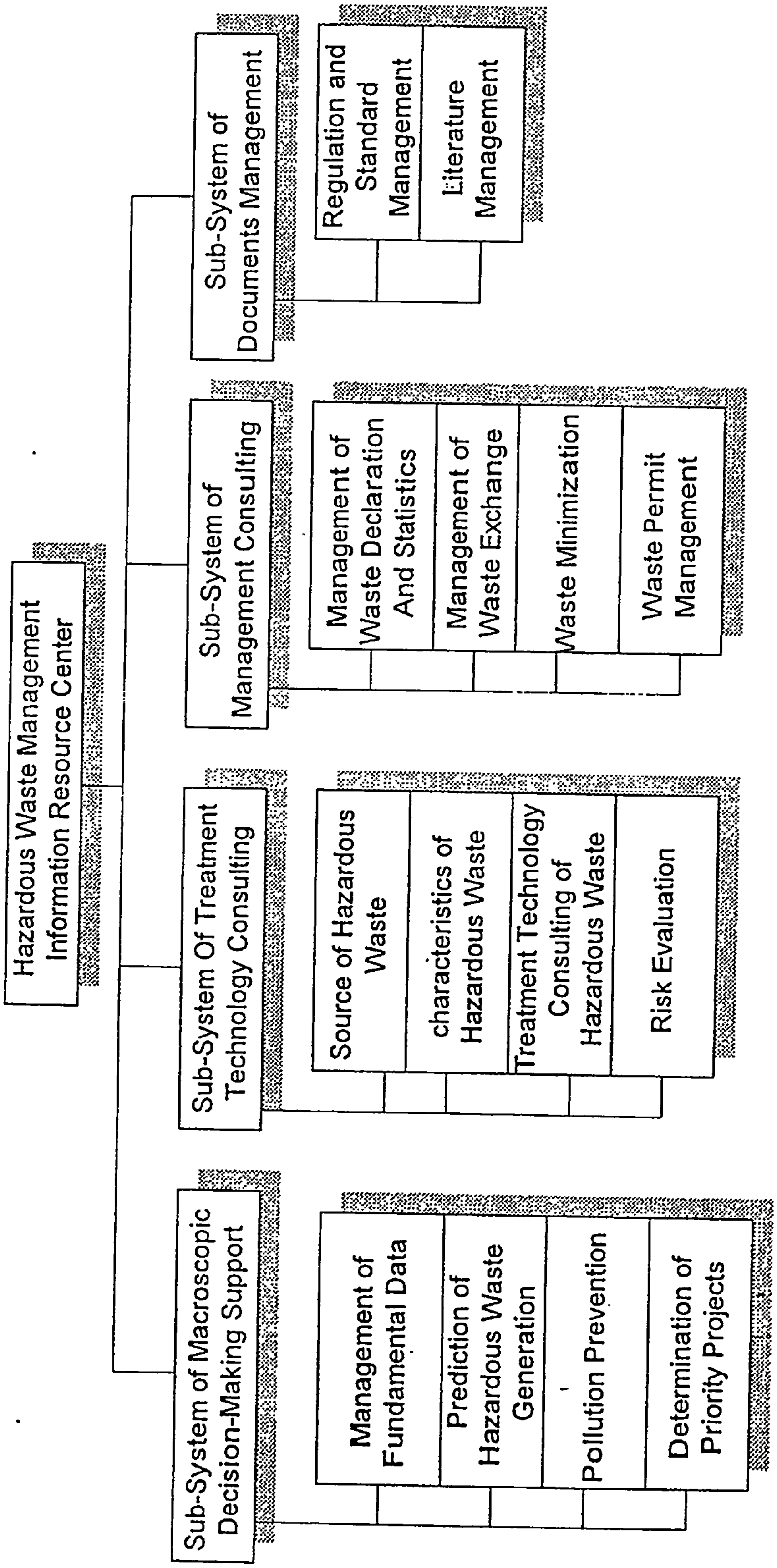

Fig. 1 Long-Term Objectives of the System

1.2 System Analysis and Design

The project mainly focuses on hazardous waste management systems. These complex engineering systems take into account such factors as social, natural, and economic factors. Some environmental information systems have been developed in China, but most do not include hazardous waste management. The development of such a system thus becomes a great challenge.

1.3 Establishment of Prototype Network

The objective of the project is to establish a prototype network of hazardous waste management information and to determine the feasibility of extending the network to other regions in China. At present, few national-level information networks exist in China. In the field of environmental protection, information management systems have been established in some provinces. The establishment of a prototype hazardous waste management information network will therefore represent progress, although its realization will inevitably be accompanied by difficulties.

The first step in designing a network is to supply the network extension, so selection of the network operating system and network structure is quite important. Careful investigation and analysis led to the selection of the Windows NT server as the network operation system and the newest client-server system structure, which is now the standard for network database systems.

On-line remote inquiry should be realized by this system to transfer information rapidly throughout the country. The client/server system can decrease the amount of data transferred via the network and make it possible to perform on-line inquiries through public telephone lines.

The hazardous waste management information system is designed for the needs of NEPA and local EPBs. A friendly interface is therefore very important. The interface characteristics of the Windows graphical user interface (GUI) are designed to make operation simple.

2 DEVELOPMENT CYCLE

The development of the hazardous waste management information network is mainly based on the structural analysis (SA) and structural design (SD) methods of software engineering. Six main stages are described in this section.

2.1 Feasibility Study

The main tasks of the feasibility study include the following:

- Investigating the demands of users and the actual environment,
- Determining the feasibility of the system from the standpoints of technology and socioeconomic conditions,
- Proposing the preliminary scheme of system demand,
- Proposing the preliminary design of the hardware and software environments, and
- Proceeding with the technological and economical analysis.

2.2 System Analysis

The main tasks of system analysis include the following:

- Analyzing the users' requirements,
- Describing the relationships between function and data,
- Proceeding with a logical analysis of the data,
- Breaking down the system functions, and
- Determining the required hardware and software environments.

2.3 System Design

System design can be divided into preliminary and detail stages. The main tasks include the following:

- Determining the structure and development scheme for the designed system,
- Designing the hardware and software environments for the system,
- Proceeding with the input and output design,
- Proceeding with the structure design of the database, and
- Proceeding with the general control design of the system.

2.4 System Implementation

The main tasks of system implementation include the following:

- Programming and debugging the modules and subsystems and
- Installing and testing the facilities.

2.5 System Testing

The main tasks of system testing include the following:

- Testing the modules and the subsystems,
- Testing the whole system, and
- Testing the network.

2.6 System Operation

The main tasks of system operation include the following:

- Establishing data files,
- Compiling the necessary documents, and
- Installing the system and testing operational steps.

Note that all the tasks are not finished at one time. Rather, user opinions should be solicited repeatedly, and the prototype system should be revised accordingly to the full satisfaction of the users.

3 HARDWARE AND SOFTWARE ENVIRONMENTS

3.1 Hardware

This system is a client/server database management system (DBMS) based on a local area network. The remote workstation connects to the computer server through public telephone lines.

The system uses the Ether_bus structure, 10BASE-5 protocol. With the NE-2000 network card and RG-58 A/U cable, the computer system supports a 10 M bps transfer rate between a local workstation and the computer server.

The Information Resource Management Center office is equipped with a computer server and a local workstation connected with a BNC connector plug.

By running the Windows NT server, the computer server accesses the network, database, and remote functions. The computer server and the remote workstation computer are connected to modems. By using a modem, the remote workstation computer can access the server computer at a 2,400 bps transfer rate through public telephone lines. At present, only one public telephone line is in place at the center office, so only one remote workstation can access the computer server. If sufficient public telephone lines are installed in the center office, this system can support up to 256 remote workstations, which can access the computer server simultaneously.

3.2 Hardware Description

- Computer server: PC 486DX2/66,16 MB RAM, 420 MB HD, CD-ROM drive;
- Remote workstation: PC 486DX/40, 4 MB RAM, 210 MB HD;
- Local workstation: PC 486DX2/66, 8 MB RAM, 420 MB HD;
- Network card: NE2000; and
- Modem: ALWA PV-BF240H (2,400 bps).

3.3 Software

The system is developed on Windows NT Net and Windows (Chinese version), using a client/server DBMS. The Windows NT server provides a basis for business solutions and has been optimized as an excellent file, printer, and applied programs server. It can be applied from small work groups to enterprises. The Windows NT server provides all services needed by shared programs, such as host computers' connection, limitless net connection, up to 256 remote computer visits, integrated tools, and reliable database management. It is a basis for the extension of the system in the future.

The Windows NT server operation system supports multi-tasking, multi-threading, and huge virtual memory transfer between processes based on Named Pipe protocol active connection and protected mode operation.

The MS SQL server is a superior and reliable multiuser DBMS. It is designed for high-capacity, routine processing on a local area network. By using the client/server structure, the applied program is divided into two parts. The client part provides a user-friendly interface (usually on personal computers); the server part manages the database and provides for information sharing and safety (usually on a host computer). Running on a Windows NT server, the MS SQL server supports links between a client and a server on most present network protocols. The MS SQL server has abundant data types, is safe, and is easy to use. The Windows NT server has multi-threading and stored procedures, which means that the MS SQL server can run at a high speed. At present, many tools are available to develop client part programs for the MS SQL server.

At the workstation, users can access the computer server through MS LANMANAGER and select Windows (Chinese version) and MS Access as operating tools. The client and server parts are connected with the MS ODBC (Microsoft-opened database connectivity), which permits MS Access to open the data stored in the MS SQL server on the computer server directly and makes it easy to develop applied programs on client computers. MS Access is one of the best DBMSs for Windows. Using Windows GUI, MS Access provides superior visual operation, so the programmer can easily transfer the real functions to applied programs.

In this system, all software products are from Microsoft Corporation. This ensures that each software program can work normally when many programs are running at the same time. Using the common international protocol, this system can connect to the Novell network and other networks easily. Considering the system structure of the Chinese environmental protection information network that is now being designed, the client/server structure of this system makes it possible and easy to connect with other information systems on environment protection and those in other management fields in China as well as abroad.

3.4 Software Description

The Hazardous Waste Management Information Center Office has the following software:

- Operation system: MS-DOS, Windows (Chinese version);
- Network system: Windows NT server, version 3.5;
- Database management system: MS SQL server for Windows NT, version 4.21; and
- Client developing tools: MS Access.

4 ESTABLISHMENT OF DATABASES

The database system used for storing information on hazardous waste management includes, at present, five subsystems: Technology Consulting, Import-Export Management, Regulation Inquiry, Standard Inquiry, and Literature Inquiry. Besides these necessary tasks, we also developed a subsystem for Solid Waste Declaration and Statistics.

4.1 Technology Consulting Subsystem

The system includes four function modules for inquiry. They are waste characteristics inquiry, leachate treatment technology inquiry, stabilization/solidification technology inquiry, and landfill technology inquiry.

4.1.1 Waste Characteristics Inquiry

Common physical and chemical characteristics of all kinds of wastes are often important. In this function module, we collect existing information to satisfy the inquiry of researchers. At present, information includes molecular formulas and weights, melting points, boiling points, Henry constant, vapor pressure, solubility, octane/water distribution coefficients, references to chronic body tissue cancer toxicity and cancer-causing risk evaluations, drinking water standards, water quality conditions, and a water toxicity database. The data source is the Risk Reduction Engineering Laboratory of the United States and the former Water Engineering Research Laboratory. Three inquiry ways are provided: CAS no. code, English name for the waste, and molecular formula. Inquiry results can be printed out and distributed.

4.1.2 Leachate Treatment Technology Inquiry

This module provides treatment methods for landfill leachate. At present, technology details about treatment method, treatment scale, quality of the treated water, concentration of the effluent, concentration removal ratio, and mass removal ratio are provided. The data source is also the Risk Reduction Engineering Laboratory of the United States. Three inquiry ways are provided: on the main component of leachate, treatment method, and their combination. Inquiry results can be printed out and distributed.

4.1.3 Stabilization/Solidification Technology Inquiry

This module allows the user to query stabilization/solidification technology about wastes. At present, this system can provide waste descriptions, waste codes, stabilization/solidification methods, mixing ratios, treatment scales, leaching experiments, leachate quantities, references, etc. The data source is the University of California at Davis. It summarizes foreign waste stabilization/solidification practices and a number of experimental achievements. Many of these data have great value for Chinese environmental researchers. Two methods are provided: combination condition inquiry and classification inquiry. Inquiry results can be printed out.

4.1.4 Landfill Technology Inquiry

Landfill technology has many advantages, including simple techniques, low cost, and ability to treat many kinds of waste. It is a suitable hazardous and solid waste disposal technology in China at present. To determine if certain waste can be added to a landfill site, we must know some important characteristics of that waste (such as volatility) and know how to calculate others. It is necessary to determine the characteristics and calculated results and provide them to users for reference. This module provides waste characteristics, including boiling point, vapor pressure solubility, Henry constant, molecular weight, diffusion coefficient, volatility degree in dry or wet soil, volatilization, etc. The data in this module are from a report by the U.S. Environmental Protection Agency (USEPA), chemical manuals, etc. Four ways of inquiry are provided: on USEPA code, English name, Chinese name, and waste classification according to the Basel Convention. Inquiry results can be printed out.

4.2 Import-Export Waste Management Subsystem

The system is developed according to "Temporary Stipulations on Controlling Wastes Imported from the EEC (European Economic Community) Countries" issued by the Chinese NEPA. It provides a convenient inquiry method.

In recent years, the movement of hazardous waste and garbage across national boundaries has become a significant problem worldwide. Developed countries ship a large volumes of industrial waste and domestic rubbish, especially hazardous waste, to developing countries by various ways. In China, many regions and districts accepted foreign rubbish only for temporary and local benefits. In fact, it is essentially pollution transfer, which not only harms the environments of importing countries but also seriously influences their socioeconomic sectors. To control this kind of transfer, the Basel Convention, which specified regulations for controlling the transboundary movement of wastes, was enacted in March 1989, and China signed the Convention. To control wastes imported into China, Chinese NEPA and the Ministry of Customs promulgated "Notification on Strict Control of Foreign Hazardous Wastes Imported into China."

Wastes are divided into three types: red, amber, and green, according to stipulations issued by the EEC (E.C. 259/93), which contain a detailed name list. Different management regulations are applied to import, export, and transfer various wastes. Green wastes for recycling are divided into three types: forbidden to import, needing examination and approval, and normal trading. Organizations that apply to import wastes that need examination and approval should obey the "Notification on Strict Control of Foreign Hazardous Wastes Imported into China."

4.3 Regulation Inquiry Subsystem

This module contains a database that includes the Chinese regulation database, U.S. RCRA regulations, and other country regulations. Users can inquire about different information. Inquiry results can be printed out.

4.4 Standard Inquiry Subsystem

Because of the lack of information sources, this system only provides the capability to inquire about relative hazardous waste standards in China. Four ways are provided. Inquiry results can be printed directly.

The classification inquiry is an inquiry that combines many conditions, including standard level waste classification and standard quality. Users can search for expected standards according to the combined conditions.

4.5 Literature Inquiry Subsystem

Three ways are provided to search for technology information about hazardous waste treatment, disposal, and management.

4.5.1 Keyword Inquiry

Keywords can be selected from the keywords dictionary. They can be combined freely according to the legends on the screen. Users can retrieve relative technology materials information according to the search conditions.

4.5.2 Author Inquiry

By inputting the name of an author according to notes on the screen, the user can retrieve all the references to an author.

4.5.3 Literature Classification Number Inquiry

By inputting the original literature classification number according to notes on the screen, the user can search all the relevant references.

4.6 Declaration and Statistics Subsystem

China generates large volumes of hazardous wastes every year. The treatment and disposal of these hazardous wastes are very important and serious problems. As an information resource center for hazardous waste management, NEPA should be committed to investigate the information about waste type, generation, transport, treatment, and disposal throughout the country. For this mandate, the analytical and statistical information should be derived to support the management of and policymaking for hazardous waste and to provide guidance for comprehensive utilization and treatment of hazardous wastes. Therefore, it is very important and urgent for NEPA to set up a complete system for hazardous waste declaration and registration.

Because of the importance of a hazardous waste declaration and registration system, the Solid Waste Division of China's NEPA set out several years ago to develop an information collection and registration system for hazardous waste. This system has led to great progress in hazardous waste management. The purpose of this subsystem is to study the method of information statistics for regional and national hazardous waste management. Other objectives are to establish a waste declaration and statistics system and to support waste management policymaking and the study of optimal hazardous waste treatment methods. The new hazardous waste declaration and statistics system will have important characteristics, which are described in the following paragraphs.

The hazardous waste declaration and registration database will be redesigned according to basic concepts to solve the problem of data redundancy. Only well-defined interrelationships will be accepted to ensure the statistical function of the system. The statistical results will be output and expressed in several ways to provide valuable data for hazardous waste management and policymaking.

Full use will be made of this information system network to alter conventional statistical methods of hazardous waste information. Through the power of new technology, efficiency and reliability will be expected to improve and make it possible to exchange information on hazardous waste among different regions.

The hazardous waste declaration and statistics subsystem will be brought into the general system; thus, users can apply various functions effectively to solve their problems. Through the network, users can acquire a comprehensive report about the status of hazardous waste in local areas.

Considering the existing hazardous waste declaration data for several cities in China, relevant tools for translating the data into the new system will be set up. Foreign hazardous waste declaration systems will be used, as will the "waste generation inquiry sheet" recommended by the World Bank's no. 93 technology report.

This system is mainly used for accounting and statistics, allowing the user to inquire about basic declaration enterprises, solid waste generation and management, organizations making use of the waste, treating and storing waste units, waste utilization, waste disposal, and equipment information for solid waste treatment. Eight ways for inquiry are provided.

5 SYSTEM MANAGEMENT

The main function of this system is to allow the user at a workstation to access the database stored in the server and to allow the workstations to exchange information with one another. The workstation in the center office holds all the database management information.

The Windows NT server is a multitasking network operating system. It simultaneously manages the database and the network. However, if the safety of the system is taken into account, a local workstation is equipped for database management.

According to the type of user and the applicable scale, two steps provide for security management of this system.

The Windows NT server introduces the concept of Domain. Domain is a logical collection of users and workstations. The Domain security information is stored in prime Domain controller (PDC) — a computer running Windows NT server. Only one server is in this system, so it secures the PDC. The system administrator establishes the workstation IDs for users permitted to connect to the server. To access the server, the user must provide an ID and password. To access the remote workstation, the user must have the right of remote access. The user must first dial the remote access server (the server computer) and then log on to the server computer. These securities are provided by the Windows NT server.

After logging on to the server, users can run programs to access the information on the server. At this time, users must log on to the MS SQL server. The system administrator can establish access for every user. The normal user can only read and select the information, while the database manager can add, change, and delete data in the database. The program is run on MS Access. The programmer can secure the information as a "read-only" document. Security is provided by the MS SQL server and MS Access.

The two-step security management system has been set up for system development in the future. The system will be expected to provide more services, such as e-mail, fax, etc. For different services, users may have different rights. Two-step security management makes it easy for the administrator to add users and set up user rights.

The network system and database are maintained by the system administrator. The Windows NT server and MS SQL server have many tools for data protection and backup. In this system, we use floppy diskettes and the hard drive for data backup. After each change in user information and security information, the administrator backs up the main database with floppy diskettes. The HWIRC_DB (hazardous waste information database) is backed up regularly by the administrator on the hard drive. With the increase in information, CD-ROM (compact disk read-only memory) can be used instead.

6 CONCLUSIONS

After more than six months of effort, the project has been completed according to our objective. Major achievements include the following:

- A hazardous waste management information resource center has been established for interchange of information. The center serves as a foundation for extension into a multifunctional (information management, technology consulting, decision-making support, etc.) system.

- A prototype network for hazardous waste management has been established, which provides an example for a wide range of extensions.

- A new client/server information system structure has been adopted, which guarantees the openness and extendability of the system.

- Windows NT server version 3.5 has been used as the operating system, which ensures the safety of network operation and convenient operation and development.

- An MS-SQL server for Windows NT version 4.2 DBMS has been used, which guarantees the safety, dependability, and consistency of the data and the further development of the system.

- Large amounts of information in hazardous waste management have been put into the system, such as regulations, standards, technological materials, characteristics of hazardous waste, treatment and disposal technologies, and import and export management information. A systematic data coding system is proposed, which is expected to lay a foundation for modernizing hazardous waste management in China.

- Five practical subsystems have been developed for the application of hazardous waste management information exchange.

- Future development of the system has been planned.

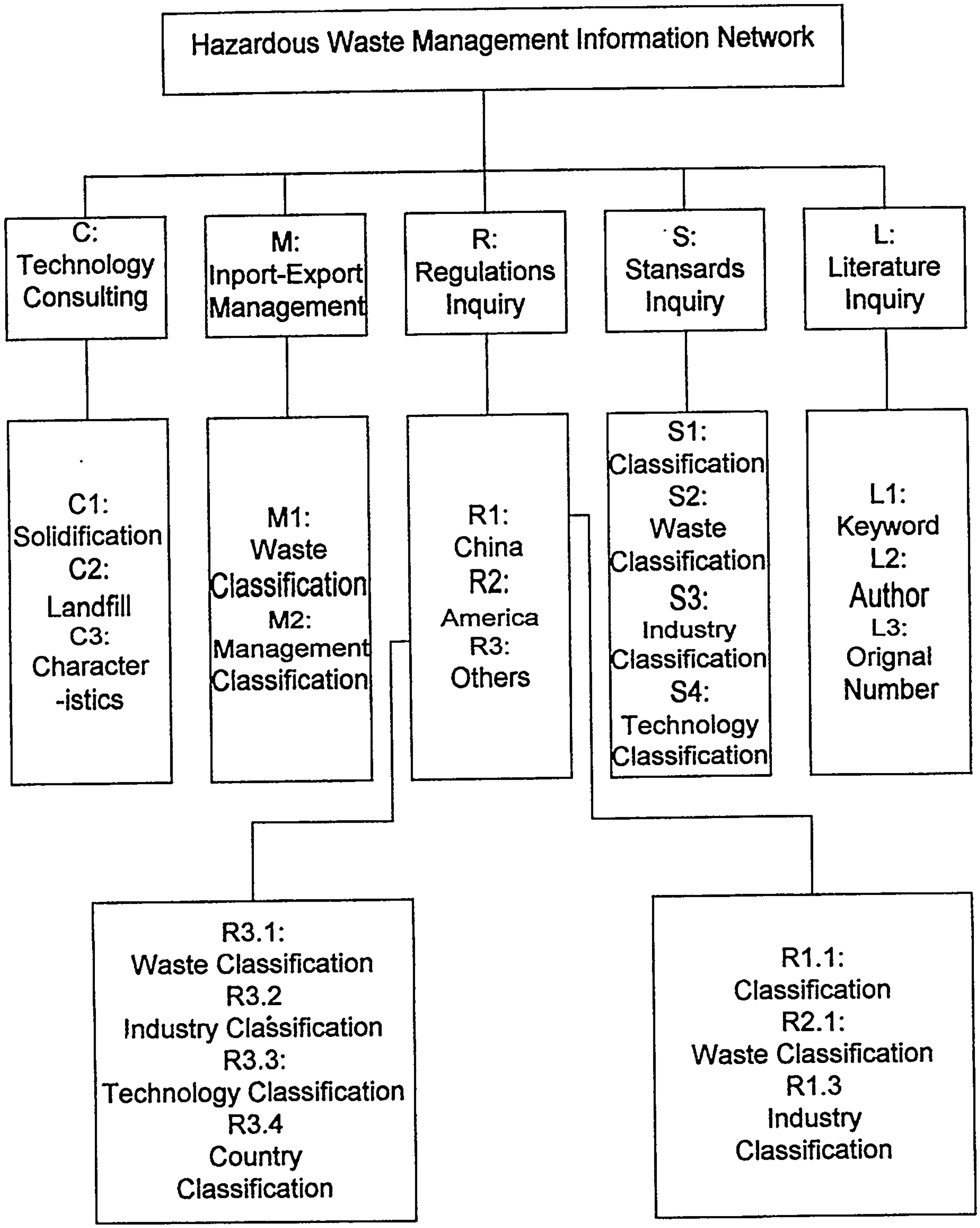

Fig. 2 Function Tree of the System

SPECIAL WASTE ISSUES

Chair: Ibrahim Bin Shafii, Department of Environment, Malaysia

CODES OF PRACTICE AND RELATED ISSUES IN BIOMEDICAL WASTE MANAGEMENT

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1 INTRODUCTION

In 1994, about five medical waste companies met in Melbourne to discuss industry problems. In particular, the meeting addressed problems related to the recently permitted practice of long haul interstate transport of medical waste. One state allowed the practice; other states did not. This variation gave rise to a significant competitive advantage for companies allowed to transport medical waste into their state. The meeting resolved to commence an approach toward harmonized national practices as a first step toward uniform legislation.

The subject of poor environmental performance by some companies working within the industry was also addressed. Subsequently, the then Commonwealth Environmental Protection Authority hosted a meeting of all the relevant state and national departments of health and environment protection. An international expert, Dr. Sig Slavik, was invited to this meeting to provide technical information on the management of medical waste in the USA and Canada. As a result of the meeting, state and national regulatory authorities recognized for the first time the range of environmental and industry issues that needed to be addressed. The issues were seen to be particularly critical in view of the rapid introduction of new technologies for treatment of medical wastes. It was acknowledged also that there was growing community concern related to what is perceived as a major risk to the community.

The Waste Management Research Unit (WMRU) was engaged to facilitate the development of a National Code of Practice. A National Medical Waste Industry Working Group (NMWIWG) was established to fund the project and to provide direct input into the code. This group, with the assistance of the WMRU, produced a draft code that was considered by a national workshop in June 1995. This workshop was funded by the EPA-Australia. It brought together a wide range of stakeholder organizations — nurses, doctors, transporters, disposers, local government authorities, and state government representatives. In particular, the Infection Control Nurses Association participated. This group was considered to be essential, as many potential improvements in medical waste management within health care facilities were restricted by overuse of "universal precautions" to prevent infectious materials from being discarded inappropriately despite the real risks being quite low.

The Code of Practice for the Management of Clinical and Related Wastes was released as a National Interim Code in March 1996. Industry members of the NMWIWG agreed in signing off on the code to have it implemented within their organizations progressively during 1996. The group also invited additional public comment during this period. It is proposed to finalize and release Version One of the code about March 1997. The development of the code has highlighted a number of technical, social and political, and research issues for future action.

In 1996, Standards Association of Australia commenced working on a standard for the management of clinical and related waste. The interim code provided a sound basis for this standard, which is currently in its third draft. It is anticipated the standard will be ready for release during 1997.

The National Health and Medical Research Council (NHMRC) of Australia released the second edition of its Guidelines on the Management of Clinical and Related Waste in 1996. Both the code and the pending standard refer to this guideline wherever practicable, so that overlaps or conflicts are minimized.

A number of states have also released their own guidelines based on the NHMRC document. Obviously this plethora of guidelines, standards, and codes is unwieldy and largely unnecessary. However, each addresses issues in a way that meets the needs of their particular constituency and political masters. In contrast, the code meets the needs of an industry dedicated to improving its environmental performance and ensuring consistent practices throughout Australia and, recently, New Zealand. In this way, the code is rapidly becoming the definitive reference point for health care facilities, government purchasing officials, and the industry nationally.

The development of the code has had additional important results. It has unified a previously highly fragmented, aggressively competitive industry. It has also unified the industry within the framework of the highly respected Environmental Management Industry Association of Australia (EMIAA). The EMIAA has strong links with the Commonwealth government and a number of state governments. This arrangement provides a strategic advantage and a cost-effective administration center for the NMWIWG. The group is now looking to develop a national training curriculum for its member organizations and to initiating research into some of the problems related to treatment efficacy, containerization, and landfill disposal.

2 NATIONAL CODE OF PRACTICE FOR THE MANAGEMENT OF CLINICAL AND RELATED WASTES

"Clinical and Related Wastes" is defined within the code as "Wastes arising from medical, veterinary, pharmaceutical or similar practices and wastes generated in hospitals or other facilities during the investigation or treatment of patients or research projects." This definition is taken to exclude general waste generated within these facilities but refers to waste that has no higher risk than generally associated with domestic garbage.

The code addresses 10 key areas:

- Industry Mission Statement
- Uniform Terms and Definitions
- Community Relations - Public Perceptions and Right to Know
- Generation, Source Separation, and Handling
- Storage Requirements
- Transportation
- Treatment and Disposal
- Disposal of Solid and Liquid Residues and Air Emissions
- Occupational Health and Safety
- Staff Awareness and Education

The first three are fundamentally important. The Industry Mission Statement requires management commitment to the implementation and day-to-day practice of the code. The second point highlights the need to achieve a common technical language for the industry. The third point represents a substantial shift in the philosophies of most participating organizations. It implies positive moves to achieve a better understanding of the real risks associated with the management of clinical wastes. It also represents a cultural change for many of the members to whom community access to real facts about the operations of the industry has been avoided in the past.

The code calls up a number of national and international standards. It also refers, where practicable, to the National Health and Medical Research Council's guidelines. This reduces duplication and contributes to uniformity.

3 DEVELOPMENT OF THE CODE

Several factors have contributed to the success of the code to date.

The development was initiated by a small number of industry participants but, for various reasons, did not include all the major operators. In hindsight, this probably contributed to progress rather than hindering the process, as it reduced immediate confrontation between some of the key stakeholders. It also kept the Working Group to a manageable size in the early stages.

The second important consideration relates to the development process. Initially, many of the industry partners thought the WMRU acted as consultants and provided a complete product for comments. Instead, the approach taken was to involve active participation at every stage. In fact, specific sections were allocated to the industry members to write in first draft form. The WMRU then professionally facilitated the Working Group meetings so that interactive discussions modified, corrected, and adapted the text to achieve general consensus. This consultative, interactive approach proved very successful once the members understood the ground rules and the need to listen to, understand, and appreciate the views of other stakeholders.

Third, members had to contribute to the costs involved in retaining the WMRU. Contributions reflected the organization's size and perceived ability to pay and benefits likely to accrue from the implementation of the code.

The Australian Nurses Federation Environmental Group was invited to be on the Working Group at no charge. The practical input from this group was invaluable, particularly because of their identification as professionals and their direct activities as an environmental lobby group.

Commonwealth and state governments were involved from the outset and provided initial credibility through their support. Subsequently, wide consultation with all sectors of the health care industry occurred at an early stage of development of the code through funding support of a national workshop. Again, this evidence of government support added to the perceived importance of the initiative and gave it wider credibility and acceptance. As the growing credibility of the code and its development process became recognized, additional industry organizations joined so that the code better covered all aspects of the Industry.

A major step was to release the code on an interim basis, with all members agreeing to implement the code during a 12-month period. Use of the interim code approach was extremely important. It provided an opportunity for those members unable to comply in every detail to openly support the code. It gave all companies a 12-month period to align their practices with the requirements of the code. This approach also meant that no organization was barred from participating in the first year!

The interim code was immediately picked up by state government purchasing departments. In some states, the code was a requirement for selection of tenders for goods and services related to health care facility waste management. This provided a financial inducement for other companies to join the Working Group.

The group decided to become a Special Interest Group within the EMIAA. This added to the credibility of the group and provided an additional path for accessing government and increasing the effective "size" of the group.

As voluntary membership grew, requests came from New Zealand organizations to join the working group. This enhanced recognition, and the trans-Tasman link has provided additional strength, particularly as the Working Group members were able to view the work through the eyes of others who had recognized its commercial value to their organizations.

Probably, most important, the facilitation process used by the WMRU ensured ownership developed and remained with the industry members. As a result, commercial benefits are seen along with the need to address outstanding technical and implementation problems. Financial support for the project continues to be provided by the members, with the larger organizations now taking greater responsibility for funding further work.

The national Code of Practice has achieved an unparalleled level of industry unity and support. The industry has come of age!

4 COMPARISON WITH OTHER CODES

There are few similar codes available in Australia. However, the chemical industry's "Responsible Care" Code of Practice provided a preliminary framework based on proven industry applicability and acceptance. The only national Australian code that had succeeded in achieving harmonization of activities across all Australian states is the "Australian Code for Transport of Dangerous Goods by Road and Rail" (ADG Code) Fifth Edition. This code also provided some framework guidance. However, development of this code was led by the Australian government through the Federal Office of Road Safety. In contrast, the medical waste industry initiated and developed their own code without direct government intervention. In fact, the move by the industry resulted in government initiatives to develop a code being curtailed.

The overall structure of the code is such that it is a practical working document for use by industry. The structure is therefore representative of the practical needs of industry rather than constrained by adherence to some preexisting format. It also does not have an extensive list of guiding principles as have some other international codes. Instead, it contains the principles in an implied form within the body of the document and the constraints it imposes. It is also important to recognize that the code set out to be nonprescriptive. This goal has not yet been achieved. There is, in fact, some moves to be more prescriptive in areas that the industry sees as essential to the achievement of uniform performance standards across all technologies currently in use or being introduced to the industry.

The important result is wide acceptance by industry. Government support and indirect involvement through the review process have also resulted in wide acceptance by government.

5 OUTSTANDING ISSUES

The WMRU's objective in facilitating the development of the code was to get the participants to accept a level of 80% or more agreement on its content. It was recognized that there would need to be some level of tolerance and compromise to achieve an operational document in a reasonable period of time. The recognition of outstanding issues and the acceptance that these would require further research and consideration to finalize are therefore important aspects of the interim code. This listing is provided immediately after the preface on page iv of the code. In effect, this listing is a *de facto* recognition of the areas of compromise and inadequate technical information that will have to be addressed in subsequent versions of the code. Some of theses issues are briefly described below.

5.1 Containment

Currently, no uniform regulations relate to the standard of containers to be used and whether bulk containerization is appropriate. Some members consider that containers must be rigid, lockable, and unable to be penetrated by sharps. Some state regulators approve the transport in plastic bags thrown into waste collection vehicles. Other companies use enclosed containers for transport of medical wastes, with the waste either in plastic bags or compressed within the container. An Australian standard is currently being developed that partly addresses these issues, but complete resolution is not in sight. The WMRU is initiating research into a risk-based assessment of the efficacy of the various approaches to containerization. Both environmental and occupational health considerations will be addressed.

5.2 Recognizability

There is considerable debate as to the meaning of "recognizability." The issue specifically relates to body parts and to blood-stained wastes or fetal residues. In some cases, waste, such as nappies and continence pads, are deemed offensive and therefore required to be rendered unrecognizable before landfill disposal. These same items are regularly seen in the domestic waste stream without being considered offensive.

Some sectors of the industry consider that shredding and maceration are essential to ensure unrecognizability unless the wastes are incinerated. However, other sectors supported by regulators in some states accept that enclosure in an opaque hessian bag confers "unrecognizability" on the offending items. The concerns expressed with this practice arise chiefly from the potential for rupture of these bags during tipping and landfill operations or when closed landfills are subsequently redeveloped.

5.3 Efficacy of Treatment

In the recent past, incineration has been the predominant means of treating clinical and related waste in Australia. Incineration has been well tested and microbiological tests developed to check the residual ash to ensure it is "safe" for landfill disposal. New systems of treating such wastes include microwave, autoclaving, and chemical processing. Autoclaving and the chemical processing have generally included maceration/shredding as a pretreatment. However, doubts remain that the chemical or steam come in close contact with all segments of the bulk waste. There are therefore doubts as to whether all infectious organisms have been destroyed. Currently, there is a reliance on the "process" and monitoring temperatures or chemical concentrations at a small number of test points within the waste to ensure the treatment process has been effective. Frequently the only requirement is for a thermometer to record that the waste at the sampling point(s) has been held at a given temperature for a specified period of time. This is then taken to indicate all the waste has been adequately treated. Insufficient research has yet been undertaken to ensure that in fact an effective kill has been achieved or at least that the residual risk is low.

5.4 Reusable Sharps Containers

There is a lot of debate about the use of reusable sharps containers, not because the containers themselves are generally regarded as inadequate, but because of the OH&S risks associated with their use. In particular, the emptying of the containers is seen to pose a hazard. Some organizations are also emptying the sharps into bulk wheelie bins for transport. The reusable containers are left on site, washed, and reused. There is considerable concern about the prospects of large bins of otherwise noncontained, contaminated sharps being transported around the country. The risk is made higher because of the inherent difficulty in securing most wheelie garbage bins to ensure that during rough transport, no needles move out of the containers.

6 CONCLUSIONS

It is obvious from many of the above considerations that the code is seen to be a vehicle for providing a level playing field for all sectors of the industry. Many concerns are associated with the newer technologies. In turn, these newer technologies involve significantly lower capital costs and operating costs. This is particularly the case when the rigorous on-line monitoring and regulatory conditions applied to incineration are not equally applied to the newer technologies. It is also apparent in some municipalities that facilities to house the new technologies have not been subject to an environmental impact assessment as is the case for all new incineration facilities.

Despite the inherent problems, the code has been produced to its present status in approximately 18 months. It has succeeded in unifying an industry and provided the capability to initiate and support research and political activity that will not only benefit the industry but will benefit both the health care industry at large and the environment.

HAZARDOUS WASTE AND ENVIRONMENTAL TRADE: CHINA'S ISSUES

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ABSTRACT

By presenting some case studies, this paper analyzes China's situation with regard to hazardous waste: its environmental trade, treatment, and management. The paper describes China's experiences with the environmental trade of hazardous waste in both the internal and international market. Regulations for managing the import of waste are discussed, as are China's major approaches to the trading of hazardous waste both at home and overseas. The major reasons for setting up the Asian-Pacific Regional Training Center for Technology Transfer and Environmental Sound Management of Wastes in China and the activities involved in this effort are also described.

1 WASTE AND TRADE: BACKGROUND

Environmental trade is a vital component in economic trade. With the emergence of global environmental issues and the upsurge of interest in global environmental protection, the importance of environmental trade has become more and more prominent. The movement of waste between countries is a sort of trade. Because developed countries must meet strict environmental standards and pay high costs for hazardous waste treatment and disposal, some companies located there have transferred their hazardous waste to developing countries to take advantage of their new, more open economic policies.

Along with opening itself to the outside world and economic trade with other countries, China has gradually begun to import industrial and municipal waste for different reasons. Chinese Customs statistics from June and August 1996 indicated that nine cases of hazardous waste from overseas, at a total weight of 1,850 tons, were seized. Since 1993, when investigations of hazardous waste from overseas were first recorded, the rate of importing such waste has rapidly increased. Table 1 lists some examples of the types of waste exported to China. Most of the waste exported to China has contained chemicals, medicines, or food, which can smell terrible and cause germs to breed rapidly. The following text illustrates what has occurred in China.

Table 1 **Examples of Hazardous Waste Exported to China**

Export Countries	Registered Items	Examined Items	Ways to Handle
Korea	Fuel oil	Chemical waste oil	Returned to the source
Germany	Waste plastic	Municipal waste	Returned to the source
Japan	Reclaimed plastic	Waste membrane	Returned to the source
USA	Waste plastic	11 green waste	Returned to the source
USA	Chemical products	Industrial waste	Returned to the source
USA	Mixed waste paper	Municipal waste	Safekeeping and waiting for handling
USA	Waste iron and steel	Iron and steel with radioactive matter	Safekeeping and waiting for handling

1.1 Characteristics of Hazardous Waste Trade in China

Our analysis of sample cases indicates that the trade of hazardous waste in China has the characteristics that follow.

1.1.1 Economic Profits Are the Main Driving Force in the Illegal Business of Waste Trade

Exporters find the transfer of municipal hazardous waste to developing countries is an easy and cheap way to treat it. Importers find waste trade to be the sort of business in which they can obtain profits without any investment:

- The cost of importing waste is low because the waste is taken in as raw materials.
- The transportation fees by exporters are given back.

1.1.2 The Names of Imported Items Are Registered in a False Way

Some imported wastes whose import is strictly forbidden have been registered under the names of imported items whose import is allowed so they will not be observed by Chinese Customs. It could be said that these export companies dump the waste to China on purpose without any concern about the pollution to China.

The negative influence of the cross-border trade of hazardous waste on China is bigger than the positive one. Because they could get profits from exporting and importing hazardous waste in developing countries, some businessmen in developed countries do their utmost to sell their municipal and medical waste, even that with radioactive matter, to developing countries. The negative influence on the environment and society of developing countries is much greater than the economic profits the waste trade brings in. The following three examples show this fact clearly.

1. Waste iron and steel from the USA: Serious radioactive pollutants have been discovered during normal commodity inspections of such waste conducted at Chinese Customs in Tianjin City, close to Beijing. Monitoring the surface of packing boxes showed that the radioactivity value was 60 times beyond the normal standard, a level that greatly threatened the ecological environment and safety of the people in the nation.

2. "Waste paper" from the USA: After containers containing this waste paper were opened, the proportion of impurity was found to be more than 50%. Most waste consisted of plastic garbage bags, washroom waste, medical waste, and other hazardous waste. Many germs appeared. This case happened in a suburb of Beijing, the capital of China, so the social and environmental influences were very serious.

3. Municipal waste from Hong Kong: The large amount of municipal waste polluted the air and water source of the local area in the Guangdong province, which was harmful to the health of local people, the environment, etc.

1.2 Problems

On one hand, some developed countries only want to sell the waste to China by various means. On the other hand, some companies at home only want to gain the economic profits that result from the low-cost, no-investment, or even "giving-money-back" business they get from the countries that export hazardous waste in cross-border trade; they could care less about the negative effects of this trade. These attitudes make the implementation of China's regulations and the ability to effectively stop importing waste much more difficult.

2 RELEVANT REGULATIONS IN CHINA

With the rapid development of China's economy and international trade, the management and enforcement of environmental protection laws during the process of trade have become more and more important. International trade requires compliance with international conventions in the field of environmental protection and the implementation of their stands on the environment, sanitation, security, etc. To strengthen the management of solid waste and prevent the environment of China from waste imports, several related regulations have been issued.

2.1 Act for the Prevention of Solid Waste in the People's Republic of China

This act, hereinafter referred to as the Act for Solid Waste Prevention, was issued at the end of 1995 and began to be implemented in April 1996. This act provides the legal basis for the prevention and management of solid waste under different levels of the Environmental Protection Bureau. It strengthens the monitoring and management of hazardous waste and imported solid waste.

2.2 Announcement on Strictly Controlling the Cross-Border Transfer of Hazardous Waste to China

Early in 1991, the National Environmental Protection Agency (NEPA) of China and the General Department of Customs of China jointly issued the Announcement on Strictly Controlling the Cross-Border Transfer of Hazardous Waste to China. As the first legal document to control the import of waste from overseas, this announcement stipulates 23 sorts of wastes from outside that are strictly controlled.

2.3 Urgent Announcement on Firmly Controlling the Cross-Border Transfer of Waste to China

In 1995, the Administrative Office of the State Council of China issued the Urgent Announcement on Firmly Controlling the Cross-Border Transfer of Waste to China. It was issued because more and more cases involving the cross-border transfer of waste to China had occurred in recent years. A discussion of the main reasons follows here.

- Environmental protection is a basic national policy of China that must be given a high amount of attention by the different levels of government and departments in the country. The regulations must be implemented strictly, and the management of waste imports must be strengthened. China cannot be considered the place for dumping and storing hazardous waste from overseas.

- The management of waste imports must be practically strengthened in China through two methods. One is to forbid the waste imports, and the other is to strictly limit the waste imports that are allowed to be taken in as raw materials.

  - Waste that China is forbidden to import: No departments or individuals can conduct business in, import, or trade in this kind of waste.

  - Waste that can be taken in as raw materials but whose import is strictly limited: Import issues must be approved by NEPA of China. No other departments or governments at different levels have any right to approve import. NEPA must make checks rigorously.

  - Waste that can be taken in as raw materials but whose import is strictly limited: Such waste would be listed in the forced-examined product catalogue by the National Commodity Inspection Bureau of China in order to conduct a compulsory examination. For the cases involving the illegal transfer of waste to China, just negotiations will be conducted with the exporting countries and regions to stop the action and to request that the waste be returned to the source.

- Serious punishment will be given to the departments and individuals in China that illegally import waste. If the activity is criminal, the responsibility for the crime will be investigated by judicial organs, etc.

2.4 Regulation on Environmental Protection Management for Waste Imports

To further the environmental management of waste imports and prevent pollution from them, the Regulation on Environmental Protection Management for Waste Imports was enacted by NEPA, the Ministry of International Economic Cooperation and Trade, the General Office of Customs, the National Commercial Bureau, and the National Commodity Inspection Bureau. It was based on China's Act for Solid Waste Prevention. This regulation updates the management of waste imports in China. Apart from some concrete managerial rules, including principles of penalty, the catalogue of waste that can be taken in as raw materials but whose import is limited was issued as well.

2.5 Weak Regulation and Management

Since regulations on managing the import of waste were weak for so long in the past, the motivation for stopping the import of waste was relatively weak. In recent years, however, the Chinese government has paid strong attention to environmental protection in the country as well as to solid waste management. The Act for Solid Waste Prevention was enacted last November, and other regulations especially related to the management of waste imports were formulated and implemented. When facing the situation of hazardous waste transfer from developed to developing countries, the Chinese government took a stance to firmly resist the import of waste. Despite these trends, more cases of waste import occurred in China, especially in 1996. This situation exposes the fact that there are weak points and holes in management.

3 APPROACHES

3.1 Environmental Trade of Hazardous Waste at Home

With regard to the domestic trade of hazardous waste, hazardous waste from different regions can be centralized in certain areas, where a cross-regional treatment center can be set up to accelerate regional and cross-regional environmental trade around the treatment center. Examples are listed in Table 2 and discussed below.

Table 2 Domestic Trade of Hazardous Waste

Location	Activity
Xinhuang	Collect mercury waste from the entire country; conduct treatment and disposal for better economic, social, and environmental profits; and further enlarge the production at a certain scale.
Shenzhen	Reuse and dispose of the industrial waste from the city and nearby at Shenzhen Industrial Waste Treatment Plant; get good economic, social, and environmental profits.
Shenyang	Set up the Industrial Hazardous Waste Treatment Plant; treat and dispose of the hazardous waste produced in the region and nearby cities (under way).
Shanghai	Will set up the Hazardous Waste Treatment Center; treat and dispose of the hazardous waste in and around the Shanghai area.

- For small amounts of certain hazardous wastes, set up a cross-regional treatment venue. Xinhuang Mercury Treatment Company in Hunan province is an example.

- For larger amounts of hazardous waste in industrial, centralized cities, set up a regional treatment center for hazardous waste. Shenzhen, Shenyang, and Shanghai cities are examples.

China is starting a combination of hazardous waste treatment and trade within the country, starting from the regional level and moving to the cross-regional level. In recent years, the internal trade of hazardous waste has been positive — profitable for both the enterprises and local treatment centers. This result shows that appropriate hazardous waste treatment conducted within a certain area could push the treatment and reuse of waste and local development; proper cross-regional treatment of hazardous waste could enhance cross-regional trade. Internal trade in this field will continue in the future.

3.2 Cross-Border Trade of Hazardous Waste

With regard to international trade, apart from certain waste that can be taken in as raw materials, the import of hazardous waste from overseas will be strictly restricted or forbidden on the basis of regulations relevant to China. China is a signatory nation to the Basel Convention. Countries that want to conduct the business of waste import must comply with the international convention and China's regulations on the management of waste imports.

In several cases involving the import of hazardous waste in China in recent months, the Chinese dealt with the matter according to the relevant Chinese regulations. Examples follow.

3.2.1 Enforcing the Administrative Management of Imported Wastes

Customs, environmental protection agencies, environmental monitoring departments, sanitary epidemic-prevention departments, commodity inspection bureaus, and other concerned units at both the national and local level went "all out" to investigate the contents of imported waste. Most of the imported waste was found to be waste that China does not allow and whose import is strictly forbidden, because it could seriously threaten the people's health and the environment in China. After negotiation, the illegal import businesses have been forced to return the waste to the sources. Some cases are still under negotiation.

3.2.2 Enforcing the Management of Exporters and Importers

If international companies dealing with the illegal import of hazardous waste are found to be cheating by registering and withholding the truth, necessary compensation will be requested, as will other measures to solve the imported waste problem according to the relevant regulations of China and the Basel Convention. In domestic cases where individuals and companies dealing with the illegal import of hazardous waste were discovered, some companies were instructed to stop operation, and some individuals received severe sanctions according to Chinese law.

3.2.3 Catalogue of Waste Whose Import Is Strictly Limited

This catalogue lists nine types of wastes that could be used as raw materials and whose import is strictly limited in China:

- Animal waste;
- Smelter residue;
- Wood waste;
- Reclaimed waste paper on paperboard;
- Textile waste;
- Basic metal waste and its products;
- Metal, electric machine, and electrical product waste;
- Waste transportation equipment; and
- Waste that needs to be imported for a special purpose.

This list provides the basis for exporters to move waste to China.

3.3 Asian-Pacific Regional Training Center for Technology Transfer and Environmental Sound Management of Wastes, Located in Beijing

In response to a request from the Basel Convention, NEPA of China established the National Training and Technology Transfer Center (NTTTC) for the management and disposal of Chinese hazardous waste in 1993 at the Environmental Engineering Department, Tsinghua University, Beijing. Then in 1995, at its third international meeting, the Extended Bureau of the Second Conference of the Parties to the Basel Convention selected Beijing as one of two sites for the establishment of the Asian-Pacific Regional Centers for training and technology transfer related to the management of hazardous waste and other waste and the minimization of their generation.

NTTTC qualified to upgrade from the National Center of China to an Asian-Pacific Regional Center. Its establishment is of great significance in strengthening hazardous waste management in the Asian-Pacific region.

The Regional Center was established as a technical service and support department for promoting hazardous waste management and implementing the Basel Convention in the Asian-Pacific region. The main objectives for setting up the Regional Center in Beijing are to improve the technical level of managers in hazardous waste management, spread technical knowledge about the management and disposal of hazardous waste, make use of advanced technologies through technology transfer, and spread effective techniques and facilities in the Asian-Pacific area.

The implementation program for the first three years has been worked out. The objectives of the Regional Center for the first three years are to:

- Satisfy the higher-priority needs for training and technology transfer related to the management of hazardous and other wastes and for the minimization of waste generation in the Asian-Pacific region; and
- Be the technical supporting unit to the Basel Convention in the field of managing the trans-boundary movement of hazardous waste, provide regional services to the Basel Convention, and gradually develop the capability to be self-funding within five to seven years.

The major activities for the first three years of the Regional Training Center are as follows:

Year One

- Discuss high-priority training subjects with competent authorities.
- Set up regional links and confirm regional needs for implementation of the Basel Convention.
- Help countries establish national centers and provide basic training for national trainees.
- Establish access for collecting and disseminating regional database and other types of information, which is essential for implementing the Basel Convention, training, and technology transfer in the Asian-Pacific area. The existing Information Center for Hazardous Waste Management in China can provide a foundation for this purpose, but it should be improved in

accordance with the Basel Convention and the needs of the countries in the Asian-Pacific region.

- Conduct two training programs to meet high-priority needs.
- Hold one workshop in the first year.

Years Two and Three

- Conduct a number of training programs, at least four courses per year.
- Invite experts from other countries to help set up the Regional Center in Beijing and lecture in training courses.
- Hold workshops, seminars, and international conferences that will be sponsored.
- Develop the Regional Center's capability, including research and development techniques, facilities, self-funding, etc.

Through conducting these activities during the first three years, (1) personnel from governments and enterprises engaged in hazardous waste management and disposal could be trained professionally while related knowledge spreads; (2) new technologies for treatment and disposal of hazardous waste could be developed through scientific research; (3) advanced technologies, facilities, and successful experiences at home and abroad could be introduced and popularized; and (4) the academic exchange of technologies to manage and dispose of hazardous wastes in the Asian-Pacific region could be effectively promoted. This work will be of great significance in strengthening the management and disposal of hazardous waste, promoting environmental protection, and realizing sustainable development both in China and the whole Asian-Pacific region.

4 Conclusion

Trans-boundary trade involving China requires compliance with international conventions and Chinese regulations related to waste movement. Companies both at home and abroad could profit from such trade by observing the international and national regulations and formalities. China will continue to strictly implement all regulations concerned with waste imports and its management capability with regard to trans-boundary waste. It will also continue to improve the technical level of its managerial and professional personnel by taking advantage of the Regional Center in Beijing in order to protect the environment of China and the Asian-Pacific region.

IT'S SLIM WITH A PLAIN GREEN COVER: AUSTRALIA'S MANAGEMENT PLAN FOR POLYCHLORINATED BIPHENYLS

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ABSTRACT

In November 1995, the Australian and New Zealand Environment and Conservation Council (ANZECC, the Council of State and National Environment Ministers) adopted a National Management Plan for PCBs. This was a significant milestone in the very long saga of Australian efforts to develop public policy and management structures for dealing with persistent organochlorine wastes.

The author was part of a four-person consultation panel that carried out a public involvement program to assist and inform the process of developing the National Management Plan. The program involved, among other things, visiting every state and territory of Australia at least twice.

This paper describes the development and delivery of the public involvement program, including ongoing interactions with governments. The latter is often a complex (and many would say an unduly complex) matter in the federal system, where primary responsibility for waste management resides in the individual state/territory jurisdictions.

The paper also attempts to draw lessons from the process. While some participants learned and acted upon some of these lessons quite early in the process, other participants (particularly governments) took longer to realize their importance and thus took longer to refrain from actions that might be regarded as not keeping faith with the activities they had set in process.

Finally, the lessons learned here are contrasted with those drawn by participants in the process that led to the establishment and expansion of the Swan Hills facility in Alberta. While the outcomes of the Australian and Albertan processes appear to be very different, a number of the essential lessons to be drawn from the two processes are virtually identical.

1 INTRODUCTION

The history of Australian attempts over the past 10-15 years to find a means of managing persistent organochlorine wastes soundly has been outlined in a series of previous papers.[1-8]

Briefly, in the late 1970s and early 1980s, there were several unsuccessful attempts, by both state governments and private proponents, to build a high-temperature incinerator in Australia. While there was a broad range of views in the community about the desirability of high-temperature incineration, each of these attempts had foundered in the face of vigorous opposition to the siting of an incinerator. Many of these failures were written off simply as examples of the so-called NIMBY (not in my back yard) syndrome, which was certainly a major determining factor. However, a readiness to jump to such a simple and single explanation of why things went wrong ignored demonstrable failures in consultative processes, including failures to be open, failures to develop clear processes, and failures to remain faithful to declared processes.

In late 1987, the governments of Australia's two most populous states (New South Wales and Victoria) and the Commonwealth Government established an independent Joint Task Force on Intractable Waste. The Task Force carried out an extensive consultative process that endeavored to achieve agreement on three major issues:

- The nature and scale of the problem being addressed,
- The need to do something to attempt to solve the problem, and
- (If something should be done), what it was that should be done.

Widespread agreement was reached on the first two issues, but there were polarized views on the third issue. There was widespread support for utilizing high-temperature incineration to solve what was essentially a historical waste problem (all of the materials involved were either no longer being produced or were in the process of being phased out of production). However, there was also strong support for waiting for some alternative destruction technology to emerge and relying on indefinite storage in the interim.

The Task Force and a representative advisory committee advised the governments that the consultation process should not run according to a fixed timetable and, in particular, that any decision about siting a destruction facility should not become a focal point for robust criticism about failures in process. The governments ignored this advice and made a siting announcement from which they retreated within less than two months in the face of strong public opposition.

Following this debacle (in late 1990), the governments appointed a three-person Independent Panel on Intractable Waste to review the situation, hold further consultations, and make recommendations on what should be done. By then, community opposition to high-temperature incineration as a destruction technology had increased dramatically, and it was widely recognized that further attempts to pursue this option were almost certainly doomed to failure. The Panel recommended, and the Australian and New Zealand Environment and Conservation Council (ANZECC, the Council of Environment Ministers of Australia, New Zealand, and the Australian states and territories) accepted, that the incineration option be removed. Instead emphasis was to be placed on a range of emerging technologies that were showing some capacity to deal with segments of the persistent organochlorine waste stream, which by now were being called *scheduled wastes*.

In October 1993, acting on the advice of a working group made up of members of the Independent Panel and government officers,[9] ANZECC agreed to implement a national strategy for the management of scheduled wastes.

2 NATIONAL STRATEGY FOR THE MANAGEMENT OF SCHEDULED WASTES

The primary aim of the national strategy is to destroy all of Australia's persistent organochlorine wastes listed on Schedule X (see Appendix A for current listing).

Neither recycling nor long-term use of the materials that give rise to these wastes is regarded as an option. As well as being a hazard to human health and the environment, any continued use of them (or a failure to collect and destroy them) risks contamination of the food chain and is a significant threat to Australia's attempts to market itself as a clean, green, food exporter.

The three off-site destruction facilities currently operating in Australia (two based on the USEPA-initiated base catalyzed dechlorination (BCD) process and one on the Canadian Ecologic process) have so far been used mainly to destroy polychlorinated biphenyls (PCBs) and some organochlorine pesticides (OCPs). At present, Australia is well short of demonstrating that it has the ability to deal with all types of wastes and, probably more importantly, all physical forms of wastes listed on Schedule X. This raises the possibility that a scheduled waste holder might be able to demonstrate that a means of destroying its particular waste is not available in Australia and use this as grounds for applying, under the Basel Convention, for export to an overseas destruction facility that very possibly uses high-temperature incineration. In the context of Australia having rejected a home-based incinerator, there would be widespread opposition to any such export application being granted. In June 1993, the former Commonwealth Government imposed a moratorium on export of scheduled wastes. As well as being clearly in step with public opinion (a poll of a small sample of the Australian community showed 86% believing export for disposal was unacceptable), this decision provided an incentive for possible providers of treatment facilities in Australia.

In view of the foregoing, scheduled waste management plans place detailed emphasis on issues related to waste identification, collection, storage, transport, and destruction but not on recycling or export.

The central feature of the national strategy is the development, through a public involvement process, of four national management plans: for PCBs, hexachlorobenzene (HCB), OCPs, and other chlorinated hydrocarbons. The wastes to be covered by each of these management plans are listed in Appendix A.

Unless some factor is found to be inappropriate, each management plan will specify:

- Threshold concentrations, threshold quantities, and notifiable quantities of chemicals to be covered;
- Phase-out dates for processes and products;
- Dates by which destruction of wastes must be finalized;
- Storage, handling, and transport requirements; and
- Standards for emissions, effluents, and residues to be achieved by any treatment/destruction facility.

Management plans are to be "based on a risk assessment of environmental and human health effects, and the social and economic impacts."[9] Thus, while the plans are to take the best available scientific information into account, such information will not be the sole, or necessarily determining, factor in developing the plan. For example, while a high-temperature incinerator may be able to meet emission standards set in a management plan, overriding social factors have led governments to determine that technology will not be used.

In addition, gaps and uncertainties in scientific knowledge have to be taken into account while making judgments about what should be done. So, while it looks good in theory, with respect to PCBs it was not found to be "possible to apply a formal risk assessment method to situations in which PCBs are found because of the numerous possible scenarios involving PCBs and the limited information on the synergistic effects of PCBs or on how to use this information in setting management provisions. . . . Likewise, while data on the bioaccumulation and bioconcentration of PCBs and the acute, sub-acute and chronic effects of PCBs on animals have been considered, it (was) not possible to use the data as the dominant basis for developing the management plan."[10]

With the exception of matters related to import/export and Commonwealth Government facilities, responsibilities for waste management lie with the states and territories. The management plans will not form the basis for national law; rather, they embody standards and principles that will be given effect by legislative and/or regulatory actions in the individual state/territory jurisdictions. In the best circumstances, it might be claimed that the plan would lead to uniform standards of performance in scheduled waste management; however, given the current variability in performance standards among the states/territories, that claim would be fanciful. However, waste management is a very much a live issue across Australia, and all states and territories are actively reviewing and upgrading their policy and legislative regimes. There is reason for optimism that implementation of scheduled waste management plans will reinforce the trend toward improved and more harmonized waste management standards across the country.

2.1 Who Is Driving the Process?

ANZECC established two groups to advise it on the preparation of management plans and, in reality, to prepare the plans.

A 14-member National Advisory Body (NAB) is made up of key stakeholders: environment groups, industry, local government, trade unions, and farmers. As well as providing key stakeholder input into the management plan, NAB was given particular responsibility for advising ANZECC on consultation processes to be followed in the development of management plans. Very quickly the NAB assumed a greater role in the consultation process than had probably been imagined at the outset. The NAB has, in fact, become the *public face* for the delivery of programs to receive public input into the management plans, with subcommittees of the NAB forming consultation panels. This activity is something that had not really been done before (at least in waste management) in Australia, and it is widely accepted that it has led to credible and effective processes.

The Scheduled Waste Management Group (SWMG) is made up of senior government environment officials from the Commonwealth, states, and territories. The SWMG and NAB work closely and (mostly) effectively together, a process that is assisted by the linkage of having one independent chairperson for the two committees.

The NAB and the SWMG are supported by an ANZECC-funded secretariat, which operates out of the Environment Protection Agency in Canberra.

2.2 Consultation Protocol

Shortly after it was established, the NAB, recognizing that genuine and effective consultation was essential to the successful development of scheduled waste management plans, developed a National Protocol for Community Consultation on Scheduled Wastes. In short, the protocol spells out the consultative aims and principles that underpin the process of developing management plans. Its purpose is to clearly lay out the rules under which the consultation process will be carried out. It describes a detailed series of undertakings by the NAB (in particular) and the SWMG on how the consultation process will be run and deliberately provides the opportunity for participants in the process to use it to measure the NAB's performance in running the consultation. It also places more limited obligations on others entering into the consultative process to behave fairly reasonably (or at least not excessively unreasonably); the protocol does not accept that responsibility for effective consultation is a one-way street.

The National Protocol was built upon previous protocols developed by panels consulting on contentious issues in the State of Victoria, namely the Brunswick-Richmond Powerline Panel and the Code Island Review Panel. At the end of the PCB consultative process, the protocol was reviewed by the NAB, and some modifications were made. A copy of the current protocol (with the modifications in bold) is provided in Appendix B.

The development of these protocols, along with a determined commitment to stick to them, is a powerful mechanism for building trust that consultation and public participation programs will be carried out with integrity. They are a very effective tool, and their proper application is highly recommended.

2.3 The Process

The general process to be followed in developing each management plan is as follows:

Initial submissions are sought by announcing the intention to develop a plan in (1) press releases, (2) direct communications to people and organizations on an expanding mailing list of several thousand, and (3) limited paid advertising.

A draft management plan is prepared by the NAB and SWMG and released for public comment, along with substantive documentation on background information and issues for consideration, which is available on request.

For PCBs and HCB, most of the work in preparing this material (which amounted to several hundred pages) was performed by external consultants. For OCPs, a full-time consultant was hired to work within the Secretariat to facilitate a team approach. The telephone-book-sized background information documents were expensive to produce and had a dedicated but relatively small readership. The eventual content of the management plans appeared to be little influenced by responses to these documents. Rather the plans were shaped more by the informed comments of people with experience in dealing with the materials in question or by sharp questioning by people with less direct experience. Therefore, for OCPs it has recently been decided not to produce our own substantive documentation, but rather to provide existing documents (such as the WHO/ILO/ UNEP red books) free to the relatively small number of people likely to request them. This will free up considerable resources to augment face-to-face consultation, which is likely to have a much greater impact on shaping the management plan and on increasing ownership of it.

Comments on the draft plan are received through written submissions and structured but relatively informal public forums. A subgroup of the NAB is appointed as a consultation panel to facilitate this process. As well as reporting back to the NAB and SWMG on the results of the consultation, the panel also prepares for each round of consultation a public report listing all of the substantive comments made and indicating how they were considered in redrafting of the plan.[11,12]

All comments received are considered as the NAB and SWMG revise the plan into a draft final management plan. This, in turn, is released for a further round of public forums, discussions, and submissions.

These comments are again reviewed by the NAB and SWMG as they prepare a proposed management plan, which is submitted to ANZECC for endorsement. Once it is agreed to by ANZECC, the plan is forwarded to state and territory governments (eight in all) for implementation through state and territory law.

3 THE PCB MANAGEMENT PLAN

The PCB plan is divided into the following sections:

1. Definitions
2. Scope
3. PCB analysis
4. Notifiable quantity
5. Equipment management and phase-out
6. PCB-contaminated land
7. PCB storage, handling, and transport
8. Emergency procedures
9. Treatment and disposal of scheduled PCB material and scheduled PCB waste
10. Treatment and disposal of nonscheduled PCB material and nonscheduled PCB waste
11. Disposal of PCB waste to landfill (limited to nonscheduled solid PCB waste)
12. PCB monitoring (in the wider environment)
13. Certification (of destruction of the waste)
14. Community-based collections
15. Community participation, education, and training
16. Review period

Appendix A. Guidance note for the disposal of nonscheduled solid PCB waste
Appendix B. Guidance note for the disposal of nonscheduled liquid PCB waste

Some of the more significant features of the plan follow.

3.1 Scope

The full provisions of the management plan apply to all materials or wastes containing 50 g or more of PCBs at a concentration of 50 mg/kg or more; these are *scheduled* PCB materials or wastes. Any material or waste containing PCBs at less than 2 mg/kg is classified as *PCB free*.

Early drafts of the management plan had no information about materials and wastes in the range between those that were scheduled and those that were PCB-free. There were known to be large volumes of oil contaminated at 2-50 mg/kg and potentially large volumes of solids contaminated at similar concentrations. Many people were concerned that these materials and wastes be handled safely and consistently; from this perspective, a failure to deal with them at all in the management plan was unreassuring. Equally, many people agreed that to subject these less-contaminated materials and wastes to the stringent controls that apply to scheduled PCBs was not necessary or desirable.

Guidance notes for the disposal of these nonscheduled wastes were appended to the plan to promote consistency of practice across all jurisdictions. In particular, provision was made for the controlled landfilling of nonscheduled solid PCB wastes and for nonscheduled liquid PCB wastes to be used as a fuel in licensed facilities or as a diluent in treatment processes.

3.2 Notifiable Quantity

Anyone holding 10 kg or more of PCBs (e.g., 1 tonne of material contaminated with PCBs at 10,000 mg/kg) at any one premise must notify the responsible environmental agency of the nature of that holding. The agency must keep a publicly accessible register of notified quantities. Holders are not allowed to split up their PCB holdings to avoid responsibility for notification.

3.3 Equipment Management and Phase-Out

The plan provides for a program, commencing 1 January 1996, for identifying, removing from service, and destroying all PCB-containing equipment over 13 years. All concentrated PCBs must be removed within 8 years. Use of PCB-containing equipment, regardless of how well it may be working, will be prohibited beyond these dates.

3.4 PCB-Contaminated Land; Storage, Handling and Transport; Emergency Procedures

These sections of the plan largely call up existing legislative/regulatory provisions to ensure their effective integration into the plan.

3.5 Treatment and Disposal of Scheduled PCB Material and Scheduled PCB Waste

This section provides for PCB wastes to be consigned for treatment in a licensed facility within one year of being removed from service or placed in storage unless the responsible environmental agency determines that viable treatment facilities are not available in Australia. Liquid and solid residues from treatment should be PCB-free. Stringent standards for emissions, effluents, and residues in line with international regulatory best practice are also set.

3.6 Treatment and Disposal of Nonscheduled PCB Material and Nonscheduled PCB Waste

Nonscheduled PCB materials and wastes at a concentration of 50 mg/kg or greater shall be disposed of as scheduled PCB wastes at the end of their useful life, while those at less than 50 mg/kg may be disposed of in a manner consistent with the guidance notes appended to the plan. Note that under no circumstances may liquid waste be disposed of to a landfill.

3.7 PCB Monitoring

A nationally coordinated and statistically valid PCB sampling and monitoring program that is based on existing and new activities is to be carried out to determine whether PCB environmental concentrations are decreasing over time. The program shall focus on breast milk and foodstuffs, sewage treatment plants and outfalls, landfill leachate and adjacent groundwater, and appropriate biological indicators, including wildlife.

3.8 Certification of Destruction

Multidocket certificate systems for the transport of hazardous waste for off-site treatment and disposal are already in widespread use in Australia. This section of the plan provides for augmentation of the transport certificate system with a destruction certificate, so that environmental agencies can confirm that PCB wastes have actually been destroyed rather than simply transported to the destruction facility. There have been occasions in the past where PCB wastes have been abandoned and also where excessive pretreatment stockpiles have built up.

This provisions, together with the notifiable quantity provision, mean that we can now track PCB wastes on premises as well as in transit.

3.9 Community-Based Collections

This section provides for a coordinated approach to any such collections and for PCBs to be collected as part of a nationally coordinated program for all scheduled wastes. ANZECC has directed the SWMG in consultation with the NAB to draw up options for a national collection program

3.10 Community Participation, Education, and Training

Licensing and operation of PCB treatment and disposal facilities are required to undergo formal consultation processes. Environmental agencies are required to make information related to the implementation of the plan available and to ensure education programs are formulated for workers and other people likely to come into contact with PCBs.

3.11 Review Period

The plan must be formally reviewed within five years to assess the effectiveness of its implementation. It can, however, be reviewed at any time should a need to do so become apparent.

The NAB has established a subgroup to review implementation of the plan by the various jurisdictions. During early 1996, the subgroup expressed considerable concern over the rate of implementation of the plan; it felt that some jurisdictions had regarded the plan more as an end point than a starting point for better PCB management. While it was recognized that the plan had resourcing implications for often under-resourced government agencies, there were concerns that a lack of clear action to implement the plan would threaten the cooperative approach that had led to its formulation. In the last few months, the subgroup has witnessed greater activity to implement the plan, particularly in the states of Western Australia and New South Wales, and it has expressed general satisfaction with this recent progress.

The response of industry remains mixed. The electricity supply industry has taken a proactive approach to ensure that its membership is well-informed of obligations under the plan. Some other sections of industry seem to be waiting for governments to tell them what they have to do. Those sections of industry that have been fully involved in the process should know their obligations in considerable detail; it is disappointing if, as seems to be the case in some circumstances, the opportunity has not been taken by the industries themselves to ensure that they are up to speed.

4 THE AUSTRALIAN AND ALBERTAN EXPERIENCES: WHAT ARE THE SIMILARITIES?

In 1985, I first became aware of the process in Alberta that led to the successful establishment of an integrated hazardous waste treatment facility, including high-temperature incinerators, outside Swan Hills.

Over the next few years, it was clear that more than a few people in Australia, particularly chemical engineers and politicians, believed that if you examined the Alberta experience closely enough, you would discover a major formula for getting communities to accept high-temperature incinerators and that you could export that formula to Australia.

Some others had the view that if you looked somewhat more deeply at what happened in Alberta, you might learn some lessons about how to solve waste management problems by enlisting community support. Those lessons might then be adapted and built upon in seeking solutions to similar problems in other places.

At the last Pacific Basin Conference, I had the pleasure of sharing the podium at a session with Al Wakelin, who spoke about a process of gaining public approval for an expansion of the Swan Hills facility.[13] Wakelin summarized his experience simply and profoundly as follows:

> We would advise a proponent to approach the process with a degree of humility. Do not assume that you have all of the answers.
>
> The best and perhaps only strategy is to ensure that the project is ecologically sound, that a full range of alternatives have been considered and that credible plans are in place to mitigate potential damage. Understand too that lay people are the real experts on what frightens them and what reassures them. . .
>
> Early involvement of local and interested public is necessary, input from all stakeholders in determining the scope of issues to be addressed as well as identifying significant environmental issues.

The essential messages are all there: involve people in the search for a solution, come to learn, leave any narrow technological arrogances at home, do not play games (but be prepared for some others to play them), run a well-managed and accountable process, and recognize the different forms of expertise through which participants can add value.

Collectively, we were considerably slower to learn many of these lessons in Australia than Alberta. However, to avoid the temptation to engage in total self-flagellation, we should recognize that the task was more difficult in Australia:

- Southeastern Australia, where most of our saga was played out, is much more complex sociopolitically than Alberta.
- While Greenpeace gave major international priority to fighting high-temperature incineration in Australia and Ireland, there were no reports of the *Rainbow Warrior* being sighted on the North Saskatchewan River.

We will never build a high-temperature hazardous waste incinerator in Australia, and this fact has meant that dealing with our stockpile of scheduled wastes was delayed for almost a decade. However, we are beginning to deal with that stockpile now and, having read the PCB Management Plan in detail for the first time in several months while preparing this paper, I have to admit to being pleasantly surprised at how comprehensive and well-crafted it seemed.

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APPENDIX A

WASTES LISTED ON SCHEDULE X

1. Polychlorinated Biphenyls (PCBs)

2. Hexachlorobenzene (HCB)

3. Organochlorine Pesticides (OCPs):
    - Aldrin
    - Pentachloronitrobenzene
    - Chlordane
    - Dieldrin
    - DDT
    - Endrin
    - Heptachlor
    - Hexachlorobenzene (from pesticide applications)
    - Isodrin
    - Lindane
    - Pentachlorophenol
    - 2,4,5-T
    - Breakdown products:
        - Heptachlor epoxide
        - DDD
        - DDE

4. Other Chlorinated Hydrocarbons:
    - Pentachlorobenzene
    - 1,2,4,5-Tetrachlorobenzene
    - Endrin aldehyde
    - 2,3,4,6-Tetrachlorophenol
    - 1,2,4-Trichlorobenzene

APPENDIX B

NATIONAL PROTOCOL FOR COMMUNITY CONSULTATION ON SCHEDULED WASTES

(Revised August 1996)

B.1 AIMS

The following consultation **and participation** aims have been agreed by the NAB and the SWMG and will be adopted in the development of management plans:

1. To enhance the development, adoption and implementation of effective management plans for scheduled wastes

2. To maximize understanding of and involvement in the debate related to the management of scheduled wastes

3. To place scheduled waste management issues clearly within the context of broader waste management issues, **including those which may arise throughout the process of development and implementation of management plans**

4. To achieve the most societally acceptable outcome possible in the development and finalization of management plans, taking account of environmental, economic and social factors

B.2 PRINCIPLES

The NAB and the SWMG, in facilitating the consultation **and participation** process, will seek to achieve clarity of roles and responsibilities, timeliness of decision making and information delivery, access to information and personnel, easily comprehensible information and processes, continuity, feedback mechanisms, openness, fairness and equity.

We will:

1. Communicate in a clear and timely manner accommodating comments on the scope, aims and expected outcomes for each stage of discussion and submissions

2. Provide comprehensive and timely information to the community to encourage fair and informed discussion of issues

3. Support, to the maximum extent possible, the consultative process by providing information requested by those seeking input

4. Establish clear and realistic timelines for all forms of input which reflect, as much as is possible, a sensitivity to the resources available to individuals and groups concerned

5. Translate key information into plain language for wider community consideration, especially when dealing with technical issues

6. Assist individuals and groups in a variety of practical ways to engage in the consultative process, within the limitations of the scheduled waste budget, paying particular attention to equal opportunity principles

7. Pay specific attention to the inclusion of people from non-English speaking backgrounds in the consultation process, within the limitations of the scheduled wastes budget

8. Provide frequent feedback, including information relating to emerging technologies, key outcomes from NAB and SWMG meetings and consultations, the nature of interested people's contributions, and final key recommendations

9. Ensure that people who enter consultative processes at different stages will, as much as possible, be able to influence the direction of management plan development

10. Stimulate conciliatory and constructive exchange of views and genuinely attempt to address, without prejudice, the major issues involved in the management plans

11. Frequently monitor and evaluate the effectiveness of the consultation program during and at the end of each stage of the management plan process

12. **Regularly review, update and activate contact lists of individuals and organizations with an interest, or a potential interest, in the management of scheduled wastes**

13. Share the responsibilities for effective consultation with those who enter into the consultative process.

While the protocol will apply to all of the management plans, each plan will require a specific implementation strategy for consultation. These strategies will include, amongst other things:

- Consideration of target groups (for example consultation on hexachlorobenzene (HCB) is likely to be more localized than that for other management plans);
- Mechanisms for effective consultation (for example, for example the approach used in consultation with the rural sector for organochlorine pesticides is likely to be very different from that used in Botany for HCB);
- Clear timelines; and
- Resourcing (levels and types of assistance will vary)

B.3 SHARING RESPONSIBILITIES

The roles of the NAB and SWMG are identified at Appendices B and C of the Report of the Scheduled Wastes Working Group (SWWG) to ANZECC, May 1993.[9] Appendix B states that the role of the SWMG is:

> "to implement, review and advise (ANZECC) on the National Strategy for the Management of Scheduled Wastes. In particular, in consultation with the NAB, the SWMG is to:
>
> - ensure that the community is adequately consulted through the NAB and other means, such as public hearings and targeted consultation, education and information programs."

Appendix C states that the role of the NAB is to advise ANZECC on:

- "community consultation/education and information programs; and
- any other relevant issue on which ANZECC or the SWMG seeks advice."

This makes it clear that while the SWMG is ultimately responsible for making sure the public is adequately consulted, the NAB has the responsibility for providing advice on consultation programs.

The NAB has considered the approach to be adopted for major public events in the consultation process. These events, including hearings and workshops, will be led by a sub-group of the NAB. The SWMG will provide technical support on these occasions.

COUNTRY CASE STUDIES

Chairs: Azni Bin Idris, Universiti Pertanian Malaysia, Malaysia
Ma Hongchang, National Environmental Protection Agency, China
Michael J. Hooper, Clemson University, USA

THE NEWEST ACHIEVEMENTS OF STUDIES ON THE REUTILIZATION, TREATMENT, AND DISPOSAL TECHNOLOGY OF HAZARDOUS WASTES

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ABSTRACT

From 1991 to 1996, key studies on the reutilization, treatment, and disposal technology of hazardous wastes have been incorporated into the national plan for environmental protection science and technology. At present, the research achievements have been accomplished, have passed national approval, and have been accepted. The author of this paper, as leader of the national group for this research work, expounds the newest achievements of the studies involving four parts: (1) the reutilization technology of electroplating sludge, including the ion-exchange process for recovering the sludge and waste liquor for producing chromium tanning agent and extracting chromium and colloidal protein from tanning waste residue; on the recovery of heavy metals from the electroplating waste liquor with microbic purification; on the demonstration project of producing modified plastics from the sludge and the waste plastics; and on the demonstration of the recovery of heavy metals from waste electroplating sludge by using the ammonia-leaching process; (2) the demonstrative research of reutilization technology of chromium waste residues, including production of self-melting ore and smelting of chromium-containing pig iron, and of pyrolytic detoxification of the residue with cyclone furnace; (3) the incineration technology of hazardous wastes with successful results of the industrial incinerator system for polychlorinated biphenyls; (4) the safety landfill technology for disposal of hazardous wastes, with a complete set of technology for pretreatment, selection of the site, development of the antipercolating materials, and design and construction of the landfill. Only a part of the achievements is introduced in this paper, most of which has been built and is being operated for demonstration to further spreading application and accumulate experience.

1 STUDIES ON PRODUCTION OF TANNING AGENT FROM ELECTROPLATING SLUDGE AND EXTRACTION OF CHROMIUM AND COLLOIDAL PROTEIN FROM TANNING WASTE RESIDUE[1]

This is a socialized and industrialized technology for treating the chromium wastewater from electroplating and recovering the chromium. The basic idea is to adopt one-step, ion-exchange technology for the electroplating industry in a rather large region with a socialized water treatment to recover chromium, which is centralized to produce tanning agent for use in tanneries; chromium and colloidal protein from the waste residue generated in the tanning process are extracted. Chromium is recycled to make tanning agent, and the colloidal protein is used for producing feedstuff. Thus, the recycling for reuse of the wastes between the electroplating and tanning industries fulfills the objective of waste minimization. This achievement has been adopted in the Yancheng area of Jiangsu Province in China. The technological flowsheet is shown in Fig. 1.1.

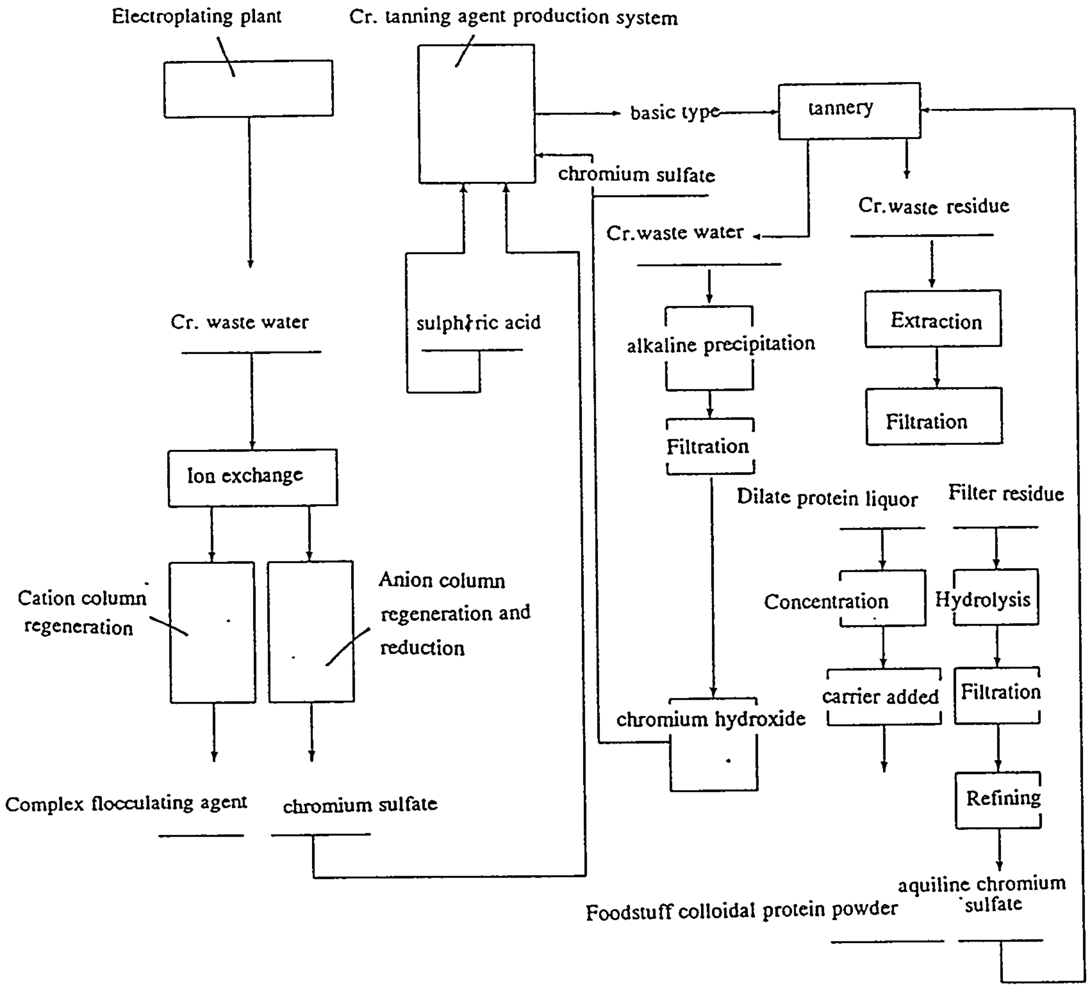


Fig. 1.1 Flowsheet for Producing Tanning Agent from Electroplating Sludge and Colloidal Protein and Chromium from Tanning Waste Residue

1.1 One-Step, Ion-Exchange Technology of Reduction and Regeneration

The electroplating wastewater containing Cr^{6+} is first treated with cation exchange and then with anion exchange, so that Cr^{6+} is adsorbed by the ion-exchange resin of weak alkaline type with large pores. In general, the regeneration uses alkali (NaOH) to wash out the anion $Cr_2O_7^=$ or $C_2O_4^=$ to form Na_2CrO_4 solution and then uses reductant to make it into chromium sulfate. In this project, two steps of regeneration and reduction are combined into one step, i.e., using acidic reductant of sodium hydrogen sulfite directly for regeneration as follows:

$$5H_2SO_4 + 2R_2Cr_2O_7 + 6NaHSO_3 = 2R_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3Na_2SO_4$$

$$7H_2SO_4 + 4R_2CrO_4 + 6NaHSO_3 = 4R_2SO_4 + 2Cr_2(SO_4)_3 + 10H_2O + 3Na_2SO_4$$

The Cr^{6+} adsorbed on the resin is directly reduced to chromium sulfate for creating the condition of chromium tanning agent production. A comparison of the traditional regeneration process with this one-step reduction and generation process is shown in Table 1.1.

Table 1.1 Comparison of Traditional Regeneration with One-Step Reduction and Regeneration

Item	One-Step Reduction And Regeneration	Traditional Regeneration
1. Regeneration	Combined with regeneration and reduction	Separated from regeneration and reduction
2. Reduction	Combined with regeneration and reduction	• Using $Na_2Cr_2O_7$ collection pool • Reducing Cr^{6+} in reactor to Cr^{3+}
3. Reduction mechanism and difficulty	Irreversible reaction rapid and perfect	Reversible reaction slow and not easily perfect
4. Regenerating and reducing agents consumption	$NaHSO_3$, H_2SO_4 $NaHSO_3$ is 1.2 times that of the theoretical amount	NaOH, $NaHSO_3$, H_2SO_4 NaOH is 2.0 times that of the theoretical amount
5. Treatment of acidic wastewater	Neutralized with line or transformed resin into OH type with NaOH	No
6. Cl^- impurity introduced	No	Yes

1.2 Development of Small-Scale Movable Automatic Ion-Exchange Facility

To make all electroplating industries, rather large regions adopt ion-exchange technology to treat and cover electroplating wastewater. The small-scale universal movable automatic ion-exchange facility should be developed to facilitate spreading the socialized application in large areas.

The developed facility is shown in Fig. 1.2, which has the following characteristics:

- The exchange column and inlet and outlet pipes can automatically reconnect through tridimensional motions to practice the automatic transfer of exchange and regeneration performance for accomplishing the process.
- The microcomputer control is used to provide operating data at all times to help production management.
- This module-type facility can be combined at random to facilitate extensive application.

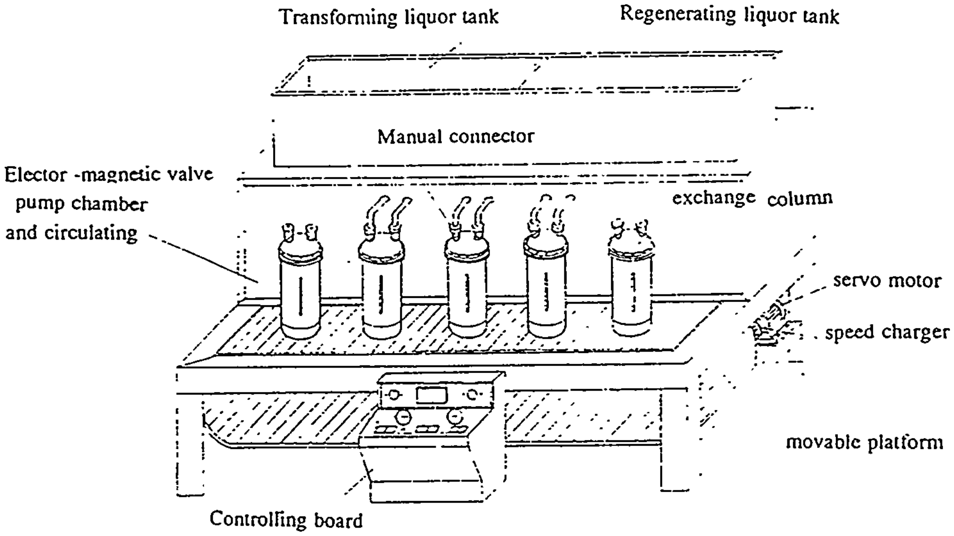


Fig. 1.2 Diagram of Movable Resin Regeneration Facilities

1.3 Production Technology of the Chromium Tanning Agent

As shown in Fig. 1.3, the chromium sulfate recovered through the ion-exchange process is concentrated and press-filtered; the filtering liquor (after modification of its alkalinity and vacuum filtration) is dried to form the product $Cr(OH)SO_4$, with the following technical indices:

Cr_2O_3 (%)	26-27
Alkalinity (%)	35-40
Iron content (%)	<0.1
Specific gravity Be'	47-48
Solubility (%)	100

1.4 Production of Feedstuff of Colloidal Protein Extracted from Tanning Waste Residue

Tanning waste residue contains more than 50% water, more than 30% protein, and less than 1% trivalent chromium. The process of extraction to separate protein and trivalent chromium is a reversible reaction, which moves the trivalent chromium combined on the protein molecule to form the free ion as well as the protein molecule. This project uses lime or calcium oxide in alkaline liquor to dissolve the waste residue in a reactor under definitive temperature and pressure, and the calcium hydroxide formed precipitates in the residuals, while the filtrate is dilute protein liquor, which after neutralizing and evaporating for concentration, is put into the carrier to be agitated, dried, and ground to form colloidal protein powder feedstuff (Fig. 1.1). Its main contents are shown in Table 1.2.

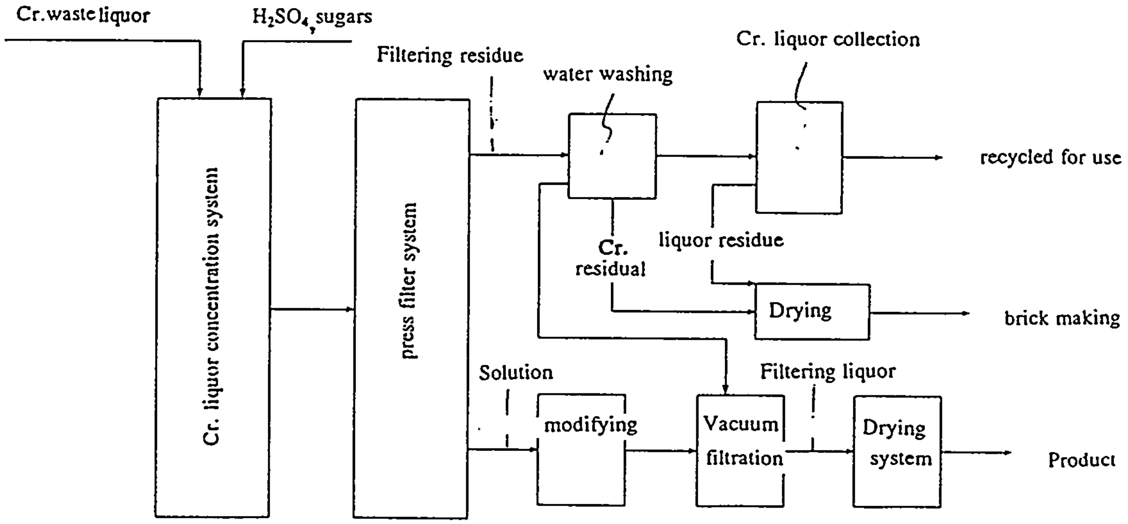


Fig. 1.3 Production Technology of Chromium Tanning Agent

Table 1.2 Main Contents of Colloidal Protein Feedstuff

Water (%)	Crude Protein (%)	Crude Fal (%)	Crude Ash (%)	Total Chromium (ppm)
<10	>50	1~2	≤10	≤45

1.5 Spreading for Application

The achievement of this project has been applied in Yansheng City of Jiangsu Province in China to set up a wastewater treatment network, covering more than 50 electroplating plants, and production lines of chromium tanning agent and colloidal protein feedstuff, forming primarily the industrial chain of waste reutilization of two industries.

2 RECOVERY OF HEAVY METALS FROM THE ELECTROPLATING WASTEWATER AND SLUDGE WITH MICROBIC PURIFICATION[2],[3],[4]

This research project has found a type of functional bacteria of SR series, which can remove efficiently the heavy metals in electroplating wastewater and sludge; developed the concentrating agent and fixing technique and the bioreactor; and set up a demonstration purification works for recovering heavy metals from electroplating wastewater and sludge.

2.1 Separation and Domestication of SR Series Functional Bacteria Type

- The SR series functional bacteria type is comprised of five species of functional bacteria of SRI, SRIV, etc., which are obtained by separation, bacteria elimination, and purification.

- The functional bacteria type does not form gemma and is arc rod in shape, with gram negative, flagellula at pole, and movement of nearing gradually in no order. It is appraised to be of Desulphoribrio SP.

- The best conditions for purifying chromium liquor by SR functional bacteria are as follows. The bacteria liquor is cultured for 24 hours and then vibrated for 24 hours at pH 6~7, 20~30°C and 5~100 μg/mL of Cr^{6+} concentration. The purification rate of chromium is 99.6%. The microbic treatment of electroplating wastewater generates sludge, which is used to extract chromium with microbic vibration of the sludge for 15 days, resulting in an extraction rate of 64%.

- The theories of toxicology, microbiology, immunology pathology, and epidemiology are integrated with the electron microscopic technique to study the safety of SR functional bacteria; it is proved to be nontoxic, nonpathogenic, and unable to sensitize, and it does not affect the growth and heredity of plants.

2.2 Development of the Bioreactor

2.2.1 Studies on the Conditions of Fixation

The bioreactor was developed to commercialize the microbic treatment technology of electroplating wastewater.

- From the fixation materials for food, fermentation and medico-chemicals, two are selected as adaptable for the fixing call in this project: PVC and sodium alginate with concentrations of 10% and 2%, respectively.

- The conditions for fixation to form shape are studied, as well as the culture conditions and medium of the functional bacteria; two media are found to be cheap for industrial application.

- The concentration technique and coagulant are studied; the bacteria can be concentrated by 10 times within 40 minutes.

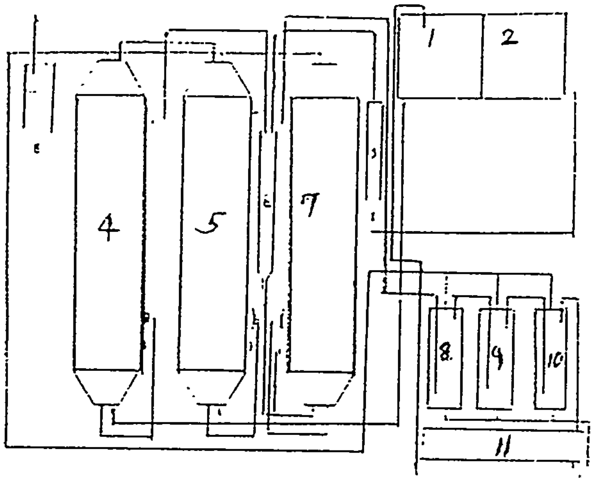
- The treating capacity of six valent chromium after fixation is higher than that of free cell by 26% or more.

2.2.2 Bioreactor

The bioreactor is composed of three columns, as shown in Fig. 2.1.

- The wastewater is first fed into a pH buffer to lower its acidity.

- The wastewater and the culture medium of the bacteria are fully mixed in mixing column 6 and then enter into reaction column 7 of fixing functional bacteria.



1. culture medium pool
2. waste water pool
3. pH buffer
4,5. Fixing column of functional facteria
6. Mixing column
7. Reaction column of fixing functional facteria
8,9,10,11. precipitation pool

Fig. 2.1 Flowsheet Bioreactor Structure

- The outflow from reaction column 7 enters into four precipitation pools 8–11 to facilitate the functions of precipitation, recovery, and bacteria elimination.
- The results of electroplating wastewater treatment with a bioreactor are shown in Table 2.1.

2.2.3 Example for Microbic Treatment of Electroplating Wastewater and Recovery of Heavy Metals

The SR functional bacteria purification and recovery of heavy metals from electroplating wastewater are applied in four electroplating plants, with the technological flowsheet shown in Fig. 2.2 and the treatment effects in Fig. 2.3. These figures show that very good effects are obtained with this microbic technology.

Table 2.1 Facilities and Effects of Four Projects of Microbic Electroplating Wastewater Treatment

Order No.	Plant Name	Wastewater Treated Daily (m^3)	Concentration of Metal (mg/L)	Bacteria Culture Pool (m^3)	Reaction Pool (m^3)	Precipitation Pool (m^3)	Treatment Effects
1	Jinjiang Electric Machine Plant	50	Cr^{6+} 66, Zn^{2+} 8, Ni^{2+} 6, Cu^{2+} 9, Cd^{6+} 3	49	14	93	Cr, Zn, Ni, Cd, Cu recovered; water recycled
2	Honguang Industrial Company	1	Cr^{6+}2658	17	12	PE filter	Cr recovered; water recycled
3	5701 Plant	175	Cr^{6+}693, Cu^{2+}5, Cd^{2+}16, Zn^{2+}43, Ni^{2+}3, Pb^{2+}5	170	103	22	Cr, Cd, Zn, Cu, Ni, pb recovered; water recycled
4	Shuangliu Metallurgical Plant	120	Cr^{6+}65, Zn^{2+}40	192	163	22	Cr, Zn recovered; water recycled

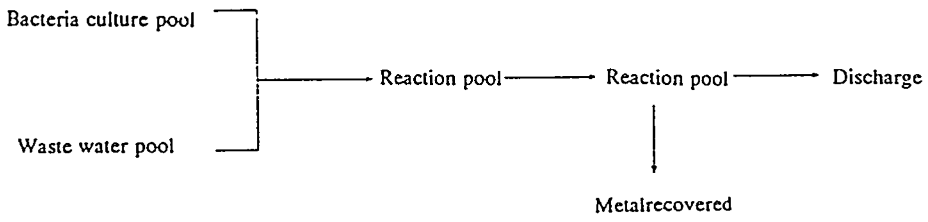


Fig. 2.2 Technological Flowsheet of Microbic Treatment of Electroplating Wastewater

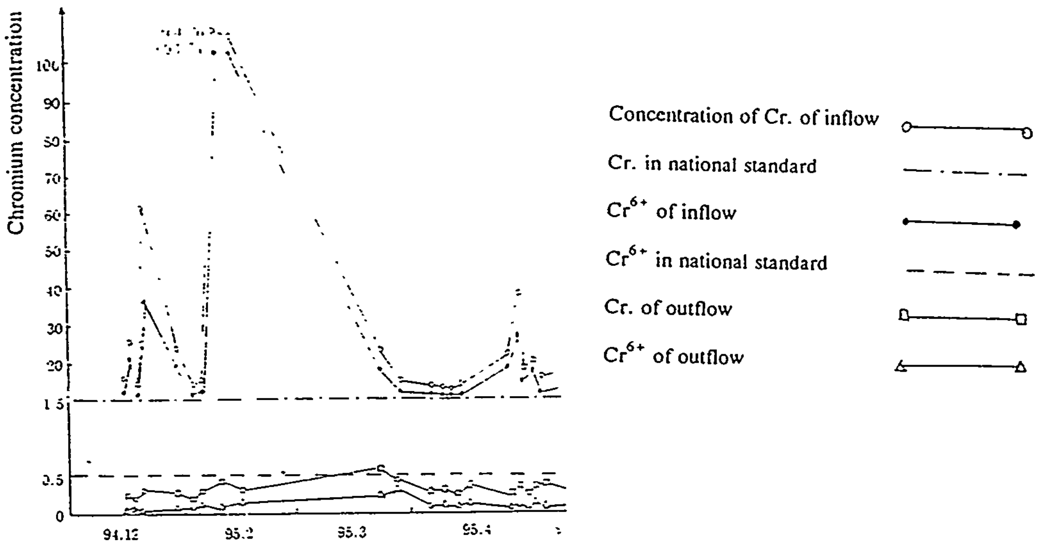


Fig. 2.3 Operation Curve of Microbe Purifying Chromium Wastewater from an Electroplating Plant

3 STUDIES ON THE DEMONSTRATIVE TECHNOLOGY FOR PRODUCING SELF-MELTING SINTERED ORE AND SMELTING CHROMIUM CONTAINING PIG IRON FROM CHROMIUM WASTE RESIDUE[5]

This research project uses chromium waste residue (containing 1–3% Cr^{6+}) as melting agent to be draft-sintered together with iron ore, using coke powder as fuel, to produce self-melting ore; the reduction rate of Cr^{6+} in the residue is up to 99% or more. The self-melting ore is smelted again in a blast furnace to form chromium containing pig iron, which may then be used as industrial raw material and made into wear-resisting casting.

3.1 Technological Flowsheet for Producing Self-Melting Sintered Ore and Smelting of Chromium Containing Pig Iron from Chromium Waste Residue

As shown in Fig. 3.1, the chromium leached residue after screening and grinding is burden and mixed for two times with iron ore and cake powder and then fed into sintering equipment. The sintered output after crushing, screening, and cooling processes forms the sintered ore product, which is also used as a quality raw material for producing qualified chromium containing pig iron with blast furnace. This pig iron can be used to make various wear-resistant materials through melting and smelting once more.

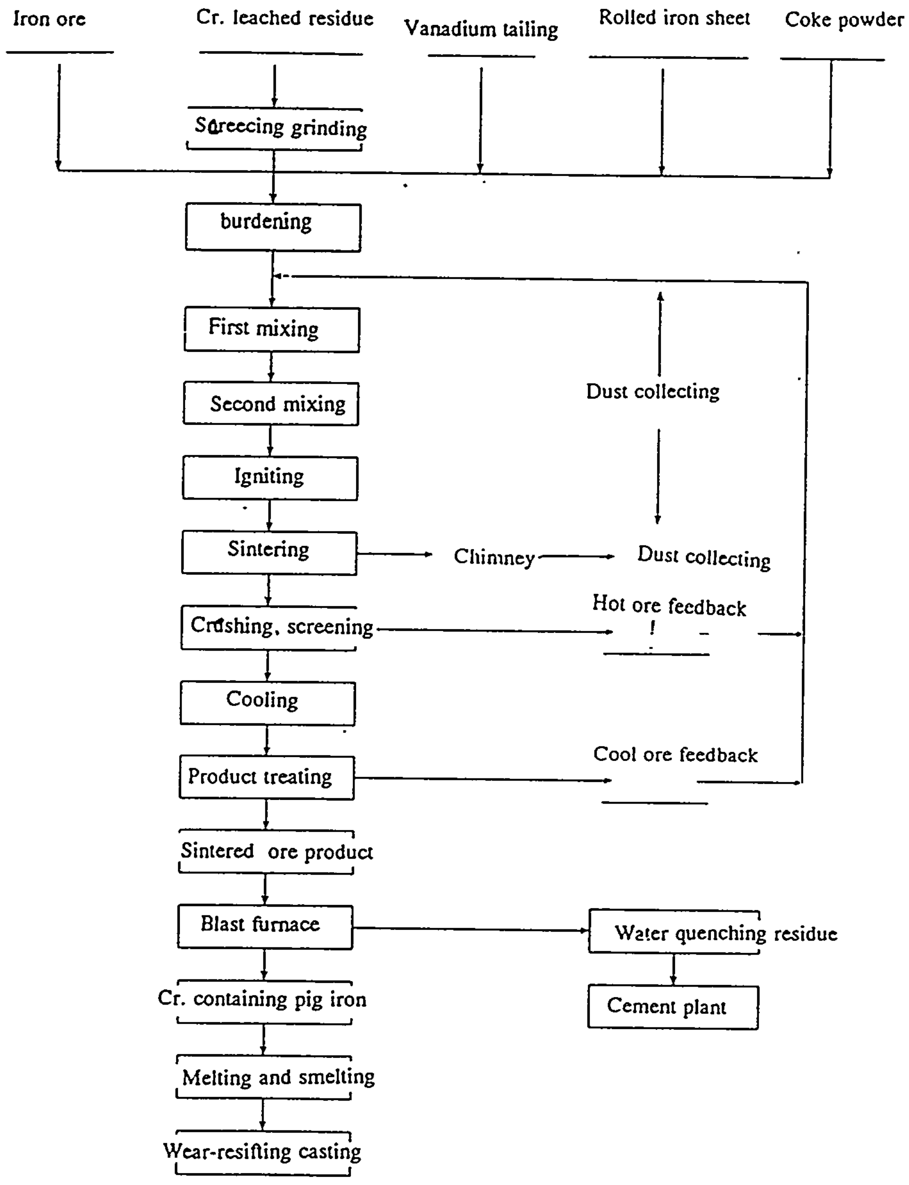


Fig. 3.1 Technological Flowsheet of Producing Sintered Ore for Smelting Iron and Wear-Resisting Casting from Chromium Residue

3.2 Several Key Techniques Resolved in the Studies

To obtain self-melting sintered ore of stable quality, the mixing ratios of sintering raw materials must be exactly calculated to ensure the sinter process is being carried out in a reducing atmosphere so as to completely reduce Cr^{6+} to Cr^{3+} in the waste residue. Research shows the mixing ratio of carbon in the sintering process should be strictly controlled to be 10–15% more than that used for producing common sintered ore, or have a natural weight ratio of 6–7%.

The reduction mechanism of Cr^{6+} is studied in detail. In the sintering process, Cr^{6+} is completely reduced in the atmosphere of many reducers generated in the furnace, such as carbon (C), iron (Fe), ferrous oxide (FeO), and carbon monoxide (CO), so that the content of Cr^{6+} in the sintered ore product is <8 parts per million.

$$2Na_2CrO_4 + 3C + O_2 = Cr_2O_3 + 2Na_2CO_3 + CO\uparrow$$

$$\Delta G = -24050 - 351.0T$$

$$2Na_2CrO_4 + 3CO = Cr_2O_3 + 2Na_2CO_3 + CO_2\uparrow$$

$$\Delta G = -565760 - 15.3T$$

The size of sintering raw materials, thickness of the material layer, vertical sinter velocity, ignition temperature, and wind amount affect the quality of the sintered ore. The studies have determined adaptable parameters of the sintering technology:

Size of the waste residue	≤3 mm occupying 70% or more
Size of the coke powder	1~4 mm occupying 60% or more
Thickness of the material layer	330~350 mm
Vertical sinter velocity	13 mm/min
Ignition temperature	1,100 ± 50°C
Drum rotating strength	≥60%

3.3 Demonstration Project

The achievement of the studies has been used in China's Jinzhou Ferroalloy Plant to establish a demonstrative project with annual treatment of 30,000 tons of chromium residue. This project is now being applied all over the country for treating the accumulated waste chromium residue of 3 million tons. The effect of removing of Cr^{6+} in this project is shown in Table 3.1.

4 ACHIEVEMENTS OF STUDIES ON THE SECURE LANDFILL DISPOSAL TECHNOLOGY OF HAZARDOUS WASTES[6]

This research project presents the achievements of the theory, design, construction, and management technique necessary for building the secure landfill site for hazardous wastes. Its design framework is shown in Fig. 4.1.

Table 3.1 Removal Degree of Six Valent Chromium

		Cr^{6+} in Raw Material			Cr^{6+} in Sintered Ore			
Period	Serial Number	Cr^{6+} in the Residue (%)	Unit Consumption of the Residue (kg/t)	Cr^{6+} Content in the Residue (kg)	(%)	(kg/t)	Removal Rate of Cr^{6+} (%)	Notes the Residue Screened
Production Period	95-7-14	1.00	275	2.75	0.0006	0.006	99.8	Size <5 mm
	95-7-15	1.05	275	2.89	0.0006	0.06	99.2	Size <5 mm
	95-7-16	0.97	275	2.67	0.002	0.02	99.3	Size <5 mm
	95-7-18	0.94	275	2.59	0.0005	0.005	99.8	Size <5 mm
	95-9-2	1.15	275	3.16	0.0005	0.005	99.9	Size <5 mm
	95-9-3	1.15	275	3.16	0.0005	0.005	99.9	Size <5 mm
	95-9-4	1.10	275	3.03	<0.0005	0.005	99.7	Size <5 mm
	95-9-6	1.10	275	3.03	<0.0005	0.005	99.7	Size <5 mm
	95-9-7	1.02	275	2.81	0.0005	0.005	99.6	Size <5 mm
	95-9-8	1.04	275	2.86	0.0005	0.005	99.8	Size <5 mm
	95-7-9	0.98	275	2.70	0.0005	0.005	99.6	Size <5 mm
	95-7-15	1.00	275	2.75	<0.0005	0.005	99.8	Size <5 mm
	95-7-16	1.15	275	3.16	<0.0005	0.005	99.9	Size <5 mm

4.1 Main Achievements

4.1.1 Receiving Conditions and Preliminary Treatment

The technology behind a secure landfill disposal for hazardous wastes is discussed in the following.

- The receiving standards for 30 kinds of hazardous wastes are presented, integrating the concrete conditions in China.
- Three solidification techniques are proposed: the methods using the glue bonds of inorganic (cement) and organic (asphalt) and the self-gluing agents.
- Three methods for decreasing volume are suggested: wet low temperation and low-pressure oxidation, mechanical compaction, and mechanical dewatering.

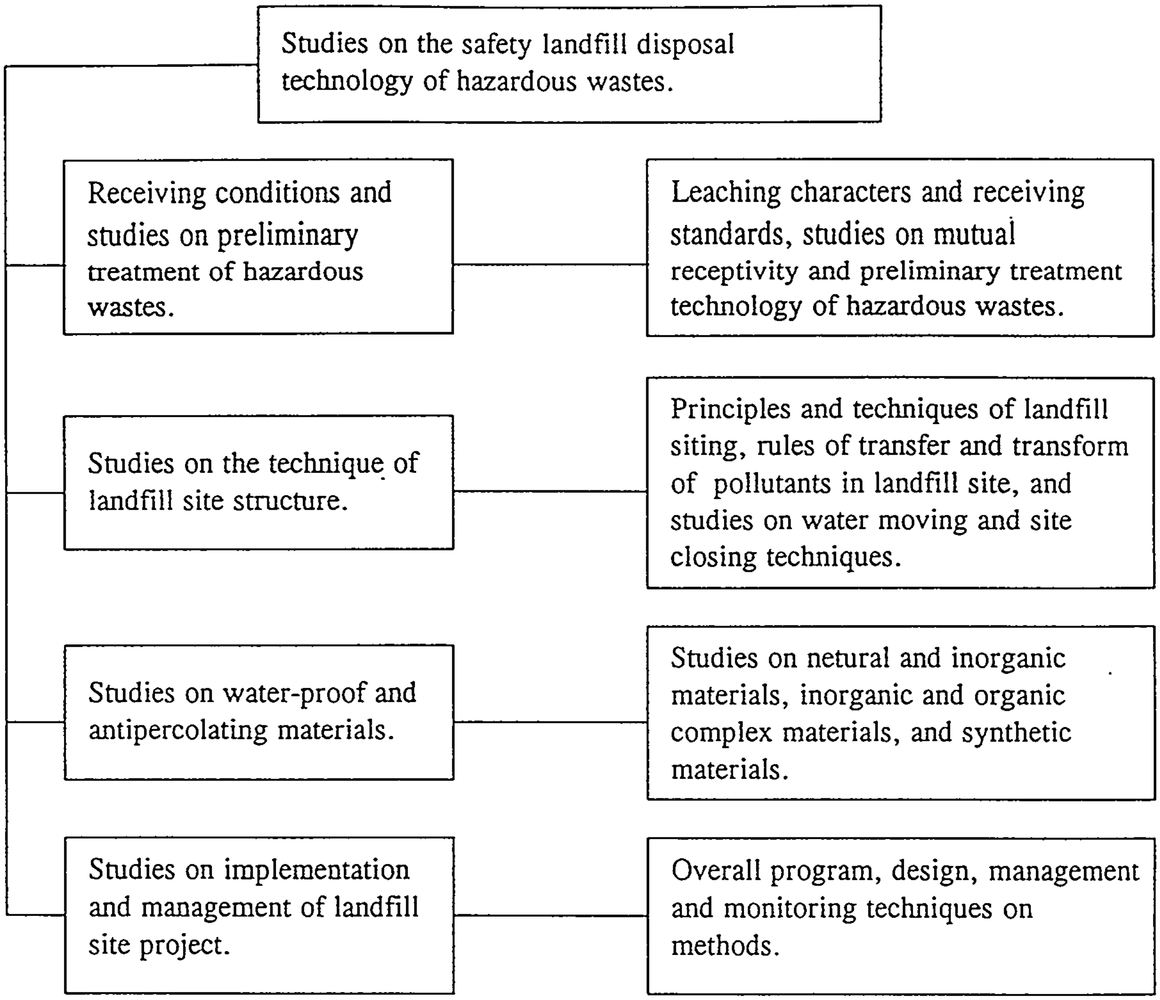


Fig. 4.1 Research Framework of the Techniques for Safety Landfill of Hazardous Wastes

- The principles and list for judgment of the mutual receptivity of hazardous wastes are determined.

4.1.2 Studies on the Technique of Landfill Structure

- The evaluation techniques and geographical information system for landfill siting and the computer software system for optimization of the siting are presented.

- The best conditions for the distribution and moving rules of pollutants in the clay layer and for the antipercolating coefficient up to 10^{-7} cm/s are proposed.

- The design software of the drainage collection system of the lining or drainage layer is presented, including prediction of the amount of leachate generated in the landfill site and the complementary design software for the site.

4.1.3 Screening and Development of Waterproof and Antipercolating Materials for the Landfill

- The research achievements for improving the property of clay and subclay layers are presented, integrating the soil and geological characteristics in China. The percolating coefficient is up to 10^{-9} cm/s.

- The inorganic and organic complex antipercolating material of polomer-cement concrete (PCC) is developed successfully

- The high-density polyethylene (HDPE), an organic antipercolating membrane, is developed successfully, and the HDPE rolling material production line is established in China. The antipercolating membrane has various specifications of 7 m wide and 0.7~2.5 mm thick.

4.1.4 Studies on Implementation and Management of Landfill Project

- The design and construction techniques of:
  - clay, PCC, and HDPE lining layers are proposed.
  - percolate control system are suggested.
  - monitoring system for the landfill are presented.
  - closing the landfill are proposed.

- The operational management technique and the guidelines of project implementation and management for the landfill are suggested.

4.2 Introduction of Some Key Techniques

4.2.1 Development of Antipercolating Manorial of Polymer-Cement Concrete

PCC is a new material made by adding polymer to the common gluing material of concrete — a two-phase complex material of cement and aggregate — to improve its gluing function. The main functional indices of PCC are shown in Table 4.1.

Table 4.1 Main Indices of PCC

Index	PCC		
	4%	8%	12%
Percolating coefficient Ks (cm/s)	4.46×10^{-11}	5.34×10^{-10}	7.50×10^{-8}
Compressive resistance (MPa)	36.1	33.8	26.4
Breaking strength	8.03	9.45	8.08

From the table it can be seen that the main functional indices of PCC fulfill the antipercolating requirements of the landfill.

- The mechanism of antipercolation is studied, and two results show that adding the polymer of propenoic acid ester for copolymerization can change the form of water-combined coagulated glue to make it more dense and to improve markedly the distribution of pores in the cement sludge so as to improve the antipercolation function.

- The design and construction techniques of antipercolating material PCC and the quality ensuring measures are proposed.

4.2.2 Design of Control System for the Percolate of Landfill

- In the studies, the pipe network with full flow of percolate has been compared with the network not with full flow, and it shows the latter has the following advantage:
  - There is enough empty space in the pipe to lead air flow simultaneously.
  - Under this condition of air flow, the decomposition of organic substances in the water can be promoted in pipe.
  - Thus, this pipe network possesses the functions of leading air flow and controlling water quality in addition to the traditional function of water discharge.

- The differences between these two kinds of pipe network in design are shown in Table 4.2.

Table 4.2 **Differences in Design of Pipe Networks with and without Full Water Flow**

Item	Pipe Network without Full Water Flow	Pipe Network with Full Water Flow
Pipe diameter calculation	50% empty space in pipe is enough to lead air flow	Without considering the air flow in pipe
Water discharge layer	Using stone flake of 50~150 mm in size	Using gravel of 5~10 mm in size
Pored pipe	Pored all over to facilitate both water and air flow	Pored only in the lower portion of the pipe
Vertical water collection or discharge	With sloping and vertical pipes to facilitate the vertical inflow of percolate and exchange of gas	Without vertical pipe and water discharge advocating to use engineering network

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PRIORITIES FOR TOXIC WASTEWATER MANAGEMENT IN PAKISTAN

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ABSTRACT

This study assesses the number of industries in Pakistan, the total discharge of wastewater, the biological oxygen demand (BOD) load, and the toxicity of the wastewater. The industrial sector is a major contributor to water pollution, with high levels of BOD, heavy metals, and toxic compounds. Only 30 industries have installed water pollution control equipment, and most are working at a very low operational level. Priority industrial sectors for pollution control are medium- to large-scale textile industries and small-scale tanneries and electroplating industries. Each day the textile industries discharge about 85,000 m^3 of wastewater with a high BOD, while the electroplating industries discharge about 23,000 m^3 of highly toxic and hazardous wastewater. Various in-plant modifications can reduce wastewater discharges. Economic incentives, like tax rebates, subsidies, and soft loans, could be an option for motivating medium- to large-scale industries to control water pollution. Central treatment plants may be constructed for treating wastewater generated by small-scale industries. The estimated costs for the treatment of textile and electroplating wastewater are given. The legislative structure in Pakistan is insufficient for control of industrial pollution; not only do existing laws need revision, but more laws and regulations are needed to improve the state of affairs, and enforcement agencies need to be strengthened.

1 INTRODUCTION

Toxic and hazardous wastes are generated from a wide range of industrial, commercial, agricultural, and even domestic activities (Batstone et al. 1989). These wastes can include solids, liquids, gases, sludges, and contaminated containers. In this study, the focus is on liquid wastes generated from Pakistan's main industries.

The inappropriate and careless handling of municipal and industrial wastes has created problems worldwide for human health and the environment. Effective control of toxic and hazardous wastes is of paramount importance for human health, environmental protection, and natural resource management. Developing countries like Pakistan, as they experience rapid industrial growth, have a particular and urgent need to initiate programs for hazardous waste management.

At this time, companies, even those having excellent past working records, must demonstrate a high level of commitment to environmental practices. This commitment must extend throughout the organization at every stage of production. Ideally, a commitment to overall quality management should automatically result in the minimization or reduction of wastes, directly at the source or simply through increased efficiency in production or supply and energy used. Such improvements have a direct environmental benefit and improve profitability.

In Pakistan, a logical first step for many companies should be the adoption of a formal environmental management system. Implementation of the National Environmental Quality Standards (NEQs) would provide a starting point for those companies really wishing to demonstrate their commitment to sound environmental practice.

All the evidence suggests that environmental awareness is still at an early stage among the industrialists in Pakistan. It is a fact that the majority thought that their industries would not be seriously affected by the enforcement of environmental legislation and NEQs. A number of companies in Pakistan claimed their activities had no impact on the environment, a claim made nowhere else in the world. Since the implementation of NEQs, the case for making regular audits of environmental performance a mandatory requirement is overwhelming, at least for all medium- and large-sized companies.

2 STATE OF THE ART

In many areas of Pakistan, industries are disposing of their wastewater in water bodies, in sewers, or on land, thereby causing unsanitary, unaesthetic, and unhygienic conditions. Industries generally use large quantities of water in production processes, resulting in huge waste streams. Traditionally, industries like to have minimum production costs, and they overlook social/environmental responsibilities. Investment in effluent treatment is naturally considered a nonproductive activity. The Government of Pakistan (GOP) *Census of Manufacturing Industries (1987-88)* indicated a total number of 4,753 industries in Pakistan (GOP 1993a).

This study aims to set priorities for industrial water pollution control through an assessment of wastewater flow from industries, BOD load, and wastewater toxicity and a review of existing treatment systems, resulting in technological as well as policy recommendations. A 1983 industrial pollution survey conducted by the GOP revealed that most of the industries discharged toxic and hazardous wastewater into the streams without any treatment (GOP 1983). Treatment units already existing are either inappropriate or inefficient to meet the satisfactory level of treatment.

2.1 Socioeconomic Impacts of Industrial Pollution

In Pakistan, 80% of illness and 40% of urban deaths are estimated to be caused by polluted water (GOP 1991). Chemicals and heavy metals in wastewater released into the water bodies have destroyed fish populations, leading to a decline in fish export — an important source of foreign exchange earnings. Agricultural lands around certain factories where wastewater is discharged have been rendered unfit for any kind of cultivation.

2.2 Water Pollution Control Legislation

A number of laws for water pollution control have been in existence since before the creation of Pakistan. In most cases, they do not meet the present requirements for environmental management. The latest additions to the legislation are the Punjab Local Government Ordinance (1979), Sind Fisheries Ordinance (1980), and Baluchistan Water and Sanitation Ordinance (1988). Pakistan's water pollution control legislation is listed in Table 1. The legislative provisions and penalties for the control and minimization of water pollution in the country are either inadequate or not clearly defined. To implement measures for pollution control in the country, the existing environmental legislation needs to be updated with more laws.

2.3 National Environmental Quality Standards

National Environmental Quality Standards (NEQs) have been implemented in Pakistan since August 1993 (Table 2). These standards allow management of waste from existing industrial units or installation of appropriate treatment methods until July 1996. Even after this deadline, however, industries not in compliance with these standards may not be penalized. Although the standards are relaxed when compared with the standards of some other countries (Fig. 1), the NEQs represent a positive sign for environmental protection in Pakistan. Strict and inappropriate standards always tend to be ignored and hence become counterproductive, causing the government's regulatory operations to be discredited. Over time, the standards may be tightened so they are brought to the level of the standards of advanced countries.

3 STRATEGIES AND METHODOLOGIES

3.1 Estimation of Wastewater Flow and Pollution Load

In Pakistan, data on water consumption and discharge of wastewater from various industrial groups are not available. However, wastewater generation was estimated for this study on the basis of (1) information on water consumption trends for various industries in Pakistan, (2) individual surveys, and (3) the limited data available. A detailed survey for this purpose has yet to be conducted.

Table 1 Water Pollution Control Legislation in Pakistan

Legislation (Year)	Agency	Offense	Penalty
Pakistan Penal Code (1860)	Provincial government	Fouling water of a public spring or reservoir	Maximum imprisonment of 3 months, or fine up to Rs 500, or both
Canal and Drainage Act (1873)	Provincial governments	Fouling the water of any canal, rendering it less fit for use	Imprisonment of 3 months, or fine of Rs 200, or both
Factories Act (1934)	Ministry of Industries	Disposing of untreated industrial waste in water bodies	Fine of Rs 500
Karachi Joint Water Board Ordinance (1949) and Rules (1956)	Karachi Joint Water Board Authority	Contaminating the water supply of water works	Undefined
Punjab Local Government Ordinance (1979)	Punjab Government	Polluting a water supply source for human consumption	The local council may rectify the situation and recover cost from the concerned party
Sind Fisheries Ordinance (1980)	Sind Government Fisheries Department	Discharging untreated sewage and industrial waste in water	Undefined
Baluchistan Groundwater Rights Administration Ordinance (1978)	Water Board under Government of Baluchistan	Discharging unlicensed industrial waste into sanitation system or water bodies	Imprisonment of one year, or fine, or both

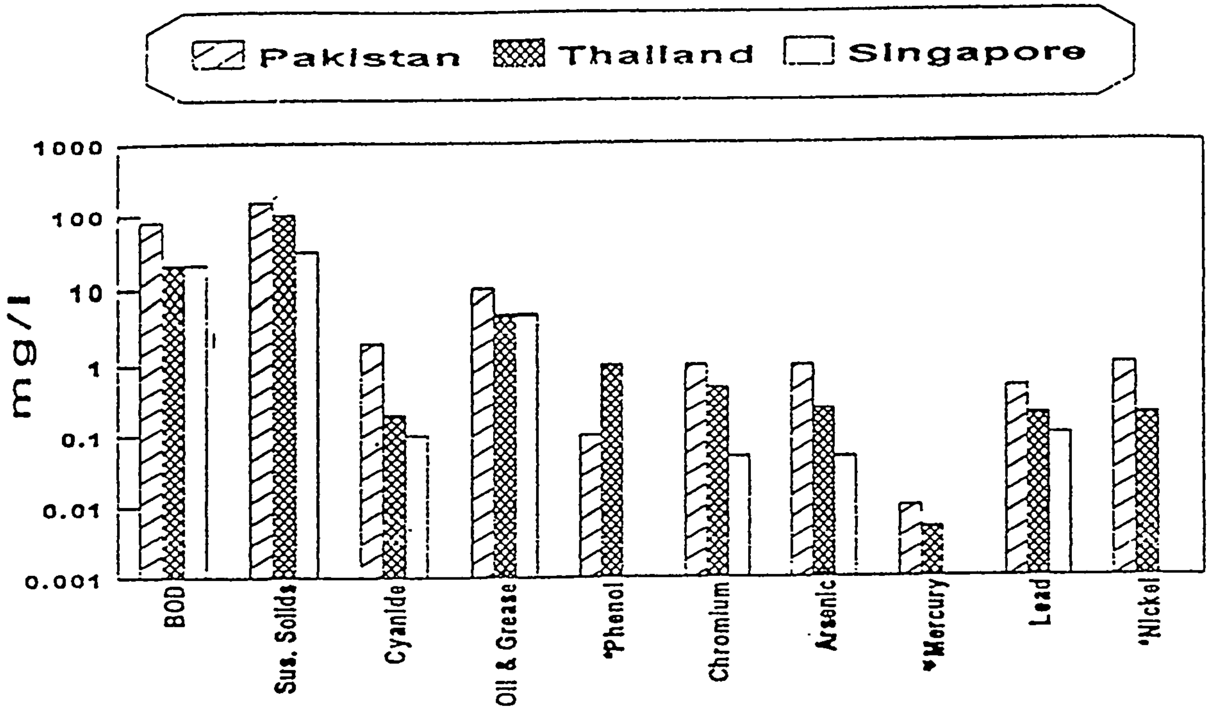
Sources: GOP (1991, 1993b).

The literature cites different values for wastewater discharge from various industrial activities. For example, Imhoff et al. (1971) states that 45-1,000 m^3 and Fresenius (1989) quotes that 50-100 m^3 of wastewater per ton of product are discharged from a textile dyeing and bleaching industry. The Environmental Protection Agency (Punjab) indicated that 1,200-3,650 m^3 of wastewater per day was generated from a medium-scale textile industry with a production level of 0.5-3.5 tons of finished product (Rahman 1994). These data indicate a higher water consumption trend for industries in Pakistan, mainly because most of them used groundwater and there was no restriction on the amount of wastewater that could be discharged into the sewer or drain. On average, a medium-sized industry uses 2,500 m^3 of raw water per day. Similar estimates for water consumption have been made for other industries (Rahman 1994). Tables 3 and 4 show the values for production, total wastewater discharged by each industrial group, total BOD load, and wastewater toxicity from small-scale industries and medium- to large-scale industries, respectively.

Table 2 National Environmental Quality Control Standards for Municipal and Liquid Industrial Effluents (values in mg/L unless specified)

No.	Parameter	Standard Value
1	Temperature (°C)	40
2	pH value	6.0-10.0
3	5-days BOD at 20°C	80
4	Chemical oxygen demand (COD)	150
5	Total suspended solids	150
6	Total dissolved solids	3,500
7	Grease and oil	10
8	Phenolic compounds	0.1
9	Chloride (as Cl)	1,000
10	Fluoride (as F)	20.0
11	Cyanide (as CN)	2.0
12	Detergents (as MBAS)	20.0
13	Sulfate (SO_4)	600
14	Sulfide (S)	1.0
15	Ammonia (NH_3)	40.0
16	Pesticides, herbicides, fungicides, insecticides	0.15
17	Cadmium	0.1
18	Chromium (trivalent and hexavalent)	1.0
19	Copper	1.0
20	Lead	0.5
21	Mercury	0.01
22	Selenium	0.5
23	Nickel	1.0
24	Silver	1.0
25	Total toxic metals	2.0
26	Zinc	5.0
27	Arsenic	1.0
28	Barium	1.5
29	Iron	2.0
30	Manganese	1.5
31	Boron	6.0
32	Chlorine	1.0

Source: PEPA (1993).



*Singapore standards require zero level

Fig. 1 Comparison of Effluent Standard Parameters

3.2 Prioritizing Industries for Water Pollution Control

The objective of priority setting is to identify a strategy for managing industrial water pollution problems in order to maximize the use of scarce resources. The source of a major share of the environmental problems in Pakistan is the industrial sector, which at present is not making any effort at controlling pollution. Thus, a systematic and easily understood method of prioritizing industries for water pollution control has been adopted on the basis of the "Multi-Criteria Choice Analysis" approach (Heredia 1993). To establish the ranking/priority of industries, criteria are valued from 1 to 10 on the basis of data shown in Table 4. For criterion 1 (No. of industries), an industrial sector composed of less than 100 industries was given a score of 1, while a sector composed of more than 900 industries got a score of 10. Similarly for criterion 2 (wastewater quantity), a flow rate of less than 10 m^3 was given a score of 1 while a rate above 90 m^3 got a score of 10. For BOD (criterion 3), less than 10 tons per day got a score of 1 and more than 90 tons per day got a score of 10.

Measuring toxicity is difficult. Toxicity is complicated by varying sensitivities of organisms to toxic compounds. Temperature, pH, dissolved oxygen, alkalinity, and salinity also affect toxicity values. For example, a reduction in dissolved oxygen from 6.0 to 4.0 mg/L can triple the toxicity of Kraft mill effluents to salmonoids (SDPI 1995). It is because of these cause-and-effect relationships that a general procedure has been adopted for valuating the toxicity level of various effluents. For

Table 3 Estimated Wastewater Discharge, BOD Load, and Wastewater Toxicity from Small-Scale Industries

Small-Scale Industry/Workshop	Approx. No. of Industries	Avg. Discharge per Factory	Estimated Total Effluent Discharge (000 m^3/d)	Avg. BOD (mg/L)	BOD Load (t/d)	Toxicity[a]
Dairy products	582	55 m^3/d	32	2,000	64	+
Tanneries	823	65 m^3/d	53	1,226	65	+++
Electroplating	1,150	20 m^3/d	23	570[b]	13	++++
Wheat and grain mills	214 (36,000 t/d)[c]	0.36 m^3/t	18	200	3.6	–
Bakeries and confectionery	918	5 m^3/d	4.6	1,500	6.9	+
Soap and detergent	586	5 m^3/d	2.9	200	0.6	++

[a] ++++ = most hazardous, +++ = moderately hazardous, ++ = potentially hazardous, + = nominal, – = no effect.

[b] COD (chemical oxygen demand).

[c] Production.

Source: Rahman (1994).

criterion 4 (degree of hazardousness), the industries were classified into three groups: (1) most hazardous industries such as pesticides, paints, acids and alkalies, fertilizers, and metal finishing (scores from 7 to 10); (2) moderately hazardous industries such as textiles, tanneries, pharmaceuticals, and pulp and paper (scores from 4 to 6); and (3) less hazardous industries such as glass, sugar, and food processing (scores from 1 to 3).

Each criterion was weighed in terms of percentage (according to its importance with regard to environmental degradation). The priority-setting exercise is represented in Tables 5 and 6, and the ranking of industries is shown in Table 7.

4 CASE STUDIES

4.1 Textile Industry

The textile industry is a major industrial sector in Pakistan that uses a large quantity of water in its production process. The existing state of matters is alarming because highly polluted and toxic wastewater is being discharged into the sewer/drain without any level of treatment. The wastewater

Table 4 Production, Wastewater Flow, BOD Load, and Wastewater Toxicity from Medium- to Large-Scale Industries

Industrial Sector and Industry	Total Production	Effluent per Unit of Production	Total Flow (10^3 m^3/d)	Avg. BOD (mg/L)	Total BOD (t/d)	Toxicity[a]
Food, beverages, and tobacco						
Food processing	1,797 t/d	25 m^3/t	45	800	36	+
Beverages	676,493 L/d	10 L/L of product	6.8	1,500	10.2	+
Sugar	6,362 t/d	2.3 m^3/t	14.6	700	10.2	+
Vegetable oil	1,797 t/d	13.7 m^3/d	24.6	900	22.1	+
Textile, apparel, and leather						
Textile manufacturing	170 t/d	500 m^3/t	85	450	38.2	++
Paper, printing, and publication						
Pulp, paper, and paper board	130 t/d	228 m^3/t	30	2,500	75	++
Chemicals, rubbers, and plastics						
Fertilizers	7,658 t/d	60 m^3/t	4.6	500	2.3	+++
Chemicals	1,797 t/d	25 m^3/d	45	800	36	+++
Paint and varnishes	52 t/d	10 m^3/t	0.5	350	0.2	++++
Basic metal industries						
Iron and steel	5,732 t/d	7 m^3/t	40.1	300	12	++
Nonmetallic mineral products						
Cement	23,000 t/d	2 m^3/t	46	[b]	–	–

[a] ++++ = most hazardous, +++ = moderately hazardous, ++ = potentially hazardous, + = nominal, – = no effect.

[b] Contains inorganic suspended solids.

Source: Rahman (1994).

Table 5 Computations for Ranking Small-Scale Industries

Industry	No. of Industry 15%	Wastewater Flow 20%	BOD Load 25%	Degree of Toxicity 40%	Weighted Average 100%	Rank
Dairy products	6	4	7	1	3.85	3
Tanneries	9	6	7	5	6.30	1
Electroplating	10	3	1	9	5.95	2
Wheat and grain mills	3	2	1	1	1.50	6
Bakeries and confectioneries	10	1	1	3	3.15	5
Soaps and detergents	6	1	1	5	3.35	4

Source: Rahman (1994)

Table 6 Computations for Ranking Medium- and Large-Scale Industries

Industrial Sector/Industry	No. of Industries 15%	Wastewater Flow 20%	BOD Load 25%	Degree of Toxicity 40%	Total Weighted Average 100%	Rank
Food, beverages, and tobacco						
Food processing	2	5	4	2	3.1	7
Beverages	1	1	2	1	1.25	10
Sugar	1	2	2	2	1.85	9
Vegetable oil	2	3	3	3	2.85	8
Textile, apparel, and leather						
Textile manufacturing	10	9	4	5	6.3	1
Paper, printing, and publication						
Pulp, paper, and paper board	1	3	8	4	4.35	3
Chemicals, rubbers, and plastics						
Fertilizers	1	1	1	7	3.40	6
Chemicals	1	5	4	7	4.95	2
Paints and varnishes	1	1	1	8	3.80	5

Table 6 (Cont.)

Industrial Sector/Industry	No. of Industries 15%	Wastewater Flow 20%	BOD Load 25%	Degree of Toxicity 40%	Total Weighted Average 100%	Rank
Basic metal industries						
Iron and steel	3	5	2	5	3.95	4
Nonmetallic mineral products						
Cement	1	5	–	–	1.15	11

Source: Rahman (1994).

Table 7 Industries Ranked in Order of Priority for Pollution Control

Medium- to Large-Scale Industries	Rank	Small-Scale Industries	Rank
Textile manufacturing	1	Tanneries	1
Chemicals	2	Electroplating	2
Pulp and paper	3	Dairy products	3
Iron and steel	4	Soap and detergents	4
Paints and varnishes	5	Bakeries and confectioneries	5
Fertilizers	6	Wheat and grain mills	6
Food processing	7		
Vegetable oil	8		
Sugar	9		
Beverage	10		
Cement	11		

Source: Rahman (1994).

from textile dyeing and finishing products is highly colored, is usually alkaline, contains a substantial amount of suspended solids, and is high in BOD/COD and temperature. The largest share of BOD comes from desizing operations. Data on the flow and characteristics of wastewater from a representative textile industry are given in Table 8.

The best practicable approach for the treatment of textile wastewater is a combination of chemical and biological processes. In-plant control measures can reduce wastewater discharges, resulting in

Table 8 Characteristics of Wastewater from a Typical Textile Industry

Characteristics	Values
Average discharge	3,000 m^3/d
Average production	3.5 tons/d
Wastewater produced	857 m^3/t of fabric
Temperature	40°C
pH	10.5
BOD at 20°C	250 mg/L
COD	640 mg/L
Total dissolved solids	5,740 mg/L
Suspended solids	620 mg/L
Chlorides	1,150 mg/L
Sulfates	83 mg/L
Sulfide	17 mg/L

Source: EPA-Punjab (1991).

lower treatment costs. The factors that obstruct small-scale factories from adopting pollution control measures include low capital investment, tight factory space, and lack of expertise.

For small- and medium-size industries to maintain competitiveness, treatment methods to be used must be effective, compact, easy to operate, and affordable. The cost of treating textile wastewater has been estimated to be U.S. $0.32 per m^3 of wastewater (Dharmappa 1992). Various waste minimization techniques, such as in-plant control measures and production process modifications, can be adopted. They can reduce the quantity of wastewater generated, thereby reducing the treatment requirements.

4.2 Electroplating Industry

Electroplating industries exist as small-scale workshops. They have been estimated to number 1,150 and are located throughout the country. Although the quantity of wastewater produced by the electroplating industry is comparatively small, the wastewater is highly toxic because of the presence of copper, zinc, nickel, cadmium, chromium, acids, alkalies, and the highly dangerous cyanides. In order of priority among small-scale industries, this industry gained second position after the tannery industry. Since a great deal of work has already been done by the tannery industry in Pakistan, the electroplating industry was chosen for a case study. The principal sources for the wastewater discharged from plating operations are drag-out from rinse vats used to remove electroplating solution films, dumps that occur during cleanup of tanks and vats, and vat blowdown and cooling water.

It is not practical for small-scale electroplaters to treat their wastewater because of the high initial investment requirements and operating expenses. A treatment system may cost up to 50% of the total investment in plating equipment (SEATEC International 1990). A careful strategy will help small-scale industries to manage their waste streams within the present structure; a rigorous enforcement of standards among small platers might cause them to close down their businesses. The strategy could include (1) waste minimization and drag-out reduction through process modification and segregation of wastewater, and (2) establishment of central treatment plants where plating wastes can be treated by removing cyanide, chromium and other metals, oil, and grease. The cost for treating electroplating wastewater has been estimated to be U.S. \$1.27 per m^3 of wastewater (Rahman 1994).

5 RECOMMENDATIONS AND GUIDELINES

5.1 Policy Planning

1. Short- and long-term plans for dealing with industrial water pollution could be framed in line with the priorities set in this study. Resources could be allocated accordingly. This effort would require a complete survey of all industrial units to obtain data on the wastewater discharged from them.

2. Political consensus should be built to foster the development, implementation, and enforcement of proper legislation, and special emphasis should be placed on industries producing hazardous wastes.

3. An awareness campaign could be launched to make people realize the pollution problems and to put pressure on industrialists.

4. Adequate, formal enforcement procedures must be defined clearly. The monitoring system also needs to be strengthened. Because the existing penalties and fines for violating the laws are inadequate, the laws have lost their significance. These should be revised.

5. Large-scale industries could be offered economic incentives such as tax rebates, subsidies, soft loans, etc., in lieu of having to adopt pollution control measures.

6. The environmental institutions must be strengthened; they are starving because of the lack of a trained workforce, monitoring equipment, and legislative support.

7. The industries should be grouped as large-, medium-, and small-scale industries, and each group should be subdivided into hazardous, moderately hazardous, and less hazardous.

8. Discharge permits should be introduced, where necessary, to make standards flexible for small-scale industries, allowing them to implement a pollution control program step by step.

9. Central treatment plants could be erected for small-scale industries; they should have an affordable treatment fee.

10. Training should be provided to assist industry in planning and implementing environmental measures.

5.2 Technological

1. The industries should adopt clean production technologies for wastewater minimization through in-plant changes and process modifications.

2. The large-scale textile industries should build their own treatment plants for removing color and BOD from wastewater.

3. The treatment technology for small-size textile factories should be chemical coagulation and neutralization of wastewater at the factory site and then discharge into the sewer till facilities of a central treatment plant for biological treatment.

4. The wastewater from electroplating industries should be required to achieve a certain degree of detoxification before being discharged into municipal sewers. At a later stage, when central treatment plants become operational, segregated wastewaters should be collected and treated for recovery/neutralization of metals.

5. If possible, the small-scale electroplating industries should be relocated near the treatment facilities, and the monitoring system should be improved.

6. The old, highly polluting equipment at the factories should be replaced with new, sophisticated equipment that is not only efficient in terms of production but also less polluting.

6 CONCLUSION

Because the existing industries in Pakistan have been indiscriminately discharging toxic substances into the water bodies, they are posing a great threat to human beings, livestock, and plants. The legislative framework requires improvements to control this situation. The textile, chemical, and pulp and paper industries have been revealed as the priority large-scale industries for water pollution control, while tanneries and electroplating industries are the primary small-scale industries that need to control pollution. The costs for treating textile and electroplating wastewater have been assessed as U.S. \$0.32 and \$1.27 per m^3 of wastewater, respectively. Total investment requirements for the whole country have been assessed to be U.S. \$98.4 million for the textile industry and \$76.1 million for the electroplating industry. It is felt that the industries discharging hazardous wastes to the environment should be stopped immediately from this practice through any means.

7 PHASE-WISE INVESTMENT SCHEDULE

Pakistan is a developing country, where the lack of resources is the main hurdle in successfully implementing a strategy. This study refers to the phase-wise implementation of a pollution control strategy for priority industries in Pakistan. Requirements for other industries could also be devised on similar lines. The total investment required for wastewater management in the textile and electroplating industries in various phases is estimated to be Rs 1,309 million (for 1995-97), Rs 1,832 million (for 1998-2000), and Rs 2,094 million (for 2001-2003). A brief implementation schedule is given in Table 9.

Table 9 Implementation/Investment Plan in Priority Industries[a]

	Pollution Control Technologies		
Industry/Investment	Year 1996-1998	Year 1999-2001	Year 2002-2004
Textile (small scale)	Chemical coagulation, flocculation/sedimentation, pH adjustment (batch)	Activated sludge process at CTP (wastewater from SSIs may be pretreated)	Tertiary treatment at CTP for color removal by ozonation, H_2O_2, if necessary
Textile (large scale)	Equalization, chemical precipitation, sedimentation, wastewater segregation, neutralization	Activated sludge process (at plant site)	Tertiary treatment by ozonation or H_2O_2 treatment
Investments	Rs 738 million	Rs 1,033 million	Rs 1,181 million
Electroplating (small scale)	Process modification, drag-out reduction, wastewater segregation, neutralization	Chemical precipitation of metals and removal of cyanide and chromium (+6) at CTP	Advanced treatment for metal recovery, ion exchange, electrolysis
Investments	Rs 571 million	Rs 799 million	Rs 913 million

[a] CTP = central treatment plant, SSIs = small-scale industries.

Source: Rahman (1994).

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LOCAL GOVERNMENT'S POLLUTION PREVENTION PROGRAM

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ABSTRACT

The pollution prevention program operated by the Health Department of Boulder County is called Business Partners for a Clean Environment (Business Partners). It is a cooperative effort among local businesses, the City of Boulder, Boulder County, and the Boulder Chamber of Commerce. This nonregulatory, incentive-based program provides industry with pollution prevention information and technical assistance necessary to reduce and/or eliminate environmental waste. This paper provides an overview of the program development, creation of partnerships and trust, and some of the results from implementation of the program. Following the first 18 months of the program, 35 businesses were recognized as Business Partners. The Business Partners program has also received an achievement award from the National Association of Counties for promoting "responsible, responsive, and effective government" and two governor's awards from the State of Colorado. Participating businesses have demonstrated that a pollution prevention program can reduce environmental waste, increase employee safety, and decrease costs.

1 BACKGROUND

The Boulder County Health Department (BCHD) established a pollution prevention (P2) program in November 1993. It was developed on the premise that preventing pollution is the most effective method for protecting public health and the environment. In addition, P2 often enables a business to operate at lower costs, to improve working conditions, to reduce environmental liability, and to require fewer regulatory requirements. The BCHD's P2 program, together with local government agencies and private-sector organizations, assists businesses in voluntarily reducing pollution. Thus far, the program has focused on small- to medium-sized businesses, such as auto repair shops, auto body shops, printers, metal finishers, and printed circuit board manufacturers. The program aims to inform businesses and regulators about available P2 technologies and to assist in implementing these alternatives by providing educational materials and on-site technical services. To date, the BCHD has established three programs. These programs are discussed in Secs. 1.1-1.3.

1.1 Business Partners for a Clean Environment

Business Partners for a Clean Environment is a cooperative effort among the City of Boulder, BCHD, and the Boulder Chamber of Commerce. This nonregulatory program is designed to encourage businesses to voluntarily prevent pollution. The program assists businesses in implementing P2 measures through industry-specific workshops, conducting on-site P2 assessments, providing technical assistance, and recognizing the participating businesses publicly.

1.2 Mentor Program

The Mentor Program, established in conjunction with the Boulder County Clean Air Consortium, facilitates the communication of P2 technologies within the local business community. The program matches a large company, which has incorporated P2 approaches, with a small business using similar chemicals and/or processes, to effect an exchange of P2 information and technology.

1.3 Regional Training Program

The Regional Training Program is an educational program designed to train government and business personnel in a nine-county region throughout Colorado to implement P2 measures. Training is provided through workshops directed at industry and local government.

Small- to medium-sized businesses are not usually considered major sources of pollution by themselves, but their accumulative effect on the environment can be significant. This, together with the realization that most of these businesses do not have the resources available to employ the staff needed to address environmental concerns, is the main reason that BCHD developed a P2 program to focus on these industries. This paper focuses on the Business Partners program.

2 DEFINING POLLUTION PREVENTION[1]

The goal of P2 is to reduce present and future threats to human health and the environment. Pollution prevention is a multimedia approach that minimizes or eliminates pollutants released to the land, air, and water without shifting pollutants from one media to another. The Pollution Prevention Act of 1990 defines P2 as:

> *...any practice which reduces the amount of a hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment prior to recycling, treatment, or disposal; and any practice which reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants.*

Facilities can implement P2 through:

- Equipment or technology modifications;
- Process or procedure modifications;
- Substitution of raw materials; and
- Improvements in housekeeping, maintenance, training, and/or inventory control.

2.1 Waste Management Hierarchy

The goal of a P2 program is to eliminate or reduce the generation of pollutants and wastes at the source through careful consideration of materials usage, production processes, and waste management practices. A P2 program should identify opportunities for reducing the use of hazardous materials and the generation of wastes or releases, as well as opportunities for protecting natural resources through conservation and more efficient use of energy and water.

The Pollution Prevention Act of 1990 includes a waste management hierarchy that assigns the highest priority to source reduction, followed by (in descending order) recycling, treatment, and disposal.

2.2 Source Reduction

Source reduction refers to the use of materials, processes, or practices that reduce or eliminate the quantity and toxicity of wastes at the point of generation. Source reduction opportunities include raw material substitutions, improved operation practices, and process and equipment changes.

Raw material substitutions means replacing hazardous materials with less hazardous (or less toxic) alternatives to reduce accidental spills and releases to the environment. Many businesses have substituted less or nonhazardous solvents for hazardous ones, replaced petroleum-based inks with vegetable-based inks, or switched to high-solids/low volatile organic compounds (VOC) paints.

Process and equipment modifications refer to changes in processes and equipment that present significant opportunities for source reduction. For example, some businesses have implemented high-volume, low-pressure (HVLP) spray guns to replace the standardized spray gun, replaced a Freon 113 vapor degreaser with a deionized water parts washer, and installed modern dry cleaning machines (closed loop) to replace the older (open loop) systems. Also, many businesses have installed a filter on parts washing units to remove contaminants, thus lengthening the life of the solvent.

2.3 Recycling

Recycling turns by-products and wastes into reusable products. Recycling includes such practices as on- or off-site recycling, materials exchange or reuse, and raw materials recovery.

Both on- and off-site recycling can help reduce dependence on expensive virgin materials by reusing spent materials. Several businesses have installed antifreeze recycling machines that filter out the contaminants, returning the antifreeze into a reusable product. Others have a distiller that recovers the lacquer thinner from paint gun cleaning operations, thus reducing the need for virgin lacquer thinner.

The concept of a materials exchange program is to turn waste from one business into a raw material for another business. This concept is often used when a company has substituted a nonhazardous raw material, but still has some hazardous material left. This hazardous material can be used by another business, which reduces the treatment/disposal costs and liabilities of the original user.

2.4 Waste Treatment

Waste treatment applies to waste after it has been generated. The goal of waste treatment technologies is to neutralize the waste and recover energy or material resources, which in turn renders the waste nonhazardous and/or reduces the volume.

2.5 Waste Disposal

Waste disposal should be considered only when all other options have been exhausted. Disposal is considered the least-favored waste management method because of the associated costs and environmental impacts. The number of permitted waste sites available for disposing of hazardous material is limited, and many within the United States are approaching capacity. Also, transport of wastes may pose hazards. Finally, recordkeeping and reporting requirements associated with the disposal of hazardous wastes are an additional burden that can be avoided through preventive measures, such as source reduction.

2.6 Pollution Prevention Benefits

Facilities gain both direct and indirect benefits by implementing P2 options. A key benefit of source reduction is a decrease in operating costs associated with waste management. These costs may include expenditures for raw materials; waste disposal; transport, handling, and storage; training; management overhead; and emergency response. Furthermore, future costs, such as remediation activities, can also be avoided with source reduction activities.

Additionally, source reduction can produce positive health and environmental benefits. Minimizing the use of hazardous materials creates a safer workplace and reduces the need for expensive health and safety protection devices. Such positive impacts quite often improve employee job satisfaction. The environmental benefits include decreases in the volume of toxic substances released to the environment from spills, leaks, and air emissions due to the reductions in the use of hazardous materials. In a time of increasingly stiff penalties for hazardous waste management, remaining in compliance with environmental regulations is a top priority.

3 GROWING POLLUTION PREVENTION FROM THE BOTTOM UP

In the United States, the Environmental Protection Agency (EPA) is the regulatory agency that governs the polluting industries at the federal level. States can apply for, and be granted, the authority to regulate businesses if they meet requirements established by the EPA. The State of Colorado has completed this task and has regulatory authority. Because of the lack of resources to adequately cover the entire state, Colorado subcontracts the regulatory inspections to local or county governments. The BCHD has been given authority to perform regulatory inspections. This is where government and industry can meet at odds, hence, the establishment of BCHD's P2 program to help government and industry work together to achieve environmental protection.

The BCHD's P2 program was designed to assist the small- to medium-sized businesses of various industry types with their environmental concerns. These are the companies that do not have the resources to provide an environmental person or staff needed to address their environmental problems. Most of these businesses learn about environmental regulations through trade associations, conferences, or when a regulator shows up for an inspection. Boulder County's P2 program assists, trains, and educates businesses not only on the environmental regulatory concerns, but also on P2 measures that lessen and/or eliminate the regulatory burden. Businesses appreciate local government support (Boulder County's P2 program) because it provides them with the information they need to make a difference rather than a "command and control" approach that offers no alternatives.

4 INTERGOVERNMENTAL COOPERATION

The city and county of Boulder have formed a partnership that combines resources and expertise to maximize the effort of promoting P2 and regulatory information to industry. The partnership was established to provide a uniform governmental approach to assist industry in understanding and applying environmental and P2 regulations. Many governmental agencies have regulations that may conflict or are vaguely written with several possible interpretations. Business Partners meets with these regulatory agencies, discusses and disseminates the regulatory information, and then forwards these results to industry. This process streamlines the regulations and can be applied on an industry-by-industry basis. This service saves industry time and money in developing and implementing individual environmental management programs.

The City of Boulder provides 30% of the funding necessary to support a full-time person dedicated to P2 at the county level, a room for the P2 workshops, food at the workshops, and any material not produced by the BCHD. The city also designed the Business Partners logo and pays for advertising when required. The BCHD selects the type of industry to focus on P2 efforts, disseminates the environmental regulations, develops P2 materials and industry-specific criteria, performs all site assessments, calculates P2 results, and decides which shops qualify for public recognition based on the P2 measures implemented. Finally, the Boulder Chamber of Commerce occasionally provides a room to hold the workshops and promotes the Business Partners program in their mailings.

5 EARLY INVOLVEMENT OF INDUSTRY

It was the objective of the BCHD to include industry and government at all levels in the development of the Business Partners program. Thus, the program was initiated through focus group meetings consisting of representatives from government, trade associations, and industry. The focus groups provided a forum for working with industry directly, learning about their ideas, listening to their concerns, and incorporating their thoughts into an industry-specific program, thus winning industry support from the start. These focus groups also determined how the Business Partners program could best be designed to facilitate P2 and regulatory information within the industry. Additionally, the focus groups established program criteria for each industry. The program criteria are industry-specific and consist of a combination of regulatory issues plus P2 options a business should investigate. In this way, the criteria were developed with input from industry representatives to obtain practical and realistic P2 goals. Getting industry involved early in the process not only created an "ownership" quality for industry, but started the "trust" process between industry and government. This approach identified what an industry can do to be environmentally proactive versus reacting to the regulatory laws.

Following the focus group meetings, industry-specific workshops were held to disseminate information on P2/compliance issues and to promote the Business Partners program to the rest of the regulated community. These workshops covered compliance issues, updates to businesses on the latest changes in regulatory requirements, P2 issues, discussions on P2 alternatives, and available P2 technologies.

6 INDIVIDUAL OUTREACH AND FOLLOW-UP

Following a workshop, a business interested in the Business Partners program was invited to receive a pre-P2 on-site assessment, which established an environmental baseline. The purpose of this assessment was to identify and prioritize environmental waste streams (hazardous wastes, solid wastes, air emissions, and water effluents); provide P2 alternatives, together with the costs and benefits associated with each P2 option; and obtain commitment from the business to incorporate P2 techniques. Business Partners established a fixed timeline of six months for businesses to create and implement a P2 program. Figure 1 gives a step-by-step description of a P2 program.

Following the six-month period, a post-P2 assessment was performed. This assessment measured the costs and environmental benefits of incorporating a P2 program. It also determined which P2 options were most effective and identified any barriers or problems associated with incorporating a P2 program.

7 QUANTIFIABLE RESULTS AND ACCOMPLISHMENTS

This section presents the results of the Business Partners program 18 months after its inception. Calculating the results of the program in terms of pollutants reduced is somewhat difficult because of the diversity of P2 measures implemented and tracking of quantities of pollutants generated at the participating shops. However, the shops provided detailed information to the Business Partners staff during initial and follow-up visits, which was the source of the information described here. The following tables summarize the participation rates, the quantity of pollution prevented as a result of the program, the environmental benefits of the measures, and the costs associated with implementing a P2 program.

7.1 Participation Rates

Table 1 presents the number of shops participating in the program and those that became fully certified by completing all of the program criteria. As can be seen from the table below, auto body shops have a participation rate of 30%, which is the highest for the three industries.

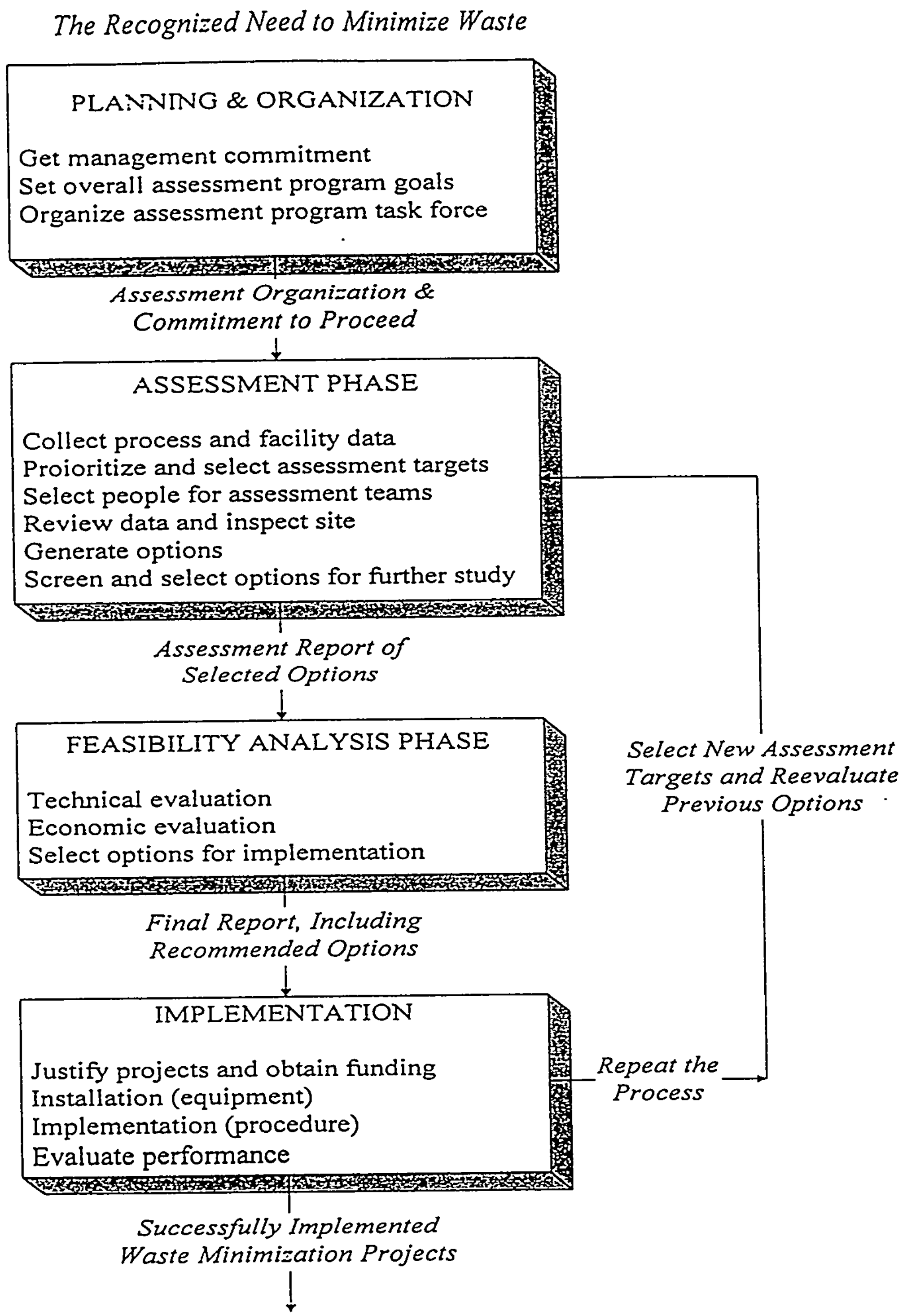

Fig. 1 The Waste Minimization Assessment Procedure[2,3]

Table 1 Summary Statistics on the Business Partners Program (Summer 1996)

Statistic Measured/Type of Shop	No. of Shops	Total (%)
Approximate number found in Boulder		
Auto repair	100	100
Auto body	20	100
Printers	35	100
Certified (both partial and full)		
Auto repair	17	17
Auto body	6	30
Printers	9	26
Fully certified (completed all criteria)		
Auto repair	12	12
Auto body	6	30
Printers	2	6
P2 measures implemented		
Auto repair	29	66
Auto body	6	100
Printers	NA	NA
Met program criteria prior to audit (% of total certified)	7	22

This is likely due to the fact that an equal amount of time was spent on each industry, and the number of auto body shops is smaller than the other two. Regarding the number of P2 measures implemented by businesses, auto repair shops have completed the most, averaging almost two measures per shop. Furthermore, auto body and repair shops were successful in completing the measures needed for certification. Repair shops completed 66% of all P2 measures needed to become fully certified, and all auto body shops became fully certified.

Since the compilation of these data, the metal finishing and printed circuit board industries have joined the Business Partners program. In fact, a metal finishing and printed circuit board P2 workshop was provided, with 50% of the total number of metal finishing and printed circuit board shops in Boulder County attending. All have expressed a desire to enroll in the Business Partners program. Additionally, 23 auto repair, 5 auto body, and 6 print shops have joined the Business Partners program since June. Figure 2 depicts the overall program participation rate through October 1996.

7.2 Quantity of Pollution Reduced

The primary pollution reductions achieved during the first 18 months of the Business Partners program are summarized in Table 2. These reductions were estimated based on initial and follow-up visits with the participating businesses. The statistics provided on the reductions achieved in air, waste, and wastewater are aggregated across industries and include a variety of pollutants within each category.

Figure 3 demonstrates air emissions reduced as part of the program.[4] Volatile organic compound emissions have been calculated from auto body shops and printers, although some hazardous air pollutants may have been reduced as well. At auto body shops, VOC emissions were reduced primarily through the use of HVLP spray guns, which reduced the amount of paint lost to overspray. Computerized paint mixing used in conjunction with HVLPs dramatically reduces the amount of waste paint generated for each vehicle. At auto body shops alone, VOC reductions were 6.1 tons per year. The remaining 2.9 tons of the VOC reductions was attributable to printers. The reduction of VOCs at printers was primarily achieved through reductions in isopropyl alcohol in fountain solutions, use of less volatile blanket and roller washers, and increased use of soy-based inks.

The hazardous waste reductions presented in Table 2 can be attributed to auto repair shops that switched from hazardous to nonhazardous solvents in their parts washers. It was assumed that the solvent is nonhazardous when leaving the shop, although it is possible that the solvent could become

Table 2 Pollutant Reductions Achieved by the Business Partners Program (Summer 1996)

Pollutant Category	Type of Pollutant Reduced	Quantity Reduced/Year
Air	VOCs from thinners, solvents, inks, paints	9.0 tons[1]
Hazardous waste	Switched solvents in parts washers	2,100 gallons[2]
Solid waste	Recycled products (oil filters, aerosol cans, paints, inks)	2.3 tons[3]
Wastewater discharge	Antifreeze discharged to POTW	960 gallons[4]

[1] Source: Toomey (1996).

[2] Estimated assuming eight parts washers with 30-gal solvents tanks serviced (i.e., hauled for recycling) every 6 weeks switched to a nonhazardous solvent serviced every 12 weeks.

[3] Estimated based on reported reductions of 5,700 filters, 2,250 cans, and 80 gal of paint, assuming filters and cans weigh 1 lb each and paint weighs 12 lb/gal. Paint reduced could be hazardous material if it contained metals. Cardboard, metal, and glass also may have been recycled, but quantities of these materials were not tracked.

[4] Estimated based on reported use of antifreeze.

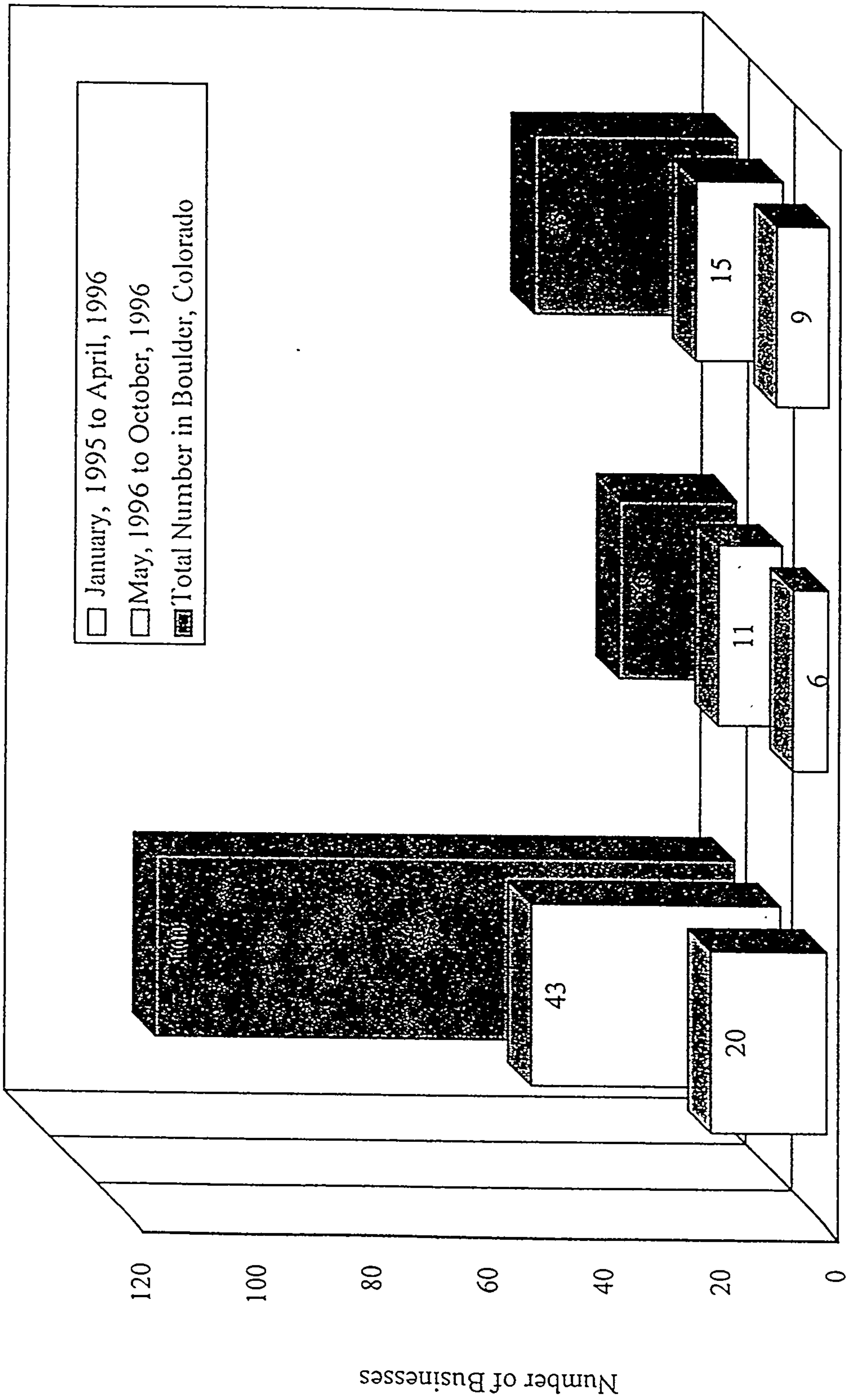

Fig. 2 Summary Statistics of Businesses Participating in the Business Partners Program

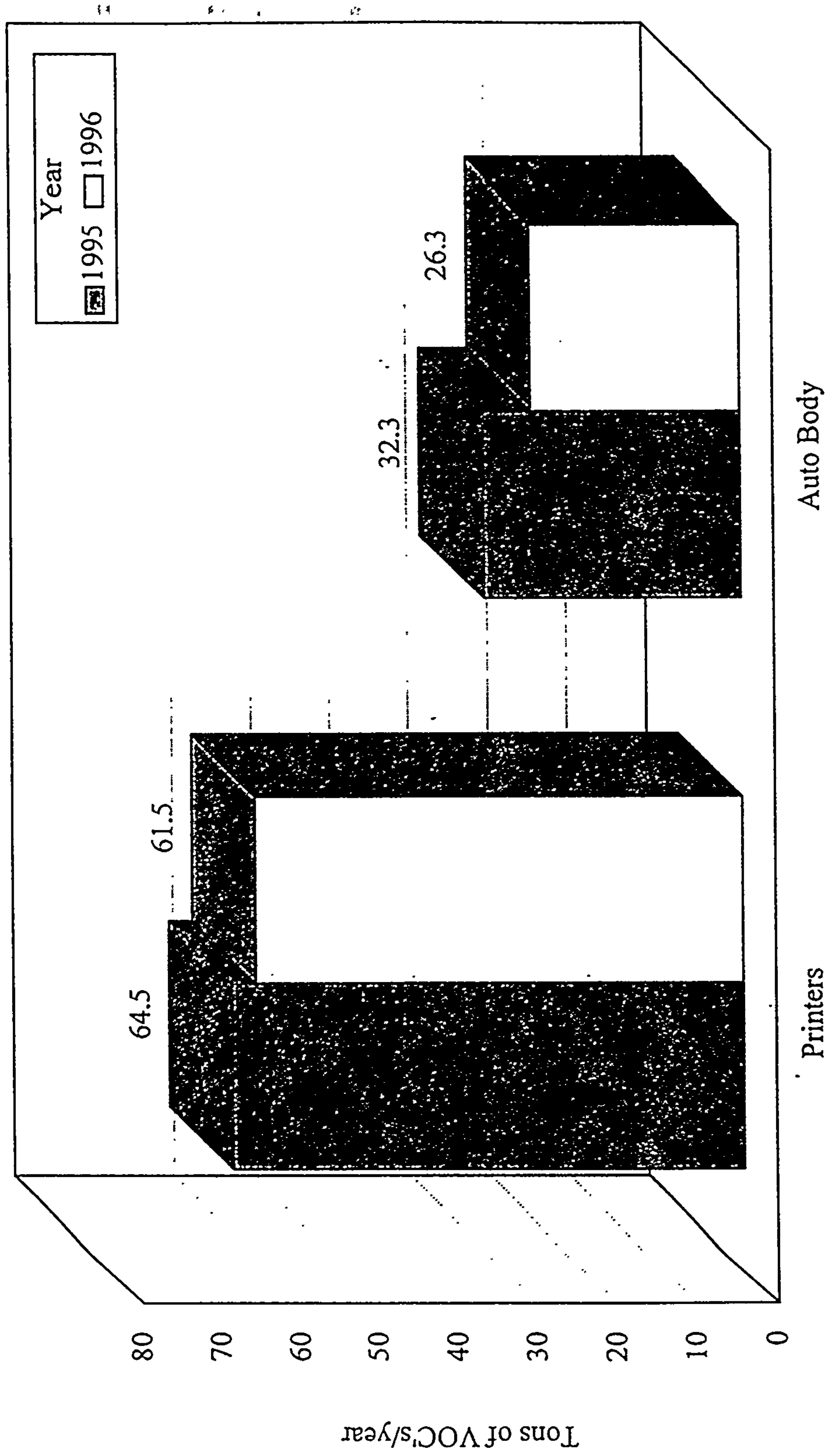

Fig. 3 Air Emission Reductions (VOCs) Achieved from Pollution Prevention (*Business Partners for a Clean Environment*)

contaminated in the shop with chlorinated cleaners, metals, or other contaminants present on the parts being washed. A total of 7 shops, one with two units, switched to nonhazardous solvents, resulting in a reduction of about 2,080 gal of hazardous waste per year. The amount of hazardous solvent reduced was conservatively estimated by assuming that it was removed every 6 weeks, rather than every 4 weeks, which is sometimes the case. Other potential hazardous waste reductions were not calculated, such as reduced paint thinner purchases resulting from the use of HVLPs or switching from metal- to nonmetal-based paints and inks.

The solid waste reductions are based on materials formerly discarded in the garbage that are now either recycled or no longer used. The items included in the solid waste estimate were spent oil filters and aerosol spray cans (cleaners and paints). Spent oil filters are generally punctured and drained by shops and thrown in the garbage. However, they can be recycled for metal content, and the Business Partners program encouraged 7 shops to recycle more than 5,000 filters each year. In addition, the program encouraged a number of shops to buy brake and carburetor cleaning fluids in bulk, rather than in individual aerosol cans. As a result, more than 2,000 aerosol cans were eliminated each year. The estimate of solid waste reduced does not include recycled cardboard, glass, aluminum cans, and batteries.

The reductions in wastewater discharges pertain to antifreeze that is often discharged to the sewage treatment plant rather than collected. Spent antifreeze is a problem for sewage treatment plants because it contains concentrations of metals, especially copper. Antifreeze can be recycled with the use of on-site units that filter the metals, or it can be collected for off-site recycling. The Business Partners program worked with the local shops that were discharging antifreeze to the sewage treatment plant to develop a recycling plan. This resulted in a reduction of almost 1,000 gal/yr of antifreeze entering the public sewage system from these shops.

7.3 Environmental Benefits

The environmental benefits of these reductions are summarized briefly in Table 3. The primary environmental benefit of the air emissions reductions was the elimination of VOCs, which contribute to ground-level ozone formation. Ozone causes smog and is known to aggravate symptoms of respiratory illnesses, such as asthma and bronchitis. The hazardous waste reductions lower worker health risks because nonhazardous solvents are less flammable and less volatile, meaning fewer fumes, than the hazardous ones. In addition, the nonhazardous solvents pose less of a risk of spill during transport to off-site treatment or recycling facilities. The solid waste reductions are beneficial in that in some cases, fewer raw materials are used, and in other cases, material is recycled. Both reduce the amount of material sent to the landfill. Eliminating the discharge of antifreeze to the sewage treatment plant is beneficial in that metals found in spent antifreeze do not contaminate the sludge generated by the local sewage treatment plant. These sludges are often land applied, and a reduction in metal content reduces the risk of metals entering the food chain.

Table 3 Environmental Benefits of Pollution Reductions Achieved (Business Partners for a Clean Environment)

Pollutant Category	Sources - Auto Servicers	Sources - Printers	Environmental Benefits Due to P2
Air emissions (VOCs)	HVLPs, solvents, thinners, paints	Blanket washes, fountain solutions, inks	Reduce formation of ozone (smog-related health effects); improved worker health and safety
Hazardous wastes	Parts washer solvents	Inks	Improved worker health and safety; reduced risk of hazardous waste spills
Solid waste	Oil filters, aerosol cans	Inks, paper, plates, film	Reduced landfill waste; reduced virgin material usage; reused materials
Wastewater discharges	Antifreeze	None	Reduced discharge of ethylene glycol and metals to sewage treatment plant

7.4 Savings from Pollution Prevention Activities

Overall, the businesses that have participated in the Business Partners program have saved money. A few of the prevention measures recommended by the program resulted in small cost increases to the business, such as recycling oil filters. Measures such as HVLP spray guns for painting vehicles or purchasing brake and carburetor cleaning fluids in bulk rather than in aerosol cans have resulted in significant annual savings. Table 4 summarizes the total annual savings due to P2 measures implemented by local businesses to meet the Business Partners program criteria.

Table 4 identifies three categories of savings: disposal, material, and operating. Figure 4 represents the average savings from these three categories by businesses due to implemented P2 measures. Generally, *disposal savings* resulted from reduced waste paint and spent thinner when HVLPs were used at auto body shops. Disposal costs result from the need to store and transport oil filters for recycling. The *material savings* resulted from buying cleaners in bulk rather than by individual aerosol can and from reducing purchases of new antifreeze due to on-site recycling. In addition, material savings accrued to auto body shops using HVLPs as they dramatically reduced purchases of paints and thinners. HVLPs used in conjunction with computerized mixing enabled shops to mix only the quantity of paint needed for each vehicle. Printers also achieved material savings by using soy-based inks, which are often less expensive than traditional petroleum-based inks. Finally, the *operating savings* were primarily due to auto repair shops that changed to nonhazardous and less-expensive solvents used in part washers. Some printers have achieved operating savings by switching to low VOC blanket washes.

Table 4 Savings Due to Implementing Pollution Prevention Measures (Business Partners for a Clean Environment Program, US$/yr)

Shop/Other Data	Disposal Savings (Cost)	Material Savings (Cost)	Operating Savings (Cost)	Total Savings (Cost)
Repair	(1,740)	5,910	(610)	3,560
Body	9,700	60,000	0	69,700
Print	0	1,500	170	1,670
Total	7,900	67,400	440	74,900
Average	1,140	11,300	150	6,200
Number of shops	7	6	3	12

Cost information differs among businesses, depending on their size and housekeeping practices. In some instances, P2 measures require the outlay of capital. The most common capital expenditures were for on-site and antifreeze recyclers, HVLPs, aqueous parts washers, and nonaerosol spray canisters for brake cleaners. Generally, material or disposal savings generate the revenue to pay back the capital expenditure (Table 5).

Table 5 Savings or Costs Associated with Pollution Prevention Measures (Business Partners for a Clean Environment)

Measure	Approximate Savings or Costs (US$)
Auto Servicing	
HVLP spray guns	Capital cost of $450; payback possible in 2 weeks.
Antifreeze recycling (on-site)	Capital cost of $1,700-$2,000; payback in about 1.3 yr.
Bulk cleaners (i.e., brake)	Savings of $0.50-$2 per aerosol can.
Oil filter recycling	Cost of $75-$100 per 55-gal barrel or $0.30 per filter.
Removal of chlorinated compounds	Generally no difference in cost.
Less hazardous solvents	Savings of $20 per servicing or $150/yr.
Printers	
Soy- or vegetable-based inks	Savings of $0.50/lb.
Fountain solutions with low isopropyl alcohol content	Generally no difference in cost.
Low VOC blanket washes	Generally no difference in cost.

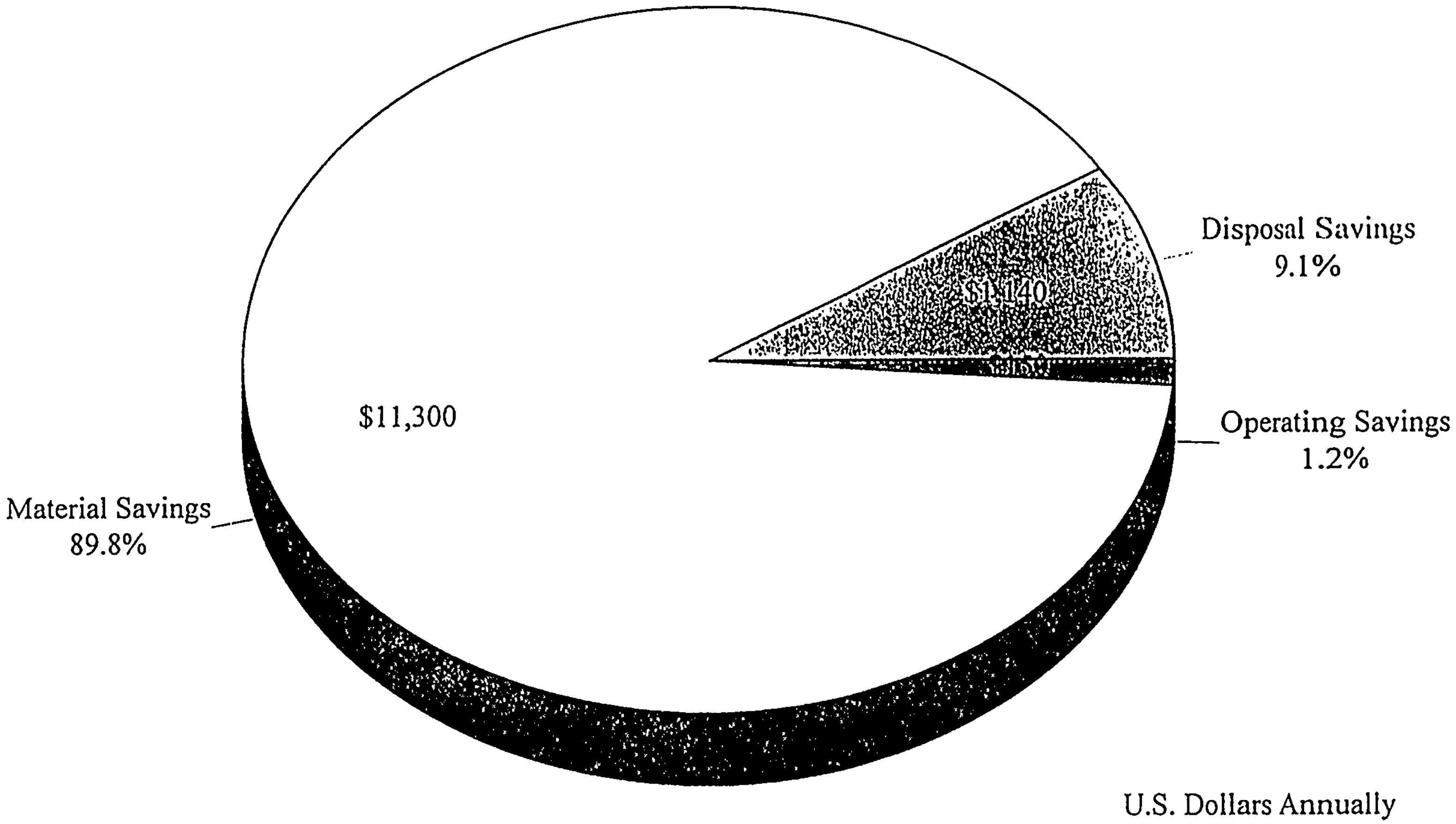

Fig. 4 Graphical Presentation of Cost Savings Due to Implementing Pollution Prevention Measures

8 PUBLIC RECOGNITION

Certification is based on compliance with industry-specific program criteria as established by the Business Partners program. Businesses that implement at least three of the program criteria are eligible for partial certification. (Partial certification entitles businesses to advertising twice a year in local publications and to be recognized at an annual awards ceremony.) Full certification is achieved when a business incorporates all of the listed criteria. Full certification entitles a business to an official Business Partners decal, together with advertising and recognition at the awards ceremonies. The awards ceremonies consist of city council members, county commissioners, other businesses, and the general public.

Another aspect of the Business Partners program is to educate the public to understand and recognize the program logo and to help support these businesses, which are proactive, thus potentially bringing more revenue into the business for their P2 efforts.

9 FUTURE EFFORTS

Efforts will be made to increase the number of certified auto repair, auto body, printers, metal finishers, and printed circuit board manufacturers, and to expand the program to other industries and municipalities. New industries currently under evaluation are hotels and motels, hospitals, and wood finishers and dry cleaners. Additionally, the shops presently participating in the program were introduced through the industry-specific workshops. One-on-one meetings with shop and telephone contact will be initiated to introduce new shops to the Business Partners program.

10 PROGRAM SUMMARY

BCHD's voluntary P2 program was designed to assist small- to medium-sized businesses with their environmental concerns. Involving businesses early in the process was a key factor to the success of the program. Businesses can save money and reduce their regulatory requirements and liabilities by implementing P2 measures. BCHD's P2 program has measured overall pollution reductions for the program; although small, these results would not have been achieved through regulatory means. In summary, BCHD's P2 program has demonstrated that government and industry can work together to achieve environmental protection, reduced regulatory concerns, improved employee safety, and an increase in the bottom line of a business.

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SOURCES AND MANAGEMENT OF HAZARDOUS WASTE IN PAPUA NEW GUINEA

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ABSTRACT

Papua New Guinea (PNG) has considerable mineral wealth, especially in gold and copper. Large-scale mining takes place, and these activities are the source of most of PNG's hazardous waste. Most people live in small farming communities throughout the region. Those living adjacent to mining areas have experienced some negative impacts from river ecosystem damage and erosion of their lands. Industry is centered mainly in urban areas and generates waste composed of various products. Agricultural products, pesticide residues, and chemicals used for preserving timber and other forestry products also produce hazardous waste. Most municipal waste comes from domestic and commercial premises; it consists mainly of combustibles, noncombustibles, and other wastes. Hospitals generate pathogenic organisms, radioactive materials, and chemical and pharmaceutical laboratory waste. Little is known about the actual treatment of waste before disposal in PNG. Traditional low-cost waste disposal methods are usually practiced, such as use of landfills; storage in surface impoundments; and disposal in public sewers, rivers, and the sea. Indiscriminate burning of domestic waste in backyards is also commonly practiced in urban and rural areas.

1 INTRODUCTION

Papua New Guinea (PNG) comprises the eastern half of the island of New Guinea and outlying islands north of Australia. Irian Jaya, a province of Indonesia, occupies the western half. The total land area of PNG is 462,840 km^2, which includes North Solomons, New Britain, New Ireland, Manus, and many other islands. Much of the interior of mainland PNG is mountainous and heavily populated, with a total population of 3.8 million in 1990 (National Statistical Office 1993), and a mean population growth rate of 2.3%/yr. The people are culturally and linguistically diverse, and many tribal groups live in relative isolation. More than 700 distinct languages are spoken. The economy of PNG depends largely on agriculture and the exploitation of natural resources. Forestry, agriculture (cocoa, tea, coffee, coconut, rubber), and, in particular, mining are significant contributors to the gross national product. Papua New Guinea has considerable mineral wealth.

Large-scale mining of gold (OK Tedi, Porgera, Misima, Mt. Kare) and copper (OK Tedi, and Bougainville, which is currently closed) takes place. The country ranks ninth among the world's gold-producing nations. Exploration continues to reveal valuable minerals, including nickel and chromium, as well as oil and gas (Kutubu, Gobe, Hides). Mining activities are the source of much of PNG's hazardous waste.

Naturally endowed with luxuriant forests, fertile soil, and mineral resources, PNG has great potential for development. The political system of the country, which became independent in 1975, represents a remarkable synthesis of traditional and Westminster democratic structures; for example, clan-based common ownership of land and modern democratic institutions, such as a federally structured parliamentary system operate in reasonable harmony (Alphonse 1991).

2 ENVIRONMENTAL PROTECTION LEGISLATION

Papua New Guinea is unique in the Pacific region in that its constitution has specifically recognized the nation's responsibility to ensure that the environment is protected and its natural resources are wisely used. The Environmental Planning Act (1978) ensures that development projects are planned to attain maximum economic, environmental, and social benefits. The Act can be enforced through voluntary or requested submission by the developer of an environmental plan, which must detail the potential effects of a project on the physical and social environment and state the actions that will be undertaken to minimize harmful effects. The conditions of an environmental plan, once approved, are legally binding.

The Environmental Contaminants Act aims to prevent and regulate the release of all harmful pollutants into the PNG environment. It provides for establishing an Environmental Contaminants Advisory Council and a Registrar of Hazardous Environmental Contaminants and requires all potential polluters to apply for a license or permit. The permit details how much of each contaminant or poison can be released into the environment (including trade wastes from factories, pesticides, and other chemicals). The legislation also covers litter, noise, and radioactivity.

The Conservation Areas Act is seen as the major way for conserving certain areas of PNG for future generations. The Act does not take land away from landowners; rather, it provides for the creation of local management committees responsible for the preparation of a management plan for the area. The Office of Environment and Conservation was established in 1974, as a result of much pressure on the government of the day and concern about the total lack of environmental and social planning. Currently, a federal minister heads the Department of Environment and Conservation. Nevertheless, PNG faces considerable environmental problems.

3 MINING BOOM

Papua New Guinea is currently undergoing a mineral exploration and development boom, especially for gold and copper, and a number of economic deposits have already been located. Like all other mineral development projects, those in PNG have associated environmental and social problems. For example, considerable publicity has arisen regarding environmental management problems of the OK Tedi, Bougainville, Porgera, and Misima mining projects. As the pace of mineral development increases so will the degree and extent of environmental impact. Such impacts will continue to be felt most keenly by the local communities whose land will be alienated or damaged and whose traditional resources will be destroyed or degraded (Hughes 1989).

4 SOURCES OF URBAN POLLUTANTS

Urban environments are affected by a large range of contaminants whose impacts vary appreciably within and between different cities. Port Moresby, the nation's capital city, lies on the southern coast of PNG, approximately 9.5°south of the equator. The city is approximately 9 km × 6 km and is expanding rapidly because of squatter settlements, urbanization, growth in population, and industry. The estimated population is 200,000. The city's climate is classified as tropical rainy, with distinct dry seasons that ensure slow flow rates in drains and creeks. The various industries and land uses associated with urban soil contamination are summarized in Table 1. In PNG, hazardous waste generated by major sectors is the main source of contaminants to the environment (PBCHWR 1988). These are described in the following sections.

Table 1 Industries and Land Uses Associated with Urban Pollution

Airport
Alcoholic beverages
Abattoir
Automotive service stations[a]
Asbestos disposal
Bakeries
Building materials
Chemicals, including soaps, detergents, matches, pharmaceuticals and paints, etc.
Cocoa and coconut processing
Dry-cleaning establishments
Electric power generation
Electroplating[a]
Film processing
Food processing
Footwear, plastic and rubber
Grain milling and feeds
Landfill sites
Mining industries
Metallurgy
Oil storage
Palm oil
Paper products, publishing and printing
Scrap yards[a]
Soft drinks
Tannery products[a]
Wood and forestry products and preservation

[a] Main sources of heavy-metal contamination.

5 MINING

Papua New Guinea's considerable mineral wealth is very important to its economy. Mining activities are also the source of much of PNG's hazardous waste. Cyanide used to strip gold from the ore is often released as waste sludge to settling ponds or directly into riverways (Pernetta 1988). Heavy metals, including copper, cadmium, lead, and zinc, are also generated in large amounts by the mining industry and have been found in very high concentrations in water samples taken down-river of mine sites (Mowbray 1986). Most of the rural population in PNG live in small dispersed farming villages. Those living adjacent to mining areas have experienced some negative impacts from river ecosystem damage and erosion of their lands.

Mining activities in PNG have the potential to cause severe localized soil contamination. The main areas affected are generally (1) in the vicinity of the mine site and (2) along riparian strips and flood plains of rivers and creeks draining from the mine site, or which are used for the disposal of mine spoil. The latter may result in long-range transport of soil contaminants and deposition on river banks many kilometers from the mine site. The main soil contaminants on river flood plains are generally directly related to the geological material being mined. Thus, for example, localized areas on the banks of the OK Tedi and Fly Rivers have elevated levels of total and available copper where the rivers have flooded and deposited sediments on the levees and flood plains. In some cases, plant-available copper levels may be immediately at toxic levels, whereas in others the sediments have the potential to weather and release high levels of copper into the soil.

6 INDUSTRY

Industry is located mainly in urban centers. Waste generated includes the following:

- Inorganic waste: acids, alkalis, scrap metals, glass, and ceramics
- Organic waste: polychlorinated biphenyls, chlorinated phenols, dioxins, furans, fuels, oils, lubricants, solvents (trichloroethylene, benzene, chloroform, and carbon tetrachloride), paints, varnishes, lacquers, enamels, soaps, detergents and toilet preparations, etc.

7 AGRICULTURE

Processing of export crops, such as palm oil, cocoa, coffee, and tea, also generates waste.

7.1 Pesticides and Herbicides

Increasing use of pesticides is the major source of contamination associated with agricultural activities. According to the PNG Department of Environment and Conservation, 193 registered pesticide products (chlorinated hydrocarbons, organophosphates, carbamates, pyrethroids, contact, systemic, and soil sterilants) are currently imported. However, the most commonly used pesticides in PNG are paraquat, DDT, aldrin, dalapon, atrazine, diuron, ametryne, tebutryne, 2,4-D, MSMA, malathion, parathion, rotenone, sodium pentachlorophenate, carbaryl, pemethrin, acephate, arsenic copper oxychloride, and their related formulations (Mowbray 1988). Use of organochlorine pesticides was banned in 1990, except for DDT (for malarial control only). Although DDT has been officially banned, it is still sporadically used illegally by some farmers who have access to DDT through old abandoned Department of Health stores scattered around the country.

No systematic survey has been done to determine pesticide residues in the agricultural and marine products around the country. Mowbray (1986) reported the presence of DDT in breast milk, and DDT, dieldrin, heptachlor epoxide, and lindane in fat samples of people in PNG at levels above the maximum permissible concentrations. This finding was also supported by a number of reported deaths related to poisoning due to paraquat, rotenone, diazinon, and sodium pentachlorophenate. Most fatalities were attributed to the use of empty containers for drinking water rather than to exposure to pesticide residues.

7.2 Paraquat Poisoning

Paraquat is used extensively for plantation crops (banana, cocoa-palm, coffee, oil-palm and rubber, etc.) and for citrus fruits, vines, and tea. On certain crops (potato, pineapple, sugar-cane, sunflower), it is used as desiccant. Careless use of paraquat can damage coffee trees, and the PNG Department of Primary Industry does not recommend the use of paraquat on small-scale coffee holdings.

Paraquat poisoning has been a matter for concern in several Pacific Island countries in recent years. Both suicidal and accidental ingestion of this very effective and toxic herbicide have led to a significant number of deaths in PNG (Taylor et al. 1985).

7.3 Poisoning of Domestic Animals, Fish, and Wildlife

Very little documented evidence exists on poisonings other than that of humans in the South Pacific region. Only isolated incidences of poisonings have been reported. In PNG, 53 cattle were sprayed with diazinon; of the 53 cattle, 44 Brahman and Brahman-Cross cattle died within 10-30 minutes. In another incident, 75 cattle died from drinking water from old discarded drums that had originally contained an organoarsenate herbicide. Also, nontargeted insects, fish, and herds have died in PNG as a result of antimalarial DDT spraying.

7.4 Problems of Pesticide Safety

Many pesticides are used in PNG. The country lacks the personnel and technical expertise and infrastructure to advise on efficient use of pesticides and to enforce effective regulations to control use and abuse of pesticides. Some pesticides used have been banned or restricted elsewhere, or classified by the World Health Organization (WHO) as extremely or highly hazardous.

Hazards arising during the application of pesticides are mainly due to lack of information, knowledge/awareness, poor supervision during spraying, absence of proper legislation or enforcement of legislation, and open market sales of highly toxic pesticides.

The information on the extent of pesticide contamination on agricultural lands in PNG is very limited. Concern is growing about possible excessive pesticide residues in agricultural produce and pesticides leaching into surface and groundwaters. At present, there are no adequate facilities and resources available to monitor pesticide residue in agricultural and marine produce. Misuse of pesticides is often the result of ignorance, which can only be dealt with by education and training of health and agriculture workers and through workshops on the safe handling of pesticides (WHO 1990).

8 CHEMICALS USED IN FORESTRY AND TIMBER PRESERVATION

Exploitation of forest resources in PNG has increased dramatically in recent years, and a number of countries have established associated timber logging, milling, and treatment facilities. Numerous registered timber treatment operations use copper/chrome/arsenic preservatives. Although forestry regulations in PNG contain adequate specification for the appropriate design of facilities and environmentally safe operations, very little monitoring is done to ensure actual compliance with requirements. Under these circumstances, mismanagement of the facilities is a possibility. Timber residues, such as sawdust contaminated with preservatives, are believed to be dumped on the land adjacent to these operations, causing considerable contamination of the underlying soils.

Among the commonly used wood preservations are lindane, heptachlor, malathion, aldrin, dieldrin, catafol, creosote, PCP, formalin sodium pentachlorophenate, permethrin, etc. However, no studies have assessed the impact of heavy metals and pesticides on the quality of environment (PBCHWR 1988).

9 MUNICIPAL WASTE

Municipal rubbish forms waste streams on domestic and commercial premises in urban areas. Little inorganic waste is found outside urban areas. The waste is divided into three categories:

- Combustibles: waste paper, newspaper, and cardboard; putrescibles, including all wastes from vegetables and from preparing, cooking, selling, and serving foods; plastics, wood, and textiles.
- Noncombustibles: ferrous and nonferrous metal, broken glass and glass bottles, ceramic, asbestos, batteries, fluorescent lights, and electronic equipment.
- Others: bleaches, insecticides, household chemicals, and cleansing agents.

10 OTHER WASTE

Hospitals generate pathogenic organisms and radioactive materials, chemicals, and pharmaceutical laboratory waste. The oil and gas industries (exploration, refinery, petrochemical products) are also emerging sources of hazardous wastes. The composition of Port Moresby's domestic waste is given in Table 2. Average collection per capita per day is 0.25 kg. The projected estimate for domestic refuse collection in Port Moresby is given in Table 3.

Table 2 Percentage Composition of Port Moresby's Domestic Wastes

Domestic Waste	Total (%)
Vegetable/putrescible materials	52.8
Paper	13.9
Metal - Iron - Nonferrous, e.g., aluminum	11.2 2.2
Glass - Colored - Clear	3.6 6.8
Textiles	1.6
Plastics	6.9
Wood	0.1
Ceramic	0.9

Source: National Capital District Commission.

Table 3 Projected Estimates for Domestic Refuse Collection in Port Moresby

Year	Population Projection	Persons/Household	Total Collection/Day (tons)	Total Collection/Year (tons)
1985	139,300	6.5	29.25	10,640
1986	145,500	6.5	30.44	11.110
1987	152,100	6.5	31.82	11,614
1988	158,900	6.5	33.15	12,136
1989	166,100	6.5	34.75	12,684
1990	173,500	6.6	35.75	13,049
1995	216,300	6.6	37.26	16,520
2000	269,500	6.6	55.53	20,268
2005	271,500	6.6	55.95	20,422
2010	312,900	6.7	63.51	23,181

Source: National Capital District Commission.

11 URBAN WASTE DISPOSAL

Under the Environmental Planning Act in PNG, every industrial facility with a license to operate must submit a contingency plan in case of a chemical emergency. The facility's plan must state the nature of transportation, disposal, and handling and describe the remedial action that would be taken in the event of a chemical spill. Absence of an enforcement policy allows industries to effectively operate as they will. However, public awareness of potential dangers of hazardous chemical waste is gradually increasing. Local resistance groups have mobilized the general public against the health hazards posed by hazardous waste in the vicinity of mines and other industrial units.

Little is known about the treatment of waste before disposal in PNG. Traditional low-cost hazardous waste disposal methods are usually practiced, such as landfill; storage in surface impoundments; and disposal in public sewers, rivers, and the sea. Table 4 shows how various mines dispose of their tailings. The OK Tedi gold mine discharges its waste, including cyanide tailings, into the OK Tedi River (Hughes and Sullivan 1989), which, after 150 km, flows into the large Fly River, which travels 800 km to the sea. A proposal was made to build a spent-cyanide destruction facility and tailings dam to break down the cyanide prior to release into the river, but this plan was abandoned when a massive landslide in 1989 destroyed earthworks associated with the constriction of the tailings dam. Bougainville Copper Ltd, when it was operating, dumped its tailings directly into the nearby Jeba River, which flows 40 km to the sea.

Table 4 Disposal of Tailings from Mines in Papua New Guinea

Mine	Tailings t d^{-1}	Mine Life (yr)	No. of Workforce	Tailing Disposal Methods
Bougainville[a]	135,000	30	4,000	Into river
OK Tedi	80,000	30	2,500	Into river. More than 10,000 t/day of fine waste rock also enters the river.
Misima	15,000	10	350	Deep ocean via submarine pipeline. 10,000 t/day of soft waste rock is dumped directly into the ocean.
Hidden Valley	10,000	10	300	Storage in tailings dam.
Porgera	9,000	18	900	Into river.
Mt. Kare	300	3	200	Into river.
Wau	1,400	9	280	Into river.
Mt. Victor	400	2	100	Storage in sealed limestone sinkhole.
Lakekamu	1,500	15	160	Virtually all rock wastes will be contained within the dredging area.

[a] Currently out of operation.

Source: Hughes and Sullivan (1989).

Most of the existing hazardous waste from urban areas (much of it low-level hazardous waste) is believed to be disposed of in municipal landfills. Very few of these sites are suitable for receiving hazardous wastes as codisposal. Liquid and semiliquid hazardous wastes are often disposed of to sewers. Again, these wastes usually, though not always, are low-level hazardous wastes and are not strictly controlled by trade waste bylaws set by the local authorities, such as the Department of Environment and Conservation or the National Capital District Commission (for Port Moresby).

The National Capital District Commission is responsible for managing municipal waste in Port Moresby. Commercial and industrial establishments either truck their wastes to the dump sites or incinerate them on their premises. Liquid wastes comprised mainly of waste oil are discharged into the storm drains or the city's sewer system. Two contractors operate in the city to collect and dispose of wastes from residential areas, including urban villages, governmental offices, schools, the University of Papua New Guinea, and various other institutions. Collection is biweekly, and the wastes are immediately transported to landfills. The dumps are located in a valley at Baruni and at 6 Mile, the start of the Magi Highway. They were established in 1979 and 1974, respectively. The oil, domestic wastes, and putrescibles are brought to Baruni, whereas the 6 Mile dump was supposedly for dry waste, such as tree cuttings, timber, car parts, cardboard, scrap metal, etc. Both waste disposal sites have attracted scavengers, and rubbish litters extensive areas around each dump.

Burning is common. Indiscriminate burning of domestic waste in backyards is also commonly practiced in urban and rural areas.

Although contaminated sites are affected by a range of potentially hazardous substances, e.g., acidic and alkaline materials and building waste products, the most common contaminants are heavy metals.

12 CONCLUSION

This paper presents an overview of waste generation and management in PNG. The projected estimates of PNG's population and industrial growth show that the volume of waste is on the rise. There is generally a lack of information and research dealing with pollution and waste management in general. PNG does not have the trained personnel or facilities capable of adequately treating and disposing of hazardous waste. An active exchange of information and experience among the developed Pacific neighbors and PNG could do much to advance the latter's capabilities to deal with such wastes.

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INDUSTRIAL WASTE AND POLLUTION IN MONGOLIA

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1 REGULATORY BACKGROUND

At present, Mongolia is experiencing a transition to a market-based economy. While this transition is necessary for continued economic growth, it strains the country's natural resources. Furthermore, at the same time, foreign relations and trade activities have increased. To address these issues, the Mongolian government has made many changes in environmental laws and regulations. These new laws and regulations are intended to help in the transition to a market-based economy and to increase active participation in international, regional, and local environmental cooperation. Mongolia is a party to four international conventions on the environment, including the Basel Convention on Transboundary Movement of Hazardous Waste, which was signed in 1989. Following translation into the national language, the Basel Convention has been submitted to the government and the Parliament for ratification.

To prepare for the implementation of the Basel Convention, the government has developed regulations in the area of waste classification and has distributed these regulations among the ministries for comments and recommendations. A technical and expert group on hazardous waste classification is preparing a National List of Hazardous Wastes. The Ministry responsible for overseeing toxic chemical and hazardous waste management is the Ministry of Nature and Environment. The Ministry has assembled an advisory group of technical and scientific experts in toxic and hazardous wastes. This group, the State Council of Toxic Chemicals, was established under the Protection of Chemical Law of July 1995 to advise the Ministry in defining and interpreting the laws. It is expected that this Council will be of substantial value to the Ministry in determining if a material falls within the definition of hazardous waste and should be regulated as such.

Finally, the Government Resolution of Mongolian Environmental Impact Assessment Procedures was enacted in 1995. These procedures require that impact assessments be conducted for users of toxic chemicals.

2 CLIMATE, AIR POLLUTION, AND WATER POLLUTION

2.1 Climate

Mongolia's continental climate has extreme variations in seasonal and daily temperatures. The climate is also very dry, which leads to about 26 dust storms each year. As a result, regeneration of the natural environment occurs very slowly. Because of this slow regeneration, planners must give more consideration to the potential adverse impacts of human activities, such as town and urban planning.

Ulaanbaatar (the capital city) lies in a valley surrounded by four mountain ranges. Because of its location, the city experiences many temperature inversions. At least 80 to 96% occur during October to April, when air temperatures range from 7.5 to 11.7°C and land temperatures range from −21 to −39°C. The average depth of the inversions is 650 to 920 m.

2.2 Air Pollution

Ulaanbaatar has many cultural and scientific institutions and organizations, and some of the country's most developed infrastructure. It also is the site for three large coal-fueled thermal power plants. Operation of these plants creates dust, ash, and smoke, which are removed almost exclusively by filtration. Smoke is released directly to the open air. Still, the employment opportunities offered in the city have attracted, and will continue to attract, people from rural areas. As evidence, the population of the city grew from 118,400 people in 1950 to five times that in 1996.

Factors that influence air quality in the city include poor planning, the use of coal as fuel, and the lack of pollution control devices. The location of the thermal power plants and the "gher" (Mongolia's traditional housing unit) west of the city demonstrates the lack of planning. The power plants emit dust and smoke. The housing area also emits contaminants from coal- and wood-heated ghers, which have short stacks that keep the smoke close to the ground. Together, the plants and the housing area produce a daily average concentration of sulfur dioxide, nitrogen dioxide, and carbon monoxide that is well above permissible air level concentrations during the winter in large cities such as Ulaanbaatar, Darkhan, Erdenet, and Baganuur.

Forty-eight percent of Ulaanbaatar's population lives in ghers and uses wood- and coal-fueled stoves for heating and cooking. These stoves do not have pollution control devices, and so they emit toxic substances such as carbon dioxide into the air. Such substances affect the population's health. Another source of air pollution in the city are the 160 coal-fired boiler heating stations. These stations use many tonnes of coal per year, storing the coal in the open, which causes dust and particulates to circulate in the air.

Finally, transportation planners in the country have usually underestimated use and have failed to address environmental issues or their importance. In the last two years, the number of private vehicles that operate inefficiently and lack appropriate air emission control devices has increased.

2.3 Water Pollution

Southern Ulaanbaatar boasts mountains that have pure rivers such as the Tuul River. Once the Tuul reaches the city, however, and flows 45 km downstream to the Songino resort, it is contaminated with chemicals. Near the city, the Tuul has four to five times as many chemical contaminants as it does near its source in the mountains. The primary reason for the poor water quality of the Tuul River is the five wastewater treatment facilities located along the river. Discharge water from these facilities is poor in quality and adversely affects the quality of the riverwater.

3 SOIL CONTAMINATION AND HAZARDOUS WASTE

Mongolia occupies 156.4 million ha and has a population density of 74 ha^2/person. Ulaanbaatar accounts for .86% of the country's total land area, or 135,800 ha, and one-third of the country's population. The capital city has 35,000 outdoor toilets and 30,000 outdoor receptacles for collecting wastewater. Most are located in the gher neighborhoods.

Each year, more than 11.3 million m^3 of industrial solid waste is collected in Mongolian cities. Domestic wastes add another 1.85 million m^3. Wastes included in these totals are sludge from the wastewater treatment plants and waste from medical care in hospitals, centers, and clinics. At present, wastes are disposed of in uncontrolled, open dumping. Of particular concern is disposed boiler ash. Open dump semidomes catch fire and attract flies, rodents, and other carriers of disease, causing a problem in nearby residential areas. It is now recognized that these open dump areas are a major source of environmental pollution, mainly because of the lack of finances and technical expertise in Mongolia. Urgent action is needed to close the existing dump sites and relocate to a new landfill site.

The volumes, types, and specific hazards of these toxic and hazardous wastes are not quantified. Unfortunately, the special means needed for transporting solid waste are not sufficient. Also, Mongolia does not have the appropriate guidelines, technologies, and recommendations for waste disposal.

At this time (1996), Mongolia has a number of primary sources that produce hazardous wastes: a leather factory, copper and gold mining industries (which use cyanide in processing), a wool fur factory, and infectious wastes from hospitals, clinics, and bioproduction. Table 1 lists the volumes of hazardous wastes discharged from the leather industry, and Table 2 presents the volumes of

Table 1 Elements and Total Content of Waste Found in Leather Industry Sludge

Element	Content (mg/kg)
Nitrogen	3.0
Phosphorus	0.2
Sodium	1.8
Chlorine	0.2
Organic matter	30.0
pH	7.5
Chromium	9.0

Table 2 Chemical Elements in Waste from the Erdenet Copper and Molybdenum Mining Industries

Element	Content (mg/kg)
Lead	76.8
Potassium	27.20.2
Copper	2,157.9
Strontium	1,026.7
Zinc	229.7
Rubidium	179.6

chemical elements found in wastes discharged from the Erdenet copper and molybdenum mining industry.

4 SUMMARY

The following list summarizes the major problems that Mongolia has in managing solid waste:

- Rapid urbanization, especially overpopulation in Ulaanbaatar
- Inadequate institutional structure and trained personnel
- Inadequate public cooperation and discipline in managing hazardous and toxic wastes
- No appropriate sanitary landfills or incineration strategies
- No application of the “polluter pays” principle to reduce waste generation
- No promotion of recycling and reutilization
- No recycling industry development
- No construction of sanitary landfills

- Inadequate collection and transportation systems
- Lack of assessment and development of management and treatment processes and capacities required for hazardous wastes
- Lack of policies and institutional requirements to implement the above

Mongolia needs the experience that other countries can offer to help improve and possibly implement remediation measures for solid waste disposal. In particular, the country is very interested in technology for collecting and disposing of solid wastes within the framework of hazardous solid waste management.

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STATUS OF INVENTORY, RECYCLING, AND STORAGE OF HAZARDOUS WASTE IN KAZAKSTAN

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ABSTRACT

Conditions associated with toxic and radioactive waste in the Republic of Kazakstan are discussed. At present, more than 19 billion tons of various wastes, including toxic, radioactive, and other hazardous waste, have accumulated in the country, and about 1 billion tons of waste are generated each year. Ecological legislation for toxic waste storage is being examined. However, the definition and classification of waste inventories are not finalized. Furthermore, the country does not have sites for salvaging, rendering harmless, or disposing of these wastes. Kazakstan also has problems with radioactive waste that are complicated by the activity at the Semipalatinsk nuclear testing site. Here, nuclear explosions occurred because of economic and other reasons. In ecologically challenged regions, high levels of pollutants from chemical, toxic, industrial, and radioactive wastes and pesticides cause many diseases. These complex problems may be resolved by establishing a governmental body to manage industrial and consumer waste, including toxic and radioactive waste, and also by developing legal and other regulations.

1 INTRODUCTION

Ecological problems in the Republic of Kazakstan have intensified in the last 20–30 years. Even early in this period, the government should have regulated the use of natural resources and protected the environment. It was believed that this problem would be resolved by social and economic development and through directives from the Union and Republican governments. However, within the framework of a command-type, centralized administration, in which economic interests take precedence over ecological interests, it was impossible to reduce or prevent pollution. Another factor was the division of territories into raw material bases and industrially developed regions, making it impossible to reduce or prevent the pollution that resulted from intensive use of the environment and inadequate regulation of human activity.

2 TOXIC WASTE MANAGEMENT ISSUES

Development of mining and a departmental approach to processing raw material have resulted in significant increases in industrial waste. More than 19 billion tons have accumulated. Because of sluggish development of low-level radioactive waste (LLW) and waste-free technologies for complex processing of raw materials and salvaging of industrial waste, only about 5% of raw materials become finished products.

In 20 years, Kazakstan's copper and nickel industries will accumulate 10–15% in technological raw material. Other metals (and their percentages) extracted from ore during the same period include lead and tungsten, 40%; zinc and tin, 50%; and molybdenum, 70%. The country's extremely inefficient use of raw material, other materials, and fuel and energy resources was inherited from the former Soviet Union. From 1989 to 1990, a smaller volume of gross national product exceeded that of the United States on such indexes of production as commodity ore by 5 times, crude ore by 11 times, pig iron by 12 times, and natural gas by 1.7 times more than in the United States.

The significant and excessive costs of material resources in Kazakstan compared with world standards is on a par with a national disaster, and resolution requires governmental action. Highly efficient economic measures for raw materials, other materials, and fuel and energy would substantially help with the costs associated with their realization, as a rule, exceeding two to three times, and often (especially for the use of some secondary resources) five to six times, less than costs required for producing the additional volume of primary resources.

Measures should take into account that economic use of resources is not only the factor needed to increase the efficiency of processing material resources. They are also a factor in decreasing the level of anthropogenic influences to the natural environment. Finally, such measures are a factor in increasing the stability of an economy with complicated resource maintenance requirements, as well as increasing the scales of natural environment pollution.

The primary danger is the growing volume of toxic waste that results from processing natural resources. Data from the State Committee on Registration and Statistics of the Republic of Kazakstan show that the annual volume of toxic waste is 84.4 million tons; of this waste, 52.4 million tons (62%) came from nonferrous metallurgy undertakings. The unused, unrendered harmless component composed 75.3 million tons (89%), and these wastes were allocated to special surface repositories in a 23,500-ha area in and around the territories involved in mining. Data also show that 1,886 million tons of toxic waste had accumulated in organized storage by 1 July 1996. Industrial waste dump sites occupy more than 90,000 ha of land.

The accumulated volume of toxic waste is stored mainly with fragmentary infringement of environmental legislation. The account and definition of their class of danger are not yet defined, and grounds for their salvaging, rendering harmless, and burial are absent.

More than 184,000 tons of waste have been allocated in unorganized storage (ravines, etc.). Of this waste, 85% of the toxic waste was delivered to city rubbish heaps from unorganized storage.

Waste composed of lead accounts for about 33% of waste in organized storage; waste composed of cobalt accounts for more than 17%. In industrial waste, toxic substances are found in inorganic compounds of fluorine, arsenic, mercury, 6-valent chromium, nickel, etc. Only 8.7 million tons of toxic waste are used from this quantity, which is only 10% of the annual volume. Such wastes as nickel and its combinations, 6-valent chromium and its compounds, and pesticides are not recycled.

Industrial waste in the Republic makes up about 1 billion ton/yr, of which 60 to 70 million tons of secondary resources are suitable for use. However, because limited volumes are processed, waste still accumulates in dumps.

The largest volume of waste comes from the largest sources, that is, building materials, fertilizers, and other production materials. In some regions, secondary resources surpass stocks of natural raw materials. Industrial waste stored in a structure that harmful substances can enter is considered to be toxic waste. Most of Kazakstan's ecological problems are related to poor waste storage because ecological standards have not been observed.

Repositories for toxic and salvaged waste have polluted water resources in Aktube Oblast by six-valent chromium and boron; in Zhambyl Oblast, by fluorine and phosphorus; and in Eastern Kazakstan Oblast by heavy metals. For example, in the last area, repositories stored more than 900 million tons of various waste. The center at Ust-Kamenegorsk has two tailing dumps holding 5.5 million tons of uranium and beryllium industrial waste and a storehouse of radioactive waste with more than 100,000 tons. About 10 million tons of slag are concentrated in industrial sites of lead-zinc factories, including more than 200,000 tons of arsenic-containing slag.

More than 7 million tons of slag are stored in a center in the village of Glubokoe, and more than 100 million tons of concentrated mill waste and 270 million tons of overburden rocks are located in the town of Zyryanovsk. A similar situation has developed in Leninogorsk. Table 1 gives data about the waste situation in several additional locations.

Repeated levels that exceed the maximum permissible concentration of heavy metals have made the water unfit for use from most right-bank sites of the Irtysh River in Ust-Kamenogorsk.

In color metallurgy, waste as overburden rocks exceeds 4 billion tons, with an annual output of 170 million tons. The rocks are partially (about 8% of current formation) used for construction of highways, erection of dams, pouring of open pits, and road-metal production.

At present, some branches of enterprises have saved more than 1.4 billion tons of tailing dumps of concentration at the rate of 55 million ton/yr. Some of the tailing dumps (7.4%/yr) are used for

Table 1 Waste Accumulations in Various Locations in Kazakstan

Waste Type	Location	Amount (tons)
Slurry	Monochromatic section at the Aktube chromium compounds plant	6 million
Electrothermic phosphorus slags	- Industrial Undertaking "Nodfos" - Chemical Industrial Undertaking "Phosphor" in Zhambyl Oblast	21 million
Waste containing mercury	Pavlodar chemical plant	34,000
Waste containing arsenic	- Industrial Undertaking "Balkhashmed," the Prikaspiisk mining and metallurgical combine - Kazzoloto mining and concentration plant - Ust-Kamenogorsk lead-zinc combine - Shymkent lead plant	44 million

laying the production areas of mines, pouring of roads, embankments, layout of platforms, and open pits.

Metallurgical slag resources, as a whole, exceed 65 million tons, which amounts to about 2.2 million ton/yr. Slag pumice is required because of the significant content in slag of color metals, which means management of their preliminary extraction and subsequent use of a mineral part for road-metal production.

In practice, the problem of using gases that accompany the extraction of oil has not been resolved. Sixty percent of these gases are burnt in flares.

The needs of the construction industry are met by extracting more than 90 million m^3 of raw materials from the mineral resources of Kazakstan. In addition, the number of small, open-cast mines that violate legislation on mineral resources is growing.

Salvaging of firm household waste (FHW) is not favorable. In the cities and urban settlements, 13.9 million m^3 of FHW is generated annually. The amount of FHW on average increases by 12%/yr on objects of warehousing. Most of this waste (97.2%) is removed and stored in unmanaged dumps. This practice results in pollution of soil, air, and underground waters and creates adverse sanitary and ecological conditions in suburban zones. Losses from environmental pollution caused by various pollutants amounts to 9 billion tenge/yr (US$130 million/yr).

Additional ground areas, including valuable agricultural lands, are allocated as dumps each year. The level of management of dumps is low. About 92% of surveyed dumps do not have hydroprotection systems, and the availability of a sanitary protective zone is only 57%. The existing methods of warehousing are labor-consuming and require (1) extensive underground sites for rendering the waste harmless and (2) substantial costs for transporting waste.

The morphological structure of FHW is shown in Table 2. This waste represents complex secondary raw material. The tax on secondary raw material for the population of Almaty provides for salvaging of metal, textiles, and spoiled sheet at a rate of 0.5–0.7% from the annual amount of FHW; that is, 7–10% from the potential contents of these components.

Table 2 Morphological Makeup of Firm Household Waste

Waste Product	Percentage of Firm Household Waste
Food waste	30-45
Paper and cardboard	20-35
Glass	4-6
Metal	3-6
Polymeric materials	2.5

The cities have in place a separate tax on firm household waste components, but they do not have a system for sorting FHW. The small amount of sorting of FHW that is performed (only selection of black metals) is executed at the Almaty rubbish conversion factory, which is unique in the Republic and the station of sorting.

Technical maintenance and educational knowledge among the population about the tax on waste materials are at a low level. Therefore, on an annual basis, up to 70% of all paper resources and up to 20% of black and color metals and other valuable materials are placed in dumps.

Changes occurring in the Republic's management structure have aggravated the waste problem. So, in connection with the transformation of the Ministry of Material Resources into a joint-stock company called "Kazkontrakt," the government body on industrial and consumer waste management was liquidated in 1992.

State control of pollution prevention of our natural environment from various wastes identified by the Ministry of Ecology and Bioresources only solves part of this problem. The economic and social-political changes in the Republic of Kazakstan have made it necessary for the Ministry of Ecology and Bioresources to perform additional functions, connected with the necessity of issuing sanctions on waste allocation. In addition, there were conditions of importation to Kazakstan and burying of toxic waste on the basis of the uncontrollable agreements with foreign firms.

It is stipulated that in countries belonging to the Organization of Economic Cooperation and Development the average cost of burying 1 ton of hazardous waste is 4,550 tenge (US$70); in Kazakstan, it is 1,300 tenge (US$20).

The essential difference in the cost of waste creates conditions for some persons to want to import into Kazakstan hazardous waste as a raw material or products. Such circumstances require maintaining control of transboundary movements of hazardous waste and their disposal on the basis of the Basel Convention (1989). This control is not yet carried out by a sufficient number of workers.

To strengthen the state control by the Ministry of Ecology and Bioresources, standard and technical documents have been developed on the following items:

- Realization of the state control of the conditions of waste allocation;
- Application and storage of pesticides and mineral fertilizers;
- Sanctions on waste allocation;
- Determination of standards for waste amounts;
- Environmental assessment for repositories; and
- Control of transboundary movements of hazardous waste and other issues.

The Ministry of Ecology and Bioresources is working on drafts of resolutions for the Government of the Republic of Kazakstan "About Measures on Reduction of Negative Influence of Industrial and Consumer Waste on an Environment" and "On Accession of the Republic Kazakstan to Basel Convention on the Control of the Transboundary Movements of Hazardous Waste and their Disposal (1989)." The latter draft still needs to obtain funding from the Ministry of Finance to make it a viable resolution. However, accounts confirm the ecological and economic expediency of the creation in the Republic of a body to implement the Basel Convention. The agreement "On Movements of Hazardous Waste" has been signed among the Commonwealth of Independent States (CIS) of the former Soviet Union.

3 RADIOACTIVE WASTE MANAGEMENT ISSUES

The radiation situation in the territory of Kazakstan is complicated by activity at the Semipalatinsk nuclear testing site, where nuclear explosions occurred out of economic necessity. Other contributors include the nuclear industrial factories, the mining and processing of raw materials with an enhanced content of radioactive elements, the exploitation of nuclear power plants, and the nature of radioactive anomalies in settlements and in underground water sources used for drinking.

The most troubled area in this respect is the Semipalatinsk testing site, where nuclear and thermonuclear testing was carried out from 1949 to 1989. During this 40-yr period, 470 nuclear explosions, including 90 air, 26 ground, and 354 underground explosions, were made on site. The air and ground explosions were made until 1963. Data from the organization responsible for the nuclear explosions show that radioactive clouds of 55 air and ground explosions and gas fractions of 69 underground explosions drifted outside the testing site boundary.

The testing site data allow us to calculate the effective doses of radiation, which were caused by radioactive fallout. The radioactive fallout in the clouds spread over an area of 304,000 km^2, where 1,624,000 people live. In the 711 settlements, the effective dose exceeded the former Soviet Union's sanitary standard of 0.1 ber/yr. The maximum is 448 ber/yr during the total time of nuclear testing.

An analysis of the data by demographic indexes of sickness and death rates in the territory around testing sites reveals the negative effects on the population's health. By presidential decree, the Semipalatinsk testing site was closed, and the surrounding territory was declared a zone of ecological distress. The radioactive situation in this territory is being studied. It has been determined that the local contaminated areas need additional study to determine the distribution and concentration of plutonium-239, strontium-90, the land recultivation.

The main difficulty that Kazakstan faces in studying the radioactive situation is that the former Soviet Union had all the radiological research institutes, laboratories, equipment, and specialists. These are now in the Russian territory, and all materials on nuclear tests are in the Russian archives. As a result, Kazakstan needs assistance from a highly qualified authoritative international organization to evaluate the radiation conditions and calculate the doses to which the population was subjected.

Apart from the Semipalatinsk testing area, 10 nuclear air-burst explosions were carried out for military purposes at the Kapustin Yar testing area in western Kazakstan. Also, 37 underground explosions were carried out for scientific research and technological purposes in a number of other regions of Kazakstan. Undoubtedly, these events still have a detrimental effect on people's health and on the environment.

These explosions emitted the radioactive fission products in the form of strontium-90 and cesium-137, which could be a potential danger on an ecological plane to mineral resources and underground waters. An analysis of geological and hydrogeological conditions during nuclear testing indicated that the potential danger of fission products penetrating underground water-bearing horizons cannot be ignored.

The lack of information about radiation conditions in the territory makes it impossible to give an objective evaluation of the effect of radioactivity, especially on the health of the inhabitants in a number of regions of the Republic, which in turn increases social and political tensions within the population. Affected regions include the Atyran, Pavlodar, Eastern Kazakstan, Karaganda Oblast, and other areas near the nuclear testing site, for example, Lob-Not in the People's Republic of China.

Therefore, it is necessary (1) to create the normative-legal base for state radioactive ecological control of radiation-dangerous factories and for their environmental and population health assessment; and (2) to solve problems connected with using and burying radioactive waste. Item 2 is on the edge because the country does not have special licensed repositories for radioactive waste.

In 1992, the state program for creating a system for collecting, recycling, transporting, and burying radioactive waste was accepted. Within the framework of this program, the concept of localizing radioactive waste was created; an official register of the quantity of radioactive waste and the places for storage was compiled.

There are 101 temporary departmental burial grounds, but all are not licensed to store waste. The cadastre data show that these burial grounds contain about 225 million tons of LLW, with total activity over 230,000 Ci, and 1.17 million tons of medium-level radioactive waste from mining, uranium-extracting industries, and nuclear-power plants, with total activity of 57,600 Ci. Moreover, about 100,000 radioisotope sources, with total activity over 2 million Ci, are in use; 7,400 sources, with total activity of 22,500 Ci, must be buried (these data are current as of 1 January 1993).

As a result of the Semipalatinsk and other nuclear tests, 5.8 million tons of radioactive waste, with total activity of 11,600 Ci, were formed on the ground surface. About 6.5 million tons of medium-level radioactive glazing waste, with total activity of about 12.8 million Ci, are concentrated in underground cavities.

Over 40% of the uranium mined in the former Soviet Union is extracted from the territory of Kazakstan. The exploitation of uranium deposits produces waste products and is accompanied by a loss of raw materials and the emergence of local centers of increased radioactivity, which is detrimental to the environment.

The uranium-extracting industry has accumulated 419 million tons of radioactive waste, with an overall activity of 252,000 Ci. Kazakstan has about 100 places where radioactive waste has been stored, and the total area of technogenic pollution amounts to over 35 km^2.

The lack of protection or enclosure means that ore dumps are used by the local population for economic purposes, such as road and building construction, including housing. The waste products of the uranium-extracting industry have now been included in the register of radioactive waste in the Republic of Kazakstan.

At present, in view of the large number of projects involving the extraction and processing of radioactive ores, the use of nuclear reactors, and the widespread use of radioactive sources in the Republic, the burial of radioactive waste is an urgent problem.

Before the formation of the CIS, all radioactive waste produced in Kazakstan was buried on Russian territory; the Republic did not have any of its own disposal sites. With the declaration of sovereignty, each Republic adopted laws forbidding radioactive waste products from being brought into, or buried in, their territory, which abruptly intensified the problem of disposal in Kazakstan, which has a considerable amount of radioactive waste products. Irrespective of the economic difficulties, the government has made certain decisions aimed at examining and improving the radiation problem in the Republic and has, as much as possible, allocated funds for immediate use.

Following an examination of the ecological implications of radiation, using different methods, 393 anomalies were found and singled out for further testing. Of these, surface testing identified 231 anomalies as areas of technogenic radioactive pollution, requiring decontamination. On the whole, areas of radioactive contamination contain low-level radiation from solid industrial waste products, by-products (oil slurry), and sources with a specific activity in terms of gamma emissions of up to 30,000 mkr/h, predominantly in the form of natural radionuclides (uranium, thorium, and radium). The anomalies noted are northeast of the village of Aktogai in Jezkazgan Oblast, and other anomalies are near the village of Dolon in Semipalatinsk Oblast.

At the present time, a full inventory is being made of all the sources of ionizing emissions used in Kazakstan. Preliminary information shows that the total number of sources of ionizing emissions in the Republic is 62,625. Their total activity amounts to over 473,500 Ci.

Surveying has commenced to choose sites for regional repositories (burial grounds) for low- and medium-level radioactive waste products in the Mangistan and Shymkent Oblasts. Representatives from the nongovernmental organization "Luch" have completed a project on refitting the repository at the RAO reactor complex "Baikal-1" for the temporary storage of used ampule sources of ionizing emissions. All the sources of ionizing emissions accounted for to date are stored in 220 specially equipped permanent or temporary departmental repositories.

At the present time, the Republic of Kazakstan has 12 department repositories for radioactive waste products, and the government is carrying out an expert review of them. The inspection of repositories involves eliminating leakage of radioactive waste products in all media and making sure that the local population does not have access to the repositories.

Work has been completed on investigating waste dumps at the Baial molybdenum-uranium deposits in Zhambyl Oblast, and work has commenced to investigate waste dumps at uranium ore plants in North Kazakstan, the Prikaspiiskii mining and metallurgical combine, and the Industrial Union "Yuzhpolimetall."

The main volumes of radioactive waste are concentrated in the uranium-extracting and uranium-processing factories in Mangystan, Kokshetau, Turgai, Akmola, Zherkasgan, Zhambyl, South Kazakstan, Kyzylorda, and East Kazakstan. The concept of localizing the storage of radioactive waste into four regions, namely, West, North, East, and South, is connected with accounting for the deposition of radioactive objects and the infrastructure of transport links.

Table 3 lists the preliminary prognosis of the annual increment of radioactive waste from all kinds of activity as of 1 January 1993. Thus, it is necessary to create special burial ground storage for low- and medium-level radioactive waste in each region. The preliminary cost of such storage is estimated to be about US$200,000. The long-term deep repository for high-level radioactive waste will be needed until the year 2005 because the use of the nuclear reactor BN-350 in Aktau has been canceled. Government resolutions on preventing environmental pollution by radioactive substances and on improving the system of collecting, processing, transporting, and burying radioactive waste

Table 3 Annual Increments of Radioactive Waste in Kazakstan as of 1 January 1993

Low-Level Radioactive Waste	Quantity (10^3 tons)	Medium-Level Radioactive Waste	Quantity (10^3 tons)
West	1,052	West	0.46
North	1,306	North	1.10
South	17	South	0.02
East	262	East	41.4
Total	2,637	**Total**	43
Total activity = 2,800 Ci		Total activity = 1,400 Ci	

have been accepted as far as 1979 and 1988. However, officials had not completely realized, for different reasons, that the construction of the burial storage at the Tselinnyi mine-chemical factory had been canceled.

Putting into operation the first part of the state's system of collecting, processing, transporting, and burying radioactive waste was planned between 1993 and 1996. As a result, one burial ground storage for low- and medium-level radioactive waste was completed in 1996.

Complete studies to locate appropriate burial sites (stable geological formations) for radioactive waste for the above-mentioned regions were conducted. Phase 1 of the refitting of the repository of the reactor complex "Baikal-1" for temporary storage of used ampule sources of ionizing emissions is complete. The repository for ampule sources has been in operation since 1995.

Work regulations for delivering sources to the storage site have been better defined. However, the question of apportioning means to burying the sources of budget organizations remains unresolved.

At present, all materials connected with the system of collecting, processing, transporting, and burying radioactive waste are handled by the national joint-stock company "KATEP," which since 1995 has been the state consumer responsible for creating such a system.

The project to establish a law "On Handling with Radioactive Waste" and to provide special instructions and methods was prepared for evaluation to ensure the safe burial of radioactive waste. This law will answer such questions as selection of the site for storing and burying radioactive wastes, transporting these wastes, controlling the environmental situation, and so on.

The studies showed the extremely destructive influence of the space vehicle launching site "Baikonur" on the environment and population health of the region: 11,000 tons of space scrap metal remain on fields contaminated by radioactivity and by very toxic asymmetric Dimetilhydrosinium.

4 CONCLUSION

At present, Kazakstan does not have a state management system to monitor, use, and render harmless industrial and consumer waste. This problem is very complex and difficult to decide on our own. Therefore, we should consider accepting assistance for solving our waste disposal problems from the international community.

To improve the management issues for hazardous waste in Kazakstan, it is necessary to implement the following measures:

- Establish the Department and the Scientific Information Center for inventorying, recycling, and storing of industrial and consumer waste, including toxic and radioactive waste.

- Allow the Republic of Kazakstan to adopt the Basel Convention on the Control of the Transboundary Movements of Hazardous Waste and their Disposal.

- Enable the Ministry of Ecology and Bioresources of the Republic of Kazakstan, together with the Scientific-Industrial Association of the Industry Ecology "Kazmekhanobr," the Ministry of Science, and the Ministry of Industry and Trade to elaborate on the following legal and normative acts in 1996:
  - the law "On Industrial and Consumer Waste;"
  - the Ecological Program of Use, Rendering Harmless, and Allocation of Hazardous Waste; and
  - the program for purchasing new technologies of waste recycling and drawing in foreign investors for waste processing.

SITE CHARACTERIZATION AND PETROLEUM HYDROCARBON PLUME MAPPING

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ABSTRACT

This paper presents a case study of site characterization and hydrocarbon contamination plume mapping/delineation in a gas processing plant in southern Mexico. The paper describes innovative and cost-effective use of passive (non-intrusive) and active (intrusive) techniques, including the use of compound-specific analytical methods for site characterization. The techniques used, on a demonstrative basis, include geophysical, geochemical, and borehole drilling. Geochemical techniques used to delineate the horizontal extent of hydrocarbon contamination at the site include soil gas surveys. The borehole drilling technique used to assess the vertical extent of contamination and confirm geophysical and geochemical data combines conventional hollow-stem auguring with direct push-probe using Geoprobe. Compound-specific analytical methods, such as hydrocarbon fingerprinting and a modified method for gasoline range organics, demonstrate the inherent merit and need for such analyses to properly characterize a site, while revealing the limitations of noncompound-specific total petroleum hydrocarbon analysis. The results indicate that the techniques used in tandem can properly delineate the nature and extent of contamination at a site; often supplement or complement data, while reducing the risk of errors and omissions during the assessment phase; and provide data constructively to focus site-specific remediation efforts.

1 INTRODUCTION

Geophysical techniques, such as electromagnetic systems and resistivity logs, were used extensively in the early 1960s for exploring conductive ore bodies in resistive bedrock. As the search for ore bodies progressed to greater depths and into more complex terrain, very sophisticated and reliable geophysical techniques, such as frequency-domain electromagnetic (FDEM) conductivity profiling, time-domain electromagnetic (TDEM) sounding systems, seismic refraction, seismic reflection, microgravity, and other similar technologies, were developed. In the early 1970s, application of these geophysical techniques to define hydrologic and geologic stratigraphies gained prominence in the oil and gas industries. By 1985, TDEM and FDEM were prevalent in deep exploration. In the late 1980s, geophysical techniques gained an enormously expanded role in general geological mapping. In the 1990s, very sophisticated electromagnetic and optical geophysical systems, such as FDEM, TDEM, cone penetrometer (CPT), rapid optical screening tool (ROST) developed by Unisys Environmental Systems, and other similar techniques, are being used extensively in the search for fresh water aquifers, and for mapping the nature and extent of soil and groundwater contamination plumes.

In the environmental field, the application of geophysical techniques gained prominence primarily in three types of investigations: characterization of natural hydrogeologic and soil conditions, assessment of soil and groundwater contamination, and detection and mapping of buried objects, such as drums and tanks. Application of geophysical techniques at several contaminated sites has yielded a very realistic and rapid assessment of subsurface conditions and has been very effective in identifying anomalous conditions, nonintrusively, and often continuously.

Surface geochemical techniques, such as soil-gas surveys, have been successfully used since the 1980s to delineate the horizontal extent of subsurface contamination. The soil-gas survey has been used in areas underlain by sandy, silty, and clay-rich soils.

Conventional hollow-stem borehole drilling and sampling have been used for variety of purposes, including geotechnical and environmental reasons. In the 1990s, new borehole drilling techniques have emerged, which include the direct-push probe using the Geoprobe system. The borehole drilling technique used at this site combines hollow-stem auguring and Geoprobe.

This paper presents the application and results of a geophysical, geochemical, and borehole investigation performed to assess the nature and extent of hydrocarbon contamination in a gas processing plant in southern Mexico. The objectives of the investigation were to (1) demonstrate the application and effectiveness of the passive and active techniques to assess hydrocarbon contamination; (2) supplement and reconfirm areas of hydrocarbon contamination identified and documented as part of an earlier investigation using passive (nonintrusive) and active (intrusive) sampling and through modified compound-specific analytical methods; (3) compare the performance of geophysical, geochemical, and borehole techniques; and (4) further delineate and define areas of suspected on-site contamination.

2 PRINCIPLES OF THE GEOPHYSICAL, GEOCHEMICAL, AND BOREHOLE DRILLING TECHNIQUES USED FOR SITE CHARACTERIZATION

This section briefly describes the basic principles involved in the three techniques used for the site characterization.

2.1 Geophysical Technique

2.1.1 Frequency- and Time-Domain Electromagnetic Techniques

Both the FDEM and the TDEM techniques determine the electrical resistivity (or conductivity) stratification (geoelectric section) of the subsurface. The basis for using an electrical geophysical method is that dissolved solids in groundwater lower the electrical resistivity. The conductivity of soil and rock strata is influenced by a number of factors, such as clay content and water/moisture content. As a general rule, there is an increase in groundwater conductivity of about 1 millimho per meter for every 25 parts per million (ppm) increase in the total dissolved solids (TDS) in groundwater.

In both FDEM and TDEM, electrical eddy currents are induced to flow in the subsurface by the primary magnetic field of a transmitter. The intensity of these currents is a function of ground conductivity, and the secondary magnetic field caused by the eddy current distribution is measured by a receiver at the surface. The value of resistivity (or conductivity) measured at the surface is influenced by the resistivities of all layers within the effective exploration depth of the tool used. This integrated value measured at the surface has been defined as apparent conductivity, or its inverse apparent resistivity.

Computer algorithms are available to derive from apparent conductivities the true conductivity and thickness of the individual strata encountered within the subsurface. Because of its high productivity, the FDEM is highly suited for deriving lateral variation in conductivity. The TDEM, on the other hand, has the highest resolution for determining vertical conductivity. Combining the FDEM with the TDEM allows for a cost-effective assessment of lateral and vertical conductivity distribution.

2.1.2 Cone Penetrometer and Rapid Optical Screening Tools

The CPT is an electronically instrumented cone that contains a friction sleeve of standard area. The cone is pushed into the subsurface continuously at a uniform rate. Signals from the cone are conveyed to the surface through cables located within the center of the push rods. The signals are processed by a computer located in an on-site truck. Real-time data are printed in the field as the test proceeds. The ratio of tip resistance to sleeve friction indicates soil type (sand, silt, clay, etc.).

The ROST uses laser-induced fluorescence spectroscopy for in-situ analysis. The laser source and detection system are located in the CPT truck. Light from the laser source is delivered to the cone along a fiber-optic cable that follows the same path as the electric cables for the CPT strain gauges. In the cone, the light is directed through a window onto the media (soil and/or groundwater). The wavelength of light is selected to be in the range that is absorbed by the contaminant (hydrocarbons). The addition of energy to the petroleum hydrocarbons causes them to emit fluorescent light of a longer wavelength than the existing light. A portion of the fluorescent light that passes through the window into the cone is collected by a second fiber-optic cable and returned to the detection system located in the truck. The incoming data are continuously processed and displayed in a fluorescence intensity versus depth (FVD) profile for the entire CPT push. The fluorescence signal from 50 consecutive laser shots (taking a total time of 1 s) is averaged for each data point displayed. The types of hydrocarbons are differentiated by acquiring a wavelength time matrix (WTM), which is a three-dimensional graph of fluorescence wavelength, lifetime, and intensity.

2.2 Geochemical Technique

Several different types and methods of soil gas survey are available. Soil gas surveys performed at the site consist of collecting soil vapor samples in a specially designed disposable teflon tubing/probe that is pushed to a desired depth. A string attached to the probe is pulled to disengage an expandable point. With the point disconnected from the probe, soil vapors are allowed to enter the hollow center of the probe string. Teflon tubing is inserted in the probe string, and vapors are drawn into the tubing by applying a vacuum to the tubing at the surface. Ambient air is evacuated from the tubing, and the soil vapor sample is drawn from the probe into an evacuated bottle at the surface.

2.3 Borehole Technique

2.3.1 Hollow-Stem Auguring

Hollow-stem auguring consists of using a truck-mounted drill rig and advancing soil borings to collect soil core samples continuously or at selected depths, if required, from the surface to total depth. This method of auguring facilitates installation of monitoring wells and collection of groundwater samples.

2.3.1 Geoprobe

A Geoprobe™ system consists of a rotary drill rig mounted on a truck, which delivers a hydraulic pull down of approximately 6,000 kg. Combining the static weight (pull down) of the rig and a pneumatic hammer powered by a compressor, a probe string of 3-5 cm in outer diameter hollow steel rods is pushed to desired depths (effective maximum of 25 m).

3 SITE BACKGROUND

The site consists of a gas plant constructed in the 1940s to extract natural gas liquids from the natural gas produced in the area. The plant used a process in which the natural gas was commingled with "lean oil" in a contactor vessel. The natural gas liquids (natural gasoline) were absorbed by the lean oil. Subsequently, lean oil was heated to extract the natural gasoline, which was stored on site prior to transport by pipeline. The lean oil was then recirculated in a continuous process loop. A site plan is presented in Fig. 1.

3.1 Site Investigation

A brief description of the site investigation, using geophysical, geochemical, and borehole techniques, is presented in the following sections.

3.1.1 Hollow-Stem Auguring

The first attempt of any environmental investigation performed at the site was a Phase I environmental site assessment (ESA) of the property performed in September 1993. The Phase I ESA consisted of site reconnaissance, regulatory records review, site interview, and site historical review using chain-of-title, aerial photographs, and land-use review. Based on the preliminary findings of the Phase I ESA, a Phase II traditional subsurface investigation was performed. In the Phase II subsurface investigation, seven monitoring wells (TMW-1 through TMW-7) were installed at the site. Soil and groundwater samples were collected and analyzed for total petroleum hydrocarbon (TPH), and benzene, ethylbenzene, toluene, and xylene (BETX). This initial investigation revealed significant hydrocarbon contamination. The hydrocarbon contamination included the presence of free-phase hydrocarbons in the groundwater, and marginal levels of hydrocarbon contamination in some portions of the site soils. Figure 1 includes data on hydrocarbon contamination in groundwater and soils at select locations.

The surfacial soil layer (Unit 1) whose thickness ranges from surface to about 20-25 ft, consists of a variety of relatively permeable units comprising mainly sands and silts. This surfacial layer overlies a red clay (Unit 2). This red clay is found in all seven borings and has a thickness of 20-30 ft. The red clay layer appears to be folded into a shallow arched (anticlinal) structure, with its axis oriented generally North 30 degrees West, passing close to TMW-7 and close to TMW-5. The folded red clay forms a trap structure for lighter than water liquids that may be encountered beneath the red clay. The red clay is underlain by a sand or silt layer (Unit 3) of much higher permeability. Groundwater that occurs within the Unit 3 sand or in the lower part of the Unit 2 red clay apparently flows from north to south.

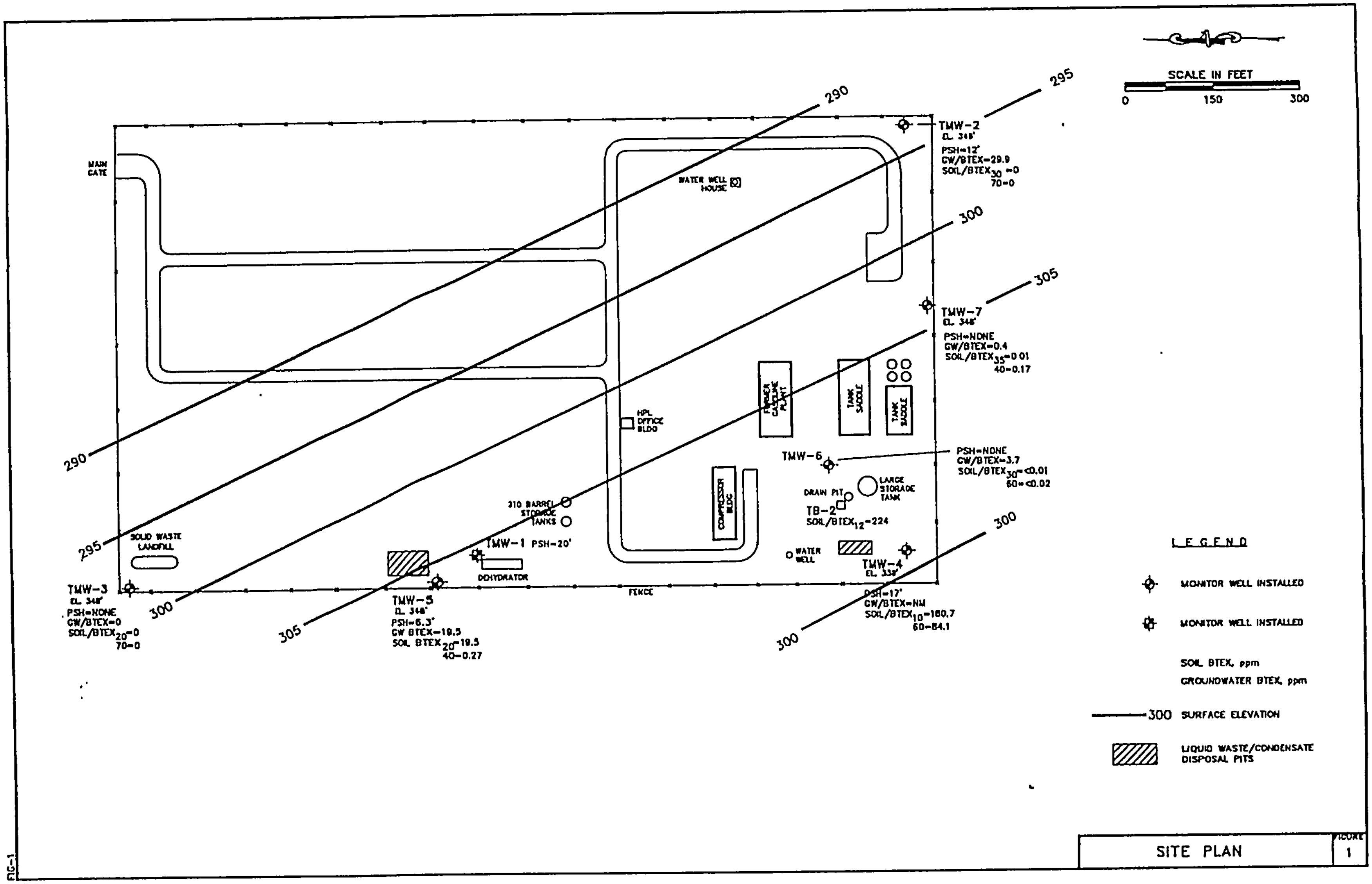


Fig. 1 Site Plan

Floating product (low-density nonaqueous phase liquid, LNAPL), ranging up to 21 ft thick, was encountered in wells TMW-1, 2, 4, and 5. The identified products appeared to have viscosities similar to motor oil or gasoline, or possibly to a broad range of paraffinic condensate, full-range naphtha, or a mixture of several products. The products were encountered on the water table at a depth of approximately 40-55 ft below ground surface (the depth to water/LNAPL interface). No floating product was encountered in TMW-3 (in the northwest corner of the site), in TMW-6 located near the former gasoline plant, and in TMW-7 located along the south property boundary. Significant thicknesses (over 10 feet) of floating products were encountered at various locations (TMW-1, 2, 4, 5, and 7). The contamination appears to be contained in the groundwater beneath a trap structure — the anticlinal fold in the red clay. The potential pathways for groundwater contamination include (1) seepage through the soil from the disposal pits near the TMW-1 location, (2) injection through a ceased disposal well, (3) seepage through the soils at the drain pit or storage tank locations, and (4) spills and waste disposal practices.

Hydrocarbon contamination in soils was present near TMW-1, TMW-4, and TMW-5, suggesting a source (liquid waste disposal pit, storage tanks, and/or dehydrator units) close to each well location. The relatively low levels of hydrocarbon contamination in the soil in other locations (TMW-2 and TMW-7) do not appear to be consistent with the thickness of floating product encountered in these wells (12 ft in TMW-2 and 17 ft in TMW-7). This suggests that contamination has probably not penetrated the relatively low permeability red clay layer (Unit 2) at the locations where substantial thicknesses of floating product have been encountered (TMW-1, 2, and 5).

The permeability of the Unit 1 soils above the red clay (Unit 2) readily explains the widespread distribution of contamination in Unit 1 due to past waste management practices. The plant's use of a liquid waste disposal pit for over 10 yr explains the presence of free-product encountered in TMW-1 and hydrocarbon contamination in the soils near the well area.

3.1.2 Geophysical Logistics and Data Acquisition

A Phase III subsurface investigation was initiated by using the geophysical technique. The geophysical field work was performed in two stages at the site. The first stage was performed in early 1994 by using a combination of the FDEM and TDEM techniques. The field investigation was performed by a four-person crew over a five-day period. During this period, four areas were investigated, which included the disposal pit area, the 210-barrel storage tank area, the large storage tank area, and the drain pit area. Five transect survey lines (AA', BB', CC', DD', and EE') covering the four areas were established for the FDEM and TDEM field surveys. The transect survey lines are shown in Fig. 2. The FDEM terrain conductivity measurements were made along all five transect survey lines using Geonics EM-34 equipment. The TDEM sounding using Geonics EM-47 equipment was positioned at select locations on the basis of the terrain conductivity data along three transect survey lines AA', DD', and EE', where anomalous high-background apparent conductivities

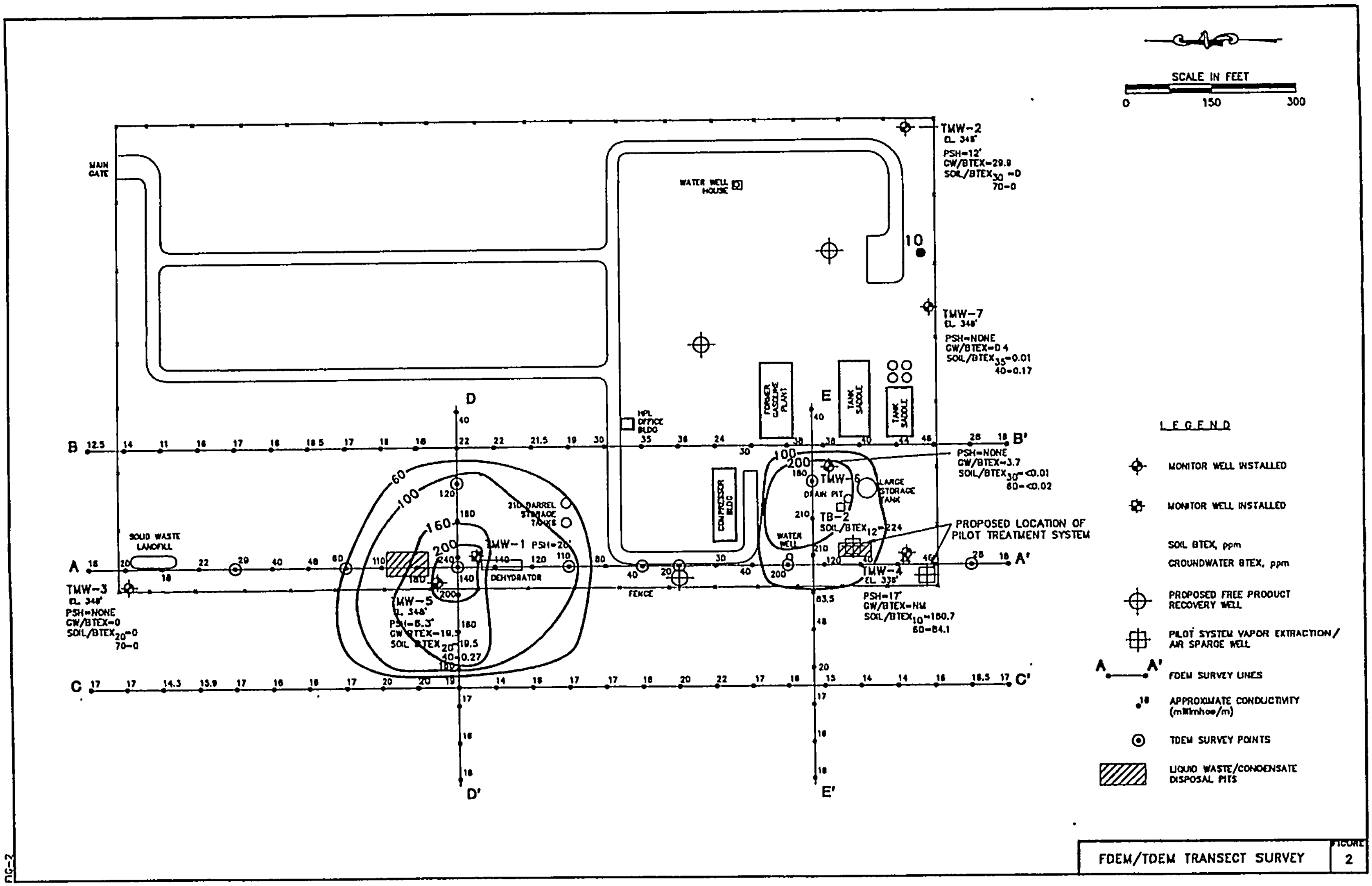


Fig. 2 FDEM/TDEM Transect Survey Lines

were observed. The apparent conductivities performed with the FDEM were contoured each day. The FDEM data were recorded in the field with a solid-state data logger and transferred to a computer at the end of each day for data reduction, inversion, and analysis.

The second stage of geophysical investigation was performed in mid-1994 by using a combination of the CPT and ROST techniques. The investigation was performed by a four-person crew over a three-day period. During this demonstrative investigation, only a limited number (10) of CPT/ROST penetrations were completed at select locations. The CPT/ROST penetration locations are presented in Fig. 3. The penetrations extended to a maximum depth of approximately 40 ft. Locations and depths were selected to illustrate the performance of CPT/ROST as a site screening method. The penetrations were located adjacent to existing monitoring wells, where hydrocarbon contamination was generally known to be present in groundwater and soils. Penetration holes were backfilled with cement-bentonite grout. One WTM was acquired at each push location at a depth where strong fluorescence intensity was observed. Tip resistance, sleeve friction, and conductivity data were collected at each location by using the CPT. The ratio of tip resistance to sleeve friction was derived, and graphs were generated. FVD profiles (depth versus fluorescence intensity, which is a relative measure of petroleum hydrocarbon concentration) were overlaid on the CPT data. A sample of the graphical representation of the CPT/ROST data showing depth versus sleeve friction, tip resistance, percent ratio of tip resistance to sleeve friction and fluorescence intensity, is presented in Fig. 4 for 2 of the 10 CPT/ROST penetrations (CPT/ROST Locations No. 3 and 4). Similar graphics depicting the CPT and FVD depth profiles were developed for all the penetrations.

The average fluorescence intensity, which is expressed as relative fluorescence standard (percent of standard) detected in 5-ft-deep intervals from ground surface to the maximum possible depth of penetration in each location, was recorded and analyzed. The fluorescence standard selected to calibrate the ROST instrument for this investigation was a liquid equivalent of unleaded gasoline spiked onto a sand matrix. FVD data, reported as "percent standard," were used to develop isoconcentration contour maps of petroleum hydrocarbon distribution. A sample isoconcentration map for the data recorded at the depth interval of 25-30 ft for the penetrations is presented in Fig. 5.

3.1.3 Geochemical Investigation

A Phase IV site investigation consisting of a soil gas survey was performed on a demonstrative basis in September 1994 at select locations of the site, which included the disposal pit area, the 210-barrel storage tank area, the large storage tank area, and the drain pit area. A sampling grid containing 100-ft centers was used; the sample density was increased to 50-ft centers in the storage tank and the drain pit areas where more detailed data were required. The sampling locations are illustrated in Figs. 6 and 7.

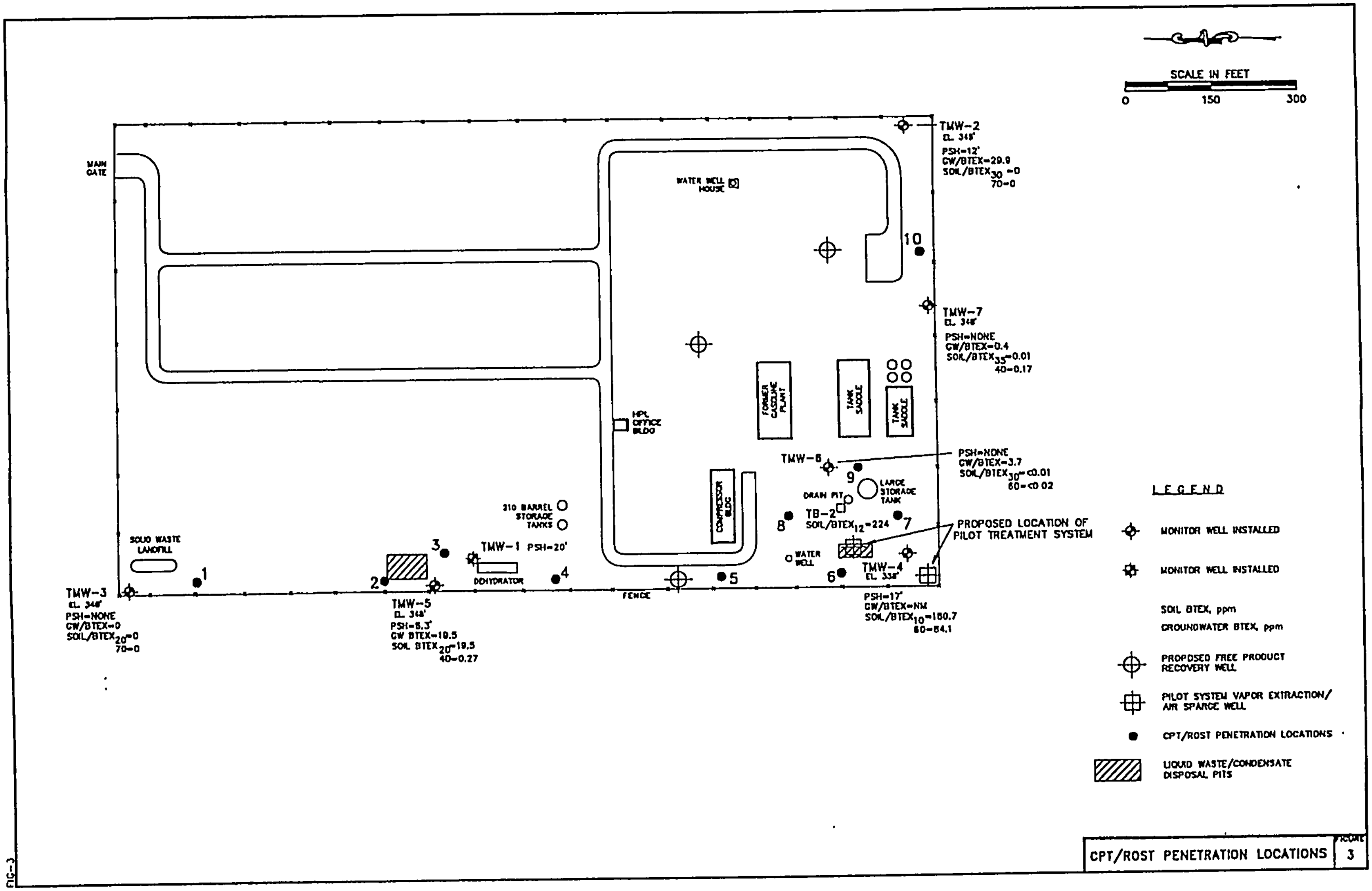
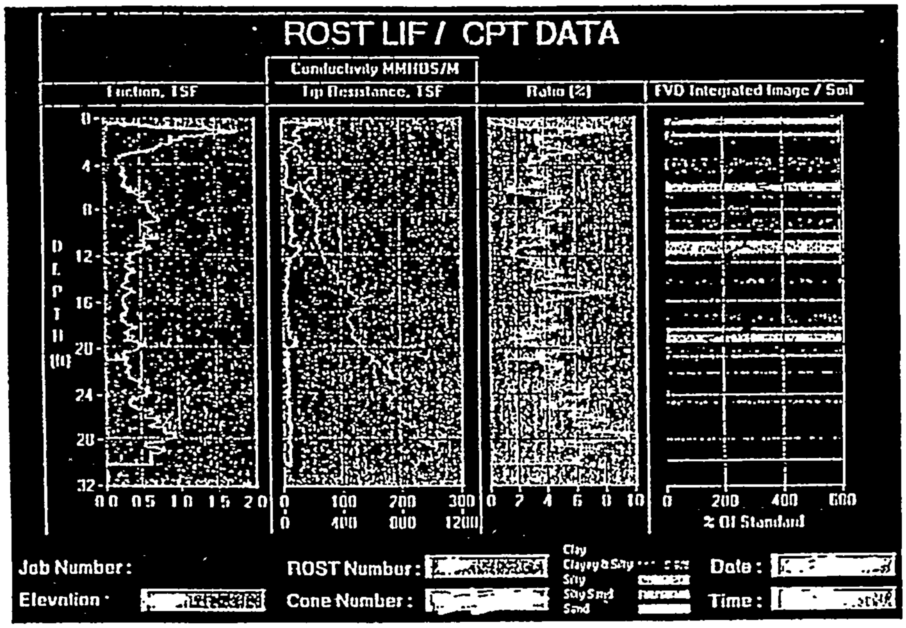
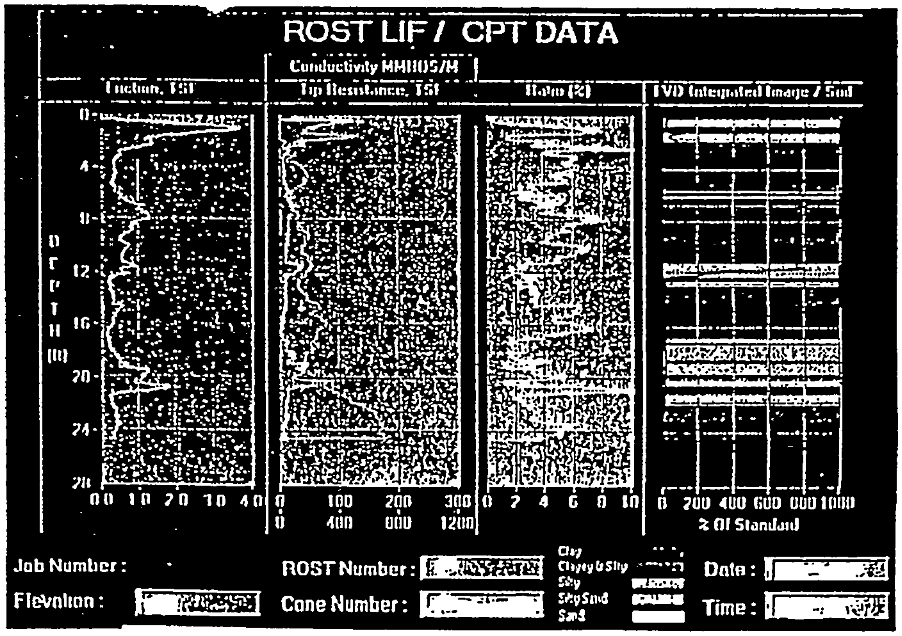


Fig. 3 CPT/ROST Penetration Locations



Location 3 CPT/ROST Data



Location 4 CPT/ROST Data

Fig. 4 **Field CPT/ROST Data for Locations 3 and 4**

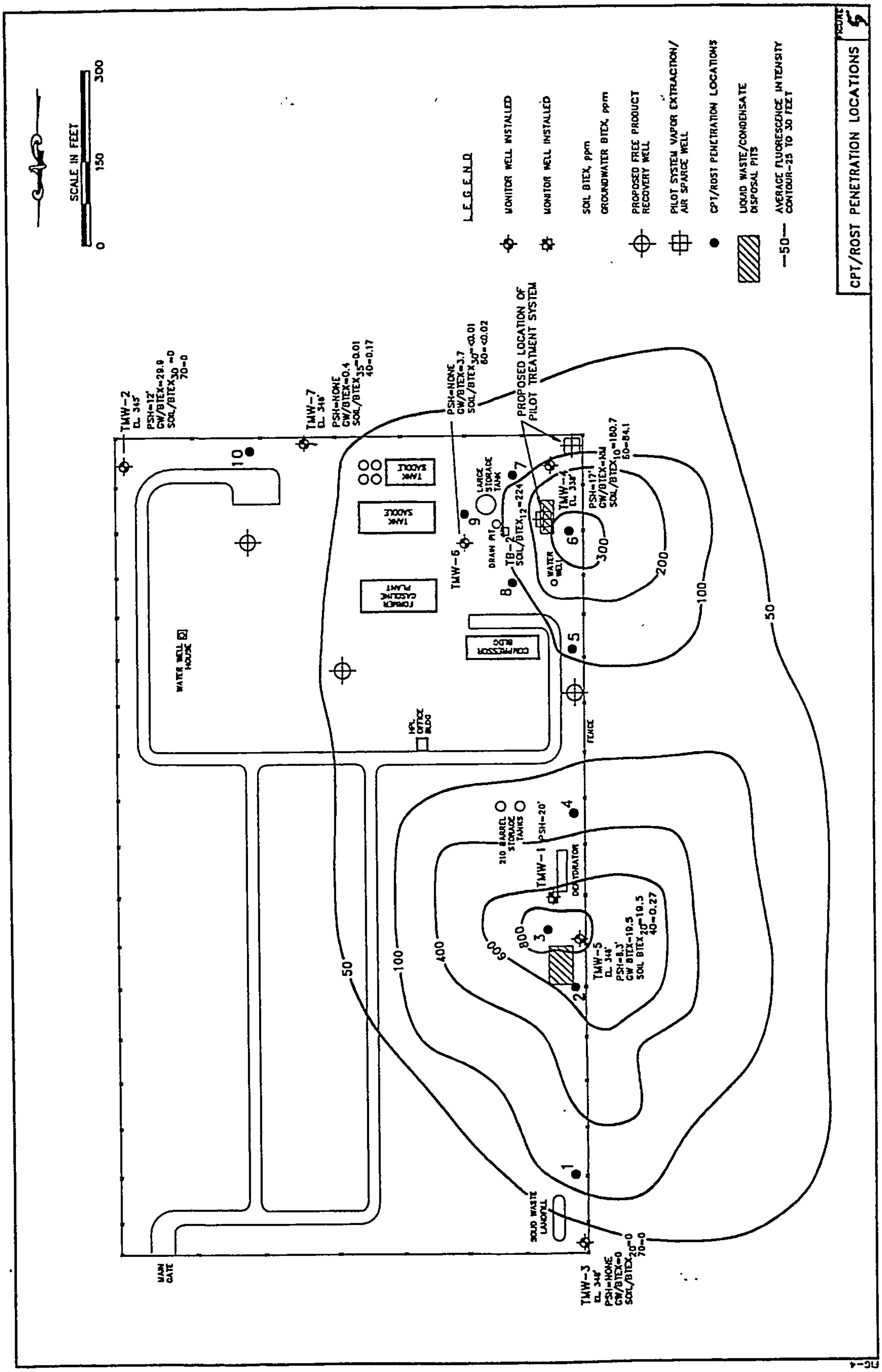


Fig. 5 CPT/ROST Penetration Locations

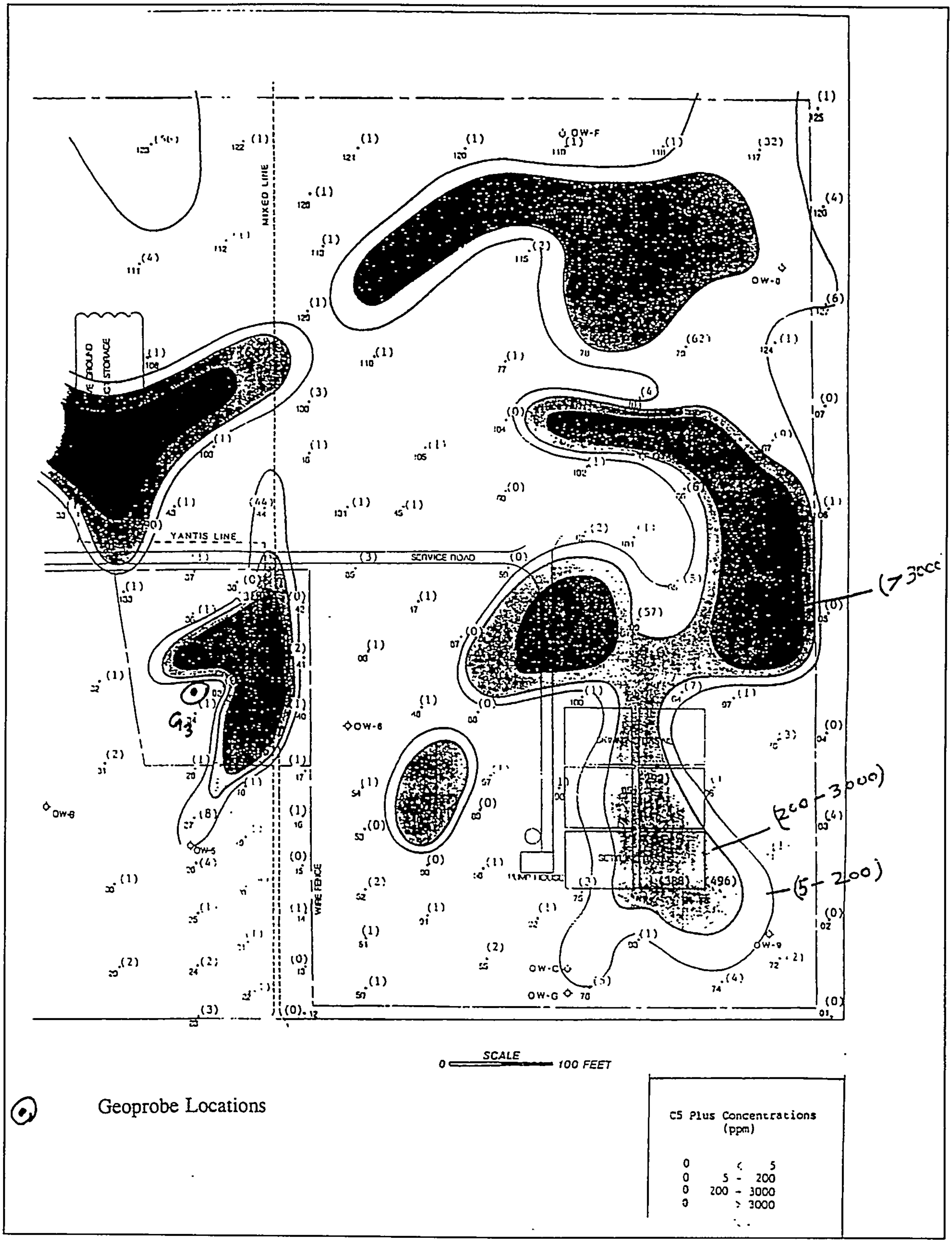


Fig. 6 Gasoline Range (C5 Plus) Hydrocarbon Plume Mapping Using Soil Gas Survey

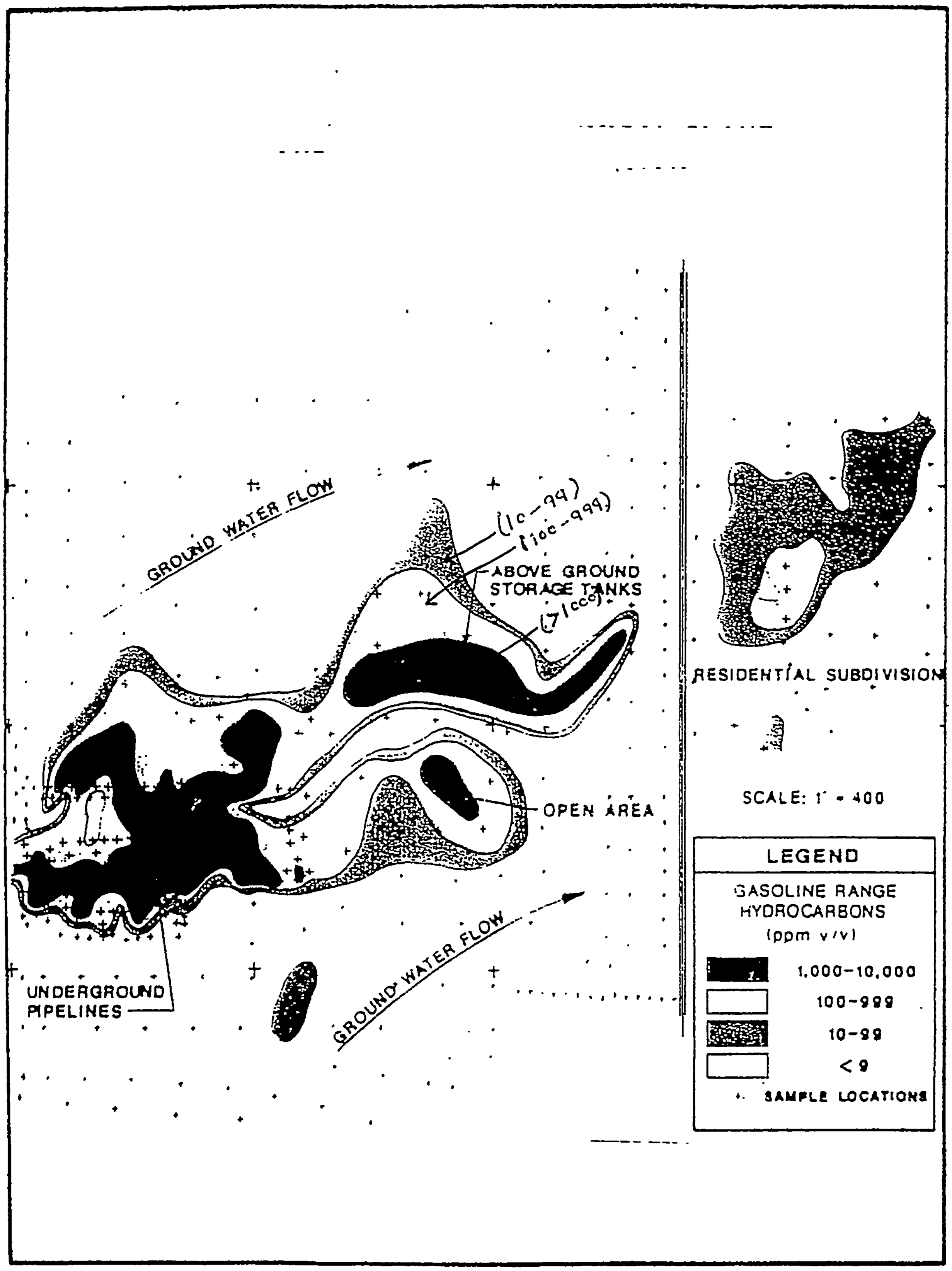


Fig. 7 Lighter Range (C1 through C4) Hydrocarbon Plume Mapping Using Soil Gas Survey

Soil gas samples were extracted by using the sampling probe and evacuated into 125-cc septum top glass bottles. Soil gas samples were analyzed in an analytical laboratory in Houston, Texas, using a modified analytical method (Method 8015) that uses flame ionization detector (FID) gas chromatography to determine gasoline range organics (GRO). This method specifically provides data on compound-specific hydrocarbon parameters. The method was used to determine methane, ethane, propane, and butanes (C1 through C4) and gasoline-range hydrocarbon (C5 plus) concentrations. These compounds were used as target analytes based on data acquired from the earlier phases of investigation, process knowledge, and site historical information.

Light hydrocarbon analyses (C1-C4) measure the most volatile constituents present in gasoline, natural gas, and other petroleum-based products. These light hydrocarbon compounds tend to dissipate rapidly with time and/or distance from the point at which petroleum products are introduced into the subsurface environment. The light hydrocarbon analyses performed for the site allowed the identification and differentiation of natural gas leaks, biogenic methane, and refined petroleum product contaminants.

Gasoline-range (C5 plus) hydrocarbon analyses yield a quantitative measure of the actual volume of "gasoline-type" vapor present in near-surface soils. Gasoline-range hydrocarbons dissipate more slowly than the lighter fraction (C1-C4) compounds and tend to identify areas where significant concentrations of petroleum constituents are present in near surface soils and/or groundwater.

By using soil gas survey data, hydrocarbon plume maps were developed for BETX-range compounds (C5 plus) as well as the lighter volatile range compounds (C1-C4). The concentration range of these compounds and plume maps for C5 plus and C1-C4 volatile range organics is presented in Figs. 6 and 7, respectively.

Data obtained from the soil gas survey facilitated the horizontal extent of contaminants plume. Soil gas plume maps were used to advance a limited number of boreholes using a Geoprobe. A brief description of the Geoprobe investigation is presented in the next section.

3.1.4 Geoprobe Investigation

A Phase V site investigation following the soil gas survey was performed in September 1994 using a Geoprobe. Soil samples were collected at five select locations and analyzed for both TPH and GRO. The locations of the Geoprobe investigation are illustrated in Fig. 6. The purpose of the Geoprobe investigation was to confirm the data acquired through the soil gas survey and the geophysical surveys.

4 RESULTS

This section presents a brief interpretation of the results obtained through the three types of investigation techniques used for the site characterization.

4.1 Geophysical Survey Results

4.1.1 Preliminary Data Interpretation of the FDEM and TDEM Surveys

The contour map of apparent conductivity derived from field measurements with the FDEM equipment (Geonics EM-34) is shown in Fig. 3. The location of TDEM sounding using Geonics EM-47 is also shown in Fig. 3.

The conclusions drawn from the conductivity data and contour map are:

- The background apparent conductivity values range from 12.5 to 18 millimho/m. These values are observed at varying distances around the areas of study (liquid disposal pit, storage tanks, drain pit, and condensate disposal pit). Similar background readings were observed in all directions around these areas, and, consequently, geological variations are not a likely factor for causing changes in apparent conductivity.

- The increase in apparent conductivity near the areas of study is attributed to, and consistent with, the hydrocarbon detection using the traditional approach. In the areas of the study, high conductive values (30 to 260 millimho/m) were observed, signifying the focal points of hydrocarbon contamination. This observation is consistent with the waste management practice followed in the past at the site.

- The background resistivity stratification, measured using the Geonics EM-47, consisted of an upper layer with a resistivity of approximately 30 ohm-m to a depth of 20 ft. A more resistive layer of 80 ohm-m was encountered at depth ranging from 20 to 40 ft. At greater depth a conductive layer was encountered.

- In one of the areas of the study, especially in very close proximity to the liquid disposal pit, drain pit, and storage tank areas, a highly conductive layer (approximately 5 ohm-m) was observed at a depth of about 45 ft. The change in conductivity in the upper 45 ft at these locations/areas was observed to be relatively small.

Based on the EM-34 and EM-47 results, it appears that the hydrocarbon contamination at the site is focused highly near the disposal pit, drain pit, and the two storage tank areas. The groundwater at the site appears to be an affected media of concern. The contour map of apparent conductivity appears to present the lateral extent of migration. The increase in apparent conductivity due to the hydrocarbon contamination is relatively symmetric around the disposal pit, drain pit, and the two storage tank areas. The hydrocarbon contamination appears to be migrating to the west/southwest of the property boundary.

4.1.2 Preliminary Data Interpretation of CPT/ROST Survey

Average fluorescence intensity in the range from 15 to 120% of standard was observed in most of the penetrations at 0 to 20 ft below ground surface, signifying the widespread distribution of hydrocarbon at low levels in the investigation area. The average fluorescence intensity data acquired for the site at the CPT/ROST penetrations near the disposal pit, dehydrator unit, 210-barrel storage tank, drain pit, and the condensate disposal pit (Penetration Nos. 2, 3, 4, and 6) at all depth intervals appear to present elevated contaminant concentrations. The average fluorescence intensity in these penetrations ranged from 300 to 950% of standard. The highest fluorescence intensity (950% of standard) was observed in the CPT/ROST penetration No. 3 at a depth of approximately 40 ft. The average fluorescence data acquired at 5-ft intervals of the penetrations were mapped. An illustration of the average fluorescence intensity isoconcentration map for the depth interval of 25-30 ft considering all the penetration data is presented in Fig. 5. Figure 5 depicts the potential intensity of hydrocarbon presence at the site at 25-30 ft.

The average fluorescence intensity map developed for all depth intervals indicated the elevated hydrocarbon concentration at deeper depth to the water table/LNAPL interface. The maps apparently depicted the migration of hydrocarbon contamination plume towards the south/southwest of the property boundary.

4.2 Geochemical Survey Results

The soil gas survey performed for the site provided supplemental data and identified the lateral extent of hydrocarbon plumes. GRO analytical results of soil gas samples indicated concentration of BETX range hydrocarbon compounds (C5 plus) from undetected to over 3,000 ppm. The survey results of select locations are presented in Fig. 6.

The soil gas survey results of lighter hydrocarbon analyses for the large aboveground storage tank area are presented in Fig. 7. Results indicate C1 through C4 gasoline-type range hydrocarbon plume concentration ranging from undetected to a maximum level of about 10,000 ppm.

4.3 Borehole Drilling and Sampling Results

Borehole drilling and sampling using the hollow-stem auger provided the basis for the remaining phases of the investigation. The drilling technique provided site stratigraphic information and samples for laboratory analysis. The TPH results confirmed the results obtained through the Geoprobe sampling. The TPH plumes were generally smaller in extent compared to compound-specific hydrocarbon parameters analyzed subsequently.

5 ECONOMICS OF SITE CHARACTERIZATION TECHNIQUES

The total cost for the traditional Phase I and intrusive Phase II investigation involving the drilling program and laboratory analysis of the groundwater and soil samples, was approximately US$75,000, excluding the disposal cost associated with investigation-derived waste materials, such as soil cuttings and purge water. The cost for the FDEM and TDEM electromagnetic survey was approximately US$35,500, which included the field survey, equipment rental, data interpretation/processing, report preparation, and other project incidentals. The cost of the demonstration CPT/ROST survey was approximately US$26,500, which covered the mobilization/demobilization of the truck and rental equipment, survey, data mapping, data interpretation, and preparation of a report. The soil gas survey, including the laboratory analysis for compound-specific parameters, was approximately US$32,000. Geoprobe investigation and analytical costs totaled approximately US$29,500.

6 CONCLUSIONS AND RECOMMENDATIONS

Application of the three different techniques (traditional sampling and analysis, the FDEM and TDEM technique, and the CPT/ROST technique) at this hydrocarbon-contaminated site illustrates the effective use of the techniques. The results of the demonstrative application of the geophysical techniques appear to confirm the laboratory analysis of hydrocarbon contamination. The cost analysis presents the geophysical and geochemical techniques as cost-effective, rapid, and reliable methods for collecting screening-level data. Similarities were observed in the results and prediction of the hydrocarbon migration at the site between the two geophysical techniques.

The geophysical techniques provided an excellent understanding of the site stratigraphy, which is very vital to predict the fate and transport mechanism of contaminants. Although the traditional methods provide similar lithological information, the method is relatively slower and expensive. The geophysical techniques provide real-time data readily in the field, which often has an advantage while performing the initial assessment, screening site locations, or conducting remediation at the site. There are no drilling fluids, soil cuttings, development/purge water generated in the geophysical techniques, which often require special handling, treatment, or disposal. The highly intrusive nature of conventional drilling methods can potentially cause cross-contamination, which does not occur in the geophysical techniques. Geoprobe sampling technique presented an excellent way to confirm geophysical and geochemical data.

Although at this site, the traditional investigation preceded the geophysical and geochemical techniques and provided baseline data, it appears that the use of geophysical and/or geochemical techniques will be an excellent screening method for informed detailed site investigation. An intrusive investigation program can be designed and implemented based on the initial data gathered through the use of the geophysical and/or geochemical techniques to address the issues directly with reduced effort and increased cost savings. It must be recognized that the geophysical and/or geochemical techniques do not substitute, but complement, the traditional sampling and analysis method. Ultimately, physical verification must be performed by using the traditional method, especially for regulatory agencies' acceptance. The geophysical or geochemical techniques merely "cut to the chase" and often focus the area(s) for detailed investigation, which has ultimate implications on the cost savings and effectiveness of the investigation.

The use of geophysical techniques is not without limitations. Large magnetic anomalies that are not the target of the investigation potentially may distort the electromagnetic signals of the instruments and can effectively mask the target anomaly. Also, potential interference from the cultural setting (e.g., buried pipelines, sewer lines, channels, etc.) in the area of the survey is possible, which would result in distorted survey readings. It is very important to gain a good understanding of the cultural settings at the site through background research or intensive surveys to identify the cultural anomaly. Similarly, the geochemical technique also has its limitations. The technique is applicable for organic compounds. The use of geophysical or geochemical techniques does not guarantee complete success and accuracy in mapping contaminants; however, they are generally very effective tools when properly integrated within a site characterization program. As with any technology, experience must be used to select the right technique and to correctly interpret the results of the survey to have a successful investigation.

One of the most important elements of this site characterization program was the use of compound-specific analysis of hydrocarbon. Analysis of TPH and GRO provided varying results and indicated no correlation between the two parameters. The extent of contamination shown by the TPH and GRO analyses differed. Confirmatory sampling performed using drilling methods tallied with the GRO analysis. The analytical program in the site characterization demonstrated the limitations of the TPH analysis and indicated the need to perform compound-specific hydrocarbon analysis, rather than conduct a broad indicator analysis, such as the TPH.

Although the site was investigated extensively, only limited data pertaining to the geophysical geochemical surveys and borehole drilling have been presented in this paper. The data presented are only a limited portion of a large data set gathered at the site through the use of the three techniques. Presentation of all and complete data was limited by both the contractual obligation with the client and limitations set by the Pacific Basin Consortium on the total number of pages for the paper. This paper is intended to mainly evaluate the three techniques and share the use and effectiveness of the techniques for site characterization.

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The views expressed and inferences made are solely mine, and as such do not represent any organization, vendors of the technology, or individuals. Any deficiencies or inadequacies in this paper are due to my contribution. This paper is based on a demonstrative effort of the geophysical technologies, and as such does not represent a full-fledged field effort. The data presented, inferences made, and cost estimates are only intended to provide a preliminary evaluation, and as such does not constitute the actual cost, which will vary very significantly depending on the field conditions, intensity of field effort, and the resolution or the level of detail required to obtain more reliable data. No guarantees or warranties are implied or expressed in the results or the techniques.

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