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Sewage sludge and wastewater for use in agriculture

*Proceedings of consultants meetings
organized by the
Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture
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IAEA Division of Physical and Chemical Sciences,
and held in Vienna, 5–9 December 1994*



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FOREWORD

Wastes have been produced by mankind since ancient nomadic tribes settled into villages and started utilizing fire and cultivating land. Archaeological evidence traces the practice of waste disposal back to antiquity. However, the concept of community-wide systematic collection, treatment, and disposal of solid wastes and wastewater did not evolve until the late 19th century.

The disposal of sewage sludge is a serious problem in many countries due to rapid urbanization. Agriculture offers one solution: land application of municipal sewage sludge is practised throughout the world, with beneficial effects on crop yields, soil organic matter, cation exchange capacity, water holding capacity and soil fertility in general. High levels of nitrogen, phosphorus and micronutrients found in sewage sludge make it an excellent fertilizer. In addition, high organic matter level can improve soil structure, particularly that of sandy soils in arid and semi arid areas. However, the presence of pathogenic organisms, heavy metals and other toxic materials from industry, necessitates treatment of sewage sludge before application to soil; liming and composting are traditional methods. Recently, gamma rays and electron beams have been successfully used on sludges and wastewater to eliminate pathogenic organisms and some toxic chemicals. Sufficient technical data are available for gamma treatment of sludges, permitting its application on the demonstration or commercial scale, but gaps in our knowledge exist for the practical application of electron-beam technology.

The IAEA's involvement in studies of radiation processing of sewage sludge dates back several years. A five-year Co-ordinated Research programme on Radiation Treatment of Sewage Sludge for Safe Reutilization, involving Canada, Germany, India, Indonesia, Italy, Japan, and the United States of America, was completed in 1990. This programme laid a solid foundation on which future programmes can be built. However, at present, information is limited on the availability of nutrients from sewage sludges to crops, its benefits as an organic amendment to soil, and the harmful effects of heavy metals on crop growth. Isotope and radiation techniques are valuable tools of potential use in finding answers to some of these questions.

From 5 to 9 December 1994, the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture held a Consultants meeting on Radiation Processing of Sewage Sludge and its Use to Increase Crop Yields, and to Preserve the Environment, with S. Kumarasinghe of the Soil Fertility, Irrigation and Crop Production Section acting as the Scientific Secretary. In parallel, the Division of Physical and Chemical Sciences held a Consultants meeting on Irradiation Treatment of Water, Wastewater and Sludges, with M. Lapidot and V. Markovic of the Industrial Applications and Chemistry Section as the Scientific Secretaries.

This publication, which contains the papers presented at the two Consultants meetings, was prepared by S. Kumarasinghe and M. Lapidot.

EDITORIAL NOTE

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**IRRADIATION TECHNIQUES FOR
SEWAGE SLUDGE AND WASTEWATER**

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CURRENT STATUS OF RADIATION TREATMENT OF WATER AND WASTEWATER



XA9745785

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Abstract

This is a brief review of the current status of radiation treatment of surface water, groundwater, wastewaters, and sewage sludges. Sources of ionizing radiation, and combination radiation methods for purification are described in some detail. Special attention is paid to pilot and industrial facilities.

1. INTRODUCTION

Currently, because of the rapid development of industry and agriculture, the problems of purification and disinfection of natural water, wastewaters, sewage sludges, flue gases etc. are intensifying in many countries. A promising way of solving some of these problems is by the application of irradiation methods.

Irradiation of any system leads to the formation of highly reactive species, for example hydrated electrons, OH radicals and H atoms in water, which can cause various radiolytic conversions of pollutants: redox reactions, decomposition of organic compounds including dyes, formation of precipitates, etc.. It is also well known that ionizing radiation has a sterilizing action. These effects are the bases for the development of radiation methods for the purification and disinfection of gaseous, liquid, and solid wastes.

The first studies on radiation treatment of wastes, predominantly for disinfection, were conducted in the 1950s [1]. In the 1960s, these studies were extended to the purification of water. Later, radiation methods were developed for the purification of flue gases. Currently, the main directions for research and technological development in this area are:

- (1) radiation treatment of surface and groundwater;
- (2) radiation purification of wastewater;
- (3) radiation treatment of sewage sludges;
- (4) radiation purification of flue gases;
- (5) radiation purification of solid wastes: hospital and airport wastes, contaminated soil, etc.

This is a brief review of the current status of radiation treatment of water, wastewater, and sewage sludge. Some related topics are also considered. Among the other publications in which the respective subjects are discussed are books [2, 3] and reviews [4-8].

2. SOURCES OF IONIZING RADIATION

Sources of γ -radiation (from Co-60 and, to a lesser extent, Cs-137) and of electron beams (from accelerators) are used. The activity of radionuclides in many treatment facilities has reached approximately 1 MCi (equivalent to approximately 15 kW).

The energy and power (equivalent to the activity of radionuclides) of electron beams from accelerators are up to about 2 MeV and 75-80 kW, respectively. Table I shows the parameters of some industrial electron accelerators utilized for the radiation treatment of water and liquid wastes. It should be noted that research and development in this area is being conducted more intensively with electron accelerators, because of their greater operational safety and higher output compared to γ -radiation sources.

3. SURFACE WATER AND GROUNDWATER

Surface water and groundwater intended for drinking can be contaminated with pathogenic micro-organisms and parasites, and hazardous chemical pollutants. Often the content of pollutants and the level of infection are low, with only small doses required for their radiation treatment.

TABLE I. PARAMETERS OF SOME ELECTRON ACCELERATORS USED FOR RADIATION TREATMENT OF WATER AND LIQUID WASTES

Type of accelerator	Producer	Energy (MeV)	Power (kW)
Transformer ELV-3	Institute of Nuclear Physics, Siberian Division of Russian Academy of Sciences (Novosibirsk) and Vladimir Il'itch factory (Moscow)	0.5-0.7	50
High-frequency accelerator ILU-6	The same	1.5-2.0	30
Insulated core transformer (ICT)	High Voltage, USA	1.5	75
Accelerator EOL-400 (with two irradiators)	Radiotechnical Institute (Moscow)	0.4	28
Cockcroft-Walton accelerator	Nissin-High Voltage, Japan	2.0	60

TABLE II. RADIATION-CHEMICAL YIELDS OF CHLORIDE IONS FROM THE RADIOLYSIS OF AERATED AQUEOUS SOLUTIONS OF HALOGENATED ORGANIC COMPOUNDS^a

Compound	Concentration (mol L ⁻¹)	G(Cl ⁻) (ion/100 eV)	Reference
1,2 Dichloroethane	5x10 ⁻⁴	4.65	[11]
	1x10 ⁻³	6.2	[11]
1,1,1-Trichloroethane	1x10 ⁻⁴	0.36	[12]
Trichloroethylene	7.6x10 ⁻⁶	1.28	[13]
	7.6x10 ⁻⁵	5.40	[13]
Tetrachloroethylene	3x10 ⁻⁵	1.08	[11]
	1x10 ⁻⁴	10.2	[11]
	1x10 ⁻³	30.6	[11]
Chlorobenzene	1x10 ⁻³	1.6	[11]
4-Chlorophenol	1x10 ⁻⁴	1.5	[14]
	5x10 ⁻³	3.96	[14]
2,4-Dichlorophenol	5x10 ⁻³	2.25	[12]

^a Initial radiation-chemical yields are given.

Doses of approximately 1 kGy were found sufficient for the purification and disinfection of natural water, in particular for the decomposition of organic compounds such as humic substances causing color, odor, etc. [1, 4, 9]. In a recent study, water from the Segezha river, discolored by natural organics and finely-dispersed particles, was effectively cleared by electron-beam treatment. The data are shown in Figs. 1 and 2: a dose of several kilograys was sufficient to reduce the color to the Russian regulatory level of 20 degrees. It should be noted that the required dose depended on the season during which the water was sampled. A higher dose was required for the autumn water than for the winter.

One important problem to be solved is the removal from natural water of chlorinated organic pollutants that are toxic and carcinogenic. These pollutants originate in the environment, and also by the chlorination of water containing some organic compounds. Researchers have found that irradiation of contaminated water decomposes chlorine-containing organic compounds [6-8]. Table II shows the radiation-chemical yields of chloride ions upon radiolysis of aerated aqueous solutions of some compounds. The yields characterize their radiation-chemical decomposition. From these data it follows

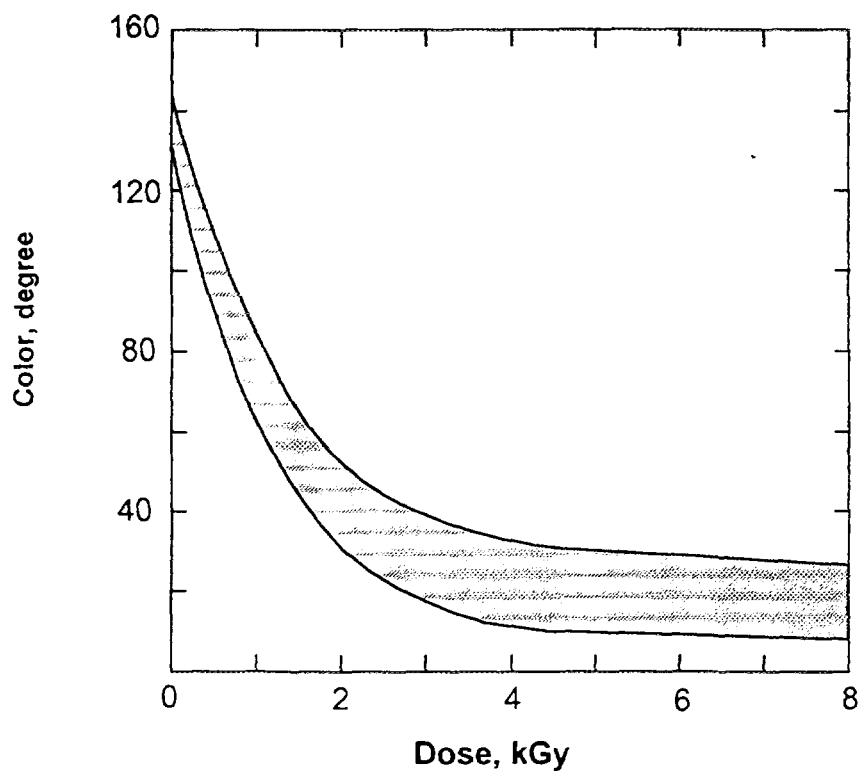


FIG. 1. Ameliorating effects of radiation on discoloured water from the Segezha river (in Karelia) taken during October and November 1993 (electron beam, energy 5 MeV, dose rate 83 kGy s⁻¹).

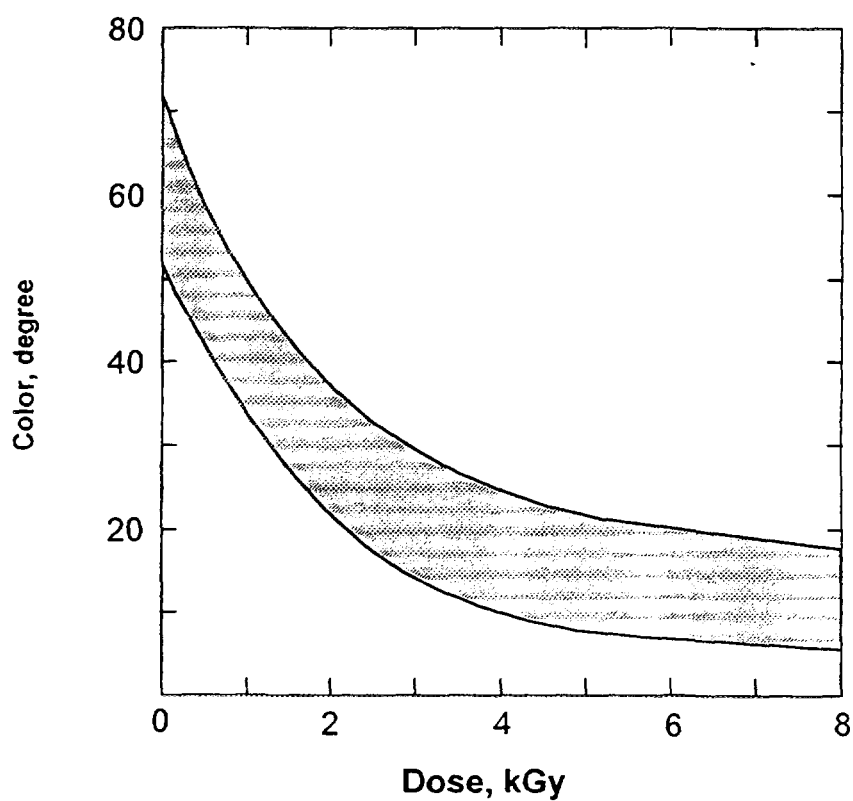


FIG. 2. Ameliorating effects of radiation on discoloured water from the Segezha river (in Karelia) taken during December 1993 to February 1994 (electron beam, energy 5 MeV, dose rate 83 kGy s⁻¹).

that, at low pollutant concentrations (10^{-4} mol L⁻¹ and less), relatively small doses (1 kGy and sometimes even less) are required for purification. For such systems, the application of radiation methods is promising.

However, it is necessary to emphasize that radiolysis of solutions of chlorinated aromatic compounds may cause the formation of other toxic compounds. For example, isomeric hydroxycyclobenzenes and phenol appear upon the irradiation of chlorobenzene solutions. Since these substances must also be decomposed, the doses required for purification increase considerably. Besides, there is a noticeable dependence of decomposition on dose rate, especially at low concentrations. Some relevant data are shown in Table III [15].

The combination of radiation treatment of water with its ozonation leads to a synergistic effect (see below) as obtained, for example, in the case of water contaminated with trichloroethylene and tetrachloroethylene [16, 17]. For example, to decrease 120 ppb trichloroethylene to a residual concentration of 5 ppb, the electron-beam irradiation requires a dose of 370 Gy. When 3 ppm ozone is added to the water before irradiation, the same decrease in trichloroethylene concentration is achieved at a dose of 45 Gy [17]. One should note that ozonation almost completely excludes the dose-rate effects in such dilute solutions [17]. In addition, ozonation protects the electron-beam treated water from the reappearance of micro-organisms and parasites during piping to houses.

Radiation treatment gives positive results also in the case of underground water supplies. First, it is successfully used for the regeneration of biologically clogged wells [18-20]. Ionizing radiation kills the bacteria causing the redox reactions of Fe(II), Mn(II), etc. and the subsequent precipitation of insoluble hydrolytic products. These precipitates clog the pores of aquifer channels, accelerating the aging of the well. The required doses are 0.25-0.4 kGy [18]. If the well is equipped with a γ -radiation source, its lifetime increases by a factor of at least 2. This method was widely applied in the former GDR [18, 21]. Seven hundred and sixty wells were equipped with Co-60 γ -rays sources (total activity was 132 kCi). However, after the reunification of Germany, all the sources were removed since the use of irradiated foodstuffs, including drinking water, is not permitted in the FRG. In former Czechoslovakia, two wells had Co-60 γ -rays sources [19], and similar studies have been conducted in the USA [20].

Secondly, in-situ irradiation of polluted underground water leads to its purification. For example, it was shown that the concentration of cyanide ions was substantially reduced when a well was equipped with a Co-60 γ -ray source and an absorber with activated charcoal [19]. During six years of operation, the concentration of cyanide in the well water was decreased by more than an order of magnitude [22].

Despite these positive results, the radiation treatment of natural water intended for drinking has not been adopted on a large scale.

4. WASTEWATER

Comparatively low doses are required for radiation treatment of municipal wastewater effluent. In pilot plants with electron accelerators, such wastewater can be disinfected at doses of 0.4-0.5 kGy, which are sufficient to decompose organic pollutants and greatly improve the taste of raw-water supplies [23, 24]. Similar doses were found to be sufficient for the disinfection of secondary effluents from sewage-treatment plants in Tokyo, but several kilograys were required to eliminate pollutants such as detergents, organic sulfides, and dyes [25]. Doses of several kilograys are usually required for the disinfection and purification of municipal wastewater, and higher doses are needed for unchlorinated than for a chlorinated effluent [6].

TABLE III. DOSE-RATE EFFECT UPON THE RADIOLYSIS OF AQUEOUS SOLUTIONS OF SOME HALOGENATED ORGANIC COMPOUNDS

Compound and its concentration	Irradiation conditions	Radiation effect	G (ion/100 eV)
1,2-Dichloroethane, 1×10^{-4} mol L ⁻¹	Aerated solution, electron beam, dose rate $\sim 1 \times 10^4$ Gy s ⁻¹	Formation of chloride ions	1.65
1,2-Dichloroethane, 1×10^{-3} mol L ⁻¹	Aerated solution, γ -radiation, dose rate 8.3 Gy s ⁻¹	The same	6.2
1,2-Dichloroethane, 1×10^{-3} mol L ⁻¹	Aerated solution, electron beam, dose rate $\sim 1 \times 10^4$ Gy s ⁻¹	The same	2.6
Chlorobenzene, 1×10^{-4} mol L ⁻¹	Aerated solution, electron beam, dose rate 6.3×10^6 Gy s ⁻¹	The same	0.43
Chlorobenzene, 4.35×10^{-3} mol L ⁻¹	Aerated solution, electron beam, dose rate 6.3×10^6 Gy s ⁻¹	The same	1.4 ^a
Chlorobenzene, 1×10^{-4} mol L ⁻¹	Aerated solution, electron beam, dose rate 6.4×10^6 Gy s ⁻¹	Formation of phenolic compounds	0.6
Chlorobenzene, 4×10^{-3} mol L ⁻¹	Aerated solution, electron beam, dose rate 5×10^6 Gy s ⁻¹	Formation of peroxide compounds	1.45

^a At low dose rate (γ -radiolysis) $G(\text{Cl}^-) = 1.6$ ion/100 eV for 1×10^{-3} mol L⁻¹ aqueous solution [11].

Industrial wastewater differs from polluted surface water and groundwater by the variety of pollutants contained and their higher concentration. Such wastewater can contain substances that are toxic and difficult to destroy: dyes, cyanides, bismuth and mercury compounds, some detergents, phenol, etc. As a rule, several dozen kilograys or more are required for the purification of these wastes, therefore researchers have developed methods that combine radiation treatment with conventional chemical, biological, thermal, or flotation procedures. Synergistic effects are often observed in the application of combination methods, the most important of which are briefly considered below .

4.1. Radiation-flotation

The radiation-flotation method for the purification of industrial aqueous wastes from mercury was developed several years ago in the former USSR [26]. The wastewater was from a plant that produced chlorine and alkali by electrolysis, with mercury as an electrode. The method consists of three steps:

- (1) preliminary flotation in the presence of a surfactant (pH of the waste is 12-13);
- (2) γ -irradiation of 1 kGy;
- (3) secondary flotation.

By this method it was possible to decrease the concentration of mercury, which was present in various forms (dissolved, as a metal, and in precipitate), to the regulatory level of $5 \times 10^{-3} \text{ mg L}^{-1}$ approved in the former USSR and Russia [26]. The radiation-chemical reduction of dissolved bivalent mercury, which does not float, to a metal and/or a slightly soluble pseudomonovalent form [$\text{Hg}_2(\text{OH})_2$ type], allowed effective removal by flotation [27, 28].

4.2. Radiation-biological

This method consists of the use of tertiary biological purification of wastewater following the radiation treatment; an industrial application is the decontamination of effluent from a plant producing synthetic rubber (see below).

4.3. Radiation-polymerization

This method was proposed 15 years ago for the treatment of wastes containing monomers [29]. Upon irradiation, the monomer is polymerized and an insoluble pollutant-capturing polymer is precipitated. No practical application has yet been found.

4.4. Thermoradiation

This method consists of irradiation and simultaneous heating, applicable predominantly to the disinfection of wastes and sewage sludge. The synergism eradicates aerobic and anaerobic spores, vegetative cells, viruses, and enzymes, with reduction in irradiation times of up to 30-fold [30].

4.5. Radiation-electrodialysis

Comparatively new, this method involves irradiation and electrodialysis [31]. Wastewater circulates at a specific speed through an electron beam and an electrodialyser. The efficiency of the combination is 2.5-10 times higher than that of radiation alone.

4.6. Radiation-coagulation

This method consists of the irradiation of wastewater with subsequent precipitation of the products of radiolytic conversion of the pollutants by means of a coagulant [32, 33]. It can be used,

for example, for the purification of wastewater from (i) poly(oxyethylene) n-nonyl phenyl ether - $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{C}_2\text{H}_4\text{O})_n\text{H}$ ($n = 7.5, 10, 20, \text{ and } 80$) - a non-ionic surfactant that it is not decomposed by biological treatment, and (ii) polyvinyl alcohol, using $\text{Fe}_2(\text{SO}_4)_3$ as a coagulant.

4.7. Radiation-adsorption

This method is based on the adsorption of pollutants from wastewater by continuously- irradiated activated charcoal [34]. The charcoal can be regenerated by radiation-chemical oxidation of the adsorbed compounds. This method is utilized, for example, to purify water from the pesticides DDT [2,2,2-trichloro-1,1-bis(p-chlorophenyl)ethane] [35] and Khlorofos [0,0-dimethyl-(2,2,2-trichloro-1-hydroxyethyl)phosphonate] [36]. In the case of DDT, the radiation-chemical yield of the decomposition in the absence of activated charcoal is as low as 10^{-4} - 10^{-3} mol/100 eV; in the presence of the sorbent, the yield increases up to 0.1-1.0 molec./100 eV [35]. Similarly with Khlorofos, the sorbent increases the radiation-chemical yield [36].

4.8. Oxyradiation

This involved irradiation of waste and simultaneous bubbling of oxygen. It is successfully used for the disinfection of sewage sludge (see below).

4.9. Radiation-ozonation

This method combines ozonation and irradiation [32, 33, 37]. A powerful oxidizing agent, ozone is sometimes used for the purification and disinfection of wastewater. However, its action is selective, being limited by unsaturated organic molecules. Irradiation intensifies the ozonation effect and synergism occurs with various pollutants (phenol, acetone, halogenated organic compounds, etc.). It is particularly applicable to the purification of groundwater polluted with chlorinated olefins.

The possible role of ozone (in addition to its direct action on pollutants) lies in the conversion of hydrated electrons and H atoms (via intermediate formation of HO_2 , O_2^- , HO_3 and O_3^-) and hydrogen peroxide to OH radicals [3]. Of course, such conversion occurs when hydrated electrons and H atoms do not react with pollutants (i.e. when pollutants have a low reactivity towards these short-lived species and/or when the concentrations of oxygen and ozone are much higher than concentrations of pollutants). Moreover, ozone combining with a poorly reactive organic peroxide free radical can convert it to a highly-reactive alkoxy radical that can initiate chain reactions.

4.10. Disinfection of dung wastes

The problem of disinfecting large amounts of dung arose in the former USSR with the construction and operation of large numbers of pig-breeding farms, and studies were made of the possibility of using ionizing radiation [38-40]. Disinfection of dung wastes is a complex problem due to high levels of infection and the high content of organic pollutants. Organic compounds scavenge the free radicals formed from water radiolysis and, in consequence, protect bacteria, viruses and parasites from the "indirect" action of ionizing radiation. Therefore, the doses required for the disinfection of the wastes are high (25 kGy and more) [40].

Of course, from an economic point of view, it is important to reduce the doses required for the disinfection. This reduction can be achieved by combining radiation treatment with conventional

disinfecting agents (chlorine, ozone, ammonia, etc.) or sensitizers (for example, KCl) [40]: it was noted that the addition of 0.2% ammonia into the waste decreased the dose required for disinfection to 5 kGy. By the radiation-adsorption method, which involves the filtration of the wastes, settling, aeration, and irradiation in the presence of activated charcoal, the dose was reduced to approximately 0.5-1.0 kGy [41].

In order to test various types of radiation technology for disinfection of dung wastes on a large scale, four pilot plants were constructed and operated for a long time in the former USSR (see Table IV) [38-40]. However, none saw adoption in practice, largely because of difficulty in obtaining a sufficiently high speed of dung-waste flow through the irradiation zone; dilution with water led to unmanageably large volumes of treated wastes.

4.11. Industrial plant

Studies on the radiation purification of industrial wastewater are being carried out rather extensively. However, they are largely confined to laboratory-scale and in some cases to pilot-scale development. So far, there is only one industrial plant for the radiation purification of wastewater, in operation at a synthetic-rubber factory in Voronezh, Russia [42-44]. The irradiation plant there has two production lines, each equipped with an ELV-type electron accelerator (energy 0.7 MeV, total power 65-70 kW). The radiation treatment is intended to remove the emulsifier Nekal from the wastewater. Nekal is a mixture of isomeric isobutylnaphthalene sulphonates. Its formula is $C_{10}H_6(R)SO_3Na$, where R is $(CH_3)_3C-$, $(CH_3)_2CHCH_2-$, or $CH_3CH_2CH(CH_3)-$, with a predominant content of the latter two butyl groups [45]; alkyl and sulfonate groups are in para-position at the same ring. These substances are refractory surfactants, and the radiation effects their conversion to biodegradable compounds.

TABLE IV. PILOT PLANTS FOR DISINFECTION OF DUNG WASTES

Location	Location source	Energy (MeV)	Power or activity
Moscow Oblast'	Electron accelerator EOL-400 (with two irradiators)	0.4	28 kW
Omsk Oblast'	Electron accelerator ILU-6	1.5-2.0	30 kW
Minsk Oblast'	Electron accelerator ILU-6	1.5-2.0	30 kW
Minsk Oblast'	Co-60 γ -ray source	1.25	0.49 kCi

It was found that 0.3 MGy was required for the complete decomposition of Nekal in a 10^{-3} mol L^{-1} aqueous solution [46]. However, for conversion to biodegradable compounds, complete decomposition is not necessary; it is sufficient to eliminate alkyl or sulfonate groups, or both [43, 45]. Indeed, it was observed that dealkylation and desulfonation (and the formation of naphthalene at high doses) takes place upon irradiation [43, 45]. The initial yield of Nekal decomposition is approximately 2 mol/100 ev. The dose required for degradation of 100-150 mg L^{-1} Nekal is 2-3 kGy. A pulse radiolysis study revealed participation of OH radicals and, to a lesser extent, of hydrated electrons [47].

After radiation treatment, the wastewater is subjected to tertiary biological purification, the second step in this combination method. Figure 3 shows the scheme of the combination electron-beam and biological treatment to remove Nekal from the wastewater. The waste is irradiated as a foam, with a density of 0.02-0.03 g mL^{-1} . The output of the plant is approximately 12,000 m^3 day^{-1} (at a beam power of 65-70 kW and dose of 3 kGy, the fraction of beam energy utilized is 0.6-0.7). If the wastewater is saturated with ozone, the output is somewhat higher and Nekal removal reaches 99.5%.

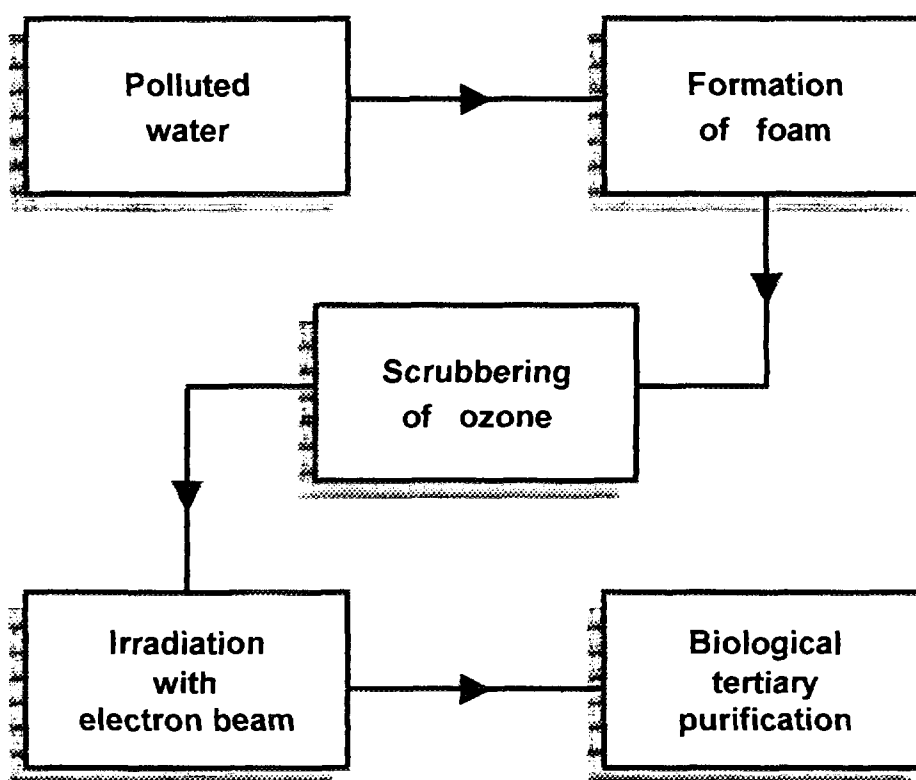


FIG. 3. Scheme of combined electron-beam and biological purification of wastewater from Nekal (a mixture of isomeric isobutylnaphthalene sulphonates).

4.12. New applications

New applications of ionizing radiation for the purification and disinfection of wastes include the treatment of hospital and airport wastes, the regeneration of activated charcoal and the purification of contaminated soil.

4.12.1. Hospital waste

Currently in the USA, there is one γ -radiation facility processing infectious hospital wastes. One relatively small γ -irradiation facility can treat all the hospital wastes generated by a city of 1 million people, and a large facility can process such wastes from a city of five million people [48].

The technology of radiation treatment of infectious hospital wastes was also developed in Russia [49]. It consists of four steps:

- (1) the separation of liquid and solid phases;
- (2) the radiation disinfection of the liquid wastes;
- (3) the radiation disinfection of the solid wastes;
- (4) the purification of the flue gases.

A facility with a Co-60 γ -rays source (Gammatok-100) was constructed with a potential output of $65 \text{ m}^3 \text{ day}^{-1}$. However, this method has not been implemented on a commercial scale.

4.12.2. Airport waste

Large international airports generate 20-30 tons (and even more) of waste per day, a quantity that can be processed by a medium-sized radiation facility. Nordion International Inc. (Canada) is planning to construct an airport γ -irradiator in the future [48].

4.12.3. Activated charcoal

Another application is the electron-beam regeneration of activated charcoal used for the purification of groundwater and aqueous wastes [50]. Charcoal with adsorbed sodium lauryl sulfonate can be regenerated by treatment with a radiation dosage of 1 MGy. Economic analysis showed that the radiation is about 8-10 times less expensive than the conventional high-temperature steam method.

4.12.4. Contaminated soil

Two procedures have been developed for the purification of contaminated soil [51-53]. The first consists of mixing the soil with water and a non-ionic surfactant, with a subsequent treatment with γ -radiation [51], which works well with soil contaminated with chlorinated dioxines. It was demonstrated, for example, that 2,3,7,8-tetrachlorodibenzo-p-dioxine was converted via step-wise reductive dechlorination to non-chlorinated dibenzo-p-dioxine with negligible toxicity. The radiation-chemical yield of destruction is of the order of $10^{-6} \text{ mol/100 eV}$. This means that the major route of destruction is "direct" action of radiation on the dioxine molecule.

The second procedure was developed for soil contaminated with volatile organic compounds (for example, trichloroethylene) [52, 53]. It consists of using vacuum extraction of pollutants from the soil and subsequent electron-beam treatment of the gaseous phase.

4.12.5. Industrial wastewater

Several projects for the construction of facilities for radiation purification and disinfection of municipal and industrial wastewater were developed in the former USSR, with plans for electron accelerators of total power approximately 0.9 MW. Some published data are given in Table V [54-56], however, given the poor economic situation in the republics of the former Soviet Union, it is unlikely that these projects will come to full fruition in the near future.

TABLE V. PROJECTS FOR THE CONSTRUCTION OF FACILITIES FOR PURIFICATION AND DISINFECTION OF MUNICIPAL AND INDUSTRIAL WASTEWATER IN THE FORMER USSR

Location	Purpose of facility	Accelerator type and its amount	Energy (MeV)	Power (kW)
Petershof (Russia) ^a	Disinfection of municipal wastes	ELV-8; 4	1.0-2.5	320
Lebyazh'e (Leningrad Oblast')	Purification of municipal wastes	ELV-8; 4	1.0-2.5	320
Riga, Avrora Factory (Latvia)	Purification of wastes from dyes	ELV-8; 2	1.0-2.5	160
Tambov, Pigment Factory (Russia)	The same	ELV; 2	-	-
Armyansk, Sivash Aniline-Dye Factory (the Crimea)	The same	ELV-8; 1	1.0-2.5	80

^aThe projected output of the facility is 110,000 m³ day⁻¹ [56].

In the USA (near Miami), a pilot plant with an electron accelerator of the ICT type, with energy of 1.5 MeV and power of 75 kW, has been developed for radiation purification and disinfection of water and wastewater, with a rate of flow through the electron beam of 460 L min⁻¹ [6, 57, 58]. The decomposition of toxic organic substances such as benzene, phenolic compounds, and chlorinated and brominated hydrocarbons has been studied.

5. SEWAGE SLUDGE

In the course of the settlement of sewage wastes, the first step in their purification, sludges consisting of insoluble solid particles (5-8%) and water (92-95%) are formed. After aeration and biological purification, a considerable fraction of the sludge is comprised of micro-organisms. These sludges can be used as a soil conditioner or an animal-fodder additive. However, being infected by bacteria, viruses and parasites and possibly containing toxic compounds, they must be disinfected before use.

TABLE VI. PILOT AND COMMERCIAL FACILITIES FOR RADIATION TREATMENT OF SEWAGE SLUDGE

Location ^a	Radiation source	Energy (MeV)	Power or Activity	Output ^b (m ³ day ⁻¹)	Reference
Geiselbullach FRG (1973-1993)	Co-60 and Cs-137 γ -rays sources	1.25 and 0.66	0.315 MCi Co-60 + 0.055 MCi Cs-137 (1990)	180 (2 kGy, 1981)	[60-62]
Munich-Grosslappen, FRG (1974 - about 1985)	Co-60 γ -rays source	1.25	-	30 (3 kGy)	[62]
Albuquerque, USA (1978-1985)	Cs-137 γ -rays source	0.66	~0.9 MCi	8 ton day ⁻¹ (10 kGy)	[63, 64]
Baroda, India (1989-)	Co-137 γ -ray source	1.25	0.15 MCi	110 (5 kGy)	[65]
Canada (project)	The same	1.25	-	80 ton day ⁻¹	[66, 67]
Boston, USA (1976-1980)	Electron accelerator of ICT type	0.8	50 kW	379 (4 kGy)	[23, 68]
Boston, USA (1980 - end of 1980s)	The same	1.5	75 kW	654 (4 kGy)	[23, 68]

^a The operation period is indicated in brackets. ^b The dose used for the treatment is given in brackets.

TABLE VI. (continued)

Location ^a	Radiation source	Energy (MeV)	Power or Activity	Output ^b (m ³ day ⁻¹)	Reference
Near Miami, USA (1984-1985)	The same	1.5	75 kW	648 (4 kGy)	[64, 68]
Takasaki, Japan (1987-)	Cockcroft-Walton accelerator	2.0	60 kW	7.2 ton day ⁻¹ (5 kGy)	[69, 70]
Near Minsk, Byelorussia (the 1980s)	Electron accelerator of ILU-6 type	1.6-2.0	30 kW	~150 (5 kGy)	[39,71,72]
Poland (project)	Linear electron accelerator	10	-	50-70 ton day ⁻¹ (5 kGy)	[73]

^a The operation period is indicated in brackets. ^b The dose used for the treatment is given in brackets.

It has been shown that the problem of sewage-sludge disinfection can be solved with irradiation [38,59]. In addition, irradiation often accelerates the filtration and sedimentation of precipitates and, as a consequence, the procedure of dewatering. Almost complete dehelminthization and inactivation of the agents of wide-spread animal diseases occur at doses of 2-5 kGy. In order to inactivate more radiation-resistant forms (for example, foot-and-mouth disease, anthrax, and pig plague) higher doses of 10 kGy and more may be required. At present, the technology for radiation disinfection of sewage sludge exists in some countries on the pilot and commercial scale, utilizing γ -radiation sources and electron accelerators (Table VI).

As in the case of radiation purification of water and wastewater, the application of combination methods for the treatment of sewage sludge leads to a decrease in the dose required. This is observed upon the use of the oxyradiation method. Bubbling oxygen during γ -irradiation allows use of lower doses (2 kGy instead of 3 kGy) [61]. A decrease in the dose also occurs upon the saturation of the sludge with an ozone-oxygen mixture and upon the introduction of some additives [62].

Economic feasibility studies show that, as a rule, the radiation treatment of sewage sludge is more profitable than conventional methods, especially when irradiation plants with high output are employed [23, 69, 74]. Undoubtedly, broader application can be found for the radiation treatment of sewage sludge.

6. CONCLUSIONS

Consideration of the current status of the application of radiation technology for purification and disinfection of water, wastewater and sewage sludge shows that ionizing radiation is an important and promising instrument in the solution of ecological problems. However, it is always necessary to prove an economic advantage and to overcome negative public opinion; in this respect, the electron accelerator is preferable to γ -irradiation. Electron accelerators with high energy, up to 10 MeV, and high power are the most suitable, for example linear electron accelerators developed in France [75] and Canada [76, 77] with energy of 5-10 MeV and power of 20-50 kW have been utilized successfully. Noteworthy is the development of a new type of industrial electron accelerator, the Rhodotron, with an energy of 10 MeV and a power of up to 100 kW [78]. A promising application of electron-beam technology, especially via the radiation-ozonation method, is for purification and disinfection of polluted surface and groundwater intended for drinking. Some combination technologies, for instance the electron beam-biological method, may find large-scale use for removal of refractory pollutants from industrial wastewater. An example of the successful application of such a method is the purification of industrial wastewater from Nekal [46, 47]. Much wider use of radiation methods is possible for the disinfection of sewage sludge.

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DISINFECTION OF SEWAGE SLUDGE BY GAMMA RADIATION, ELECTRON BEAMS AND ALTERNATIVE METHODS

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Abstract

Sewage sludges generally contain high concentrations of pathogens, even after digestion or other conventional treatments for stabilization. Disinfection can be effected by irradiation (e.g. gamma or electron beam), by heat treatment (pasteurization or thermophilic stabilization), and by changing the pH (lime treatment). Irradiation is a simple and reliable process for disinfection, with special advantages and favorable side-effects. Irradiation can be combined with oxygenation, heat or other treatments, with favorable synergistic effects. The total costs for the irradiation treatment of sewage sludges are comparable to those of alternative disinfection methods. Most of the worldwide practical experience has been obtained at the sewage-sludge irradiation plant in Geiselbullach (10 km west of Munich, Germany), which was continuously in operation from 1973 to 1993. A multidisciplinary research programme was conducted during the first 8 years. In subsequent years, the plant was operated commercially for sewage-sludge disinfection, without public funds. Other demonstration or research plants for sewage-sludge irradiation have been reported in the USA, India, Russia, Japan, Austria, Germany, and Hungary.

1. HEALTH RISKS

1.1. Pathogens in sewage sludges

The most important pathogens in sewage sludges are bacteria (e.g. salmonellae), viruses (e.g. poliovirus) and parasites (worm eggs, e.g. taenia). Full detection of pathogens is difficult, expensive and time consuming. Therefore, for orientative investigations, indicator organisms are often used: enterobacteria, faecal coliforms, or *E. coli* for the detection of salmonellae, for instance.

In Germany, digested sewage sludges have been found to contain 10^6 salmonellae per liter, 10^3 viruses per liter and 10^2 parasites per liter.

In the countries of central Europe salmonellae are generally the most important pathogens, whereas in some developing countries parasites are more important. In general, viruses in sewage sludges are considered to be less important for disease control.

1.2. Infection dose

Although the human infection dose of salmonellae is about 10^3 to 10^5 (depending on the type of salmonella and the size and condition of the person), infection by virus or parasite is possible from fewer than ten organisms.

1.3 Infection cycle

Various investigations, especially in Germany and Switzerland, have shown that salmonella diseases in animals may originate from infective sewage sludges used in agriculture [1-4].

Salmonella diseases are still a problem in Europe, even in countries that are "highly developed". The official number of salmonella infections in Germany has increased during the past twenty years from 10,000 to more than 80,000 per year.

With disinfection as part of the sewage-treatment process, the cycle of infection, man → sewage sludge → agriculture → plants/animals → food → man, can be broken.

1.4 Regulations for sludge disinfection

In most European countries, no strict hygienic requirements are made for the reuse of sewage sludge in agriculture; most often there are only general requirements. In Germany the use of non-disinfected sludges on fields is prohibited from the beginning of the year until after harvest, and sewage sludges are generally not allowed on fields where vegetables are cultivated.

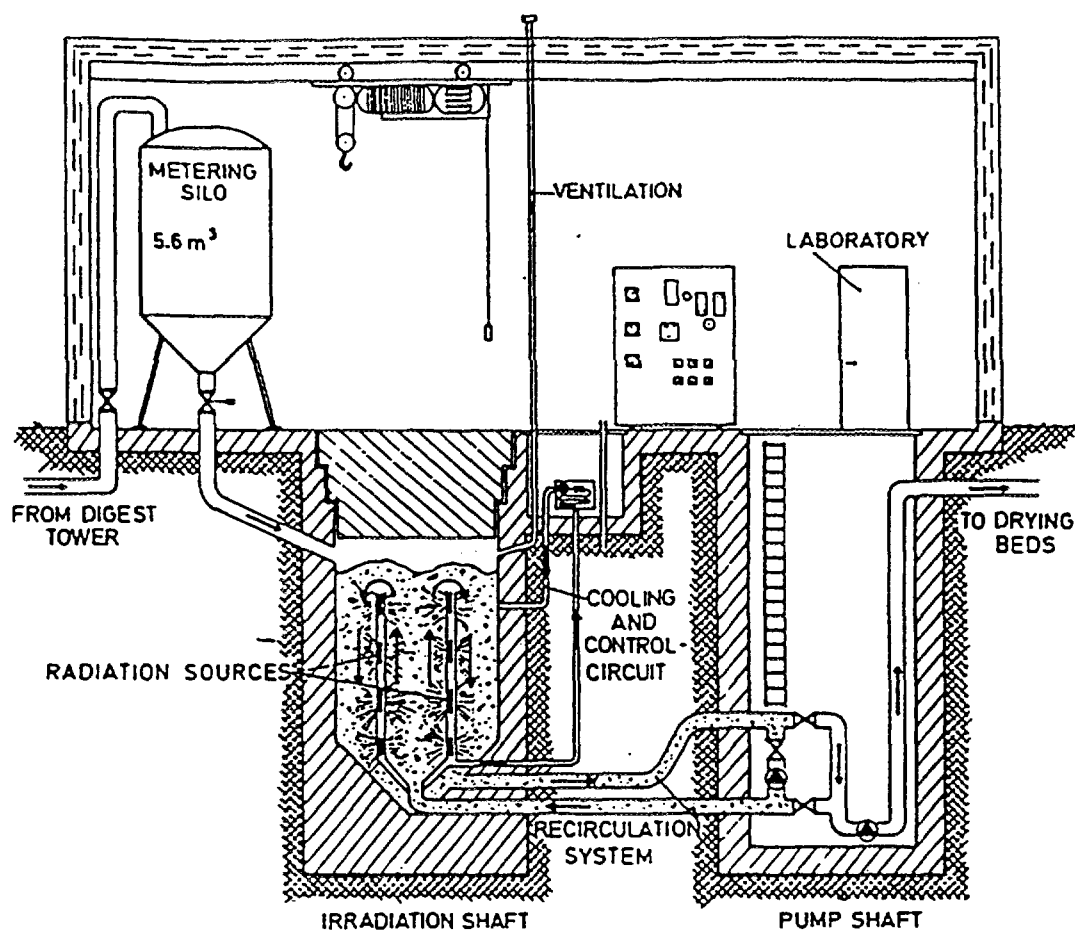


FIG. 1. Schematic diagram of the Geiselbullach Sludge Irradiator.

Switzerland was the first European country to pass a Sewage Sludge Act, in 1981. This law requires disinfection of all sewage sludges that are reused on green land or fodder-plant areas. The law defines a sludge as disinfected if it has been treated especially for this purpose and contains, at the time of distribution, no more than 100 enterobacteria per mL and no infective worm-eggs. Furthermore, storage of sludge is required for at least three months before application.

2. IRRADIATION OF SEWAGE SLUDGES

2.1. Gamma irradiation

2.1.1. General remarks

Gamma rays penetrate well in water and sludges; the half-value thickness of Co-60 γ -rays (1.3 MeV), for instance, is about 28 cm in water and not less than 25 cm in normal liquid sludges. Such deep penetration ensures the irradiation effect in thick layers of sludge.

The most common industrial γ -radiation sources utilize Co-60, which is produced by exposing non-radioactive Co-59 to a neutron flux in a nuclear reactor. After prolonged use of these sources (e.g. 20 years, which represents almost four half-lives) the residual activity has to be deposited in special storage for radioactive waste. After 20 years, Co-60 still has over 6% of its original activity.

Cs-137 can also be used, in principle, as a γ -source. This material (in the form of the salt CsCl) can be obtained as a by-product of the spent-fuel reprocessing cycle. Its radiation energy, 0.66 MeV, assures a half-value thickness of 24 cm in water, with a half-life of about 30 years. Since CsCl is water soluble, it is regarded as less safe in the event of a source leak or accident. For this and other reasons, it is not widely used in γ -irradiation plants that require high activity.

2.1.2. The sewage sludge γ -irradiation plant in Geiselbullach

2.1.2.1. General aspects

The sewage treatment plant in Geiselbullach, 10 km west of Munich, was designed for the mechanical and biological treatment of 50,000 m³ of sewage water per day, the equivalent of approximately 250,000 inhabitants. The plant operates at about 70% of its capacity. The sludge is digested at 32°C for 20 days, and then used as a soil conditioner and fertilizer on agricultural land in liquid (6-7% dry solids) or dewatered (22% dry solids) form. Currently about 20% of the total sludge quantity from Geiselbullach is used for agriculture.

In Germany today, farmers hesitate to use sewage sludge on their fields because industrial processors request "ecological," meaning "sludge-free," agricultural products. Therefore, the portion of sewage sludge used in agriculture has decreased from 35 to 20% during the past five years.

2.1.2.2. Plant technology and operation

A schematic plan of the Geiselbullach facility is shown in Fig 1. The plant consists of two underground components, the irradiation shaft with a built-in central tube, and the pump shaft containing the recirculation and evacuation pumps, the valves and the piping system.

Above ground, the building houses a metering silo, the control equipment, a crane and a laboratory. The irradiator was operated in a batch mode, treating approximately 5.6 m³ of sludge containing 4% solids to an adsorbed dose of 3 kGy.

For irradiation, the sludge flowed from the silo into the irradiation shaft, where it also entered the connection pipes. To provide a homogenous dose distribution, the sludge was mixed with a recirculation pump. After a preset time, which depended on the installed radioactivity and the required dose, the sludge was pumped out by evacuation.

The batch-wise operation ran automatically for 24 hours a day. All pumps, valves, indicators and control equipment were located either in the permanently accessible pump shaft or in the building above ground, so that services and inspections were possible at any time, without need for special safety precautions.

The operation of the plant was stopped in the springtime of 1993 for major repairs, and at that time new regulations in Germany disallowed further use of sewage sludge on grassland and areas for fodder production. As only those areas required the disinfection of sewage sludge, the treatment was no longer necessary and the decision was taken to stop operation of the irradiation plant.

2.1.2.3. Radiation sources

The radiation sources had a cylindrical form (diameter 30 mm; length 300 mm). Each contained 30 plaquettes of Cobalt-60, which were doubly-encapsulated with an initial activity of about 18,000 Ci. As the half-life of Cobalt-60 is about 5.5 years (corresponding to a decay of 13% per year), additional sources had to be installed every two or three years.

In 1984, nine Caesium-137 sources, with a total activity of approximately 70,000 Ci were installed in the Geiselbullach irradiation plant, in addition to the 380,000 Ci of Cobalt-60 sources. These Caesium-137 sources were obtained from the USA under a bilateral national contract. Their transportation and installation were supported by the German Ministry for Research and Technology. They were dismantled at the plant and transported back to the USA in 1992.

2.1.2.4. Safety features

The irradiation shaft, where the sources were located in a stable position between the two walls of the central tube, was situated underground and covered by 2.0 m of concrete. The room under the concrete cover was a restricted area, to be entered only by specially skilled staff of the supplier. All other areas were unrestricted, not requiring a personal dosimeter. The distance to the irradiation shaft and the bent connecting pipes allowed access to the pump shaft without any radiation precautions.

The radiation sources were located between the two walls of the central tube. They had no contact with the sludge and were controlled by a secondary circuit of demineralized water, which provided the leak test and cooling in case of emergency.

The radiation dose was controlled in the operation room; whenever it increased to more than double that of background, the plant was flooded with water and the electricity supply disconnected. The same happened whenever the cover was lifted before a distantly located key switch had been turned, or when the radiation-dose control was disconnected. In such cases, an alarm would sound at the local police station. The safety features were checked each year by the responsible authority.

2.1.2.5. Economics

The investment costs in 1973 for the Geiselbullach sewage sludge irradiation plant were:

underground and aboveground construction	420,000 DM
machinery, control equipment and auxiliaries	<u>710,000</u>
Total	<u>1,130,000</u>

plus the costs for the initial loading of Cobalt-60 sources.

Prices for concrete and construction work, machinery and other equipment increased in Germany by about 120% from 1973 to 1994; therefore, for a similar facility in 1994, the stated costs would have to be more than doubled.

The annual operating costs for 1985 were:

Addition of radioactivity (3.04 DM/Ci Co-60)	158,000 DM
Electric power (0.22 DM/kWh)	17,000
Other operational materials	1,000
Staff, repairs, services	39,000
Insurance	<u>3,000</u>
Total	<u>218,000</u>

With an annual capacity of 42,000 m³, these total operational costs resulted in a specific operational cost of 5.19 DM/m³ in 1985. The mean inflation rate from 1985 to 1994 was about 38%. On the basis of these data, the total annual and specific costs for 1994 can be estimated as:

- Investment costs:

Plant	1,130,000 DM
Sources 600,000 Ci x 2.50 DM/Ci	1,500,000
Annuity (8% interest, 15 years amortization)	
= 10.2% x (1.13 + 1.50 = 2.63 million DM) =	268,000 = 47%
- Operating costs (218,000 DM x 1.38) = 301,000 = 53%

Total	<u>569,000 = 100%</u>
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The specific cost was 13.55 DM/m³ in 1994.

2.1.3. Other gamma-irradiation plants

2.1.3.1. Germany: Munich-Großlappen

A pilot plant for the treatment of a maximum of 30 m³ per day (dose 3 kGy) was built in 1974 at the Bavarian State Institute for Water Research in Munich-Großlappen. It was used primarily for investigation of the effects of γ -irradiation on the destruction of chemical compounds in industrial wastewaters. Operations ceased around 1985. Some reports of the work were published, most of them in German [5].

2.1.3.2. USA: Albuquerque

A pilot and demonstration plant for the treatment of dewatered and composted sludges, also mixed with other solid wastes, was built and commissioned in 1979, at the Sandia National Laboratories in Albuquerque, New Mexico. It was designed to operate with Cs-137 sources (as CsCl, maximum 1,000,000 Ci). The design capacity was 8 t day⁻¹ of dried sludge (about 50% dry solids), which was carried in buckets along the sources, the required dose being 10 kGy. The material had to be transported to and from the plant, which was located at the Laboratories, and not at a sewage-water treatment plant. Operation of the plant was stopped around 1986. Many reports were presented at international meetings and published in journals [6, 7].

2.1.3.3. India: Baroda

A pilot and demonstration plant for the treatment of liquid sewage sludges was built and commissioned in 1988, in Baroda, by the National Nuclear Research Centre. Little has been published about the research work. It seems that the plant is not yet in full operation [8, 9].

2.1.3.4. Other reports

There are other reports of experiments or plans regarding gamma plants for the disinfection of sewage sludge, in Russia, Hungary and Germany (Company Leybold-Heraeus in Hanau) [10-12]. Most of the experiments were performed at laboratory irradiation plants or with multi-purpose irradiator, but not much is known of the research activities associated with these projects.

2.2. Electron-beam irradiation

2.2.1. General remarks

Electron beams can transfer more power into aqueous media than can γ -radiation. Therefore the capacity of electron beam plants is generally higher.

The energy of accelerated electrons can achieve 3 MeV with conventional and relatively low-cost machines, and up to 10 MeV with linear accelerators that are significantly more expensive.

The penetrative power of accelerated electrons in water is about 3 mm per MeV (Fig. 2). Therefore most electron-beam plants require that a very thin layer of sludge be passed under the beam. Since sewage sludges generally contain particles bigger than this layer thickness, prior homogenization is necessary. Nevertheless, obtaining a homogenous dose distribution in such sludges is a major problem in the case of electron-beam irradiation.

Electron-beam plants can be shut off when not in use, for service work or emergency repair, and therefore have important safety advantages in comparison with gamma plants.

2.2.2. Electron-beam irradiation plants

2.2.2.1. USA: Deer Island, Boston

A pilot and demonstration plant for the treatment of liquid sewage sludges was built and commissioned in 1976 at the Deer Island sewage-water treatment plant in Boston. Design and supervision were by the Massachusetts Institute of Technology. The accelerator had a power of 50 kW (0.85 MeV, 60 mA) and the capacity of the plant was reported to be 400 m³/day at a dose of 4 kGy. Many tests were made of various methods of passing the sludge in a thin layer (maximum 2 mm)

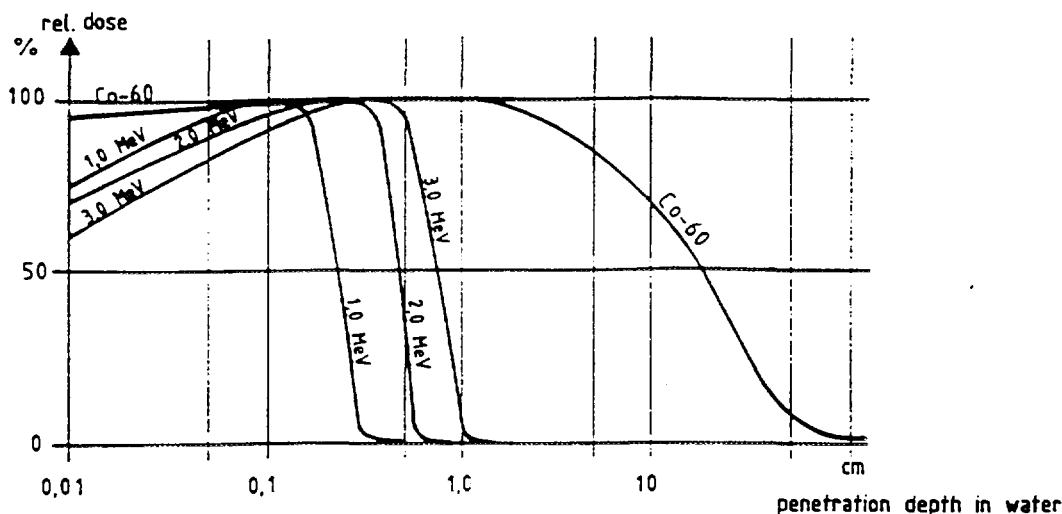


FIG. 2. Dose distribution of accelerated electrons and gamma quants of Co-60.

under the electron beam. However, these investigations were made in laboratory and not scaled-up conditions. Continuous operation was not achieved, and the plant was decommissioned in 1984 [13].

2.2.2.2. USA: Virginia Key, Miami

A commercial plant for the treatment of very liquid (maximum 2% dry solids) biological excess sludge was built during 1981-1983 at the sewage-water treatment plant in Virginia Key (Miami, Florida). The supplier of the sludge ceased activities before the plant was commissioned, and the owner, the Miami Dade Water and Sewer Authority, tried to find an alternative source to get the plant into operation. The power of the accelerator was 75 kW (1.5 MeV, 50 mA), allowing a daily capacity of 645 m³ at a dose of 4 kGy. Originally it was planned that eight irradiators in parallel would disinfect 5,000 m³ per day. A thin layer was produced by a free-falling "curtain" of sludge in front of the electron beam [14].

2.2.2.3. Germany: Wedel, near Hamburg

A research plant was developed in 1980 and used until 1982 at the AEG-irradiation centre in Wedel. The sludge was passed under the e-beam on an inclined plane. The power of the accelerator was 50 kW (1.0 MeV, 50 mA); the capacity was designed to be 500 m³ per day at a dose of 4 kGy. Some research and development work was performed over the two-year period [15, 16].

2.2.2.4. Germany: Stuttgart - Hohenheim

In 1976-77, scientists at the University of Stuttgart-Hohenheim investigated the possibility of sewage-sludge disinfection at a multi-purpose plant with an e-beam of relatively low energy, 0.4 MeV (34 kW, 75 mA). As the penetration of these low energy electrons is only 1 mm, the treatment was effected in batch operation with thicker layers (max. 12 mm) and a multi-recirculation (maximum 40 times), in part with additional injection of air, to produce more turbulence and a homogenous dose distribution [17].

2.2.2.5. Austria: Seibersdorf

A research plant (12,5 kW, 0.5 MeV, 25 mA) at the research centre in Seibersdorf was used in 1975 for sewage treatment. It was found that the turbulence, generated by the wall fraction of the inclined plane, assured a sufficiently homogenous dose distribution in waste-water layers that were thicker than the penetration range of the electrons [18].

2.2.2.6. Japan: Takasaki

A research plant (30 kW, 2.0 MeV) was built in 1987 at the laboratories of the National Atomic Centre in Takasaki. This plant was designed to irradiate composted sludge (7.2 t day^{-1} at a dose of 5 kGy). Research work was performed for three years, but no practical application followed until 1994 [19].

3. RESULTS FROM RESEARCH AND PRACTICAL EXPERIENCE

3.1 Some operational aspects of the Geiselbullach plant

3.1.1 *Limited supply of Cobalt 60*

With a half life of 5.5 years (13% decay per year), Cobalt-60 requires source replenishment from time to time. To maintain activity, additional sources with about 30% of the required total activity were installed at Geiselbullach every two or three years. Although the plant operator tried to get several offers for source delivery, and three suppliers showed interest, only one offer was finally made each time, always by the same producer. During 18 years of practical operation, there was no competition for the delivery of Co-60. The producer who delivered the sources to Geiselbullach informed the operator twice of temporary shortage of Co-60 with delivery delays of six to twelve months. Recently other producers entered the market, offering to supply Co-60 upon request.

3.1.2 *Integration into a sewage treatment plant*

The incorporation of the gamma plant into the existing sewage treatment plant did not cause any particular problems, since it did not require specially skilled workmen, complex safety measures, or personal radiation surveys.

3.1.3 *Precipitates*

At the Geiselbullach plant, the formation of $\text{Mg}(\text{NH}_4)\text{PO}_4$ precipitates occurred after seven months of continuous operation. They formed as a result of a pH increase in the sludge to 8.0 or above, caused by stripping of CO_2 during recirculation. With a thickness of between 1 and 5 cm, the layer of particles significantly reduced the irradiation effect.

The precipitates were dissolved by rinsing with 5% formic acid ($\text{pH} \approx 1.8$) without significant damage to the concrete and steel components. However the asbestos-concrete wall of the irradiation shaft was slightly damaged and was coated later with stainless steel. Further precipitation was avoided by switching off the forced ventilation during irradiation. As a result, the CO_2 gas buffer above the sludge prevented excessive stripping and the pH increased from 7.1 to 7.4 only.

3.1.4. Availability

The Geiselbullach gamma irradiator had an operational frequency of 93 % over a period of 15 years. Non-operative days were caused by defects in [20]:

- conventional components (pumps, electrical equipment, etc.)	3.7%
- radiation technical equipment (the central tube, cooling circuit, etc.)	2.1%
- inspection and loading additional sources	<u>1.0%</u>
Total	<u>6.8%</u>

This percentage corresponds to 25 days per year, therefore the plant was operational on average for 340 days per year.

3.1.5. Avoidance of "dead" zones in the recirculation system

Investigations showed lower efficacy of disinfection at the plant than in the laboratory experiments. This effect was caused mainly by the existence of "dead" zones in the recirculation pipework system, for example in branches from the main stream to the valves. The sludge residing in those areas was not irradiated, thus re-infecting the by-passing sludge flowing in the main stream. The length of the branches was reduced by relocating valves as near to the main stream as possible (about 10 cm), producing significant improvement in operational efficacy.

3.1.6. Reducing of "down" time

"Down" time occurred between batches, with the relocation of valves, with slow responses to the control equipment, with the evacuation of the irradiated sludge, and with refilling with a new batch. At the Geiselbullach plant, "down time" was significantly reduced by installation of quick-response control equipment, and by replacement of the electrically-driven valves by pneumatically-driven valves. Plant capacity was thus improved by about 8%.

3.2. Optimization by the use of synergistic effects

Besides the optimization of plant technology, the optimization of process technology was possible and no less important. Laboratory research has indicated that the effects of radiation can be increased by the presence of gases, oxygen, air, ozone, chlorine, nitrogen, or by combination with heat treatment: "thermoradiation".

3.2.1. Thermoradiation

Thermoradiation has been investigated in particular in the USA. It was established that the sludge temperature should be at least 47°C for synergistic effects on losses of bacteria, viruses, and parasites, and on sludge sedimentation. Temperatures of more than 60°C cause pasteurization and are of no utility with irradiation.

At Geiselbullach, the first tests with heated sludge (40 - 45°C) created obnoxious odors and were discontinued.

3.2.2. Oxiradiation

The synergistic effects of oxygen and irradiation are known from the literature (Fig. 3) [21]. At the Geiselbullach plant, the technical feasibility and the economics of oxiradiation were intensively studied. Investigations from 1978 to 1984 included the effects of using air or pure oxygen, methods of application, oxygen concentrations, oxygen yield, rate of the decomposition of oxygen, pathogen inactivation capability, and the influence of oxygen concentration on physical characteristics of the sludge.

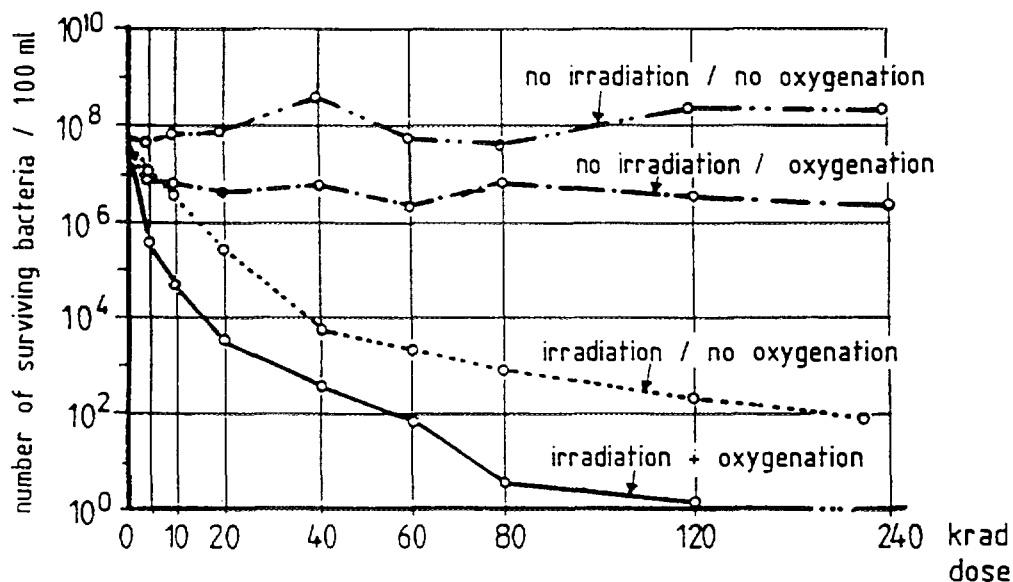


FIG. 3. Effect of irradiation on faecal coliform bacteria in treated sewage water with and without oxygenation [21].

Results from the comparison between the injection of air and oxygen into the sludge during the irradiation treatment are summarized as follows [20]:

- the maximum oxygen concentration in the sludge with aeration was 9.4 mg O₂ L⁻¹, whereas with oxygenation it was greater than 30 mg O₂ L⁻¹;
- with aeration, sludge pH increased from 7.0 to 8.2, whereas with oxygenation the increase was only from 7.0 to 7.2;
- the increase in oxygen concentration in the sludge was 2 to 10 times faster with oxygen than with air;
- the O₂-efficiency for oxygenation was between 5 and 40 times (a typical value was 15) better than the efficiency for aeration.

These results led to the introduction of pure oxygen during the first five minutes of each batch, to create a concentration in the sludge of about 5 mg O₂ L⁻¹. With recirculation times of more than 40 minutes, oxygenation was repeated after half of the irradiation time. Since relatively low quantities were needed, liquid oxygen was used, stored in an isolated tank next to the irradiation plant.

3.2.3. Pathogen inactivation experiments

Pathogen inactivation experiments were conducted with 5.6-m³ batches of sludge, enriched with salmonellae to counts of 10⁶ to 10⁷ cells L⁻¹. At a dose of 1 kGy, inactivation rates were 15 to 38 times higher with an oxygen concentration of 5 mg L⁻¹ than without oxygenation. As reported in the literature (Fig. 4), higher concentrations of oxygen in the sludge (15 and 25 mg L⁻¹) did not improve disinfection [21]. Likewise, higher dose rates with varied oxygen concentrations did not significantly affect pathogen inactivation.

It was shown at Geiselbullach that oxiradiation with a dose of 2 kGy had at least the same effect as conventional irradiation alone. Further reduction of the dose to about 1.5 kGy or even less is probably possible, but this had not been proven in experiments to date.

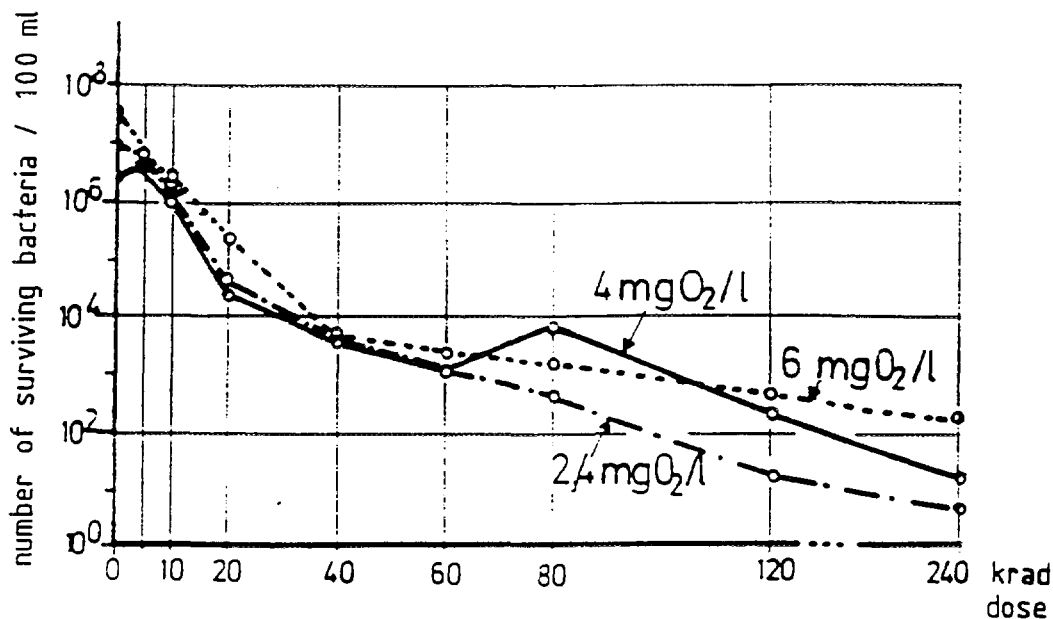


FIG. 4. Effect of irradiation on faecal coliform bacteria in treated sewage water at three concentrations of dissolved oxygen [21].

3.2.4. Precipitates

At Geiselbullach, deposition of $\text{Mg}(\text{NH}_4)\text{PO}_4$ occurred when the pH increased to 8.0 or higher, for example with the injection of air. Oxygenation increased the pH to 7.2. Therefore, aeration was deemed unsuitable for normal operations

3.3. Proposal for oxiradiation plant for sewage sludge

The results of investigations at Geiselbullach convinced officials of the need for a new sludge-irradiation concept [20]. This concept utilized a traditional batch-type irradiator for liquid sludges, but also incorporated provisions for addition of O_2 , as illustrated in Fig. 5.

4. ALTERNATIVE METHODS FOR SLUDGE DISINFECTION

Although considerations of hygiene resulted in the development and introduction of sewage-treatment technology in Europe about 130 years ago, controlled disinfection is still the exception in wastewater-treatment plants today. Improved hygiene is often regarded as a side-effect of the usual treatment processes. The conventional treatment for sewage sludge involves stabilization by aeration or digestion (at about 35°C) to reduce the numbers of pathogens, especially of bacteria such as salmonellae by 1 or 2 log units. To obtain a safe hygienic sludge, further reduction of pathogens by about 3 log units is necessary.

Several methods of disinfection of sewage sludges have been practiced for about 25 years in Europe.

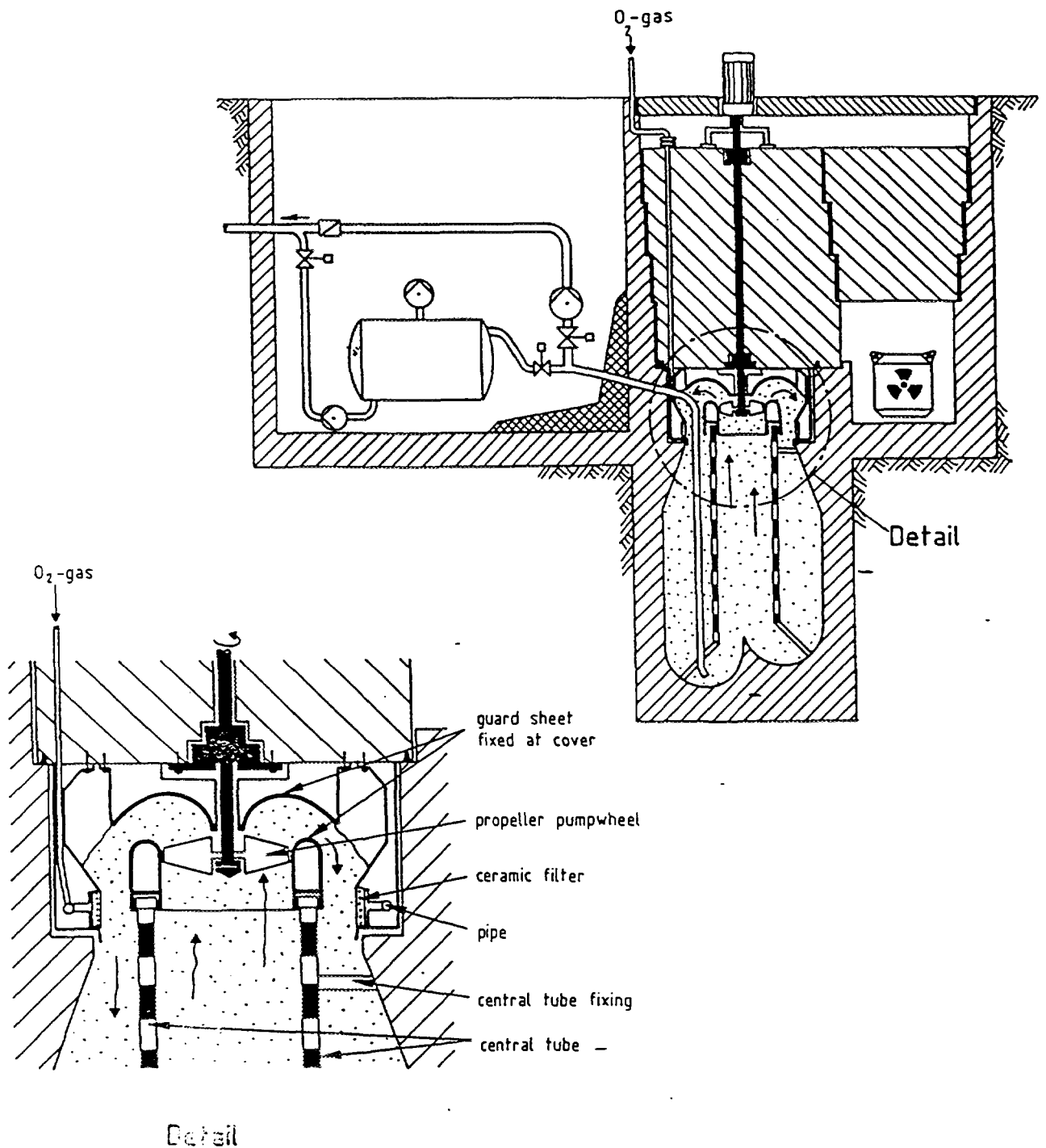


FIG. 5. Proposed oxiradiation plant for sewage sludge [20].

4.1. Pasteurization

A traditional method, broadly accepted early in disinfection technology, is pasteurization. The (liquid) sludge is heated to between 65 and 100°C; the retention time varies between 3 minutes at 100°C and 30 minutes at 65°C.

Homogenization of the sludge is necessary before treatment. To avoid recontamination or regrowth of surviving pathogens, the sludge must be pasteurized before digestion.

A heat-recovery installation (heat exchangers) reduces energy consumption. Heat treatment causes the generation of obnoxious odors.

4.2. Aerobic-thermophilic treatment

By injection of air or oxygen into liquid sludge, exothermic biological reactions effect self-heating. Disinfection is assured if the temperature reaches at least 55°C and is maintained for at least 24 hours. Practical experience has shown that an external heat source is necessary to assure such conditions. The total retention time in the system should be at least 5 days. This aerobic-thermophilic treatment has been practiced primarily in treatment plants not bigger than for about 100,000 equivalents, and is followed by digestion.

The aerobic-thermophilically treated sludge produces significantly lower quantities of methane gas during digestion.

4.3. Composting

Composting requires dewatering of sludge as a first step, by centrifuging, filter pressing, or air-drying should the climate allow it. The disinfecting effect of composting is achieved primarily by self-heating, caused by exothermal biochemical reactions. The reactions require certain relations of carbon, nitrogen and phosphorus, which often can be assured only by adding carbon-containing materials like saw dust, tree bark, straw or organic garbage. The water content must be between 40 and 60%, and ventilation is necessary.

Disinfection is assured if the temperature in all parts of the reactor maintains at least 55°C for three weeks. In temperate countries, these conditions can be achieved only in covered and isolated reactors.

4.4. Thermal conditioning

Thermal conditioning is achieved by heating the sludge to about 200°C at about 12 bars pressure. This is normally done as a pre-treatment for dewatering in filter presses, with disinfection a favorable side-effect. The risk of recontamination and regrowth of bacteria is high, and sewage sludges so treated normally generate obnoxious odors.

In Germany, thermal conditioning installations were shut down after it was found that toxic organic compounds (such as dioxins) were created.

4.5. Incineration

Incineration, like composting, requires dewatered sludge. The ash is free of pathogens, but cannot be used in agriculture. Incineration is several times more expensive than other disinfection processes and therefore not applicable for disinfection alone. It is used for volume reduction and for conversion of the organic matter.

4.6. Lime treatment

This is achieved with raw lime (CaO) or slaked lime (Ca(OH)₂). While dose administration of Ca(OH)₂ is easier, the use of CaO is preferable, because of the double effect on the pathogens - through the heating and the increase in pH. For a safe disinfection of liquid sludge, a minimum pH of 12 must be maintained for at least 24 h. When CaO is used, temperatures of at least 60°C can occur, which decreases the time requirement at the high pH.

Lime treatment is generally easy, but it can cause problems through the production of ammonia gas, which has to be evacuated by forced ventilation necessitating a closed system. Another disadvantage is the fact that significant portions of dry materials are added to the sludge, and this increases the quantity to be transported and deposited.

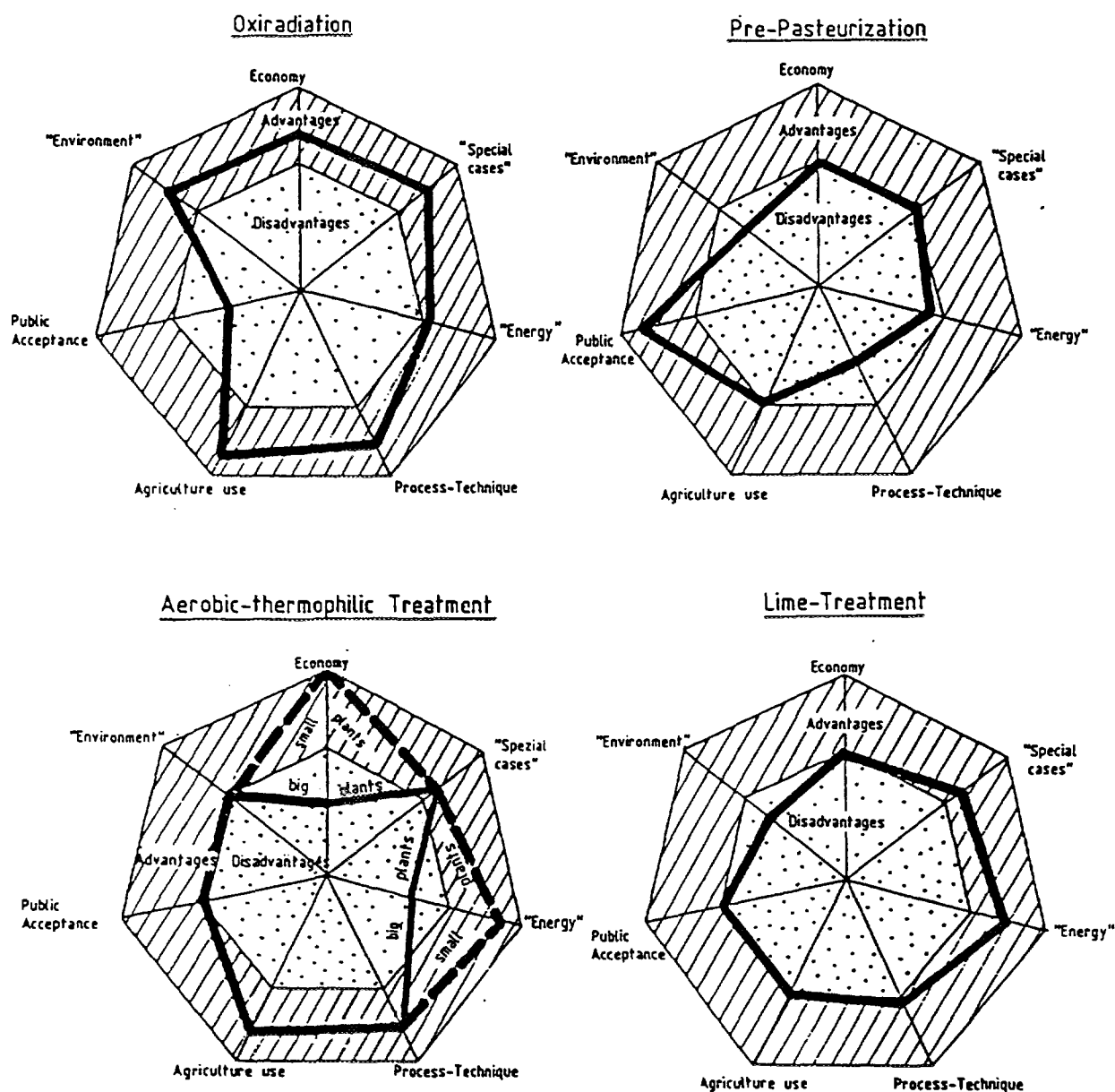


Fig. 6. Snow-crystal diagrams showing the advantages and disadvantages of alternative processes for sewage-sludge disinfection [22].

4.7. Long-term storage

The storage of liquid sludges for more than a year is generally regarded as a disinfection process. Since significantly large areas are necessary, this method is applicable only for small treatment plants.

TABLE I. TOTAL COSTS FOR DIFFERENT SLUDGE-DISINFECTION TREATMENTS

Treatment	Condition of sludge	Costs for		Side-effects that can influence further treatment costs	Remarks
		Pre-treatment (DM / t dry m.)	Disinfection treatment (DM / t dry m.)		
Gamma-irradiation (3 kGy)	Liquid (≈4% dry matter)	---	350	Improvements in sedimentation, dewaterability.	Size of treatment units limited to approx. 300 m ³ /day.
Gamma irradiation (10 kGy)	Dewatered (≈70% dry m.)	150-300 ^a	300-400	Reduction of obnoxious odor.	
Oxiradiation (Gamma, 2 kGy)	Liquid (≈4% dry m.)	---	200-300	Production of ozone gas.	
Electron-beam-irradiation (4 kGy)	Liquid (≈2% dry m.)	40 - 60 ^b	150-400	Production of obnoxious odor.	High investment costs, also for small plants. Reasonable total costs.
Pasteurization (65°C/30 min.)	Liquid (≈5% dry m.)	40 - 60 ^b	200-400		
Aerobic-thermophilic treatment	Liquid (≈5% dry m.)	40 - 60 ^b	300-400	Decrease in gas yield.	
Composting	Dewatered (≈35% dry m.)	100 - 250 ^a	150-400		Product sale (depends on market conditions) may reduce the total costs.
Thermal conditioning (200°C/15 bar)	Liquid (≈5% dry m.)	---	350-500	Obnoxious odor. Risk of re-contamination.	
Incineration	Dewatered (≈35% dry m.)	100 - 250 ^a	600- 1200		Ashes cannot be used in agricult.
Lime-treatment (CaO)	Liquid (≈5% dry m.)	---	200-300	Dewatered product can be used in landfills.	
Lime treatment (Ca(OH) ₂)	Liquid (≈5% dry m.)	---	250-350	Important increase in the sludge dry m. quantity. Production of ammonia gas. Improvement in dewaterability	

^a for dewatering.^b for homogenization.

5. COMPARISON OF DIFFERENT TREATMENTS AND COSTS

Direct comparisons of the various methods are difficult due to their different characteristics. Fig. 6 shows advantages and disadvantages of four treatments [22]. The information in the literature for total treatment costs varies over a wide range, even for a single treatment technique. The data in Table I reflect information from the literature that are regarded as well documented and based on practical experience (conditions in Europe for the year 1994).

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A COMPARATIVE VIEW OF RADIATION, PHOTO AND PHOTOCATALYTICALLY INDUCED OXIDATION OF WATER POLLUTANTS

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Abstract

Water resources are presently overloaded with biologically resistant (refractory) pollutants. Several oxidation methods have been developed for their degradation, the most efficient of which is irradiation treatment, particularly that based on e-beam processing in the presence of O_2/O_3 . The next-best method is photoinduced pollutant oxidation with VUV- and/or UV-light, using H_2O_2 or H_2O_2/O_3 as an additional source of OH radicals. The photocatalytic method, using e.g. TiO_2 as a catalyst in combination with oxidation agents such as H_2O_2 or H_2O_2/O_3 , is also recommended. The suitability of these three methods is illustrated by examples and they are briefly discussed and compared on the basis of their energy consumption and efficiency. Other methods, such as ozone treatment, the photo-Fenton process, ultrasonic and electrochemical treatments, as well as the well known biological process and thermal oxidation of refractory pollutants, are briefly mentioned.

1. INTRODUCTION

Current water resources are strongly overloaded with biologically resistant pollutants, as a result of global population growth and the development of certain industries in the past few decades. The disposal of chemical waste in rivers, seas and oceans has contributed to possibly-irreparable destruction of marine life. The application of fertilizers, pesticides etc. in modern agriculture has exacerbated the situation. Hence, urgent measures are necessary for remediation of water resources.

For the degradation of water pollutants, a number of oxidation methods, based on processes initiated by ionizing radiation, UV- and visible light, photocatalytic induced reactions, as well as combinations of these, have been developed. Technologies for water remediation are compiled and presented in Table I.

From the technical point of view, the most efficient treatment of water is irradiation by electron-beam in the presence of O_2 and O_3 [1-3 and references therein]. Photoinduced pollutant oxidation utilizes various combinations of VUV- and/or UV-radiation [2] using H_2O_2/O_3 , as well as the photo-Fenton process [4] (see also Table I), as an additional source for OH-radicals. Photocatalytic methods, using semiconductors such as n- TiO_2 as catalysts in combination with H_2O_2 , H_2O_2/O_3 etc., are also rather promising [3, 5, 6]. All these techniques are briefly reviewed in this paper.

TABLE I. METHODS FOR WATER REMEDIATION

No.	Method
1	Radiation induced oxidation of pollutants using: electrons, γ -rays, x-rays; synergistic effect in the presence of O_3/O_2 , eventually H_2O_2 as additive.
2	Photoinduced oxidation by UV (149 & 254 nm), or UV/ O_3 , UV/ H_2O_2 and UV/ O_3/H_2O_2 , resp.
3	Photocatalytic treatment: UV/VIS light using TiO_2 , ZnO etc. as catalyst
4	Ozone treatment: O_3 or O_3/H_2O_2
5	Photo-Fenton process: UV/ H_2O_2/Fe^{2+} or UV/ $H_2O_2/O_3/Fe^{2+}$ (acid media)
6	Ultrasonic treatment (sonolysis of water)
7	Electrochemical oxidation
8	Biological process for biodegradable pollutants, used for wastewater treatment
9	Thermal oxidation of pollutants, used for liquid industrial waste

2. RADIATION PROCESSING OF POLLUTED WATER

2.1. Radiation units

Some useful units and conversion factors in radiation technology are presented below¹.

¹Output power of electron accelerator, in kW:

$$kW = mA \times MeV \text{ (mA = electron current, MeV = electron energy).}$$

Radiation yield: G-value = number changed molecules per 100 eV ($1.6 \times 10^{-17} J$) absorbed energy; to obtain $\mu mol J^{-1}$, multiply the G-value by 0.10364.

Absorbed dose: 1 rad = $100 \text{ erg g}^{-1} = 6.24 \times 10^{13} \text{ eV g}^{-1}$

$$100 \text{ rad} = 1 \text{ Joule kg}^{-1} = 1 \text{ Gray (Gy)}$$

$$1 \text{ krad} = 10 \text{ J kg}^{-1} = 10 \text{ Gy}$$

$$1 \text{ Mrad} = 10^4 \text{ J kg}^{-1} = 10^4 \text{ Gy}$$

$$1 \text{ kW} = 3.6 \times 10^6 \text{ J kg}^{-1} = 360 \text{ Mrad kg}^{-1} \text{ h}^{-1}.$$

2.2. Radiolysis of water

For a better understanding of the subject matter, the primary reactions of water radiolysis and their yields (G-values)¹ as a function of pH are briefly described.

As a sequence of radiation absorption at 10^{-15} s, the water molecules can become excited (H_2O^*) or ionized, with formation of H_2O^+ (radical cations) and secondary electrons (e^-). The latter lose energy by interaction with surrounding molecules (formation of further H_2O^* , H_2O^+ and e^-) and thermalizing to e_{th}^- , which finally become solvated (e_{aq}^-) within about 3×10^{-12} s. Major primary processes of water radiolysis are compiled as a set of reactions in Fig. 1. The primary radicals resulting from water radiolysis are involved in a number of reactions with each other [1, 2].

It should be noted that the yields (G-values) of the primary products of water radiolysis are strongly dependent on the solution pH. This fact is illustrated by the data shown in Fig. 2.

2.3. Radiation-induced decomposition of water pollutants

As mentioned above, radiation processing of water (by means of electrons or γ -rays) in the presence of air, is an efficient method for degrading pollutants. This fact is illustrated by the radiation-induced decomposition of trichloroethylene ($\text{Cl}_2\text{C}=\text{CHCl}$) and phenol ($\text{C}_6\text{H}_5\text{-OH}$).

The radiolysis of trichloroethylene, in the presence of air, is illustrated by taking Cl^- formation as an indicator of the process. Fig. 3 shows the yield of Cl^- as a function of dose, observed by the radiation-induced degradation of $10^{-3} \text{ mol L}^{-1}$ $\text{Cl}_2\text{C}=\text{CHCl}$, in the presence of air. The Cl^- yield is higher than that expected by the attack of the primary radicals of water radiolysis $\{G(\text{OH} + \text{e}_{\text{aq}}^- + \text{H}) = 6.1\}$. This is because multiple hydrolysis of the transients is also involved.

The decomposition of diluted $\text{Cl}_2\text{C}=\text{CHCl}$ is presented in Insert 1 of Fig. 3. In this case a rather small dose of about 150 Gy is sufficient for complete degradation of the pollutant. The oxidative radiolysis of $\text{Cl}_2\text{C}=\text{CHCl}$ leads also to the formation of aldehyde, as shown in Insert 2 of Fig. 3.

Although many laboratory studies have been performed, complete reaction mechanisms of the radiation-induced degradation of $\text{Cl}_2\text{C}=\text{CHCl}$ and related compounds are still not completely elucidated. However, the main reaction steps (1) to (20) are given below for better understanding of the subject matter [7].

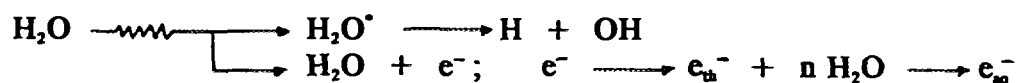
2.3.1. The effect of ozone

The effect of ozone with respect to water purification is well established, and has been applied in practice in many cases [8, 9].

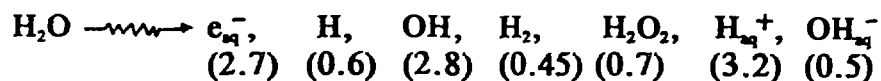
2.3.2. The synergistic effect of radiation and ozone combination treatment

The synergistic effects of radiation and ozone treatments have been studied by various authors [10-16]. A particularly efficient application of ozone is observed in the case of pollutants having double bonds, such as olefinic and aromatic compounds. Ozone combines at the double-bond position and after some transformations a hydrolysis takes place, resulting in decomposition of the pollutant. This is illustrated in the degradation of $\text{Cl}_2\text{C}=\text{CHCl}$ by Reactions (21) and (22).

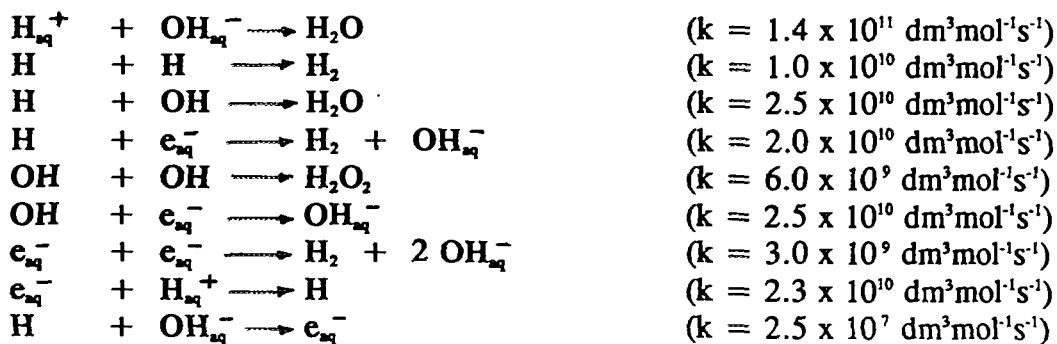
Primary reactions:



Gross reaction of water radiolysis (the G-values at pH 7 are given in brackets):*



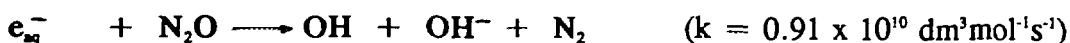
Major primary reactions:



In the presence of oxygen:



In the presence of N₂O:



In the presence of H₂:



*) G-value = number of changed molecules per 100 eV ($1.60 \times 10^{-17} \text{ J}$) absorbed energy.
For conversion into SI-units: multiply the G-value by 0.10364 to obtain G(x) in $\mu\text{mol.J}^{-1}$.

Fig. 1. Radiolysis of water and some primary reactions.

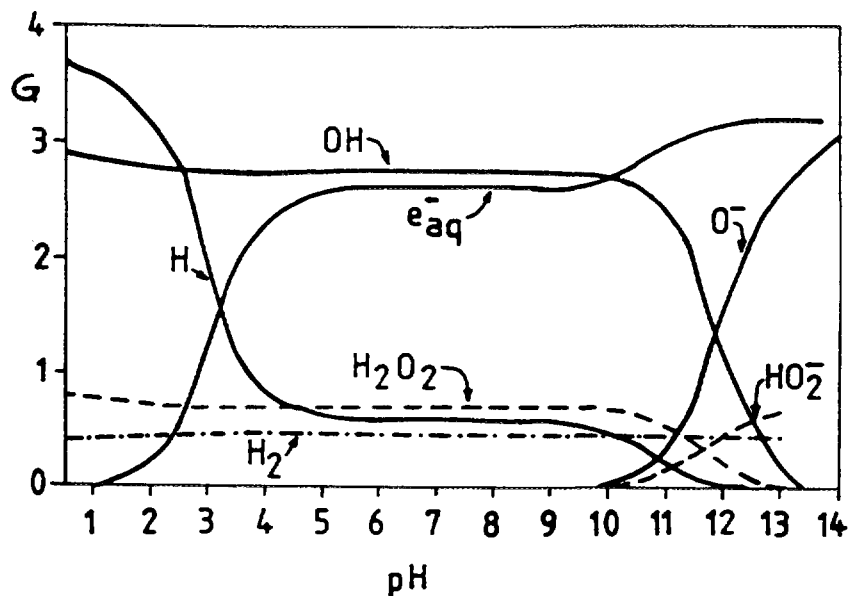
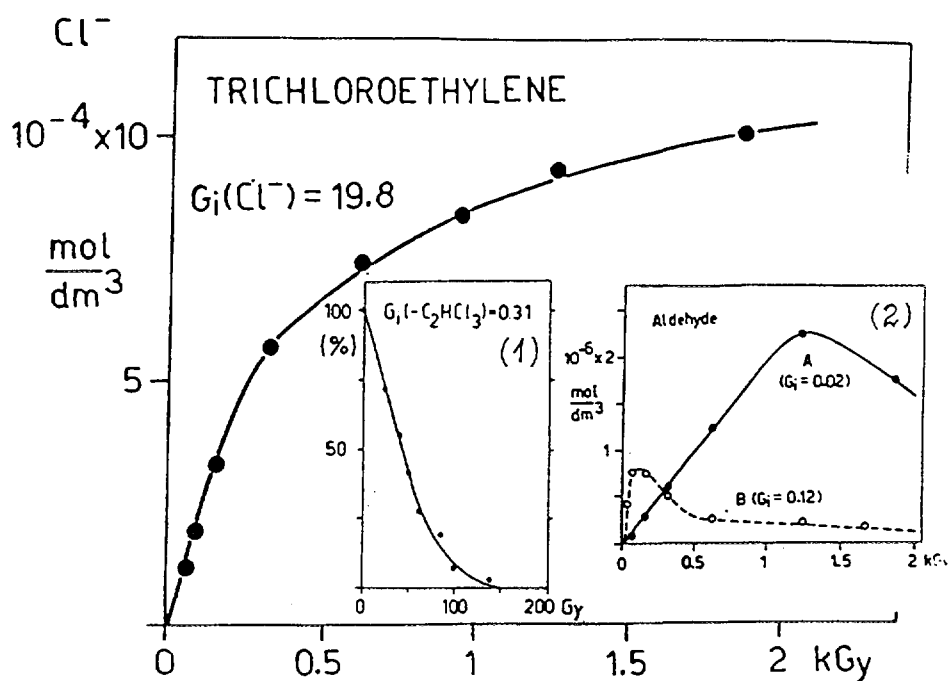


Fig. 2. *G*-values of the primary products of water radiolysis as a function of pH.

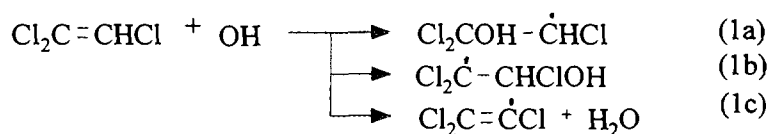


Insert 1: Decomposition of $2.74 \times 10^4 \text{ mol.dm}^{-3} \text{ Cl}_2\text{C=CHCl}$ irradiated in the presence of air (pH = 6.5) as a function of dose.

Insert 2: Aldehyde formation resulting from: (A) 10^3 mol.dm^{-3} and (B) $10^4 \text{ mol.dm}^{-3} \text{ Cl}_2\text{C=CHCl}$ irradiated in the presence of air (pH = 6.5) [2].

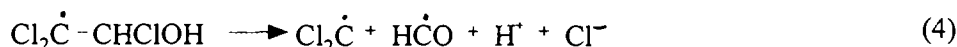
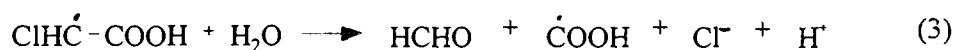
Fig. 3. Dose-dependence of Cl^- formation from $1 \times 10^3 \text{ mol.dm}^{-3}$ trichloroethylene irradiated in the presence of air (pH = 6.4).

OH - attack:



$$k_1 = 3,3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

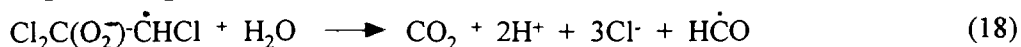
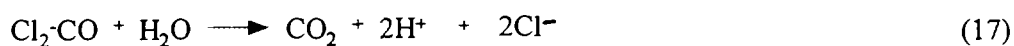
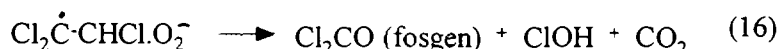
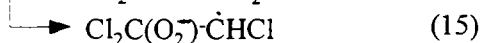
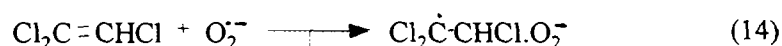
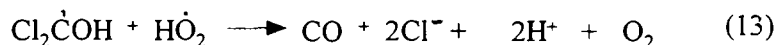
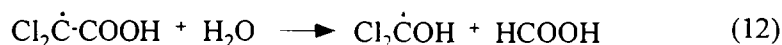
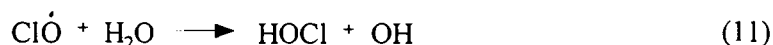
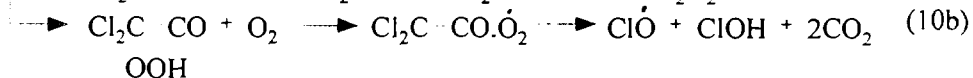
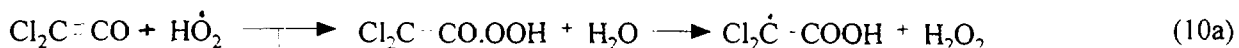
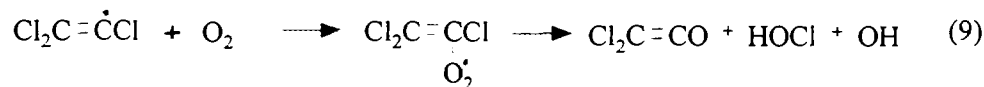
Multiple hydrolysis:

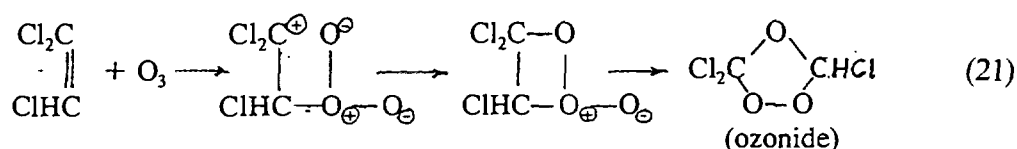
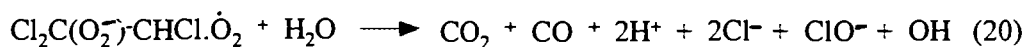
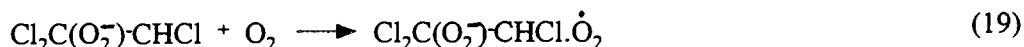


The HCO species disappear according to the reaction (5) and (6) or are scavenged by O₂ (s. Table 1) :

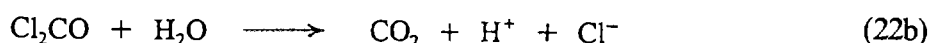
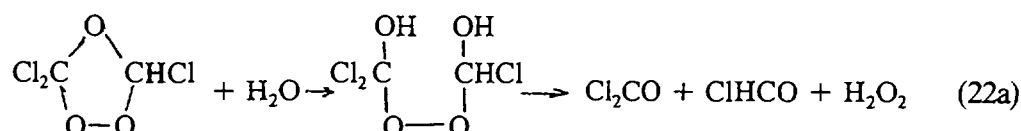


Addition of oxygen and H $\dot{\text{O}}_2$ / O₂^{•-} radicals:





The ozonide undergoes hydrolysis, whereby two carbonyl compounds (phosgene and aldehyde) as well as H_2O_2 are formed:



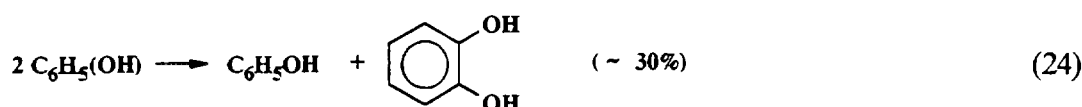
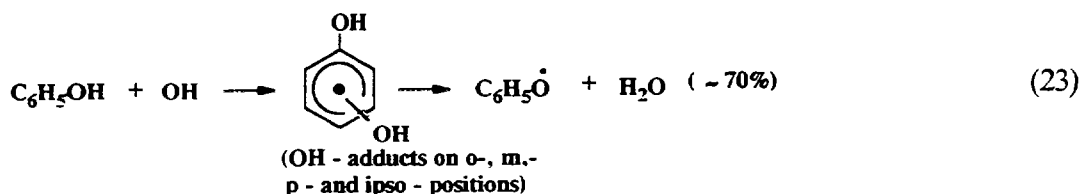
The halogenated aldehyde can likewise undergo hydrolysis.

2.3.3. The radiation-induced degradation of phenol

The radiation-induced degradation of phenol is discussed as an example for other aromatic pollutants. The highest decomposition yield of aqueous phenol in the presence of air is obtained by using a very low dose rate. The substrate concentration is also a determining factor. Micic et al. [17] observed - for aerated $2 \times 10^{-2} \text{ mol L}^{-1}$ phenol solution - that the $G(-\text{PhOH})$ value increased from 2.6 to 250 upon decreasing the dose rate from 100 to 13 Gy h^{-1} . Similar data were obtained by other authors [2, 10, 18]. This effect is explained by a chain reaction, initiated by OH and $\text{O}_2^{\cdot -}$ species, and propagated mainly by the $\text{O}_2^{\cdot -}$ transients.

The decomposition of oxygenated 10^{-5} to $10^{-3} \text{ mol L}^{-1}$ phenol is presented in Fig. 4-I as a function of applied dose (dose rate: 82 Gy min^{-1}). The diluted solutions (10^{-4} and $10^{-5} \text{ mol L}^{-1}$ phenol) require a dose of about 1 kGy for their destruction. However, the substrate radiolysis results first of all in several products that are shown in Fig. 4-II. Hence, for complete destruction of all products originating from phenol, a much higher dose is needed.

The major radiation-induced reactions involving aerated phenol, (23) to (27), were studied previously [2, 3, 19]. Major products are shown in (29).



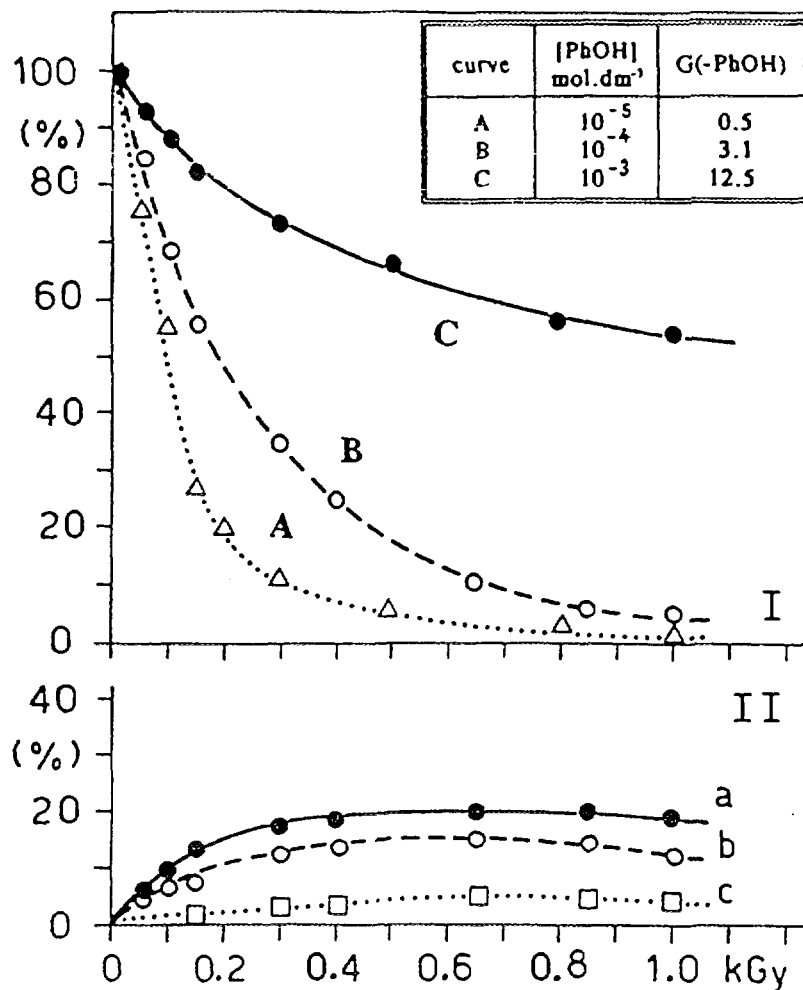
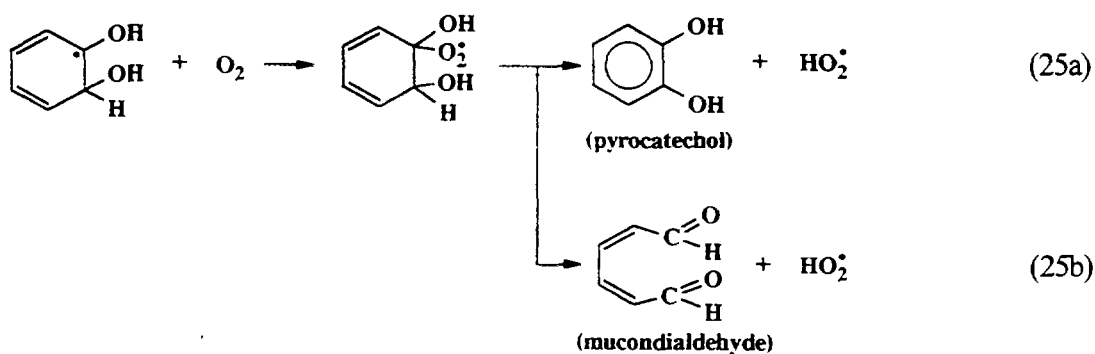
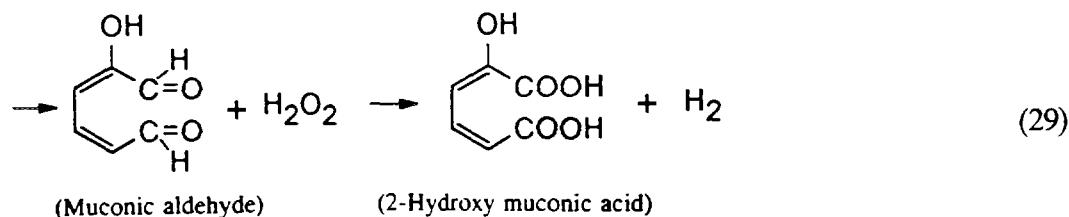
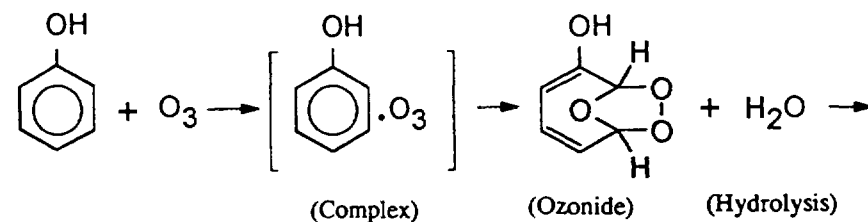
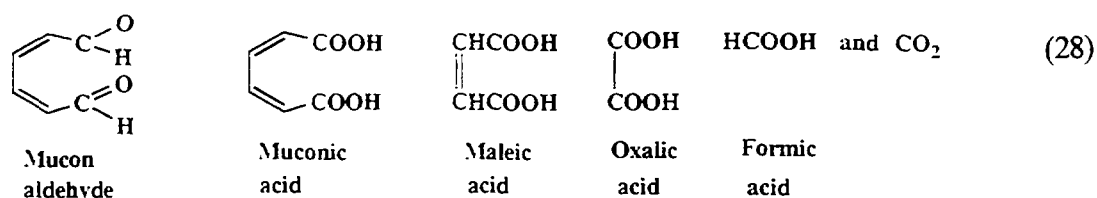
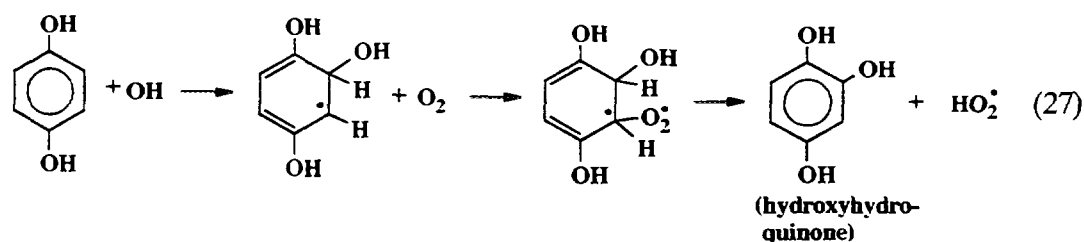
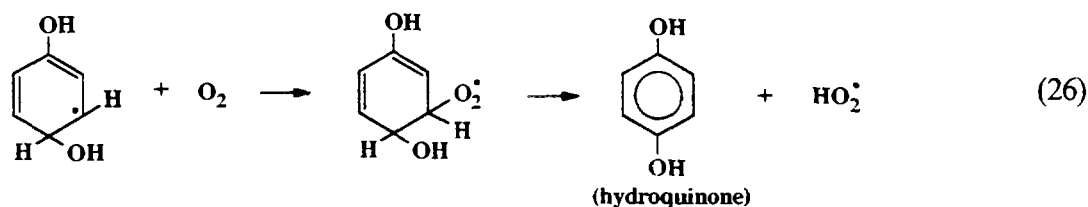


Fig. 4. (I) Radiation-induced decomposition of aqueous phenol, at various concentrations, as a function of dose, in the presence of $1.25 \times 10^3 \text{ mol.dm}^{-3} \text{ O}_2$ (pH ~ 6.5 at 25°C).

Insert: $G(-\text{PhOH})$ observed at 10^{-5} to $10^{-3} \text{ mol.dm}^{-3} [\text{PhOH}]$.

(II) Major products resulting from solution (B) as a function of dose: (a) pyrocatechol, (b) hydroquinone, and (c) hydroxyhydroquinone [1, 2, 19].





As already pointed out, the synergistic effect of ozone and radiation is very efficient with respect to pollutant degradation. In the case of phenol, the action of ozone is illustrated by several reaction steps presented in (29). It explains also the formation of muconic acid under these conditions.

Some experimental data concerning the radiation-induced decomposition of 4-chlorophenol under various conditions are summarized in Table II. The combination of radiation and ozone (even at very low concentrations) results in a higher degradation yield.

To conclude, it can be stated that water remediation by radiation treatment is a powerful and efficient method. Schemes for electron-beam processing of drinking water and of industrial wastewaters are presented in Fig. 5.

3. PHOTOCHEMICAL TREATMENT OF POLLUTED WATER

The photoinduced decomposition of pollutants of water can be based on indirect or direct photolysis, as well as on both processes. In the first case the primary transients of water photolysis

TABLE II. SOME USEFUL DEFINITIONS, RADIATION UNITS AND CONVERSION FACTORS

<u>Output power of electron accelerator (in kW):</u>	
$\text{kW} = \text{mA} \times \text{MeV}$	
$\text{mA} = \text{electron current, MeV} = \text{electron energy}$	
<u>Radiation yield:</u> G-value = number of produced or decomposed molecules per 100 eV absorbed energy. For conversion into SI-units: multiply the G-value by 0.10364 to obtain G (x) in $\mu\text{mol.J}^{-1}$.	
<u>Absorbed dose:</u>	
1 rad	$= 100 \text{ erg. g}^{-1} = 6.24 \times 10^{13} \text{ eV.g}^{-1}$
100 rad	$= 1 \text{ Joule.kg}^{-1} = 1 \text{ Gray (Gy)}$
1 krad	$= 10 \text{ Joule.kg}^{-1} = 10 \text{ Gy}$
1 Mrad	$= 10^4 \text{ Joule.kg}^{-1} = 10^4 \text{ Gy}$
1 kW	$= 3.6 \times 10^6 \text{ J.kg}^{-1} = 360 \text{ Mrad.kg.h}^{-1}$

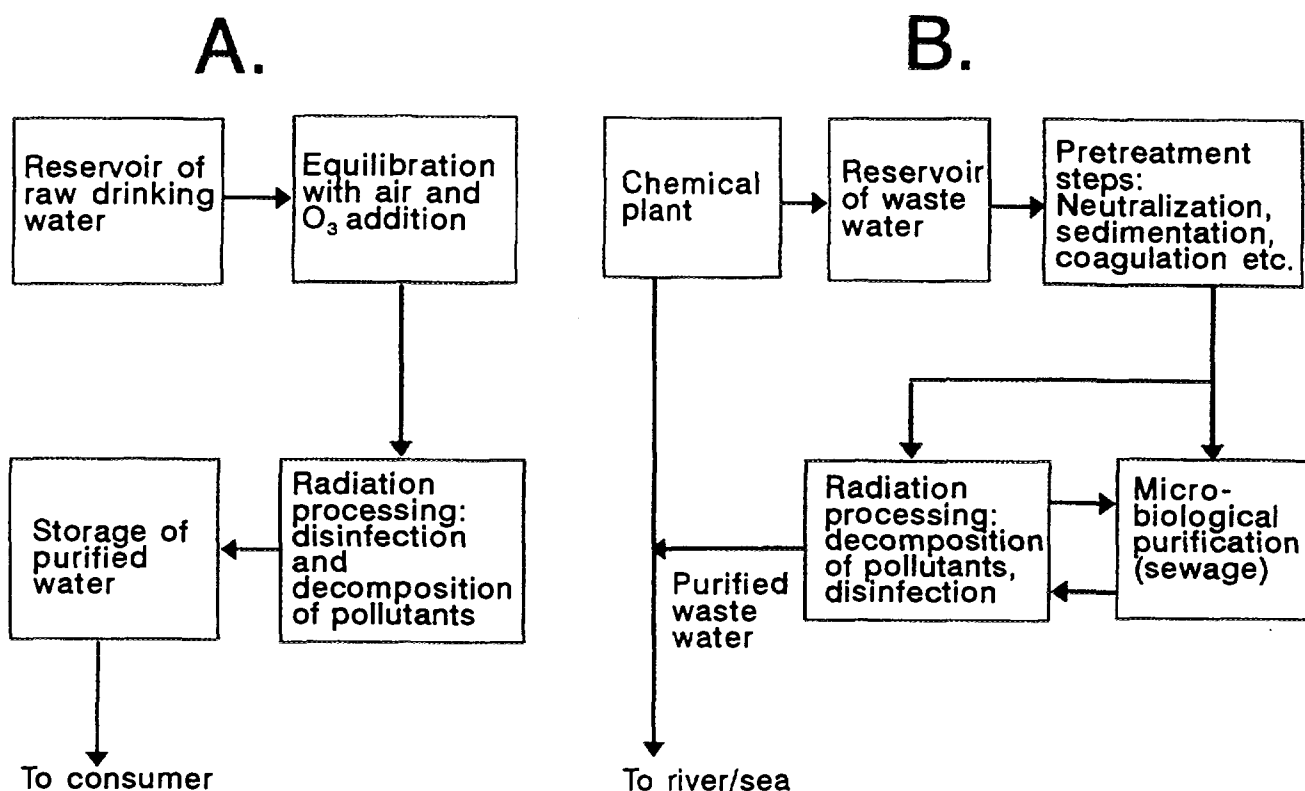


Fig. 5. Scheme for purification of drinking water (A) and of industrial wastewater (B) by electron processing.

are OH, H, and e^-_{aq} (solvated electrons), and, in the presence of oxygen, OH, HO^*_2/O^*_2 species attack the dissolved compound, whereas in the second case the substrate absorbs the incident light directly. As a result, the substrate molecules become electronically excited and can undergo various kinds of reactions depending on the experimental conditions.

3.1. Water photolysis

Fig. 6 shows the absorption spectrum of water as well as the quantum yield (Q) of H, OH and e^-_{aq} of the primary products of water photolysis, for three VUV-lines [20-24]. Electromagnetic radiation of 123.6 and 147 nm can be produced by special electrodeless lamps [24]. The VUV-light at these two wavelengths is of no practical interest in this regard, but is rather important with respect to ozone chemistry in the upper atmosphere.

As can be seen from Fig. 6, the VUV-line at 184.9 nm (produced by low-pressure mercury lamp) is absorbed by water, likewise the 123.6 and 147 nm lines. Hence, water can be photolytically decomposed [22, 24]:

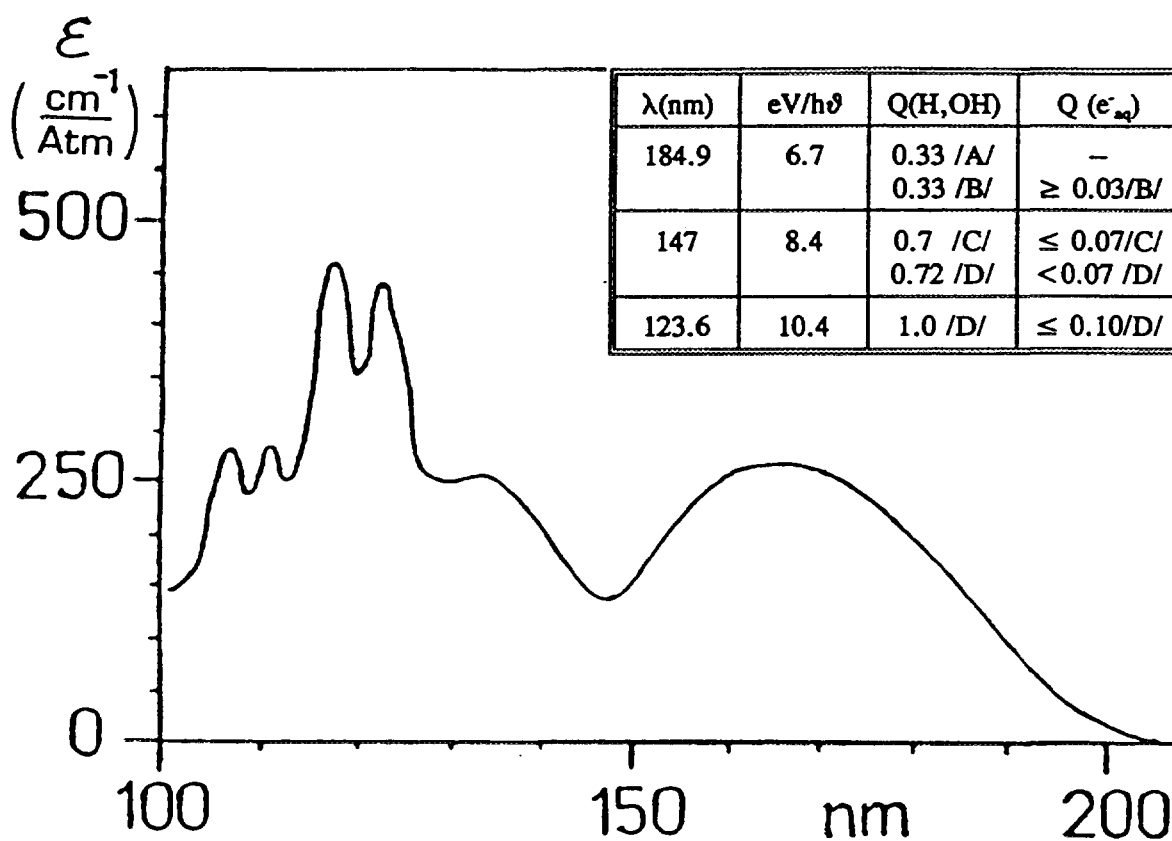


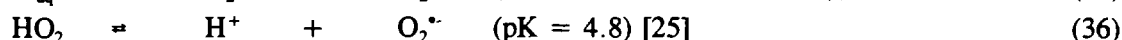
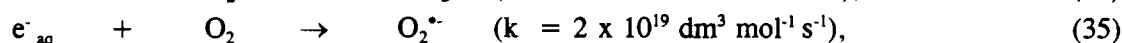
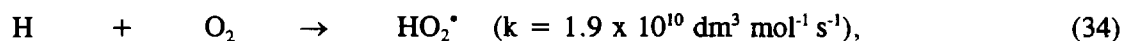
Fig. 6. Absorption spectrum of water [20].

Insert: Quantum energy (eV/hν) and quantum yields (Q) of the primary products of water photolysis with VUV-light at 123.6, 147, and 184.9 nm.

(A) - [21], (B) - [22], (C) - [23], (D) - [24].



The quantum yields of the primary products (H, OH, e^-_{aq}) are given in the Insert of Fig. 6. The free radicals so produced, OH, H and e^-_{aq} , can initiate the decomposition reactions of water pollutants. In the presence of air, both H and e^-_{aq} are converted into peroxy-radicals.

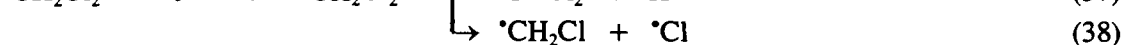
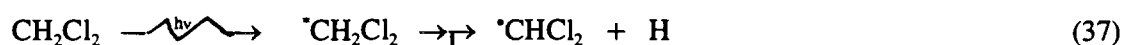


It should be mentioned that the HO_2^* species are generally more reactive than $\text{O}_2^{\bullet -}$. The absorbed energy per quantum at 184.9 nm is: $E = 6.7 \text{ eV}/h\nu$, which was taken as the basis for calculation of the photochemical G-values² of: $G_{\text{ph}}(\text{H}, \text{OH}) = 4.92$ and $G_{\text{ph}}(e^-_{\text{aq}}) = 0.45$, at pH 7.

3.2. Photolysis of dichloromethane

The major absorption band of dichloromethane lies in the VUV-range (Fig. 7B). Using VUV of 184.9 nm, both processes, direct electronic excitation of the substrate as well as photolysis of water, take place simultaneously [1]. The yield of the photoinduced Cl-cleavage is determined as a function of the absorbed energy, and is taken as an indicator of substrate degradation (Fig. 7A). Up to a dose of about $4 \times 10^{16} \text{ hv mL}^{-1}$ the Cl^- formation is linear with the absorbed VUV-quanta, and then tends to saturation. This effect is due to the reduced pollutant concentration and the involvement of secondary competition reactions.

As mentioned above, in addition to water photolysis (Reactions 30 - 33) a direct excitation of the substrate by the 184.9 nm VUV also takes place, namely:



The H-atoms as well as e^-_{aq} are scavenged by O_2 (see Fig. 1, Reactions 34 to 36) at pH 7 resulting in $\text{O}_2^{\bullet -}$ species that can oxidize the pollutant. Besides, both transients, ${}^1\text{CHCl}_2$ and ${}^1\text{CH}_2\text{Cl}$ react with O_2 and the resulting peroxy-radicals lead to the formation of phosgene (OCCl_2), which hydrolyses [1, 7, 25].



²In the case of water hydrolysis, the yields of the primary radicals at pH 7 are:

$G(\text{H}) = 0.60$ $G(e^-_{\text{aq}}) = 2.7$ $G(\text{OH}) = 2.8$ (see Fig. 2).

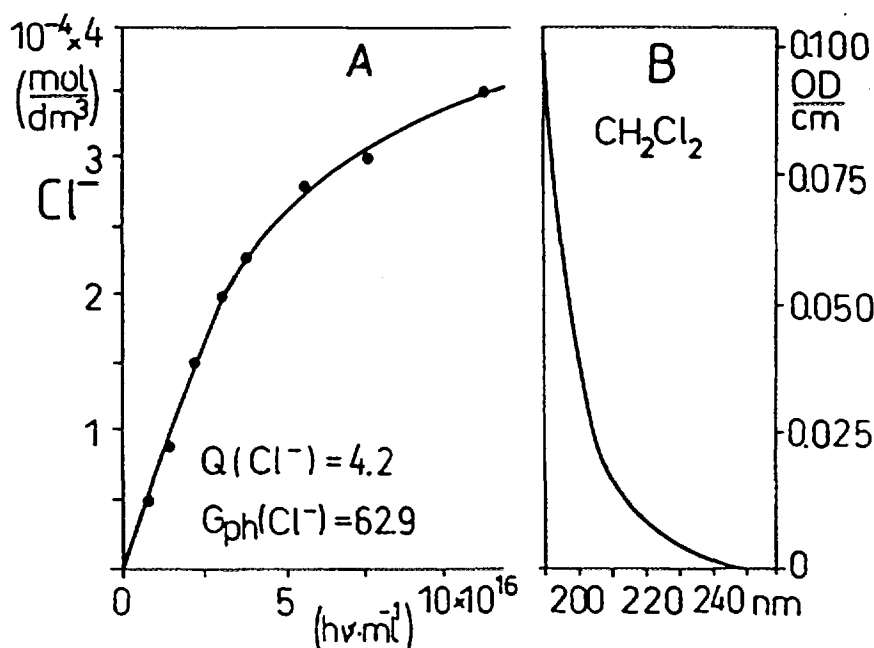
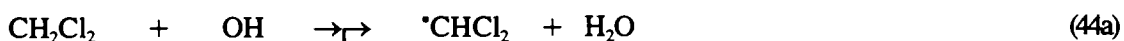


Fig. 7. A: Photoinduced Cl-cleavage from CH_2Cl_2 in $2 \times 10^{-4} \text{ mol.dm}^{-3}$ aqueous, air saturated solution, at $\lambda_{\text{exc}} = 184.9$. B: Absorption spectrum of CH_2Cl_2 in $10^{-4} \text{ mol.dm}^{-3}$ aqueous solution (pH ~ 7) [1, 3].

It is known that the reactivity of peroxy radicals is increasingly enhanced with the number of halogen atoms in the molecule [26, 27]. Hence, $^{\bullet}\text{O}_2\text{CHCl}_2$ species react more strongly with organic substances than do $^{\bullet}\text{O}_2\text{CH}_2\text{Cl}$:

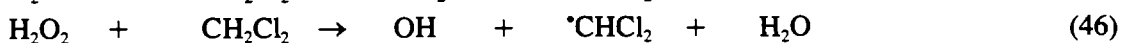
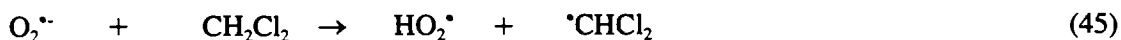


The OH radicals originating from the water photolysis (Reactions 30 and 33) as well as from Reactions (39 and 40) can also attack CH_2Cl_2 :



$$k_{14} = 0.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The $^{\bullet}\text{CHCl}_2$ and $^{\bullet}\text{CH}_2\text{Cl}$ transients are involved in several reactions as shown above. The peroxy-radical anions ($\text{O}_2^{\bullet-}$) and H_2O_2 also contribute to the degradation of CH_2Cl_2 .

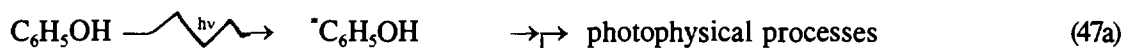


On the basis of the yield of Cl^- ions, the quantum yield (Q) and the "photochemical" G-value of the Cl^- ions were calculated, and are given in Fig. 7A. The very high degradation yield obtained is due to chain reactions initiated by the OH radicals and transients resulting therefrom.

3.3. Photolysis of phenol

The photoinduced degradation of phenol is discussed below for comparison to its above-mentioned decomposition by ionizing radiation. It has been previously studied in the presence of oxygen and small amounts of ozone [3, 28].

One should first mention that electronic excitement of aqueous phenol, as well as of a number of other organic and inorganic compounds, leads to the formation of e^-_{aq} in addition to other processes [3, 29]. In the case of phenol, the following photoinduced processes take place:



The quantum yields (Q) of e^-_{aq} resulting from S_1 - and S_2 -states for phenol are: 0.03 and 0.06. For phenolate, irradiated with UV of 253.8 nm the $Q(e^-_{aq})$ is 0.17, and for 228.8 nm it is 0.27 [3]. In the presence of oxygen, e^-_{aq} and H-atoms are converted into peroxy-radicals (see Reactions 34, 35).

The photoinduced degradation of phenol, using UV of 253.7 nm in the presence of oxygen and small concentrations of ozone in neutral solutions, is shown in Fig. 8. The Q- and G_{ph} -values achieved, as well as the absorption spectrum of phenol and phenolate, are given as Inserts in Fig. 8.

The major reaction step leading to the decomposition of phenol may start with the formation of phenoxyl radicals, as in Reactions (47b) and (47c), which exist in several resonance structures, each

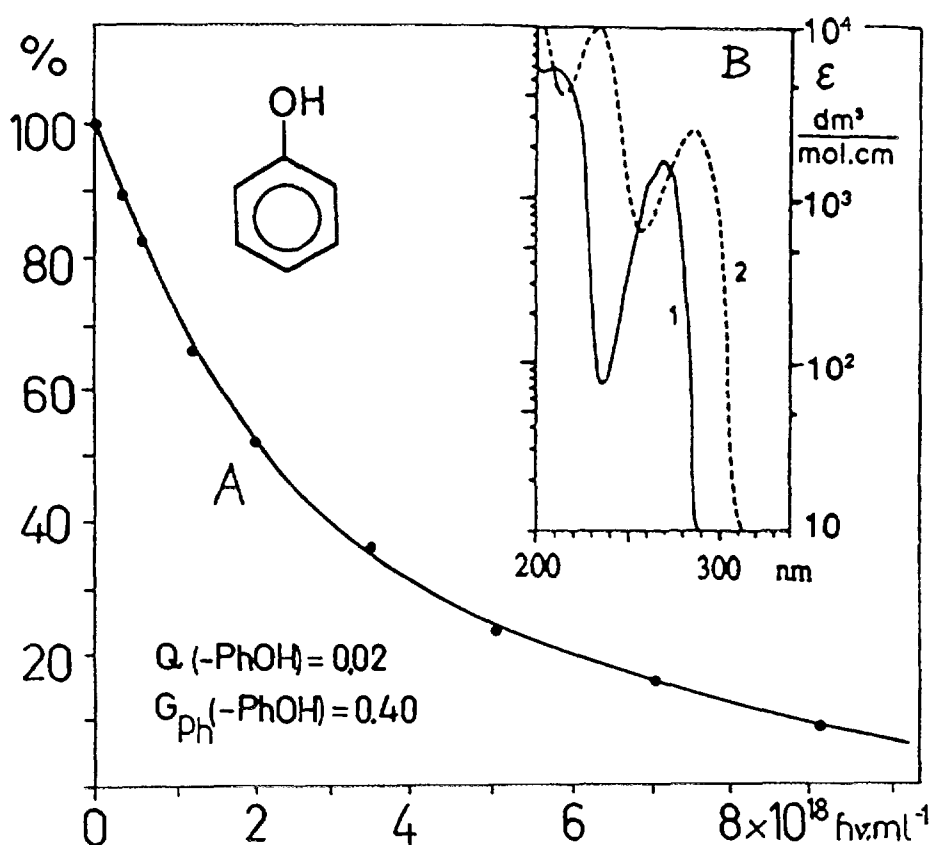


Fig. 8. (A) Photolysis (in %) of $1 \times 10^{-4} \text{ mol.dm}^{-3}$ phenol, in the presence of $1.25 \times 10^{-3} \text{ mol.dm}^{-3} O_2$ and $1.1 \times 10^{-5} \text{ mol.dm}^{-3} O_3$ (pH = 7.5), as a function of absorbed UV-dose ($\lambda = 254 \text{ nm}$). (B) Absorption spectrum of phenol (1) and phenolate (2).

of which leads to a different final product. These reactions are not discussed in detail. However, it is noteworthy that the peroxy species initiate a number of reactions discussed above (Reactions 23-28) that lead to degradation of the phenol. It might also be mentioned that in addition to the OH, H and e^-_{aq} resulting in the VUV-water photolysis, the triplet state of the pollutant as well as the singlet oxygen (1O_2) can also be involved in the photochemical decomposition process in the presence of air.

4. PHOTOCATALYTIC TREATMENT OF POLLUTED WATER

This method is based on the application of semiconductors (TiO_2 , $SrTO_3$ etc.) as photocatalysts, which were primarily developed for H_2 -production from water by means of solar energy [3, 30-35]. The principle of the method is illustrated in Fig. 9. Upon illumination of a TiO_2 particle immersed in aqueous solution with light of $\lambda \leq 450$ nm, an electron rises from the valence band (ϵ_v) to the conductivity band (ϵ_c) resulting in a charge separation (Fig. 9A). Each type of semiconductor has a characteristic band-gap ($\epsilon_G = \epsilon_c - \epsilon_v$, in eV; 1 eV = 23 kcal/mol; for TiO_2 , $\epsilon_G = 3$ eV). Hence, each particle represents a redox-system and can promote oxidation or reduction reactions depending on the experimental conditions.

The photocatalytic decomposition of pollutants on, for example, the TiO_2 -surface, is visualized schematically by Fig. 9B. As a result of the charge separation, the illuminated part (positively charged holes, h^+) is able to decompose the absorbed H_2O molecules to OH and H^+ species. The OH radicals can initiate pollutant degradation by oxidation. On the other hand, the shaded part of the TiO_2 particle becomes negatively charged, hence electrons can be transferred to absorbed O_2 , H^+ , or to a pollutant molecule, initiating a number of processes.

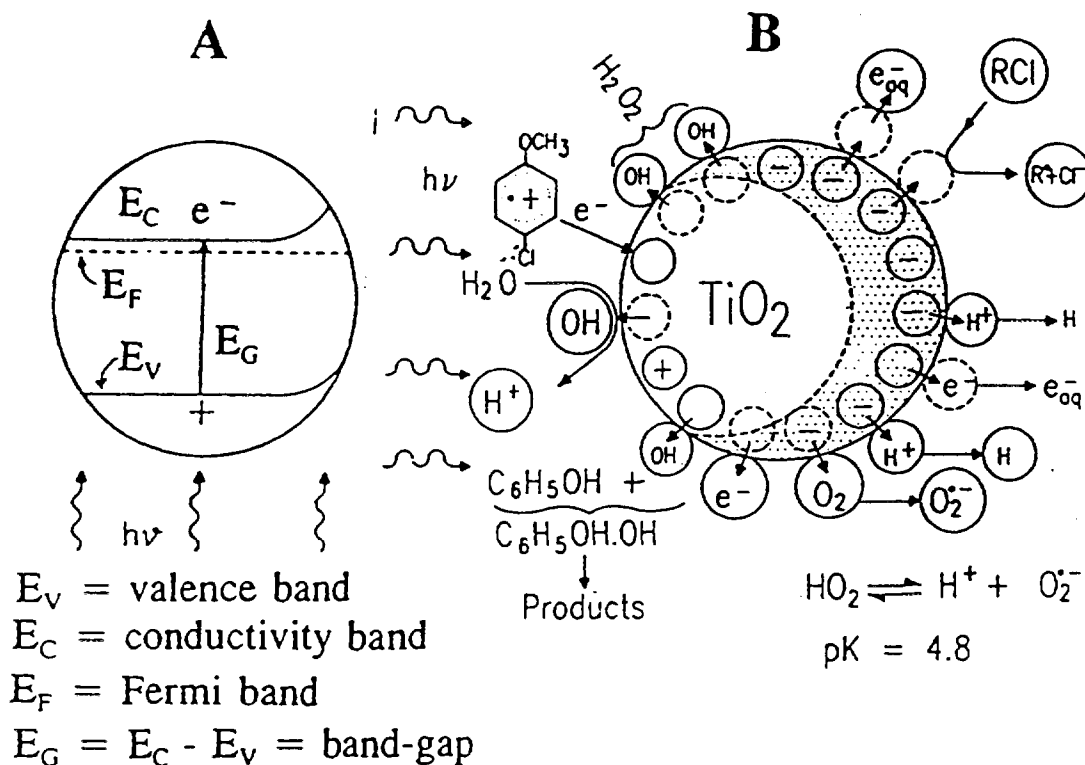


Fig. 9. (A) Simplified scheme of the energy levels of the illuminated n-type semiconductor particle, e.g. TiO_2 (B) Photoinduced reactions on the surface of TiO_2 particles in polluted water [3].

Illuminated side:



Shaded side:



Using TiO_2 as a photocatalyst, it is possible to decompose various pollutants in water [3 and references therein]. This method can also be used in combination with other techniques, for example in the presence of H_2O_2 , in order to increase the OH concentration in the solution. Depending on the "action spectrum" (absorption range) of the semiconductor employed, the photocatalytic method can be operated also by solar energy [5, 6, and references therein].

5. CONCLUSION

Comparing the yields of radiation-induced degradation of pollutants with those obtained by VUV- and UV-radiation, it is clear that the latter are much higher. This fact is based in the first place on the direct excitation of the pollutant molecule by VUV and/or by UV, and in some cases (e.g. phenol) on the additional photoinduced formation of e^-_{aq} . In the case of VUV, water photolysis also takes place, resulting in higher yields of OH and H radicals.

From the practical point of view, however, when processing very large quantities of polluted water, treatment with high-energy electrons is to be given preference over the photochemical and photocatalytic methods [36]. This is because the radiation energy needed can be provided by powerful modern electron accelerators. Photocatalytic processes can be of interest for countries with predominantly sunny weather; they are still under development.

TABLE III. INITIAL YIELDS (G_i)* OF THE DECOMPOSITION OF 10^{-4} MOL.DM⁻³ 4-Cl-PHENOL, AS WELL AS OF THE FORMATION OF Cl⁻ IONS AND OF ALDEHYDES, OBSERVED UNDER VARIOUS IRRADIATION CONDITIONS AT pH 6.5 [16]

In the presence of:	$G_i(4\text{-ClPhOH})$	$G_i(\text{Cl}^-)$	$G_i(\text{Aldehy.})$
Argon	2.7	1.15	0.28
0.25 mM O ₂	2.0	1.50	0.23
1.25 mM O ₂	2.8	1.30	0.22
1.25 mM O ₂ 0.011 mM O ₃	3.7	8.30	1.00

* G_i = initial G-value is calculated from the linear part of the dose-yield curve.

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RADIATION INDUCED OXIDATION FOR WATER REMEDIATION

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Abstract

The action of ionizing radiation on halogenated hydrocarbons, in the presence and absence of ozone, was studied in water and wastewater. The combined ozone/electron-beam irradiation process was found especially suited for remediation of low-level contaminated groundwater. This combined treatment was often more effective than irradiation alone for wastewater decontamination. It reduced the COD without a simultaneous increase of BOD. Introduction of gaseous ozone directly into the irradiation chamber improved the water-flow turbulence, allowing treatment in layers thicker than the penetration range of the electrons, with increased decontamination efficiency.

1. INTRODUCTION

Unlike drinking water, which is well-defined, wastewater is usually a mixture of substances with various reactivities, and can be characterized only by group parameters such as total organic carbon, adsorbed organic halogens or UV-absorption properties.

The kinetics of transformation of such group parameters depend on their actual composition. Because this composition changes as the reaction proceeds, no general kinetic laws - based on group parameters - can be formulated.

Although the overall pollutant concentration in wastewater is rather high, it is generally below 1 mol L^{-1} at which no direct action of radiation occurs. Accordingly, pollutant decomposition is caused by free-radical species only. For all data presented in this paper this condition applied.

2. WATER IRRADIATION

The action of ionizing radiation upon water results in the formation of almost equal amounts of oxidizing and reducing species. This hybridity is often a serious problem with regard to the efficiency of pollutant decomposition, as illustrated by the radiation-induced decomposition of trace amounts of chlorinated ethylenes in groundwater.

2.1. Irradiation of groundwater

In air-saturated groundwater containing trichloroethylene (TCE) and perchloroethylene (PCE) as micropollutants, most of the solvated electrons and $\cdot\text{H}$ -atoms are scavenged by oxygen, forming the superoxide radical anion $\cdot\text{O}_2^-$ and the hydroperoxyl radical $\text{HO}_2\cdot$ respectively. The latter is in an acid-base equilibrium with the $\cdot\text{O}_2^-$ ($\text{pK}=4.7$). At the usual pH-values of groundwater, the equilibrium is shifted towards $\cdot\text{O}_2^-$, i.e. most of the reducing species are converted into the superoxide anion $\cdot\text{O}_2^-$ (Fig. 1).

What happens to the $\cdot\text{O}_2^-$? Its probable fate is disproportionation into H_2O_2 and O_2 , which means that more than 50% of the radiation energy is lost for pollutant decomposition.

Generally, only OH free radicals remain as active species for pollutant decomposition in irradiated groundwater. Under the conditions given, and as long as the nitrate concentration is low,

only bicarbonate ions seriously compete for OH free radicals - due to their high concentration.

For nitrate concentrations higher than a few ppm, scavenging of solvated electrons and subsequent formation of nitrite ions cannot be ignored. Nitrite scavenges OH free radicals effectively, and considerably worsens conditions for pollutant decomposition. This can be demonstrated by comparing pollutant decomposition in water at various concentrations of bicarbonate and nitrate.

2.2. Decomposition of perchloroethylene

In de-ionized water containing neither bicarbonate nor nitrate, decomposition of perchloroethylene (PCE) proceeds rapidly. With Vienna City drinking water containing 195 ppm bicarbonate and about 6 ppm nitrate, the decomposition rate is slower, but the reaction is still of a first order. Seibersdorf water contains 252 ppm bicarbonate and 60 ppm nitrate, and the rate of PCE decomposition is decreased by about one order of magnitude; the kinetics change from first to a higher order. This is the effect of the nitrate (Fig. 2), which is reduced by electrons to form nitrite which, in turn, is oxidized back to nitrate by OH free radicals. In this way, electrons and OH free radicals are lost for pollutant decomposition. This problem, illustrated by the nitrite/nitrate system, is not specific to groundwater, but rather is fundamental to radiation processing of water, especially so for wastewater treatment as demonstrated by experimental data presented below.

3. WASTEWATER TREATMENT

Experiments were performed with different types of wastewater, each treated with:

- ozone alone
- irradiation alone
- combination of ozone with irradiation.

In all cases, irradiation alone was the least effective.

3.1. Effluent from processing of molasses

Fig. 3 shows that both oxidation processes - ozone and combined ozone/ionizing radiation - effected a remarkable COD reduction in an aqueous effluent from a molasses-processing plant, but it was not possible to successfully use the OH free radicals generated by the irradiation alone.

The combined ozone/ γ -irradiation process does not use ozone as oxidant: instead, the oxidant is the hydroxy free radical. A process that generates and uses OH free radical is termed an advanced oxidation process (AOP). In the present case, the AOP was more effective than ozonation. Moreover, a continuation of both processes results in another reduction in COD by the combination, but in almost no further COD reduction by ozone alone. The products of ozonation do not react with ozone, but rather with OH free radicals, as indicated by further COD reduction after 300 min with ozone. Since the pH value of the wastewater was around 8, there should be OH free-radical production by hydroxyl-ion OH^- promoted ozone decomposition. For the first 200 min treatment time, the OH radicals were probably scavenged by substances that are not reflected in the COD. The scavenger was removed sometime after 200 min. From that moment, the OH free radicals would contribute to the COD reduction.

Besides the COD reduction, the BOD changes are of importance for comparison of these two processes. The decrease in COD occurred with a considerable increase in BOD - above the limit value for emission. The subsequent reduction, recorded after 300 min, was due to the already-mentioned

OH free-radical generation by ozone. In other words: ozonation finished sometime after 100 min and turned into an AOP thereafter.

The AOP, on the other hand, reduced the COD by an order of magnitude without simultaneous BOD increase, attaining both limit values required for emission. The AOP represented a residue-free resolution of the wastewater problem, which is an encouraging result.

3.2. Landfill leachate

Another preliminary experiment involved the treatment of leachate from municipal-waste landfill. Although the composition of such wastewater is quite different from that of the molasses effluent discussed above, surprisingly similar tendencies were observed: with all three treatment processes, irradiation alone gave the poorest result: almost no COD reduction at a dose of 10 kGy.

Ozonation reduced the COD from about 2400 ppm to about 1000 ppm, and was again accompanied by a simultaneous distinct BOD increase. The AOP finally resulted in even greater COD reduction without simultaneous BOD increase.

3.3. Biologically pre-treated effluent from pulp bleaching

The similarity of the above results, obtained with two very different types of wastewater, is, however, mere coincidence. With a biologically pre-treated effluent from a pulp-bleaching process, almost opposite results were obtained, with one exception: irradiation alone again produced the poorest results, therefore those data are not included in the next figure.

Fig. 4 shows that both oxidation processes increased BOD and AOP even more than ozonation. The differences in the COD decrease and the BOD increase were not pronounced at 100 min. This, again, is an indication that ozonation is converted into an AOP with continuing treatment. When tested with samples from both oxidation processes after 300 min, there was decreased toxicity of fish only after ozonation. The AOP did not alter toxicity in comparison with the untreated sample, a further indication that ozonation and AOP may result in different products.

3.4. Native chlorination-stage effluent from pulp bleaching

The treatment processes discussed above had in common that the wastewater was already biologically treated and contained almost no biodegradable substances. This has economical implications. Fig. 5 shows results for the pulp-bleaching effluent, but without biological pre-treatment, as indicated by an initial BOD value of 490 ppm. Whereas, in the experiments with pre-treated wastewater, ozonation always resulted in a BOD increase, the BOD of the untreated water decreased with ozonation, indicating that the ozone reacted preferentially with the biodegradable substances. However, both ozone and ionizing radiation are too expensive for oxidation of biodegradable substances and, therefore, are used only for the decomposition of refractory pollutants.

3.5. Some important aspects of radiation-induced wastewater treatment

Summarizing briefly some important aspects of radiation-induced wastewater treatment processes, the following should be considered:

- biological treatment prior to the irradiation process
- toxicity tests afterwards
- economy: competition with
 - ozone + biological treatment
 - other AOPs.

4. COMPARISON OF THE OZONE/ELECTRON-BEAM PROCESS WITH CONVENTIONAL AOPs

There is a fundamental difference between the so-called conventional AOPs and the AOP based on the combination of ozone with ionizing radiation.

4.1. UV-irradiation of aqueous ozone and hydrogen peroxide

When aqueous solutions of ozone or hydrogen peroxide are irradiated with UV (Fig. 6), the radiation energy is absorbed by the ozone or hydrogen peroxide and not by the water. In the case of ozone, the action of UV leads to the formation of an oxygen radical, which immediately reacts with water forming hydrogen peroxide. H_2O_2 is a weak acid and the deprotonated form, HO_2^- , transfers its electron to the ozone. An ozonide anion is formed, which decomposes immediately after protonation into OH. The limiting factor here is the poor solubility of ozone in water.

As an alternative to UV-irradiation, direct addition of H_2O_2 to aqueous solutions of ozone is also used.

UV-photolysis of H_2O_2 is a convenient method of generating OH free radicals. However, H_2O_2 has a very low extinction coefficient at 254 nm; the OH free-radical yield is, therefore, rather low. Nevertheless, in all three cases there is always only one single source for the OH free radicals: ozone or H_2O_2 .

When ionizing radiation is used, the situation is completely different in that the energy is absorbed entirely by the water and not by any solute.

4.2. Irradiation of water in the presence of ozone

The action of ionizing radiation in water is known to result in the formation of ions, and of molecular and free-radical species (Fig. 7). Solvated electrons and H-atoms are reducing species, formed in almost the same amounts as OH free radicals. In the presence of ozone they act as promoters for ozone decomposition into OH free radicals. As a consequence, there results a unique AOP that is based on two simultaneously-operating sources for OH free-radical generation; this means that more OH free radicals are produced than can be supplied by conventional AOPs. The advantage of the combination of ozone with ionizing radiation has been verified with experimental data.

4.2.1. Decomposition of TCE in simulated Niederrohrdorf water

There is an ozone/UV plant for groundwater remediation in Niederrohrdorf, Switzerland, which was manufactured by WEDECO in Germany. The groundwater contains 402 ppm bicarbonate, 30 ppm

nitrate, and 0.5 ppm DOC, and is contaminated with about 100 ppb trichloroethylene (TCE). To lower the TCE to just below 10 ppb, 1.3 kg ozone h⁻¹ is necessary, which corresponds to about 7 ppm initial ozone concentration in the water.

The decomposition of 100 ppb TCE, in simulated Niederrohrdorf water, was studied and the results shown in Fig. 8 were obtained. Whereas the O₃/UV required about 6-7 ppm O₃ to decrease the TCE from 100 to just below 10 ppb, the ozone/electron-beam combination achieved the same result at about 2 ppm initial ozone concentration.

Applying 5-6 ppm O₃ resulted in a residual TCE concentration of nearly 1 ppb, almost an order of magnitude better than the O₃/UV process, a clear indication of a higher OH free-radical concentration with the ozone/electron-beam process.

4.2.2. Wastewater from processing of molasses

Similar results have been obtained also with wastewater. Fig. 9 shows that for the same amount of COD reduction, the ozone demand of the O₃/H₂O₂ combination is much higher than that of the O₃/γ-combination.

5. RADIATION PROCESSING OF WATER

The so-called waterfall technique, an open system, is a simple, robust and convenient means of treating wastewater. Its chief limitation occurs with highly volatile pollutants. The water layer that can be treated is determined by the penetration of the electrons. Experiments performed in a closed system showed that under turbulent-flow conditions water, layers thicker than the maximum penetration range of the electrons can be treated successfully.

5.1. Decomposition of perchloroethylene

Fig. 10 shows the results obtained with 3-mm layers and 500 keV electrons that have a maximum penetration range of only 1.4 mm. At very low turbulence, PCE decomposition takes place in the irradiated layer only. But under high turbulence, the PCE decomposition increased by almost an order of magnitude.

5.2. Decomposition of trichloroethylene

Fig. 11 shows results obtained for electron-beam decomposition of TCE at three water thicknesses, under turbulent-flow conditions. Even a 4.5-mm water layer was treated successfully with 500 keV-electrons.

5.3. Effect of gaseous ozone

Optimum turbulence during irradiation can be achieved by introducing ozone into the irradiation chamber in the gaseous state. Such a process has, moreover, two other important benefits:

- the density of the gas/water mixture is less than that of water, therefore the penetration range of the electrons increases, and
- because the ozone in the water phase is consumed more rapidly during irradiation, it crosses the gas/water boundary faster.

As a consequence, much higher efficiencies may be attained as compared with aqueous ozone addition, as shown by Fig. 12.

6. SUMMARY AND CONCLUSIONS

Drinking water cannot be treated with ionizing radiation alone because of nitrite and hydrogen peroxide formation. These problems do not arise when the irradiation is performed in the presence of sufficient ozone. The addition of ozone, before or during irradiation, converts the irradiation into a pure oxidation process (a so-called advanced oxidation process, AOP) [1-5].

The ozone/ionizing-radiation combination is unique among AOPs because of two outstanding features:

- the energy absorption proceeds via the water to be remediated, initiating
- two different OH-generation processes simultaneously.

Compared to other AOPs a higher OH concentration results, which results in a lower residual pollutant concentration (when the same ozone concentration is considered) or a lower ozone consumption (when the same residual pollutant level is considered). Moreover, there is high efficacy at low pollutant levels, allowing throughput capacities of about 5-6 million gallons a day or more, at competitive costs. Accordingly, the ozone/electron-beam irradiation process is especially suited for remediation of low-level contaminated ground water. The ozone concentrations necessary in such a remediation process are usually higher than those needed for disinfection of drinking water, therefore, drinking water treated with an ozone/ionizing-radiation process is also effectively disinfected.

In wastewater-treatment processes, irradiation in combination with ozone is often more effective than irradiation alone. Such a combination is able to decrease COD without simultaneous increase of BOD. Accordingly, a single-stage residue-free treatment process results as an attractive alternative to the conventional two-stage process of ozonation plus biological treatment, in which sludge is produced as a residue [6].

With respect to the radiation processing of water, introduction of gaseous ozone directly into the irradiation chamber effects turbulence that makes possible the treatment of water layers thicker than the maximum penetration range of the electrons. Moreover, the efficiency of pollutant decomposition is enhanced [4].

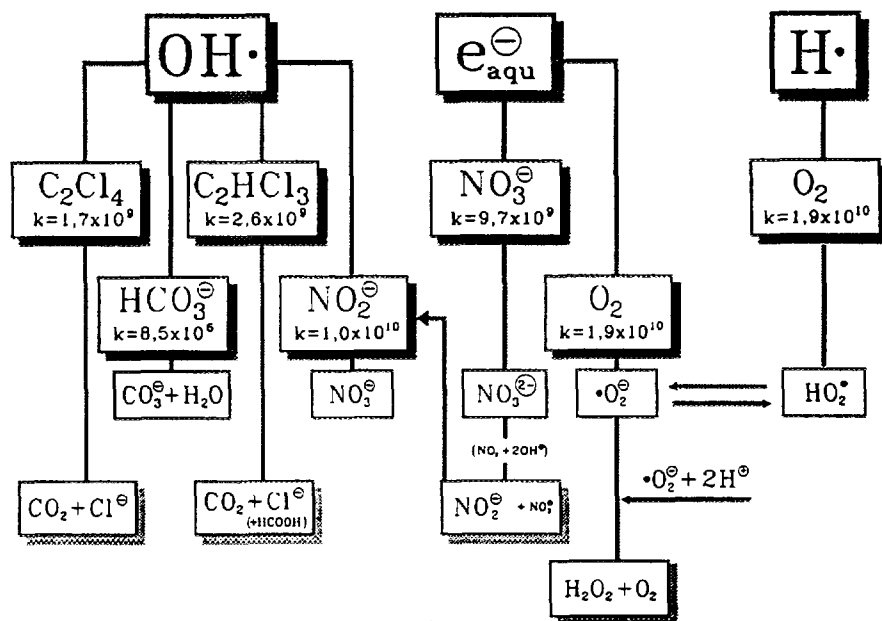
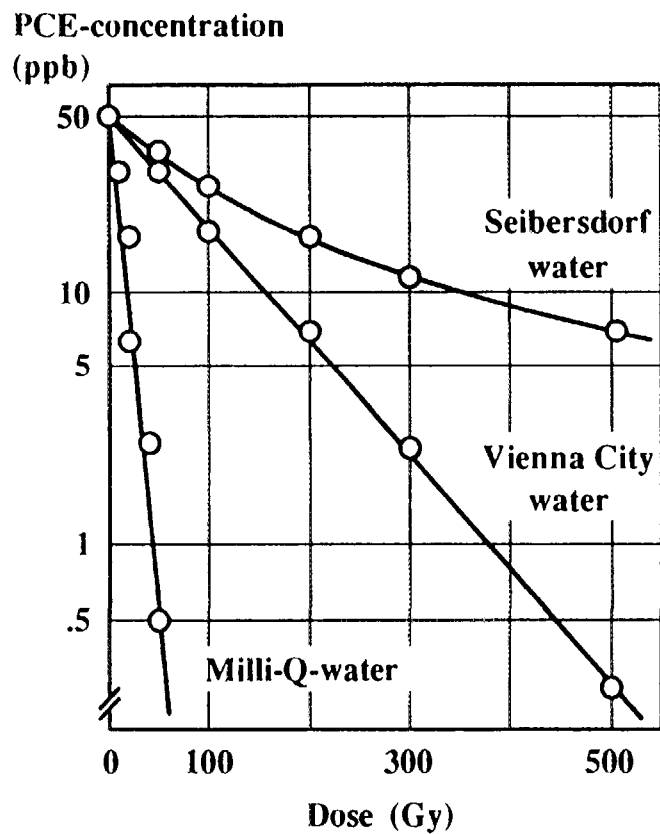


FIG.1. Irradiation of groundwater. Competition between natural solutes and chlorinated ethylenes. *k*-values given are bimolecular rate constants.



VIENNA CITY WATER

4 mval/L

195 ppm

6.5 ppm

4.5 ppm

30.5 ppm

0.6 ppm

total
hardness

Bicarbonate

Nitrate

Chloride

Sulfate

TOC

SEIBERSDORF WATER

8.6 mval/L

252 ppm

60 ppm

42 ppm

112 ppm

1 ppm

FIG. 2. Decomposition of 50 ppb perchloroethylene in various groundwaters.

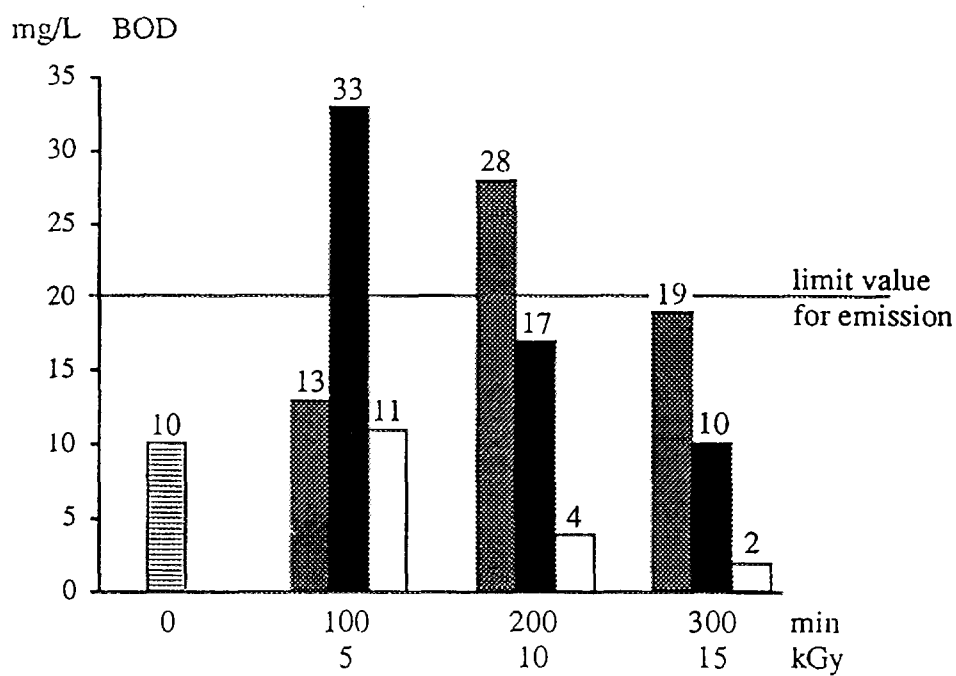
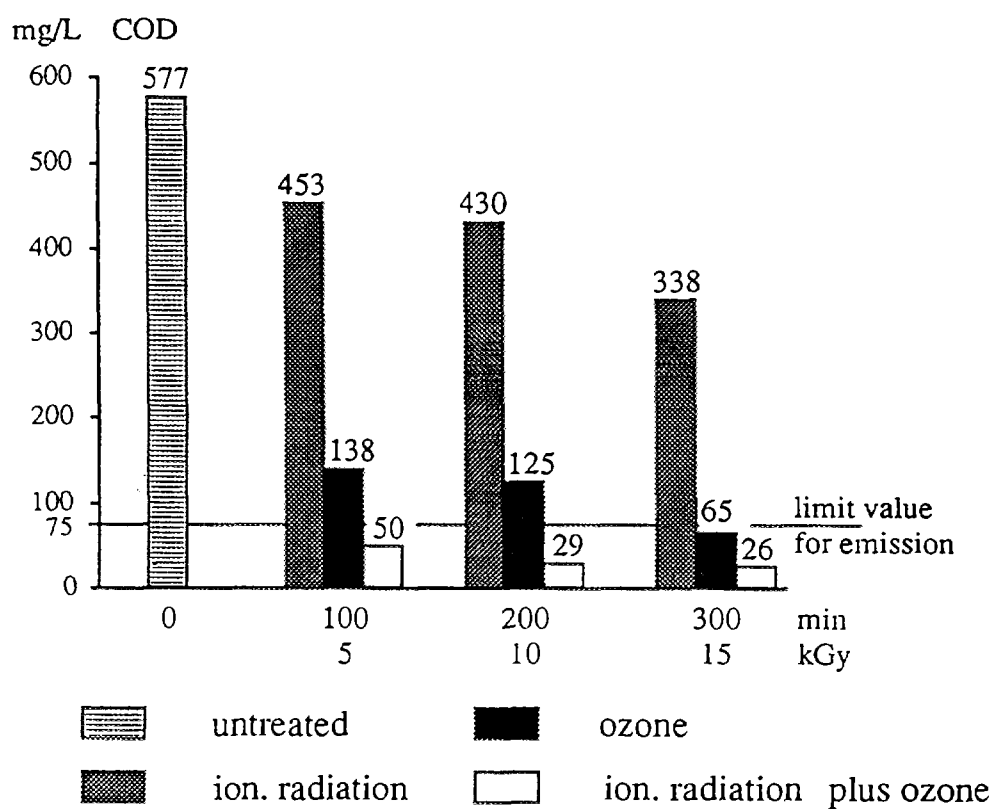


FIG. 3. COD and BOD changes, by different treatment processes applied, in effluent from molasses processing.

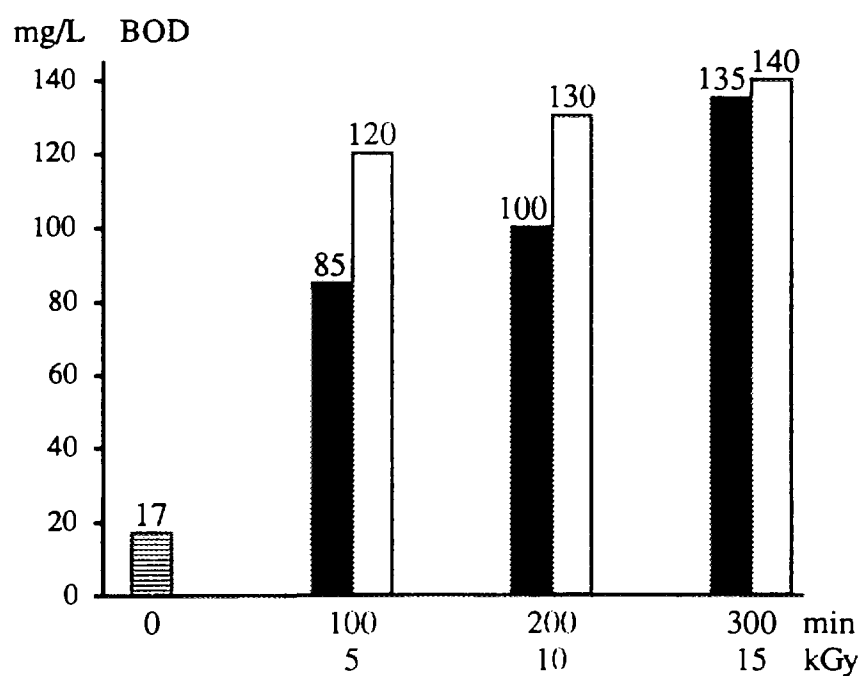
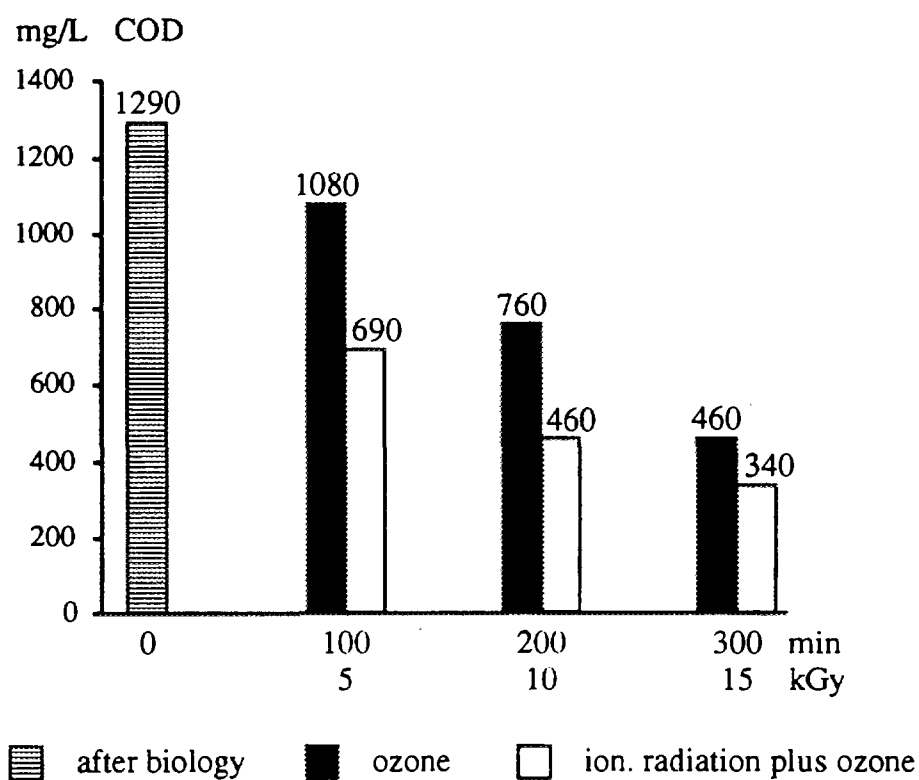


FIG. 4. COD and BOD changes, by ozonation and advanced oxidation, in a biologically pre-treated effluent from a pulp-bleaching process.

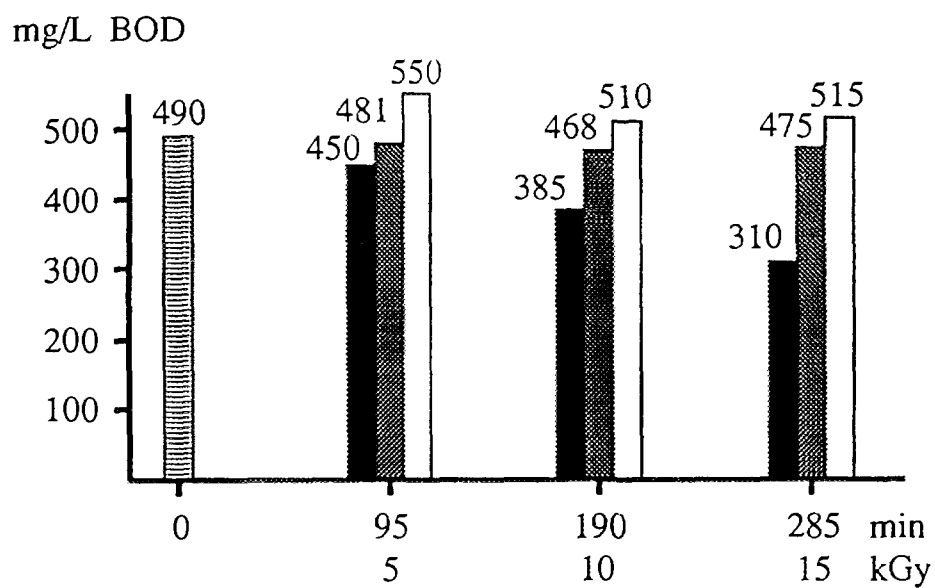
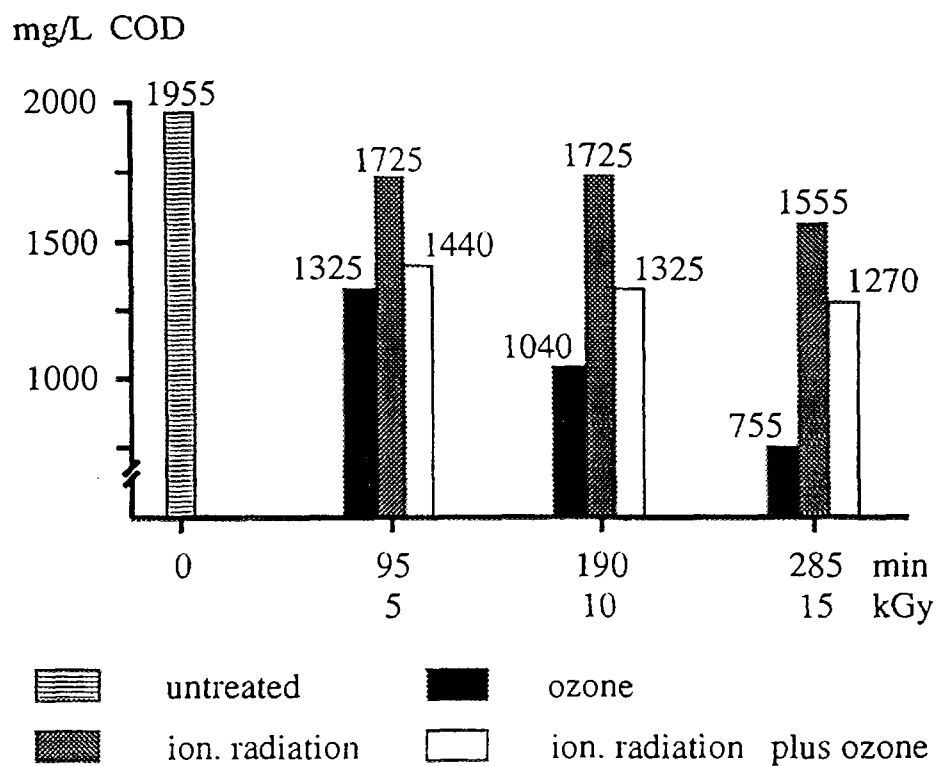
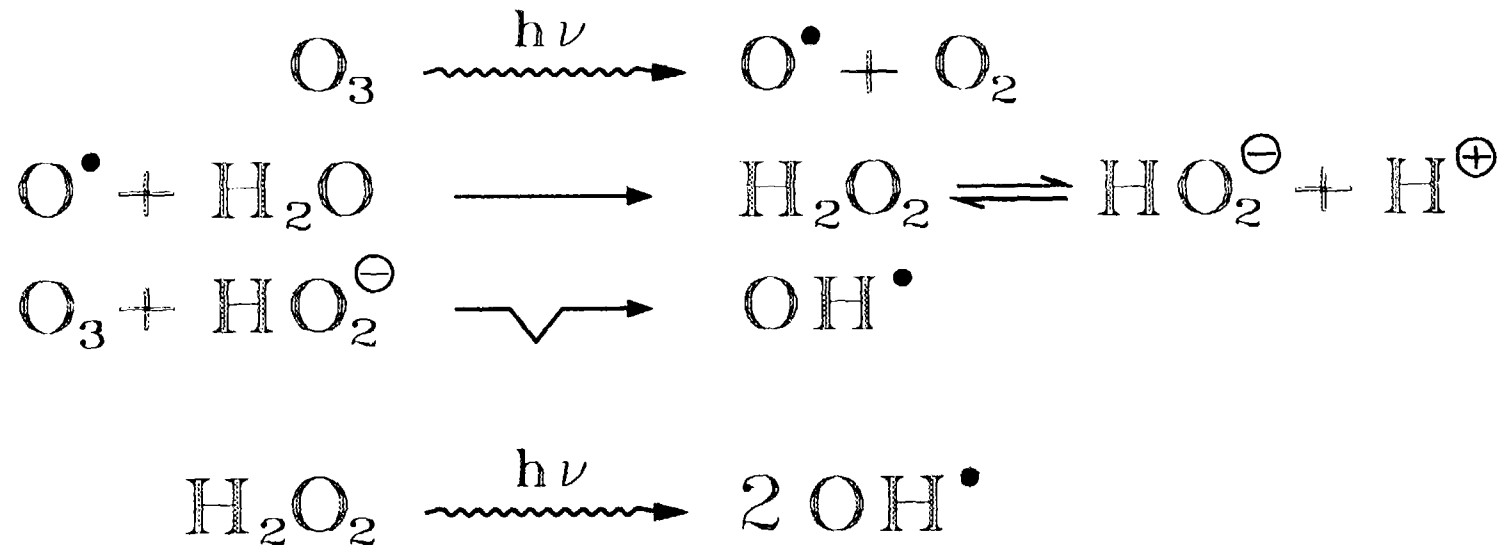
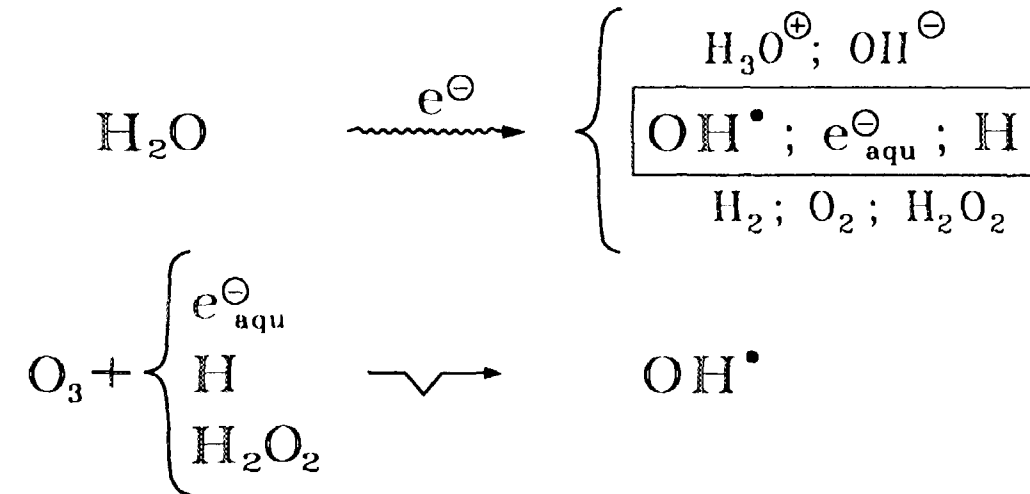


FIG. 5. COD and BOD changes in a native chlorination stage effluent from a pulp-bleaching process, by irradiation, oxidation and advanced oxidation.



Radiation energy is absorbed by solutes only, NOT by the water!
There is always just ONE OH• source: O₃ or H₂O₂

FIG. 6. Hydroxy free-radical generation by UV irradiation of aqueous ozone and hydrogen peroxide, respectively.



Radiation energy is absorbed by the water NOT by any solutes!
 There are now TWO OH • sources simultaneously:
 water radiolysis PLUS ozone decomposition
 higher OH • concentration!

FIG. 7. Sources of hydroxy free radicals in water when irradiated in the presence of ozone.

100 ppb TCE

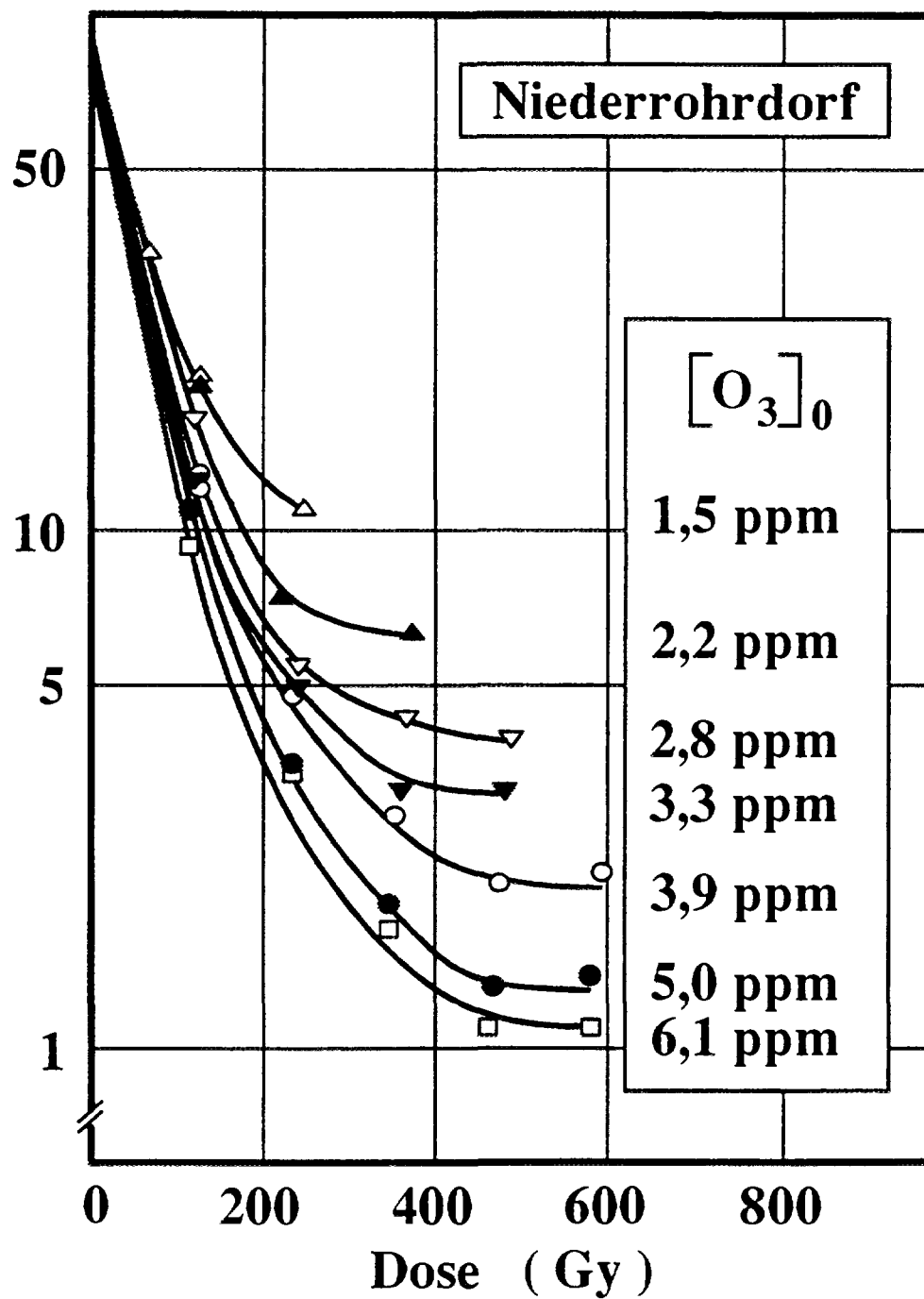


FIG. 8. Decomposition of trichloroethylene (TCE) in simulated Niederrohrdorf water by ozone/electron- beam irradiation treatment as a function of the initial ozone concentration and radiation dose.

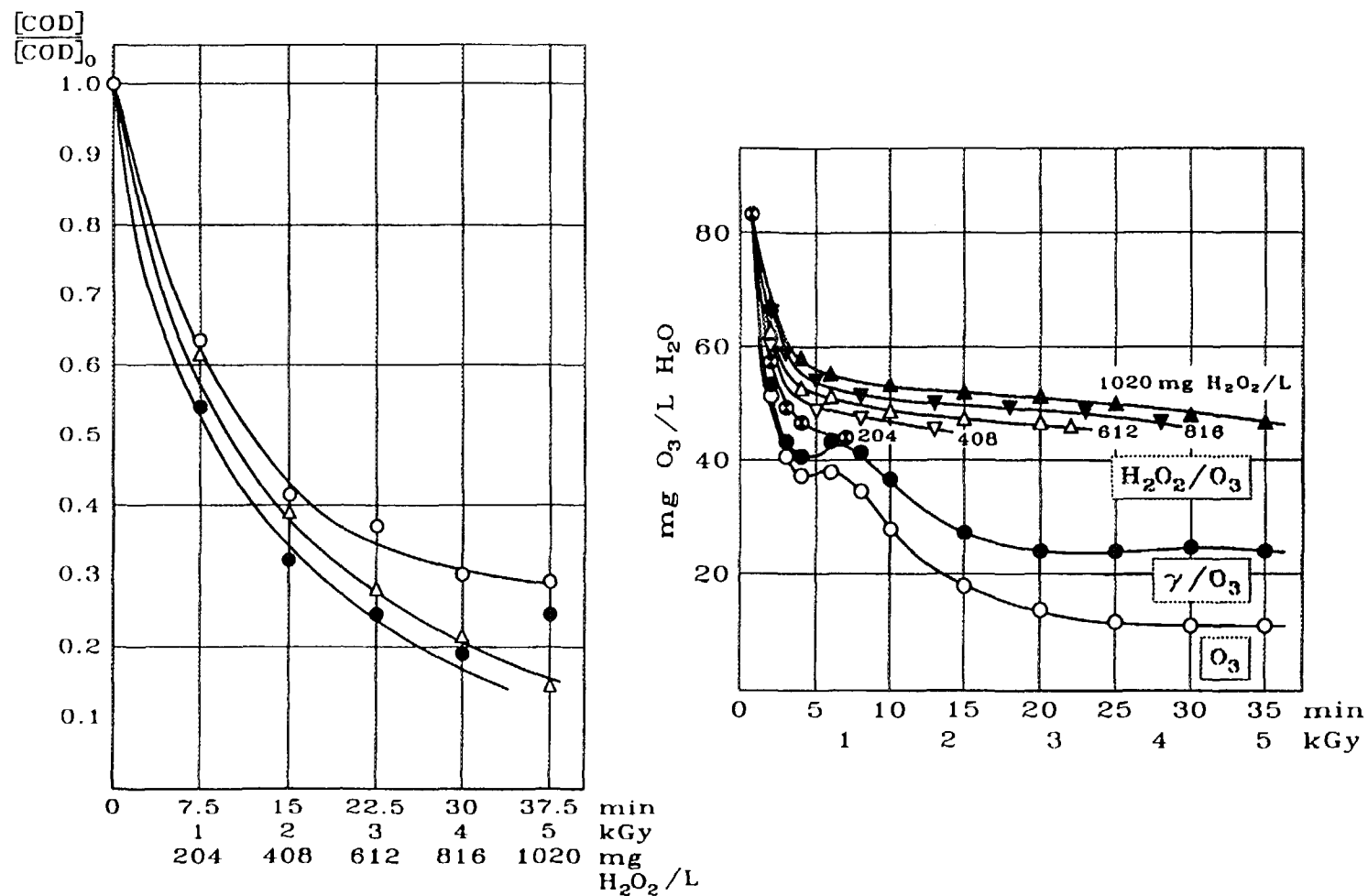


FIG. 9. COD changes and ozone consumption in wastewater from molasses processing with regard to different ozone-based treatment processes (ozone alone (\circ); ozone/ γ -irradiation (\bullet); ozone/hydrogen peroxide (Δ)).

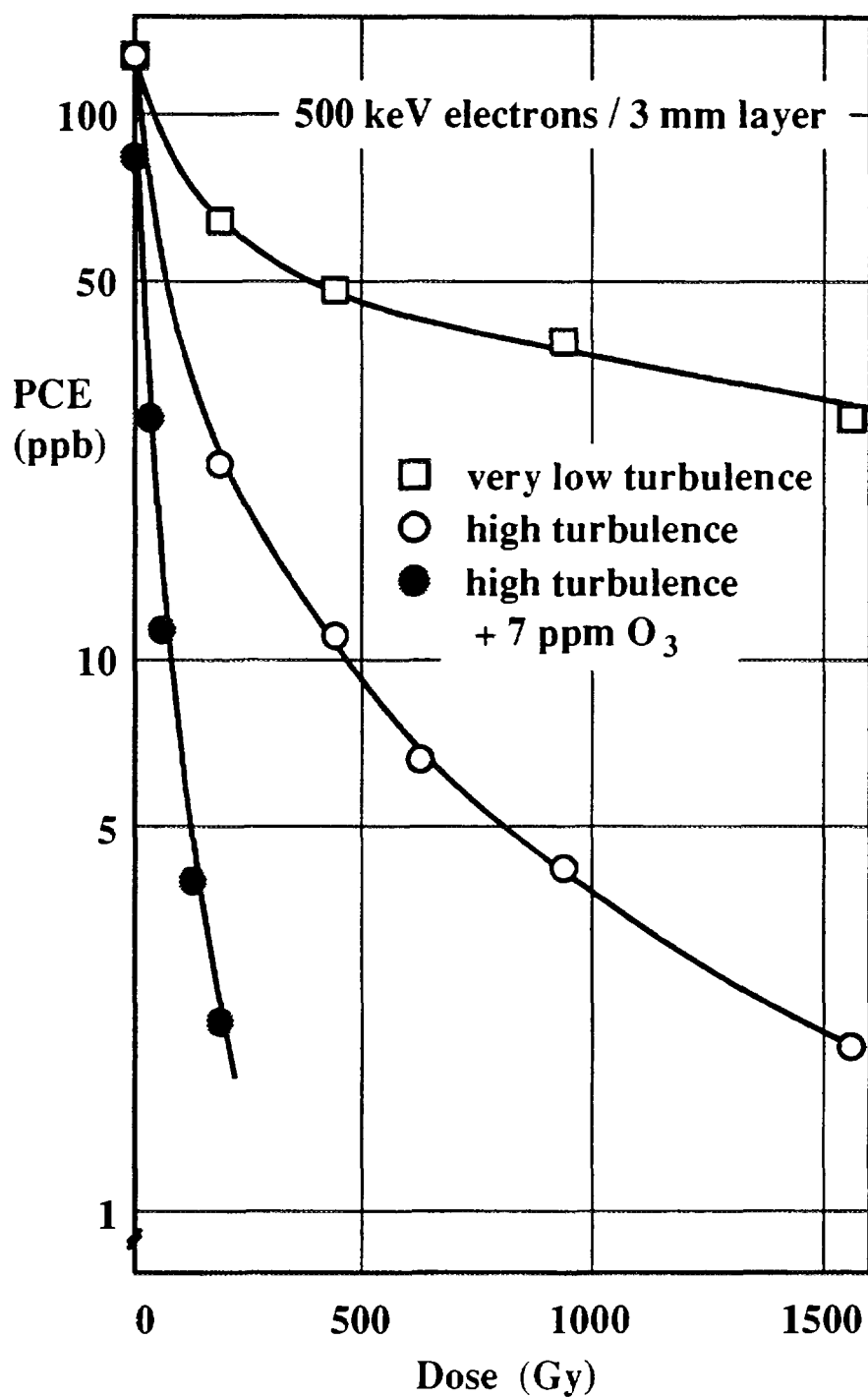


FIG. 10. Decomposition of perchloroethylene by electron beam irradiation with and without ozone under different flow conditions (in a water layer twice as thick as the maximum penetration range of the electrons applied).

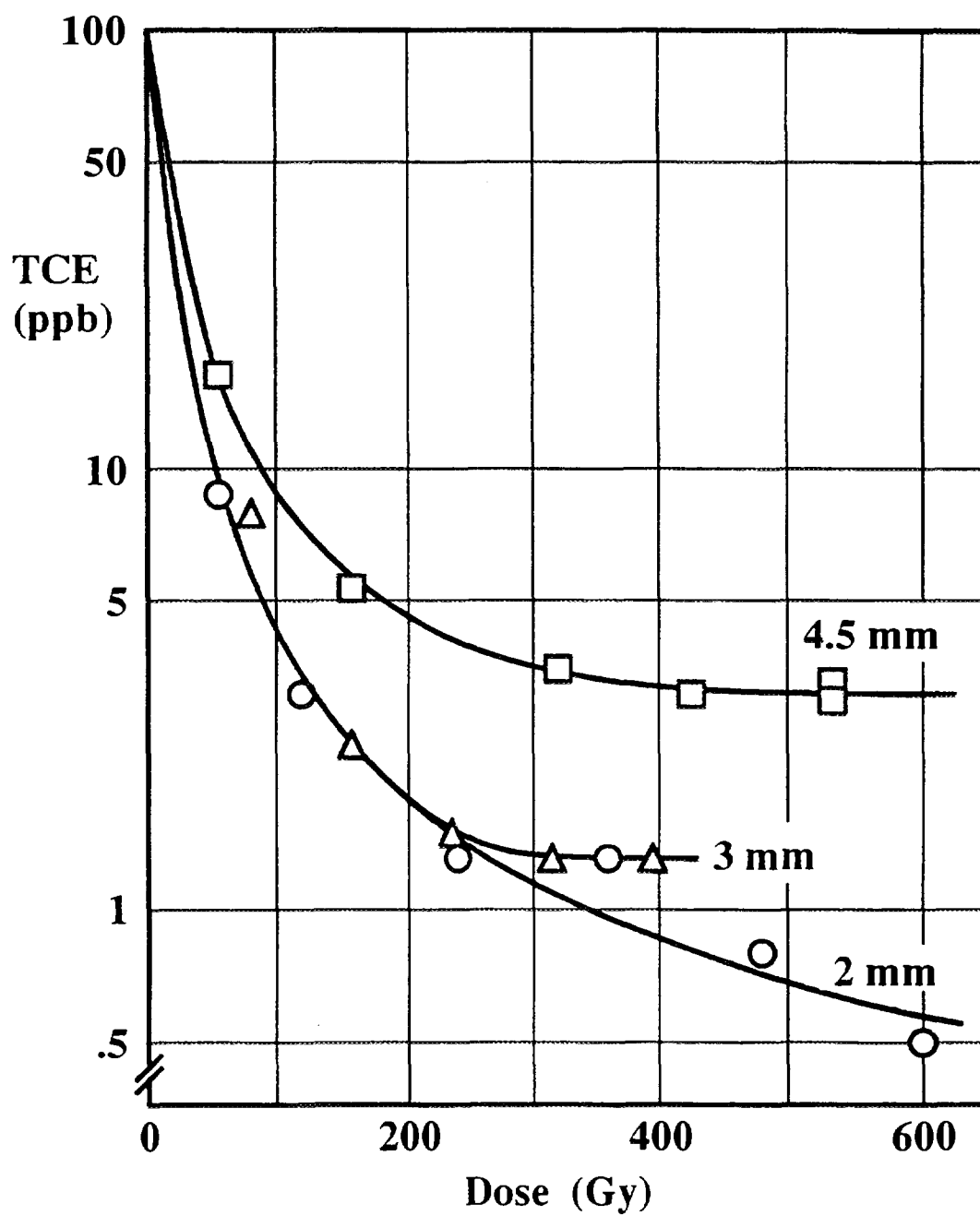


FIG. 11. Decomposition of 100 ppb trichloroethylene by ozone/electron beam irradiation treatment as a function of radiation dose and water layer thickness. Initial ozone concentration - 2 ppm; maximum penetration of 500 keV electrons in water is 1.4 mm.

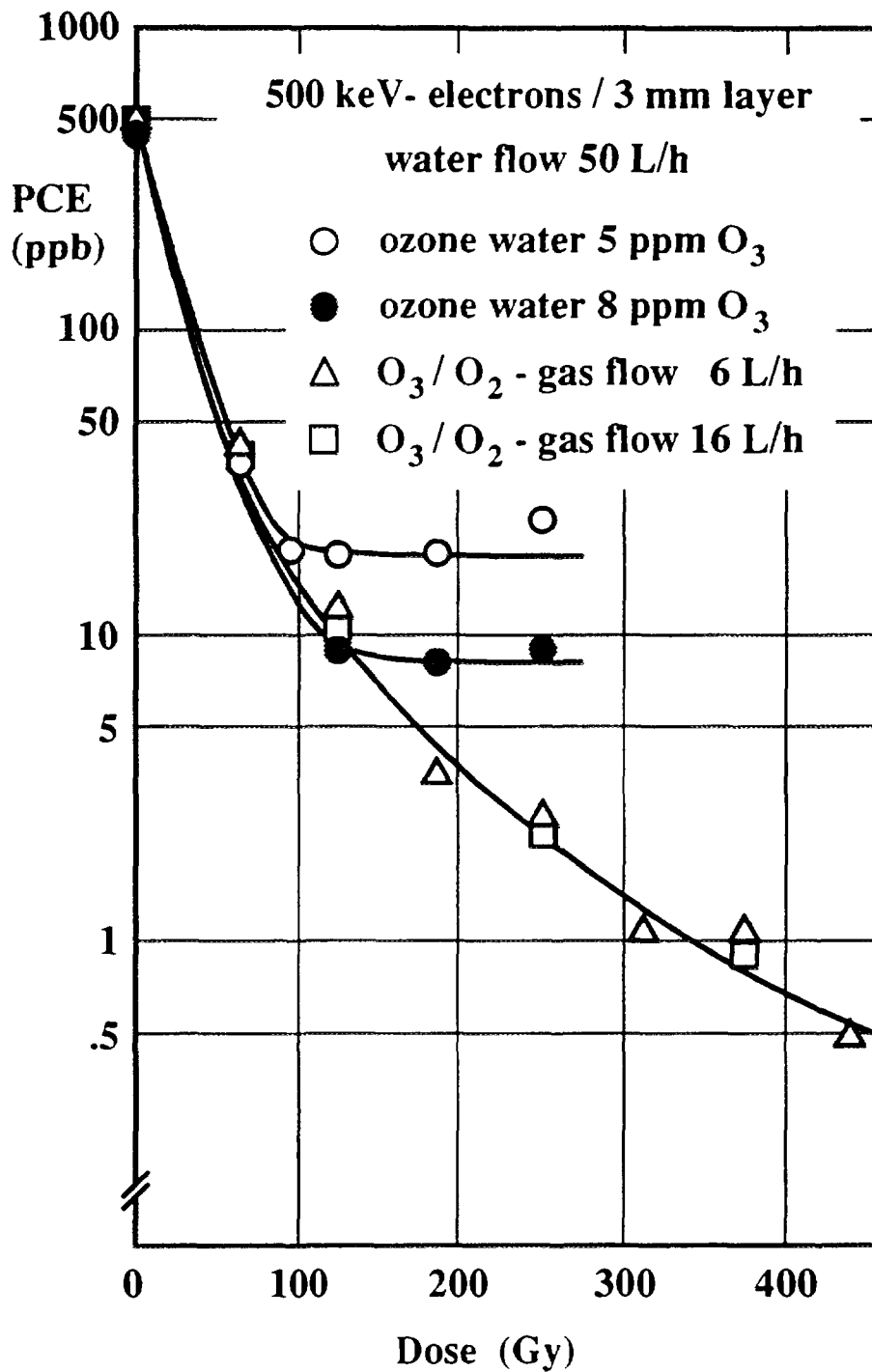


FIG. 12. The effect of gaseous ozone introduction as compared with aqueous ozone addition in an ozone/electron beam irradiation treatment process, applied for the decomposition of 500 ppb perchloroethylene in Vienna City drinking water.

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SEWAGE SLUDGE DISINFECTION BY IRRADIATION (ENEA-ACEA COLLABORATION)

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Abstract

The Municipal Association for Electricity and Water (ACEA) of Rome and the Lazio Regional Administration are implementing a programme of intervention aimed at protecting the water quality of the hydrogeological basin of Lake Bracciano. With support from ENEA, a pilot plant is being constructed for sewage-sludge disinfection by irradiation with accelerated electrons, in order to use the sludge as fertilizer for agriculture, as is practised abroad mainly in Germany and the United States. The work to be carried out within the ENEA-ACEA agreement includes: sludge digestion, drying, and sterilization by irradiation. Results achieved so far, including preliminary analyses of irradiated sludge, are presented. The irradiation plant and processes involved are also described.

1. INTRODUCTION

The Municipal Association for Electricity and Water (ACEA) of Rome and, more recently, the Lazio Region Administration, have initiated studies and research activities to plan a programme of intervention that will protect the hydrogeological basin of Lake Bracciano.

Lake Bracciano is designated as a drinking-water reservoir in the Rome Urban Water Supply Plan. The reservoir is intended to help cover the peak demand for water (projected as being about $8 \text{ m}^3 \text{ s}^{-1}$ above the average summer flow in 2015) and to cope with emergencies when one or other of the aqueducts supplying the city has to be closed for maintenance.

As a source of drinking water, the lake must be protected from pollution by raw sewage from urban and tourist developments on its shores. It should be stressed that the rate of renewal of lake water is slow, since the source of recharge consists almost exclusively of sub-lacustrine springs.

Therefore, ACEA devised an Action Plan to prevent pollution of the lake and comply with the highest drinking-water standards. Financed by the Lazio Regional Administration, the plan is almost fully implemented: most of the construction is at or near completion. About 27 km of circumlacustrine pipe has been laid and connected to the terminal treatment plant (main contractor: the S.I.T.A. Company in Rome). ENEA is assisting in the construction of a pilot plant for sewage-sludge disinfection by irradiation with accelerated electrons, to render it useful as fertilizer in agriculture, a practice that has been adopted abroad, mainly in Germany and the United States [1].

2. THE SEWAGE-TREATMENT PLANT AT BRACCIANO

The sewerage system, aimed at protecting the waters of Lake Bracciano from pollution, consists of a main that encircles the shore, collecting sewage from residential and tourist developments in the region. The sewage is pumped to the Consorzio Bracciano Idrico Sabatino (CoBIS) treatment plant by 21 booster stations and purified effluent is piped into the Arrone River, which flows out of the lake at a point outside the basin.

The CoBIS plant started operations in July 1983 and currently has the capacity to serve 45,000 (25,000 residents and 20,000 visitors). It is envisaged that it will eventually serve a population of 90,000. The treatment process consists essentially of: sand removal; oil and grease removal; aeration; primary settling in tanks; oxidation and aeration; secondary settling; sludge recycling; sludge thickening; dewatering.

One multi-processor system controls the main sewer around the lake and transmits pre-processed information to the data-acquisition and storage system. A similar system provides process control of plant operations, and also transmits data to the acquisition system. The third system is concerned essentially with the acquisition of operating data (consumption, maintenance, storage, etc.), using pre-processed data transmitted from the first two systems.

Instruments for measuring chemical oxygen demand (COD), conductivity, redox potential, dissolved oxygen, and residual chlorine and ammonia, were installed to acquire a historical record of plant-operating data and to provide warning if any of the parameters moves outside pre-set limits.

3. THE SEWAGE-SLUDGE PROBLEM

After treatment of sewage, residual sludge must be disposed of by storage and/or incineration; both present problems, the most important of which are related to spatial and environmental impact.

When the CoBIS plant was under consideration, the following values were predicted for the incinerator:

- throughput capacity: 400 L h⁻¹
- ashes: 35 kg h⁻¹
- fuel consumption: 19 L h⁻¹.

The possibility of using sewage sludge as agricultural fertilizer was considered to be an attractive alternative, provided that bacteria and viruses could be destroyed by treatment with γ rays or accelerated electrons, using irradiation technologies similar to those employed for the sterilization of medical products (syringes, gauzes, cotton, etc.).

Gamma rays used in industrial radiation processing are generated by radioisotopic sources (Cobalt-60 or Caesium-137). Electrons are produced in acceleration machines and can be employed directly, or be converted into X-rays by means of a metallic target.

Microorganisms are damaged when exposed to electrons or γ -rays. The extent of damage is proportional to the radiation dose (measured in Gray) absorbed by the organism. With sufficiently high doses, commercial sterilization becomes possible. Irradiation plants for sewage-sludge disinfection have operated abroad with excellent results. A Miami (USA) plant uses an electron-accelerator source, and one near Munich used a 60-Co source for sewage-sludges treatment in the liquid phase.

A pilot system, which provided much of the basic data for the planning of other γ -irradiation plants, was operated at Sandia National Laboratories in Albuquerque, New Mexico, where sewage sludge was irradiated at various levels of dehydration including the dry state.

4. THE ENEA IRRADIATION FACILITY

The choice of irradiation method depends above all on economic considerations and on the particular context in which a plant is to operate. The ENEA facility at the CoBIS plant will use a linear electron accelerator (E=6 MeV; P=4 kW maximum) [1].

The plant will process the sewage sludge by digestion, drying, and sterilization by irradiation, and have the following components:

- a primary sludge thickener
- an anaerobic digestion system with bio-gas production
- a second sludge thickener
- a dewatering station
- a bunker of reinforced concrete (biological shielding) with a thickness of 200-220 cm; the inner space of the bunker constitutes the irradiation cell
- safety systems connected to the control console, photo-electric cells, personnel indicator footboard, "scram" systems for the source, visual and acoustical systems that mark the beginning and the end of irradiation processing
- a ventilation system in the irradiation cell
- water and powder fire-extinguishing systems
- a control room with an operating console, where visual and aural alarms signal any malfunctioning in the various sectors
- a sewage-sludge transportation system, with transporter rollers for automatic insertion and outlet of materials
- a drying station
- central services, warehouses
- a loading and unloading area, with systems for automatic transfer of sludge
- a packaging and shipping section.

5. MATERIALS AND METHODS

Within the research programme defined by the ENEA-ACEA agreement, preliminary studies were carried out on the degradation, by electron-beam irradiation, of halogenated organic compounds and pesticides that are often present in sewage sludges [2, 3].

The compounds were placed in glass containers and irradiated both dry and in solution (of distilled water). For the irradiation, a 5 MeV LINAC accelerator (Fig. 1) was employed, with a 10-Hz repetition frequency; the doses were in the range of 0.5 - 8 Mrad (5 - 80 kGy) [4]. The irradiation dosimetry was determined with perspex slides and the calorimetric method, and analyses were performed by gas chromatography. The initial concentrations of the treated compounds are shown in Table I.

Municipal sewage sludges from the CoBIS water-treatment plant were γ -irradiated (Co-60) at ENEA's Calliope plant at Casaccia, to determine effects on physico-chemical characteristics and microbial populations.

6. RESULTS

The results for radiation-induced degradation of atrazine, 2-ethylexylphthalate (D2EHP), hexachlorobenzene (HCB) and parathion are shown in Table I and in Fig. 2. Maximum degradation was achieved when the compounds were dissolved in water. Atrazine and parathion were easily degraded, even at low doses of accelerated electrons (5 kGy).

Analytical determinations of heavy metals (Pb, Hg, Cd, Zn, Cr), halogenated organic compounds, detergents, infestant seeds and other chemical parameters (Table II) demonstrate that irradiated sewage sludge from the CoBIS plant can be used for agricultural land application, as defined by current national standards.

Table II also shows the marked reductions in microbial counts with γ -irradiation, for the principal pathogens often present in sewage sludge. Destruction of the microbial populations was almost complete, with more than 99% reduction in total counts. Salmonella contamination, detected only in two samples, was eliminated by radiation.

Fig. 3 charts the flow of the activities started in 1985; "experimental operations" refers to the optimization of plant parameters, both conventional and in the irradiation unit. The plant is self-sufficient in energy through bio-gas production.

Field experiments near the plant will follow the product to its final application, in collaboration with the local farmers and colleagues in agronomical research.

7. CONCLUSION

The Lake Bracciano project has fostered the acquisition of knowledge necessary for the development of radiation technology that is needed at the national level for the processing and safe utilization of sewage sludge.

TABLE I. EFFECTIVENESS OF ELECTRON-BEAM RADIATION FOR DEGRADATION OF ENVIRONMENTAL POLLUTANTS

Substance	Quantity or concentration treated	Doses of radiation (MRad)	Degradation (%)
Atrazine	21.2 μ g (dry)	0.5 - 8	4 - 89 ^a
	1.9 ppm (water)	0.5 - 8	99.9 ^b
D2EHP	18.8 μ g (dry)	0.5 - 14	5 - 54 ^c
	1.0 ppm (water)	0.5 - 15	54 - 70
HCB	23.8 μ g (dry)	0.5 - 8	0 - 7 ^c
	3.6 ppb (water)	0.5 - 8	66 - 77 ^c
Parathion	23.8 μ g (dry)	0.5 - 8	18 - 89 ^a
	1.4 ppm (water)	0.5 - 8	99 ^b

^aLinear dose/effect relationship.

^bAt the minimum dose of 0.5 Mrad.

^cNo linear dose/effect relationship.

TABLE II. PHYSICO-CHEMICAL AND MICROBIOLOGICAL EFFECTS OF γ -IRRADIATION OF SEWAGE SLUDGE PRODUCED AT THE CoBIS PLANT

Physico-chemical component	06-19-90		07-03-90	
	Unirradiated	Irradiated	Unirradiated	Irradiated
pH	6.2	6.6	6.3	7.5
Density	0.96	1.06	0.99	1.06
Total Solids at 105°C	25.4	20.9	19.7	23.3
Volatile Solids at 550°C	69.3	70.6	69.8	70.8
Organic Carbon	45.2	41.6	44.3	39.5
Total Nitrogen	2.5	2.4	5.4	3.4
Total Phosphorus	1.09	1.58	2.79	1.53
Potassium	0.45	0.40	0.44	0.60
Carbon/Nitrogen Ratio	18.1	17.3	8.2	11.6
Cadmium	< 1	< 1	1.3	1.5
Copper	285.1	189.9	177.2	293.5
Nickel	< 1	< 1	16.8	19.7
Lead	73.2	32.1	101.0	135.9
Zinc	1238	1309	1364	1236
Chromium	18.2	23.0	27.2	24.7
Mercury	< 1	< 1	8.6	2.8
Total Phenols	61.6	19.7	< 1	< 1
Anionic Detergents	3750	6728	4863	4248
Total Fats	4900	4869	4920	3186
Chloroform	< 1	< 1	327	633
Dimethylketone	-	-	14.3	18.8
Trichloroethylene	< 1	< 1	< 5	< 5
Benzene	< 1	< 1	< 5	< 5
Tetrachloroethylene	80	20	-	-
Polychlorodiphenyl	< 0.5	< 0.5	< 0.5	< 0.5
Hexachlorobenzene	< 0.5	< 0.5	< 0.5	< 0.5
Parathion	< 0.5	< 0.5	< 0.5	< 0.5

TABLE II. (continued)

Microbiological component	06-19-90		07-03-90	
	Unirradiated	Irradiated	Unirradiated	Irradiated
Infestant Seeds	0	0	0	0
Total Coliforms	3.10^9	200	2.10^{10}	0
Fecal Coliforms	4.10^8	100	8.10^9	0
Fecal Streptococci	2.10^8	120	7.10^9	0
Total Bacterial Count at 22°C	8.10^{10}	7.10^4	5.10^{10}	8.10^3
Total Bacterial Count at 36°C	4.10^{10}	5.10^4	3.10^{10}	6.10^3
Parasites (eggs)	0	0	0	0
Salmonella	0	0	5.10^3	0

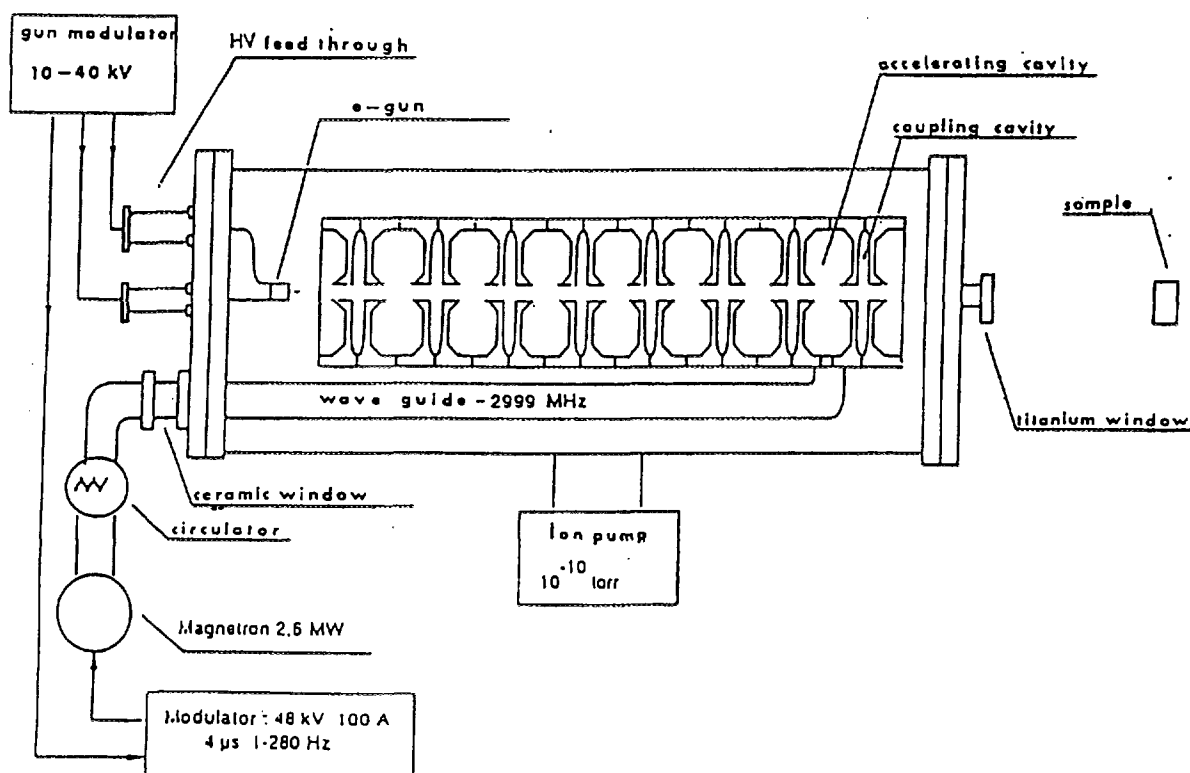


FIG. 1. Drawing of the linear accelerator.

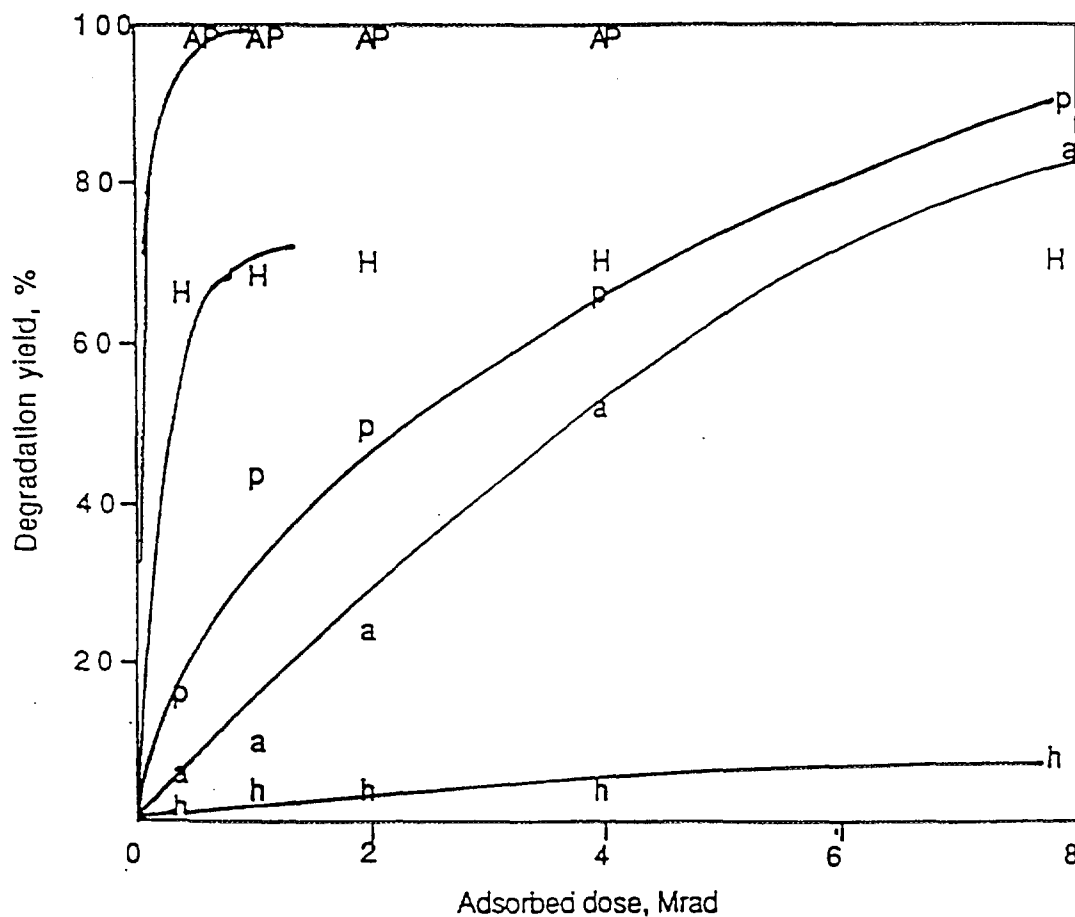


FIG. 2. Degradation of selected pesticides by electron-beam irradiation.

Legend: Atrazine: a - solid, in air (20 μ g), A - in aq. solution (1.9 mg/l)
Hexachlorobenzene: h - solid, in air (24 μ g), H - in aq. solution (5.5 mg/l)
Parathion: p - solid, in air (24 μ g), P - in aq. solution (1.4 mg/l)

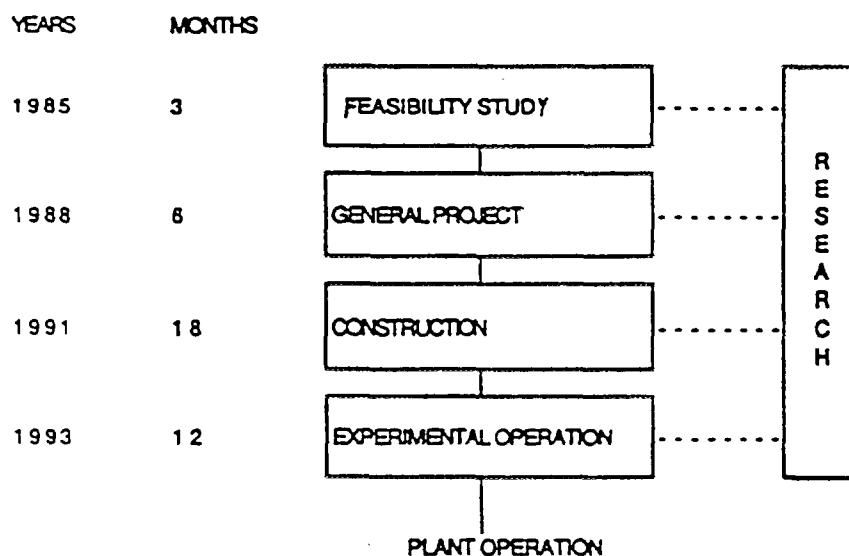


FIG. 3. Flow-chart of project activities.

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APPLICATION OF SEWAGE SLUDGE IN AGRICULTURE

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SOME LONG TERM EFFECTS OF LAND APPLICATION OF SEWAGE SLUDGE ON SOIL FERTILITY¹

(Abstract)

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Metals may affect the growth of plants, soil microbial activity, and soil fertility in the long term. Less is known of the adverse long-term effects of metals on soil microorganisms than on crop yields, since the effects of metals added to soils in sewage sludge are difficult to assess, and few long-term experiments exist. This paper reviews evidence from controlled long-term field experiments with sewage sludges in the UK, Sweden, Germany and the USA.

Adverse effects on microbial activity and populations of cyanobacteria (blue-green algae), *Rhizobium leguminosarum* bv. *trifolii*, mycorrhiza, and total microbial biomass have been detected, in some cases below the European Community's maximum allowable concentration limits for metals in sludge-treated soils. For example, N₂-fixation by free-living heterotrophic bacteria was found to be inhibited at concentrations (mg kg⁻¹) of 127 Zn, 37 Cu, 21 Ni, 3.4 Cd, 52 Cr and 71 Pb. Fixation by free-living cyanobacteria was reduced by 50% at concentrations (mg kg⁻¹) of 114 Zn, 33 Cu, 17 Ni, 2.9 Cd, 80 Cr and 40 Pb. Numbers of *Rhizobium leguminosarum* bv. *trifolii* were decreased by several orders of magnitude at metal concentrations (mg kg⁻¹) of 130-200 Zn, 27-48 Cu, 11-15 Ni, and 0.8-1.0 Cd. Important factors influencing the severity of toxicity are soil texture and pH; higher pH and clay and organic C contents decrease metal toxicity considerably.

The evidence presented in this review of long-term field experiments suggests that adverse effects on microbial parameters occur at modest concentrations of metals in soils. It is concluded that prevention of adverse effects on soil microbial processes, and ultimately on soil fertility, should be a factor that influences soil-protection legislation.

¹Data presented are already published: Long-term effects of sewage sludge on soils, microorganisms and plants. *Journal of Industrial Microbiology* 14 (1995) 94-104.



REVIEW OF STUDIES ON IRRADIATED SEWAGE SLUDGE AND CHICKEN MANURE AND THEIR USE IN AGRICULTURE IN INDONESIA

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Abstract

Studies on radiation treatment of sewage sludge and chicken manure to eliminate pathogenic bacteria and on their use to increase yields of corn have been done at the Centre for the Application of Isotopes and Radiation (CAIR) since 1984. The parameters measured for irradiated sludge were: total bacteria and pathogenic bacteria content, nutrient value, pH, BOD, COD, suspension rate, water content, optimum radiation dose, combined treatment of irradiation and sun-drying, and storage time after irradiation. Results showed that, when combined with sun-drying, the γ -radiation dose needed to eliminate the pathogenic bacteria was decreased from 6 kGy to 2 kGy. The application of 5 ton/ha of irradiated sludge to corn gave the same beneficial effect as 90 kg/ha of triple superphosphate. Irradiated sludge and chicken manure can be considered as valuable resources for improving soil fertility and increasing crop yields.

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1. INTRODUCTION

Radiation technology makes significant contributions to the metallurgical, chemical, food, and pharmaceutical industries. Commercial-scale sterilization of medical products is now well established, and at present more than 140 radiation plants are in operation throughout the world. Pollution and public health controls are relatively new areas in which research and development are in progress for utilization of radiation[1].

Sludge is the residue of solid material that collects during the process of wastewater treatment. Sewage sludge and chicken manure contain valuable inorganic components such as N, P, and K, and the organic fraction can have a soil-conditioning effect. Therefore, effort is being expended to recycle sludge and chicken manure as fertilizer, soil conditioner, and animal-feed supplement.

However, sewage sludge and chicken manure can contain pathogens, toxic compounds, and heavy metals, therefore, for environmental protection, they should be processed to eliminate pathogenic organisms such as *Escherichia coli* and *Salmonella* [2, 4] and to reduce heavy metals and toxic chemicals to safe levels, before distribution for public use.

Disinfection of sewage sludge and chicken manure can be achieved using ionizing radiation or thermal pasteurization. Thermal pasteurization has disadvantages, such as increasing the volume during steam heating. In contrast, radiation treatment offers several advantages: (i) the energy required is less than that for heat pasteurization, (ii) there is no chemical residue in contrast with chemical treatment, (iii) the operation is simple, (iv) sewage sludge and chicken manure can be disinfected continuously and completely, and (v) odour production is reduced.

Since 1984, several studies on irradiated sewage sludge and chicken manure have been conducted at the Centre for the Application of Isotopes and Radiation (CAIR), Jakarta, with promising results. However, because of lack of sufficient knowledge and appropriate environmental regulations, the use of sewage sludge and chicken manure has not met with broad public acceptance [5-9].

There are two approaches for pathogen reduction in sludge:

- processes to significantly reduce pathogens (PSRPs), which include aerobic digestion, air drying, anaerobic digestion, low-temperature composting, lime stabilization, and other techniques giving equivalent pathogen reduction,
- processes to further reduce pathogens (PFRPs), which include pasteurization (70°C for 30 minutes) and γ -radiation.

Some of the sewage sludge from Jakarta city is treated by aerobic digestion as a PSRP in a plant with a capacity of 300 m³ sludge per day, located at Pulo Gebang, Jakarta. It is collected mostly from septic tanks in housing areas, and also from an open-air sludge reservoir at Tangerang, a suburb [10-11].

Studies on isolation and determination of pathogenic microbes from municipal sludge have been reported. Watanabe et al. [12] found total bacterial and coliform counts of up to 3.0×10^9 and 3.5×10^8 g⁻¹, respectively, in dewatered sludge; the coliforms in dewatered sludge were eliminated with a dose of 5 kGy, whereas liquid sludge required only 3 kGy.

Studies on the nutritive value of sewage sludge have been carried out by several investigators [13-15].

This report reviews work at CAIR on the effects γ -radiation on sewage sludge and chicken manure, with particular emphasis on their utilization as fertilizer to improve soil fertility and increase crop yields.

2. CHEMICAL COMPOSITION

Chemical composition, as an indicator of nutritive value, of dewatered sludges (Sludge I from a sewage-treatment plant in Jakarta city, Sludge II from a suburban sewage reservoir) and of chicken manure (from a farm near Ciputat, south Jakarta) are shown in Table I. Sludge I consisted mostly of human waste, whereas Sludge II was a mixture of human and other domestic wastes. The compositions were calculated from samples of 15 to 20% moisture content.

The Kjeldahl N content of Sludge I was similar to that of Sludge II, whereas it was higher in the chicken manure probably due to the presence of husks. These values for N are similar to those in the dewatered sludge used by Stark et al. [16] and Smith et al. [17] as supplements for animal feed. Radiation doses of up to 8 kGy did not cause significant change in chemical composition or in pH values, which were 7.0, 6.10, and 7.5, in Sludges I and II and the manure, respectively.

3. BOD, COD, AND PHYSICAL CHARACTERISTICS

The effects of γ -radiation (2, 4, or 6 kGy) and storage (2 or 4 weeks in polythene bags as an oxygen barrier and to retain moisture, at a room temperature of $29 \pm 2^\circ\text{C}$), were examined on BOD and COD, solid suspension rate, particle size, and sedimentation rate of liquid sludge (70-75% water).

The results are presented in Tables II-VI. No radiation effects were observed, except that sedimentation rate was decreased.

4. MICROBIOLOGY

Bacterial counts are shown in Tables VII (not irradiated) and VIII (irradiated, 2 kGy); radiation decreased the numbers by at least 90%, and in most cases by >99%. It is noteworthy that *Salmonella* was detectable in all three substrates, and was eliminated by radiation. In the samples investigated, there was no evidence of presence of *Shigella* or vibrios. About 50% of the isolates from dewatered sludge were gram-negative bacteria. The chicken-manure samples were contaminated with lice.

A comparative study was conducted, on the counts of total bacteria, coliforms and *E. coli* in sludge in liquid (70-75% water) and dewatered (20-25% water) forms, with results shown in Table IX. Total bacterial counts were higher in the liquid than in the dewatered sludge, but coliforms and *E. coli* were lower in number in the liquid form.

UV radiation has detrimental effects on bacteria. Wavelengths between 200 and 310 nm have the most lethal effects on microorganisms, with maximum microbiocidal action at around 260 nm. Therefore, sun-drying of sludge can decrease bacterial counts more effectively than does air-drying. The combination of sun-drying and radiation (2 kGy) eliminated the *Enterobacteriaceae*, faecal coliforms including *E. coli*, and faecal streptococci (Table X).

At the end of 12 weeks of storage, total bacterial counts were similar to those at time zero irrespective of γ -radiation dosage (0-3 kGy; Fig. 1). However, the combination of radiation (2 kGy) and sun-drying led to the elimination of faecal coliforms at 4 weeks of storage (Fig. 2). In a third experiment, the combination of sun-drying and radiation of 2 kGy killed the pathogenic bacteria, whereas after air-drying a dose of up to 6 kGy was required (Fig. 3).

5. EFFECTS ON CORN

Two pot experiments were conducted to compare the effects of irradiated sludge and chicken manure, and TSP fertilizer, on the growth of corn. The parameters observed were total-P uptake, P availability from the different sources of fertilizer, and dry-matter yield.

The experiments consisted of the following treatments:

Experiment I

1. Control
2. + ^{32}P
3. TSP (90 kg $\text{P}_2\text{O}_5/\text{ha}$)
4. TSP (90 kg $\text{P}_2\text{O}_5/\text{ha}$) + ^{32}P
5. Sludge, 5 ton/ha

Experiment II

1. Control
2. + ^{32}P -TSP (45 kg P_2O_5)
3. Sludge, 5 ton/ha
4. Sludge, 5 ton/ha + ^{32}P -TSP (45 kg P_2O_5)
5. Manure, 5 ton/ha

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|----|------------------------------------|--|
| 6. | Sludge, 5 ton/ha + ^{32}P | 6. Manure, 5 ton/ha + ^{32}P -TSP (45 kg P_2O_5) |
| 7. | Manure, 5 ton/ha | |
| 8. | Manure, 5 ton/ha + ^{32}P | |

^{32}P = Isotope ^{32}P carrier free in KH_2PO_4

^{32}P -TSP = ^{32}P labelled TSP, 45 kg P_2O_5

Sludge = Irradiated Sludge I

Pots containing 8 kg of air-dried latosol from Pasar Jumat, Jakarta, were used and irradiated sludge and chicken manure were applied at 20 g/pot, equivalent to 5 t/ha, with TSP at 0.8 g/pot and ^{32}P labelled TSP at 0.4 g/pot. Isotope ^{32}P carrier free was used at 0.4 mCi/pot at planting time. N and K fertilizer were applied at 0.8 g/pot and 0.6 g/pot, as urea and KCl respectively. Soil moisture was maintained around field capacity ($\text{pF}=2.54$). Soil pH at planting time was around 6.5. The crop was harvested at 80 days after planting.

The results of Experiment I are shown in Fig. 4. The irradiated sludge and TSP similarly increased dry matter production over the control, and chicken manure was even more effective. Similar trends were observed for total P uptake and source P uptake.

The results of Experiment II are in Fig. 5. In this case, the irradiated sludge gave a similar dry-matter yield as did the irradiated chicken manure. However, the manure gave a higher total-P uptake than did the sludge. In the combined treatments (4 and 6 above), the presence of the TSP did not appreciably improve dry-matter yields or total-P uptake.

5. ON-GOING WORK

Studies on the use of irradiated sludge and chicken manure fertilizer for increasing and sustaining the yields of several vegetables crop such as sweet corn, tomato, asparagus are continuing. They will also involve environmental considerations. The use of irradiated chicken manure as a feed supplement for crayfish (*Ospharonemus gouramy*) will receive renewed emphasis.

6. CONCLUSIONS

- The combined treatments of radiation at 2 kGy and sun-drying of sludge acted synergistically to eliminate pathogenic bacteria; with air-dried sludge, up to 6 kGy were required.
- Coliforms that survived the combined sun-drying/radiation treatments died within 4 weeks of storage.
- Application of 5 ton/ha of irradiated sludge has a similar effect as 90 kg/ha of TSP based on dry-matter production and P uptake by corn.
- Future prospects are promising for the safe reutilization of irradiated sewage sludge and chicken manure as fertilizer for improving soil fertility and sustaining crop yields and in an environmentally-sound manner

TABLE I. COMPOSITION OF DEWATERED SLUDGE I, SLUDGE II, AND CHICKEN MANURE

Component	Sludge I	Sludge II	Manure
	(%)		
Dry matter	85.0 \pm 5.0 ^a	80.0 \pm 8.4	81.1 \pm 4.2
Kjeldahl N	1.66 \pm 0.07	1.86 \pm 0.10	2.25 \pm 0.04
Crude protein (N x 6.25)	10.4	11.2	14.1
P	2.36 \pm 0.2	1.91 \pm 0.2	3.35 \pm 0.52
Fe	3.20 \pm 0.2	4.60 \pm 0.2	1.94 \pm 1.10
(mg/kg)			
K	150 \pm 10	190 \pm 8	1,150 \pm 290
Ca	84 \pm 20	210 \pm 20	6,170 \pm 750
Mg	72 \pm 15	14 \pm 40	1,390 \pm 30
Na	630 \pm 20	410 \pm 100	670 \pm 100
Mn	48 \pm 80	9 \pm 30	120 \pm 50
Cu	10 \pm 1	13 \pm 3	3 \pm 0.2
Zn	63 \pm 2	90 \pm 30	25 \pm 1

^aMean \pm standard deviation (n = 5).

TABLE II. EFFECTS OF RADIATION AND STORAGE TIME ON BOD (ppm) OF LIQUID SEWAGE SLUDGE I

Storage time (weeks)	γ -radiation dose (kGy)			
	0	2	4	6
	(ppm)			
0	1.49 \pm 1.01 ^a	1.54 \pm 1.20	1.82 \pm 1.27	2.05 \pm 0.61
2	1.69 \pm 1.22	2.73 \pm 1.52	2.35 \pm 1.37	1.56 \pm 1.02
4	1.39 \pm 0.45	1.72 \pm 0.44	1.82 \pm 0.52	1.76 \pm 0.63

^aMean \pm standard deviation (n = 5).

TABLE III. EFFECTS OF RADIATION AND STORAGE TIME ON COD (% W) OF SEWAGE SLUDGE I

Storage time (weeks)	γ -radiation dose (kGy)			
	0	2	4	6
	(%W)			
0	13.9 \pm 5.31 ^a	28.4 \pm 10.3	31.3 \pm 11.9	32.3 \pm 14.5
2	16.8 \pm 7.00	28.7 \pm 7.60	30.7 \pm 8.96	36.0 \pm 9.45
4	11.4 \pm 3.40	25.6 \pm 7.84	31.7 \pm 11.1	38.9 \pm 19.6

^aMean \pm standard deviation (n = 5).

TABLE IV. EFFECTS OF RADIATION AND STORAGE TIME ON SUSPENSION SOLIDS (mg/mL) OF LIQUID SEWAGE SLUDGE

Storage time (weeks)	Interval time ^a (h)	γ -radiation dose (kGy)			
		0	2	4	6
		(mg/mL)			
0	6	46 \pm 15 ^b	50 \pm 10	55 \pm 9.8	54 \pm 9.6
	24	41 \pm 13	43 \pm 10	46 \pm 9.6	49 \pm 9.9
	48	31 \pm 10	38 \pm 9.8	39 \pm 10	41 \pm 9.8
	72	28 \pm 11	34 \pm 9.6	33 \pm 10	36 \pm 9.7
2	6	46 \pm 10	58 \pm 10	53 \pm 10	61 \pm 10
	24	37 \pm 10	47 \pm 10	44 \pm 9.7	50 \pm 10
	48	28 \pm 10	38 \pm 10	34 \pm 9.9	41 \pm 10
	72	25 \pm 10	33 \pm 9.9	32 \pm 10	36 \pm 10
4	6	44 \pm 10	51 \pm 9.7	52 \pm 10	59 \pm 9.7
	24	38 \pm 3.0	44 \pm 10	45 \pm 10	48 \pm 9.6
	48	33 \pm 10	38 \pm 10	38 \pm 10	40 \pm 10
	72	30 \pm 11	34 \pm 10	35 \pm 10	38 \pm 3.0

^aAfter shaking.

^bMean \pm standard deviation (n = 5).

TABLE V. EFFECTS OF RADIATION AND STORAGE TIME ON PARTICLE SIZE (mm x 10⁻⁴) OF LIQUID SEWAGE SLUDGE I

Storage time (weeks)	Interval time ^a (h)	γ -radiation dose (kGy)			
		0	2	4	6
		(mm x 10 ⁻⁴)			
0	1	14 \pm 2 ^b	24 \pm 34	12 \pm 3	11 \pm 1
	5	6 \pm 1	6 \pm 1	6 \pm 2	5 \pm 1
	24	3 \pm 1	3 \pm 1	3 \pm 1	2 \pm 1
	28	2 \pm 1	1 \pm 0.5	1 \pm 0.5	2 \pm 1
2	1	12 \pm 2	10 \pm 1	10 \pm 1	11 \pm 1
	5	5 \pm 2	5 \pm 1	5 \pm 1	5 \pm 1
	24	3 \pm 1	2 \pm 0	2 \pm 0	2 \pm 1
	28	2 \pm 1	1 \pm 0	1 \pm 0	1 \pm 1
4	1	11 \pm 1	12 \pm 2	11 \pm 1	2 \pm 2
	5	5 \pm 1	6 \pm 1	5 \pm 4	5 \pm 1
	24	2 \pm 1	2 \pm 4	2 \pm 4	3 \pm 1
	28	1 \pm 1	1 \pm 0	1 \pm 0	1 \pm 1

^aAfter shaking.

^bMean \pm standard deviation (n = 5).

TABLE VI. EFFECTS OF RADIATION AND STORAGE TIME ON SEDIMENTATION RATE (cm/week) OF LIQUID SEWAGE SLUDGE I

Storage time (weeks)	γ -radiation dose (kGy)			
	0	2	4	6
(cm/week)				
0	11.3 \pm 2.35 ^a	4.35 \pm 1.62	3.38 \pm 1.40	2.28 \pm 0.94
2	12.2 \pm 4.34	4.44 \pm 1.74	3.32 \pm 1.32	2.68 \pm 0.95
4	12.2 \pm 4.02	5.82 \pm 1.80	4.54 \pm 0.95	3.32 \pm 1.00

^aMean \pm standard deviation (n = 5).

TABLE VII. MICROBIAL COUNTS IN NON-IRRADIATED SLUDGE AND CHICKEN MANURE.

	Sludge I	Sludge II	Manure
	(cells/g)		
Total bacteria	$(1.1 \pm 1.0) \cdot 10^8$ ^a	$(1.8 \pm 0.5) \cdot 10^8$	$(1.7 \pm 0.9) \cdot 10^7$
Coliforms	$(6.0 \pm 2.0) \cdot 10^4$	$(5.2 \pm 0.6) \cdot 10^5$	$(3.5 \pm 1.0) \cdot 10^6$
<i>E. coli</i>	$(6.1 \pm 1.0) \cdot 10^4$	$(6.3 \pm 0.9) \cdot 10^4$	$(10.5 \pm 0.6) \cdot 10^5$
<i>Staphylococcus</i>	$(4.7 \pm 2.3) \cdot 10^4$	ND ^b	$(8.0 \pm 0.4) \cdot 10^5$
<i>Streptococcus</i>	$(6.3 \pm 4.4) \cdot 10^2$	ND	$(1.8 \pm 0.05) \cdot 10^3$
<i>Pseudomonas</i>	$(2.0 \pm 1.5) \cdot 10^4$	ND	$(0.8 \pm 0.01) \cdot 10^2$
<i>Salmonella</i>	+ ^c	+	+

^aMean \pm standard deviation (n = 5).

^bNot determined.

^cPresent in small numbers.

TABLE VIII. MICROBIAL COUNTS IN IRRADIATED (2 kGy) SLUDGE AND CHICKEN MANURE.

	Sludge I	Sludge II	Manure
	(cells/g)		
Total bacteria	$(1.1 \pm 3.0) \cdot 10^6$ ^a	$(7.6 \pm 1.3) \cdot 10^4$	$(1.5 \pm 0.8) \cdot 10^5$
Coliforms	$(1.5 \pm 0.3) \cdot 10^2$	$(2.7 \pm 0.2) \cdot 10^3$	$(2.7 \pm 1.0) \cdot 10^4$
<i>Staphylococcus</i>	$(2.5 \pm 2.1) \cdot 10^3$	ND ^b	$(1.8 \pm 0.1) \cdot 10^3$
<i>Streptococcus</i>	- ^c	ND	$(3.8 \pm 0.05) \cdot 10^2$
<i>Pseudomonas</i>	-	ND	-
<i>Salmonella</i>	-	-	-

^aMean \pm standard deviation (n = 5).

^bNot determined.

^cAbsent.

TABLE IX. COMPARISONS OF LIQUID AND DEWATERED SLUDGE I FOR WATER CONTENT, pH, N CONTENT, AND MICROBIAL COUNTS

	Water content (%)	pH	N content in dry matter (%)	Total bacteria	Coliforms (cells/g)	<i>E. coli</i>
September						
Liquid	74	5.95	0.52	$(8.3 \pm 0.5) \cdot 10^7$ ^a	$(4.6 \pm 0.5) \cdot 10^4$	$(1.8 \pm 0.1) \cdot 10^3$
Dewatered	22	5.23	1.87	$(3.6 \pm 0.3) \cdot 10^6$	$(1.6 \pm 0.2) \cdot 10^5$	$(5.0 \pm 0.9) \cdot 10^4$
October I						
Liquid	75	7.05	1.57	$(8.2 \pm 0.8) \cdot 10^7$	$(3.6 \pm 0.4) \cdot 10^3$	$(1.8 \pm 0.2) \cdot 10^2$
Dewatered	37	6.15	4.43	$(7.0 \pm 1.0) \cdot 10^6$	$(1.7 \pm 0.3) \cdot 10^4$	$(8.9 \pm 0.9) \cdot 10^2$
October II						
Liquid	73	6.03	0.53	$(1.7 \pm 0.1) \cdot 10^9$	$(3.4 \pm 0.3) \cdot 10^4$	$(1.9 \pm 0.2) \cdot 10^3$
Dewatered	22	6.10	1.67	$(7.0 \pm 2.0) \cdot 10^6$	$(5.2 \pm 0.6) \cdot 10^5$	$(6.3 \pm 0.9) \cdot 10^4$

^aMean \pm standard deviation (n=5).

TABLE X. EFFECTS OF DRYING TREATMENT COMBINED WITH RADIATION (2 kGy) ON MICROBIAL COUNTS IN SLUDGE I

	Sun-dried		Air-dried	
	Non-irradiated	Irradiated	Non-irradiated	Irradiated
	(cells/g)			
Total bacteria	$(6.3 \pm 0.9) \cdot 10^8$ ^a	$(1.0 \pm 0.1) \cdot 10^7$	$(9.8 \pm 1.0) \cdot 10^9$	ND ^b
<i>Enterobacteriaceae</i>	$(1.6 \pm 0.7) \cdot 10^4$	- ^c	$(1.0 \pm 0.1) \cdot 10^5$	$(6.9 \pm 1.5) \cdot 10^3$
Coliforms	$(1.0 \pm 0.1) \cdot 10^3$	-	$(1.3 \pm 0.8) \cdot 10^4$	$(4.5 \pm 0.3) \cdot 10^2$
<i>E. coli</i>	$(3.2 \pm 1.0) \cdot 10^2$	-	$(8.9 \pm 1.0) \cdot 10^2$	$(2.5 \pm 0.7) \cdot 10$
faecal <i>Streptococcus</i>	$(1.9 \pm 0.8) \cdot 10^5$	-	$(4.0 \pm 1.0) \cdot 10^5$	$(0.3 \pm 0.7) \cdot 10$

^aMean \pm standard deviation (n = 5).

^bNot determined.

^cAbsent.

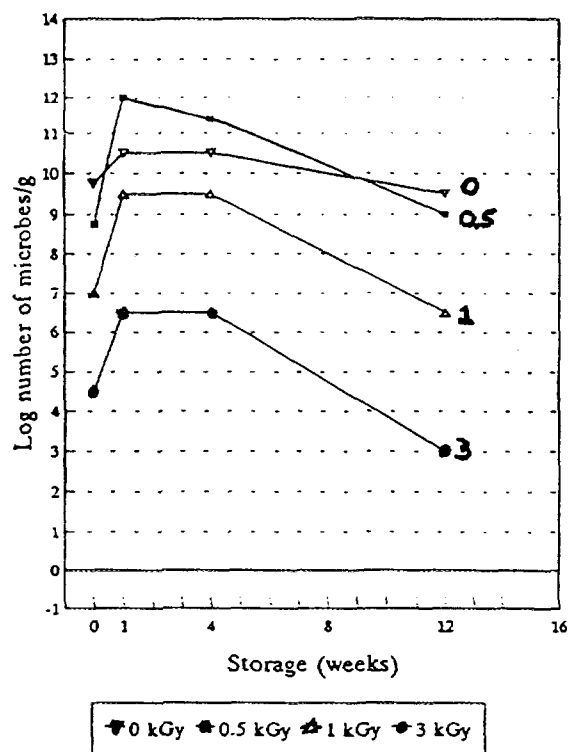


FIG. 1. Effects of storage time on total bacterial counts of unirradiated and irradiated sun-dried sludge.

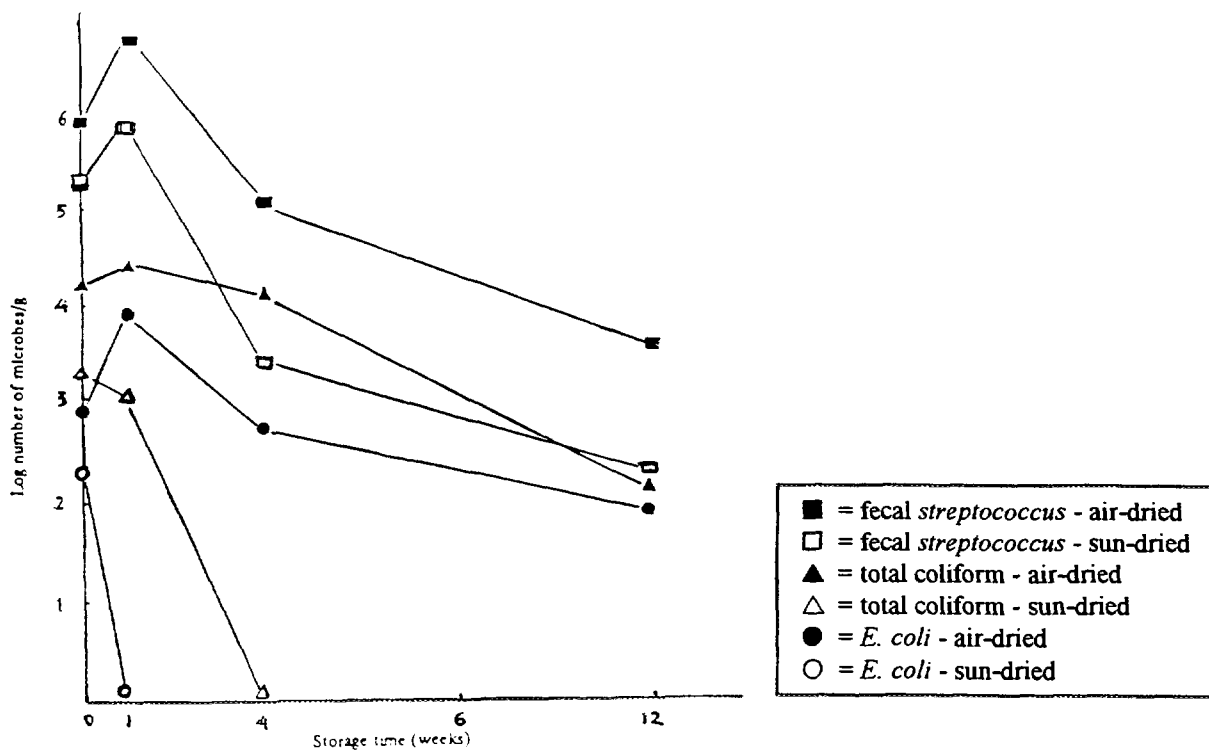


FIG. 2. Effects of storage time on pathogenic bacteria content of unirradiated sun- and air-dried sludge.

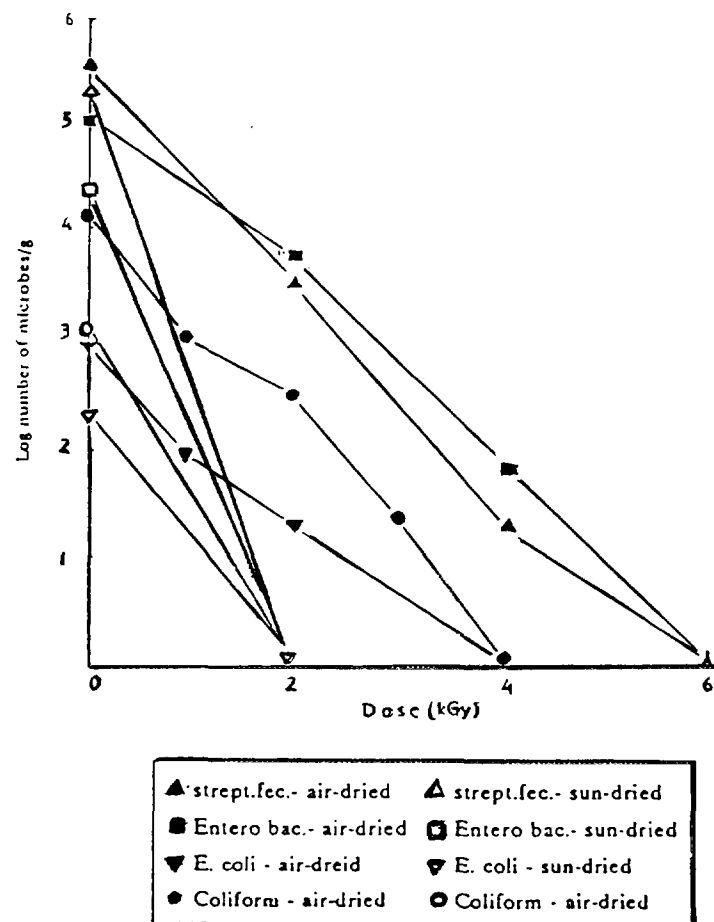


FIG. 3. Effects of irradiation dose on decreasing the pathogenic bacteria content of sun- and air-dried sludge.

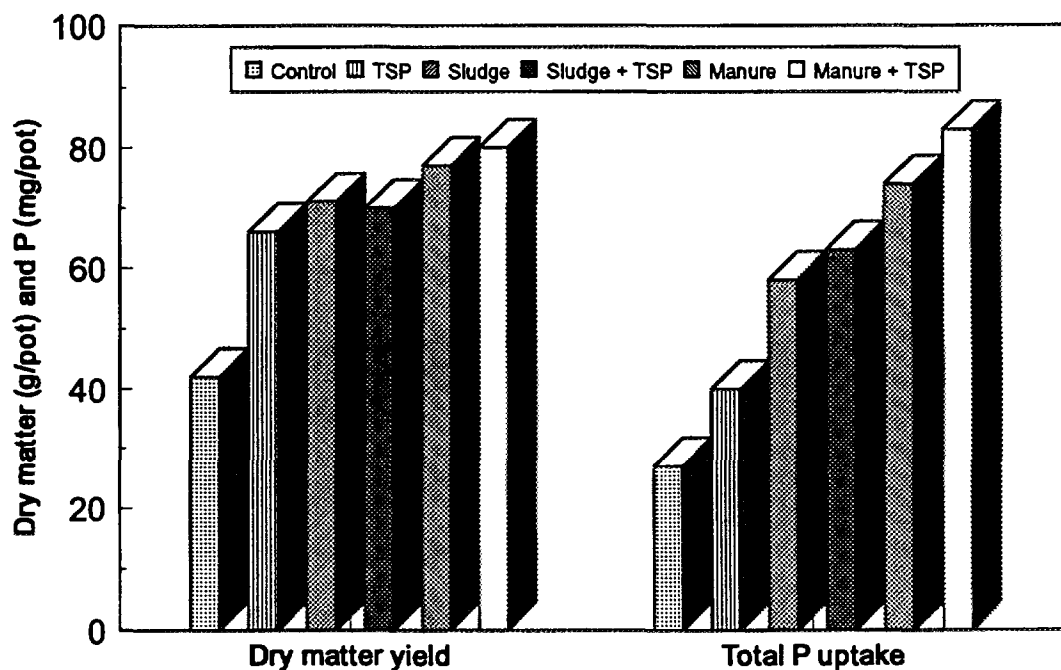


FIG. 4. Effects of treatment with phosphate fertilizer, irradiated sludge, and chicken manure on dry matter production, total P uptake, and source (phosphate fertilizer, irradiated sludge, and chicken manure) P uptake by corn.

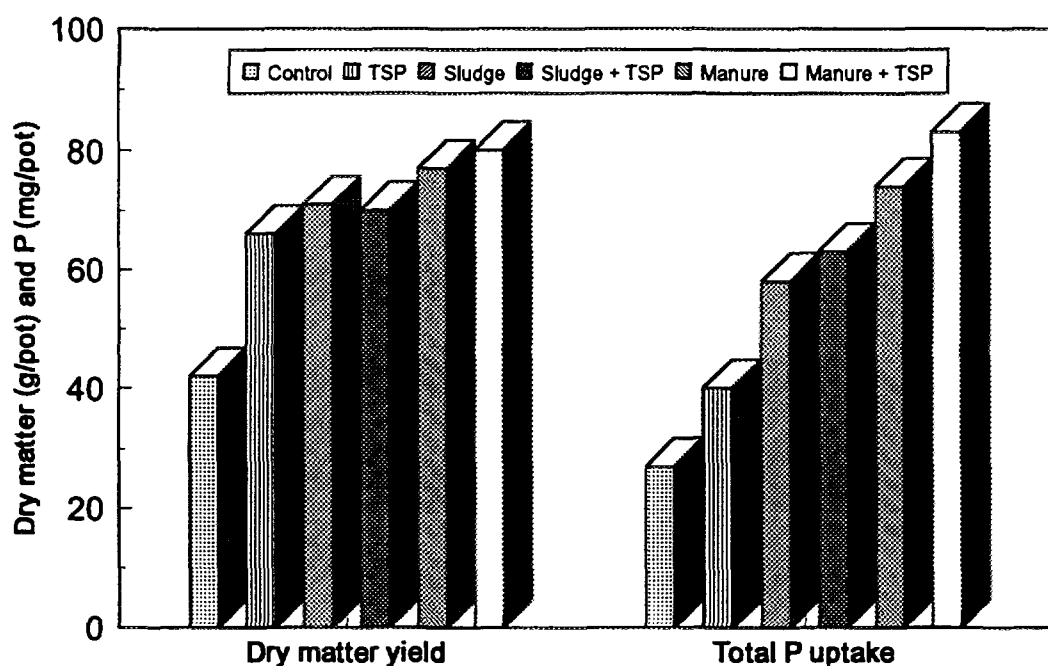


FIG. 5. Comparison of dry matter production and P uptake by corn in the presence of different sources of nutrients.

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**USE OF NUCLEAR TECHNIQUES IN
STUDIES OF UPTAKE AND METABOLIC
FATE OF XENOBIOTICS IN PLANTS¹**
(Abstract)



XA9745792

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The use of municipal sewage sludge as a fertilizer in agriculture is a convenient method of disposal. However, sludge is often contaminated with toxic organic compounds such as dioxins, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), with implications for soil fertility and quality of crops for human and animal consumption. These compounds can be assimilated by intact plants or in-vitro cell-culture systems. The amount of uptake depends on the plant species and on the physico-chemical conditions that influence, for example, molecular configuration; uptake rates are higher with low-molecular-weight and polar compounds. The xenobiotic can be converted to polar conjugates and hydroxylated metabolites that may also be toxic. In some cases, large amounts of the compound and/or its metabolic products are incorporated into non-extractable residues. The bound residues, especially those associated with carbohydrate fractions of the cell wall, are partly degradable enzymatically, therefore the association and type of binding to cellular polymers enables conclusions to be drawn on their bioavailability. Although the amounts of uptake and degradation of a compound differed between whole-plant and in-vitro cell-culture systems, the patterns of metabolite formation were similar. Therefore, cell cultures provide a convenient, rapid means of evaluating the metabolic fate of xenobiotic compounds.

¹Abstract only. The data that were presented are published in Bioaccumulation and metabolic fate of sewage sludge derived organic xenobiotics in plants. Science of the Total Environment 185 (1995) 94-104.

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USE OF SEWAGE SLUDGE FOR AGRICULTURE IN JAPAN

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Abstract

In Japan, the use of sewage sludge and composted sewage sludge is gradually increasing. They are applied not only to agricultural land, but also to golf courses, parks, etc. The presence of heavy metals and pathogens poses a major problem for such utilization of sludge. Composting is a traditional method of sewage treatment. Laws have been introduced and guidelines prepared for proper and safe use of these materials by farmers. Public acceptance plays a crucial role. At a time when environmental preservation is a major issue in almost every aspect of life, greater emphasis will have to be placed on making sludge and compost hygienically acceptable with minimum contamination from pathogenic organisms and heavy metals. The advantages of using sludges as fertilizer for improving and sustaining soil fertility and crop production are many. This paper reviews studies conducted on the use of sewage sludge in agriculture in Japan.

1. INTRODUCTION

With recent increases in the the number of sewer systems, sewage-sludge production has also increased rapidly in Japan (Fig. 1). Prior to the 1920s, night-soil generated in houses was utilized largely as agricultural manure, a natural recycling. The establishment of the Japanese chemical industry resulted in a shift among farmers from night-soil to chemical fertilizers.

Agricultural utilization of human wastes was briefly revived before and after the second world war, but it completely died out with Japan's economic growth in the 1960s. Many sewage treatment plants were built throughout the country, and the disposal of sludge has become a major problem from the point of view of environmental protection and energy consumption. Recycling of sewage sludge for crop production by application to the land is potentially an efficient and useful method of disposal.

2. PRODUCTION OF SEWAGE SLUDGE AND COMPOST IN JAPAN

Sludge produced by the public sewer system amounted to 2,360,000 m³ in 1993 and was disposed of as shown in Table 1. Landfill and coastal reclamation accounted for 50% of the total, 24% (574,000 m³) for agriculture, and 26% for other uses. The greater part of the sludge utilized in agriculture was as a fertilizer rich in organic matter, N and P. The sludge-turned-fertilizer is used in the form of dewatered cake, dry cake, or composted, and to a small extent as slurry (liquid digested sludge). By volume, dewatered cake is the predominant form (Table II). Such use of dewatered cake, however, poses the following problems.

- Environmental: emission of unpleasant odours during sludge decomposition.
- Health: presence of pathogens, eggs of parasites and pests, and seeds of weeds.
- Application: difficulties in preserving, transporting and spraying.

TABLE I. DISPOSAL OF SEWAGE SLUDGE, APRIL 1992 - MARCH 1993

Disposal form	Landfill	Coastal reclamation	Effective use	Others	Total
	(x 10 ³ m ³)				
Dewatered cake	795	430	392	176	1,465 (71) ^a
Ash	150	116	87	7	360 (15)
Dry sludge	8	0	89	22	119 (5)
Digested/ thickened sludge	11	0	6	399	416 (28)
Total	964 (41) ^a	218 (9)	574 (24)	604 (26)	2,360 (100)

^a(%)

For these reasons, dewatered sludge should be aerobically fermented and composted to decompose organic substances and reduce water content, and to kill pathogens, parasite eggs and weed seeds, before application to farmland.

In recent years, interest has been growing in the use of organic fertilizer to improve the fertility of soils adversely affected by intensive farming with high chemical inputs. This has resulted in an increased demand for sewage sludge as an organic fertilizer. This increased demand can be met if there is technology to produce high-quality sludge-turned-compost in large quantities.

3. COMPOSTING OF SEWAGE SLUDGE

Sewage sludge is composted directly by local municipalities and by fertilizer manufacturers using dewatered municipal sludge. Dewatering may be achieved by heating, by application of organic materials such as wood chips, sawdust or rice hulls, or by addition of water-absorbing inorganic materials such as vermiculite or zeolite.

When biodegradable organic substances are exposed to an aerobic atmosphere in the presence of moisture, microbes feed and grow on them. The heat that accompanies the fermentation kills pathogens and other pests, while expelling moisture from organic materials, converting them to compost. The process takes one to two weeks, and temperatures above 65°C should prevail for more than 48 h. Furthermore, to ensure stability, the compost must then be stored for about one month with

TABLE II. EFFECTIVE USE OF SEWAGE SLUDGE, APRIL 1992 - MARCH 1993

Form of sludge and use	Dewatered cake	Ash	Dry sludge	Compost	Digested sludge	Total
	(x 10 ³ m ³)					
Land application						
Produced by local municipalities	113	0	16	28	0	157
Commissioned to private companies	279	7	2	43	6	337
Subtotal	392	7	18	71	6	494
Used as construction material	0	80	0	0	0	80
Total	392	87	18	71	6	574

occasional turning or enforced aeration. When woody materials are used as moisture adjusters, a secondary maturation period of more than 3 months seems to be necessary to ensure decomposition of phytotoxic substances. If the compost contains too much moisture, it is hard to handle. On the other hand, if it is too dry it is liable to be carried away by wind and is not suitable for application. For this reason, the moisture content is standardized at 30 to 40% for ease of handling. If the compost contains too much easily decomposable organic compounds, it can cause root rot.

During composting, increases in pH can cause loss of N by ammonia volatilization. This can be minimized by addition of materials of high C:N ratio, and total enclosure of the system minimizes release of strong odours.

Irrespective of whether the raw sludge has been treated with slaked lime or polymer, the fermentation process stabilizes the pH of commercial compost at 7-8. For farming and gardening purposes, it is essential that hazardous heavy metals, Cd, As, Hg, etc., are present only at acceptable levels. In this regard, legally enforced standards must be met.

4. REGULATIONS ON HEAVY-METAL CONCENTRATIONS IN SEWAGE SLUDGE AND SEWAGE-SLUDGE COMPOST USED AS COMMERCIAL FERTILIZER

The greatest concern in sludge utilization is with respect to heavy metals. Many people consider that application to soil should not be permitted without resolving this constraint. Since heavy metals may be present in relatively high concentrations, they can accumulate in soil with continuous application, resulting in harmful effects on crop production and human health by entering the food

chain. The important metal contaminants are Zn, Cu, Ni, As, Hg, and Cd. With emphasis on environmental protection, several studies have been carried out on concentrations and chemical forms in order to elucidate heavy-metal characteristics and behaviour in the soil/plant system. The concentrations in sludges and composted products are high when compared with those in natural organic matter: the average concentration of Zn in sludge is approximately 1,000 mg/kg dry matter, ten times higher than in rice-straw compost, although the heavy-metal levels in Japanese sludges in general are lower than in other countries.

Taking into consideration the fact that various kinds of sludges and processed materials are already marketed in Japan, the Ministry of Agriculture, Forestry and Fisheries set up, in 1971, limits for concentrations of heavy metals in fertilizer derived from waste materials including sludges (Table III). When sewage sludge is applied to agricultural land, it has to meet standards defined by the Fertilizer Law. The upper limits for Cd, Hg, and As, are 5, 2, and 50 mg/kg, respectively. Analytical data indicate that Hg and Cd concentrations in sludge occasionally exceed these limits.

At present, many kinds of recycled organic matter are applied to farmland, in increasing quantities. In order to prevent soil pollution by high concentrations of heavy metals in sludge, the Environmental Agency of Japan in 1984 published guidelines for permissible levels in soil, as follows.

- Heavy-metal accumulation in farmland soils will be controlled with reference to Zn content.
- The upper limit for Zn will be 120 mg/kg dry soil.
- The Zn content in surface soil will be determined by atomic absorption spectrophotometry after acid digestion.

TABLE III. CRITERIA FOR EVALUATION OF SLUDGE-BASED FERTILIZERS (FERTILIZER LAW, 1976)^a

	Leachate test (mg/L)	Content test (mg/kg)
Cadmium	0.3 or less	5
Arsenic	1.5	50
Mercury	0.005	2
Cyanide	1	
Phosphoric pesticide	1	
Lead	3	
Hexavalent chromium	1.5	
Alkyl mercury	not detectable	
PCB	0.003	
Trichloroethylene	0.3	
Tetrachloroethylene	0.1	

^aThe leachate-test criteria must be applied in parallel with the content-test criteria.

Many municipalities apply sludges in accordance with these guidelines. The 120 mg/kg value was reached after readings were made from about 700 agricultural plots where normal cultivation had been practised without addition of any waste or sewage material. That is to say, Zn concentration of 95% Japans' cropland is below 120 mg/kg. Also it is noteworthy that this guideline is based on the principle that current Zn concentrations in soil favour crop growth [1]. Zinc was chosen as the indicator element because its concentration in soil and sewage sludge is usually above those of Hg, Cu, or Cd. It is believed that by regulating the amount of Zn applied, we can prevent not only adverse effects of Zn on crops but also avoid excessive loading with other heavy metals from sewage-sludge applications. In fact, the efficacy of this guideline has been proven in many investigations of sewage- sludge use as fertilizer.

5. HEAVY-METAL CONCENTRATIONS IN SEWAGE SLUDGE

Considering how rapidly heavy metals may accumulate in soil, sludge application to agricultural land may have to be restricted. Therefore, several studies have been carried out on sewer systems to determine if heavy-metal levels can be decreased.

Table IV shows heavy-metal concentrations in sewage sludge originating from industrial and non-industrial cities. As shown by Kumazawa [2], metal contamination in the industrial sludge was higher than in the non-industrial. Therefore, it was recommended that sewage sludges from non-industrial cities be used for agricultural purposes in preference to those from heavily industrial areas.

Much effort has also been made to reduce heavy-metal content in wastewater. Since 1976, metal flow from industry into sewer systems has been restricted, and concentrations in sewage sludge, including Zn and Cu, have markedly decreased. Fig. 2 shows trends in heavy-metal concentration in sludge produced at a sewage treatment plant at which 6% of the incoming wastewater is of industrial origin.

Mercury is sometimes found in sewage sludge at concentrations higher than the recommended guidelines. In the past, it was used in the soda, vinylchloride, acetaldehyde, and pesticide industries, but nowadays there is no chemical industrial use of Hg. Pesticides containing Hg are prohibited, and Hg battery cells are fast disappearing. Mercury in sewage water is thought to originate mainly from hospitals, because of Hg thermometers, mercuric antiseptic solutions and reagents that are still used in treatments, and from amalgam used in dentistry. Table V shows Hg concentrations found in hospital sinks and basins [3]. Since the establishment of countermeasures to avoid contamination of wastewater, by protecting Hg thermometers with thin film, use of electronic thermometers, batch separation of wastes, etc., Hg concentrations in dehydrated sludge have decreased substantially below the legally permitted level (Fig. 3) [3].

Table VI shows little difference in heavy-metal contents between sewage-sludge fertilizer and night-soil (sludge from septic tanks). This demonstrates that heavy-metal contamination in sewage sludge from industry has reached a low steady-state level.

To further decrease heavy-metal levels in sewage sludge, we must understand their origins in domestic wastewater from taps, baths, toilets, laundry, and kitchen. Table VII shows the amounts of heavy metals in domestic wastewater in Yokosuka and Hakodate cities. A similar survey has been done in Hachinohe [4]. The amounts of Cd, Ni, Mn, Cu, Zn, in faeces showed similar values among the cities, indicating few difference between locations in Japan in the kinds and quantities of food consumed. The tap water from Yokosuka had higher levels of Ni, Pb, Cr, Mn, Cu. Concentrations

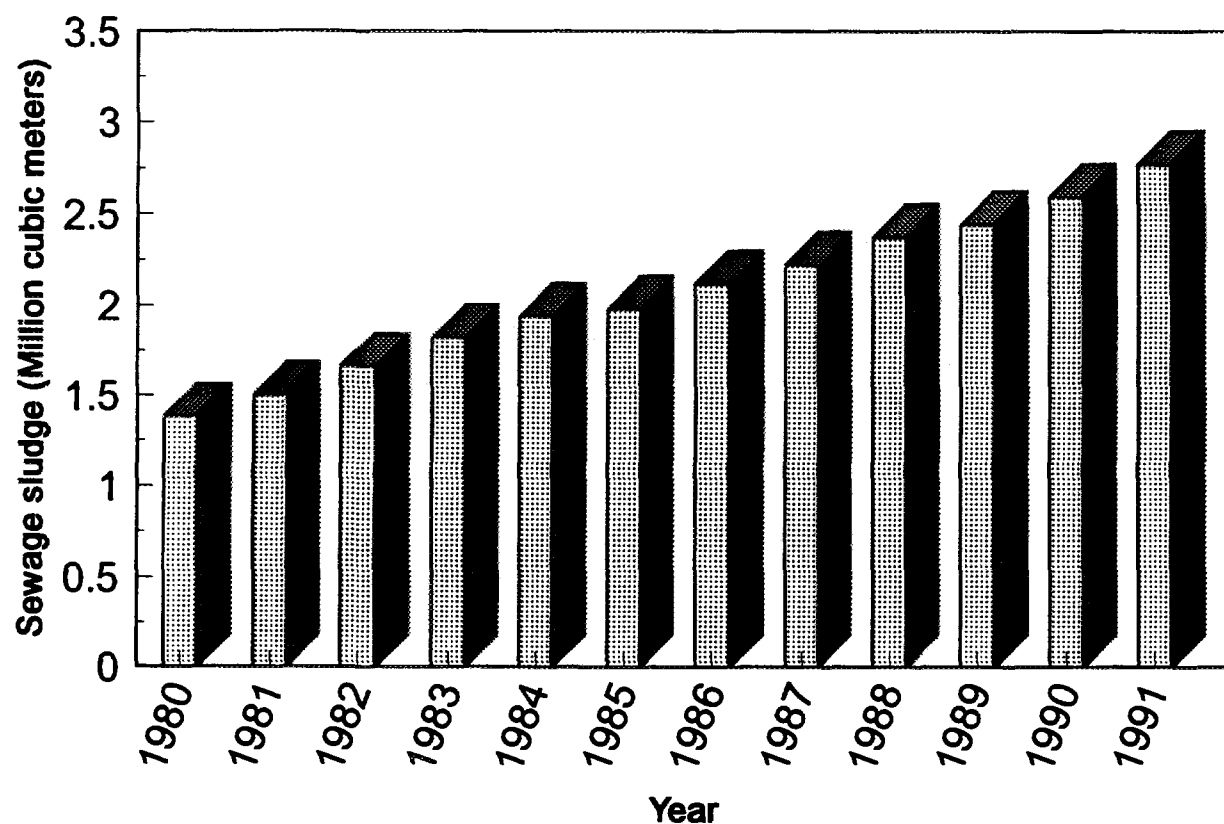
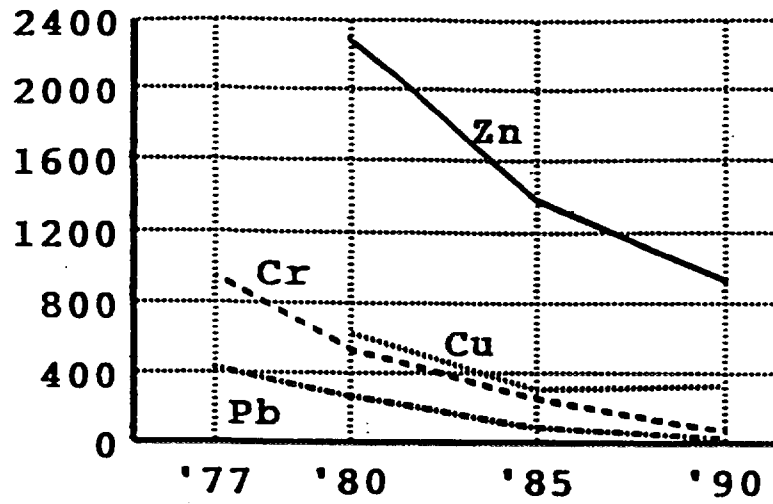


FIG. 1. Annual production of sewage sludge in Japan.

TABLE IV. HEAVY-METAL CONCENTRATIONS IN SEWAGE SLUDGE

	Industrial cities		Non-industrial cities	
	mean	range	mean	range
(ppm)				
Cd	4.4	3.1-7.1	2.1	1.5-2.8
Pb	149	102-216	84	55-88
Ni	124	39-269	18	11-24
Cu	359	139-654	145	86-187
Mn	624	394-940	334	220-501
Zn	1,817	1,030-3,220	1170	930-1,420
Cr	105	31-249	15	10-18
Fe	42,100	29,600-54,600	32,100	17,800-41,300

(mg/kg-dry)



(mg/kg-dry)

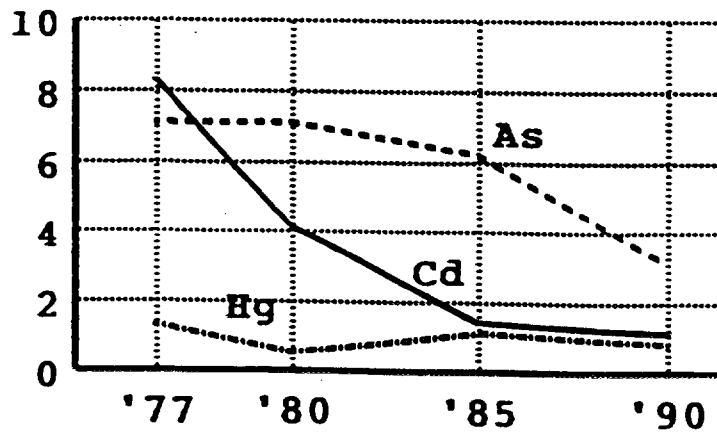


FIG. 2. Heavy-metal trends in sludge.

(mg/kg-dry)

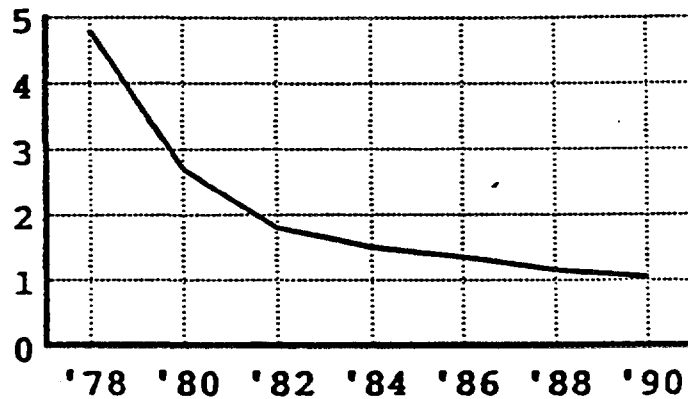


FIG. 3. Trends in mercury concentration in dehydrated sludge [3].

TABLE V. MERCURY LEVELS IN
VARIOUS HOSPITAL AREAS

	Hg conc. (mg/L)
Nurses' cleaning sluices	0.25-67
Floor cleaning sluices	1.2-8.3
Waste disposal units	1.7-4.1
ICU ^a disposal units	0.052
OT ^b catch basins	8.7
General catch basins	0.02-0.39

^aIntensive care unit.

^bOperating theatre.

TABLE VI. HEAVY-METAL CONTENT OF SEWAGE
SLUDGE AND NIGHT-SOIL SEPTIC SLUDGE

	Sewage sludge fertilizer ^a		Night-soil septic sludge ^b	
	mean	range	mean	range
	(mg/kg dry matter)			
Cd	2.3	0.71-12	2.4	0.71-6.3
Hg	0.98	0.30-2.0	4.2	0.5-17
As	5.6	1.9-18	1.2	0.14-2.7
Cu	255	100-495	139	45-292
Zn	979	310-1,475	848	340-1,990
Pb	53	12-97	16	0.76-80
Ni	40	22-77	23	6.0-79
Cr	69	22-151	22	5.0-61

^a59 samples.

^b57-58 samples.

of tap-water Zn and Cd were almost the same in both cities. The amounts of Cd, Pb, Cr, and Zn in tap water expressed as a fraction of total input were 18-52%, 11-76%, trace-28%, and 7-16%, respectively, and in faeces they were 20-61%, 1-7%, 2-17%, and 20-59%, respectively. Most of the Mn came from faeces (60-93%).

In a special case, a family surveyed in Yokosuka used a hair-treatment liquid containing a high concentration of Zn (1,360 ppm). Heavy metals in bath wastewater, especially Cu, probably come from steam boilers.

TABLE VII. PER-PERSON DAILY HEAVY-METAL CONTRIBUTIONS IN TAP WATER, DOMESTIC WASTEWATER, AND FAECES, IN TWO CITIES

City and source	Cd	Ni	Pb	Cr	Mn	Cu	Zn	Fe
	(μg/person/day)				(mg/person/day)			
Yokosuka								
Tap water	42 (22) ^a	388 (23)	3,110 (47)	217 (28)	1.6 (20)	8.4 (15)	3.0 (7)	25 (23)
Bath	73 (38)	676 (41)	2,979 (44)	196 (25)	0.37 (5)	43 (78)	28 (62)	49 (43)
Laundry	27 (14)	243 (15)	465 (7)	284 (37)	0.69 (8)	1.7 (3)	3.0 (7)	25 (22)
Kitchen	12 (6)	150 (9)	95 (1)	65 (8)	0.57 (7)	0.70 (1)	1.8 (4)	3.9 (4)
Faeces	38 (20)	204 (12)	94 (55)	13 (2)	4.9 (60)	1.6 (3)	8.9 (20)	8.5 (8)
Total	192	1,661	6,753	775	8.2	56	44	111
Hakodate								
Tap water	45 (52)	100 (23)	380 (76)	trace	0.33 (5.1)	0.45 (14)	3.8 (16)	11 (36)
Bath	5.6 (6)	63 (14)	39 (7)	136 (59)	0.02 (0.3)	0.33 (11)	5.2 (21)	2.4 (8)
Laundry	2 (2)	37 (8)	42 (8)	41 (18)	0.07 (1)	0.21 (7)	2.6 (11)	3.8 (12)
Kitchen	2 (2)	20 (5)	12 (2)	14 (6)	0.05 (0.8)	0.13 (4)	2.6 (11)	1.2 (4)
Faeces	34 (38)	224 (50)	33 (7)	39 (17)	6.0 (93)	2.0 (64)	10 (41)	12 (40)
Total	89	444	506	230	6.4	3.1	24	30

^a(%)

6. PROPERTIES OF SEWAGE SLUDGE AND SEWAGE-SLUDGE COMPOST

Sewage-sludge compost contained higher levels of heavy metals than did common compost (Table VIII).

Table IX shows heavy-metal contents of various organic materials and manures. Some of these, such as septic sludge, pig dung, and rice straw, contained Zn, Cu or Mn at levels as high as sewage sludge.

7. EFFECTS OF LONG-TERM APPLICATION OF SEWAGE SLUDGE AND SEWAGE-SLUDGE COMPOST ON THE ACCUMULATION OF HEAVY METALS IN SOIL

The behavior of metals in the ecosystem is influenced by several factors: soil properties, plant species, climatic conditions (rainfall and temperature), management practices (irrigation, drainage, liming, fertilization), and heavy-metal composition of sewage sludge. Therefore, long-term field trials have been carried out under diverse soil and climatic conditions in Japan.

7.1. Experiment at the University of Tokyo, Tanashi, Tokyo

Two kinds of sewage sludge composts and a dried sludge were applied separately to a volcanic-ash soil (Andosol) twice a year at 10 t/ha for 12 years, from 1978 [5]. In this region, the surface soil contains relatively high amounts of Zn and Cu, i.e., 137 and 165 mg/kg, in comparison with average values for Japan of 60 and 19 mg/kg, respectively (Table X). Summer corn and winter barley were grown every year.

Table XI shows average concentrations of Zn and Cu in sawdust and rice-husk composts, dried sludge and chemical fertilizer. The average concentrations of Zn in sawdust and rice-husk composts were 675 and 646 mg/kg, respectively, and of Cu, 161 and 104 mg/kg respectively.

TABLE VIII. CONCENTRATIONS OF HEAVY METALS IN SEWAGE-SLUDGE COMPOST AND COMMON COMPOST

	Sewage-sludge compost			Common compost		
	Number of samples	Mean (mg/kg dry matter)	Range	Number of samples	Mean (mg/kg dry matter)	Range
Cd	76	2.8	0.01-6.9	54	0.82	0.00-2.9
As	68	4.6	0.07-16	42	2.2	0.01-4.8
Hg	56	1.4	0.03-3.3	24	0.11	0.01-0.32
Cu	76	184	3.0-680	62	28	2.0-62
Zn	76	1,109	167-3,315	56	82	15-222
Pb	70	87	1.2-130	48	9.5	0.2-46.9

TABLE IX. HEAVY-METAL CONCENTRATIONS IN VARIOUS ORGANIC MATERIALS

	Al	Fe	Mn	Zn	Cu	Ni	Pb	As	Hg	Cd
	(% of dry matter)		(mg/kg dry matter)							
Rice straw	1.25	0.89	1,307	83	30	30	7.8	0.72	0.21	
Equine dung	1.5	1.25	896	135	32	54	10	2.0	0.21	
Cattle dung	0.51	0.43	398	95	21	13	7.6	1.2	0.22	
Swine dung	0.23	0.81	1,105	738	244	16	9.5	1.4	0.20	
Poultry dung	0.18	0.30	327	218	34	11	12	0.30	0.18	
Bark	0.92	0.78	327	225	40	12	10	1.5	0.19	
Septic sludge	0.60	1.8	684	948	143	15	26	4.6	1.8	1.4
Sewage sludge ¹	1.2	4.1	982	940	173	31	31	3.6	1.7	0.87
Sewage sludge ²	1.8	2.8	713	1,046	201	32	36	11	1.8	3.3
Raw sludge	0.75	4.5	1,197	640	127	24	58	40	0.67	1.8
Cattle dung + bark	0.54	0.49	324	76	15	15	6.1	0.65	0.29	0.19

^aWith inorganic amendment.^bWith organic amendment.

Assuming applications of 10 t/ha, the amounts of Zn introduced would be 6.76 kg/ha from sawdust compost and 6.46 kg/ha from rice-husk compost. The amounts of Cu introduced would be 1.61 and 1.04 kg/ha, respectively. Therefore, the increases in Zn concentration in the soil would be 6.75 and 6.46 mg/kg dry soil, respectively, and in Cu, 1.61 and 1.04 mg/kg dry soil, respectively.

The patterns of accumulation of Zn and Cu in the surface and subsurface soils over the 12-year period are in Figs. 4 and 5. Increases in Zn levels in subsurface soil were not detected until 1987, 10 years after the inception of the experiment.

7.2. Experiment at Niigata University, Niigata

This soil is a coarse sand of low clay content (1-3 %) and low CEC (2.7 meq/100g). Sewage-sludge compost was applied for 10 years, from 1978 [6]. Average concentrations of Zn and Cu in the compost were 679 mg/kg and 124 mg/kg, respectively, and Table XII shows the accumulation of Zn and Cu in the soil. Within the first five years, Zn in the surface soil increased from 3.5 to 26 mg/kg, then more gradually reached a plateau of 31 mg/kg. In the sub-soil the Zn increased to 12.3 ppm after 6 years and subsequently varied little, indicating leaching deeper into the soil. Copper moved more slowly than Zn into the sub-soil.

TABLE X. PHYSICO-CHEMICAL PROPERTIES
OF HUMIC VOLCANIC-ASH SOIL

Property	Unit	
Soil texture		Sandy loam
pH (1:2.5 H ₂ O)		6.0
Total organic C	(%)	5.2
Total Zn	(mg/kg)	
Surface soil		137
Subsurface soil		119
Total Cu		
Surface soil		165
Subsurface soil		171
Cation exch. capacity	(meq/100g)	26.1
Exchangeable Ca		10.1
Exchangeable Mg		2.5

TABLE XI. ZINC AND COPPER CONCENTRATIONS IN
MATERIALS APPLIED IN THE TANASHI FIELD EXPT.

Material	Plot designation	Zn	Cu
		(mg/kg)	
Dried sludge	D ^a	3,220	432
Sawdust compost	S	675	161
Rice-husk compost	H	646	104
Fertilizer	F	56	7.4

^aIn Figs. 4 and 5.

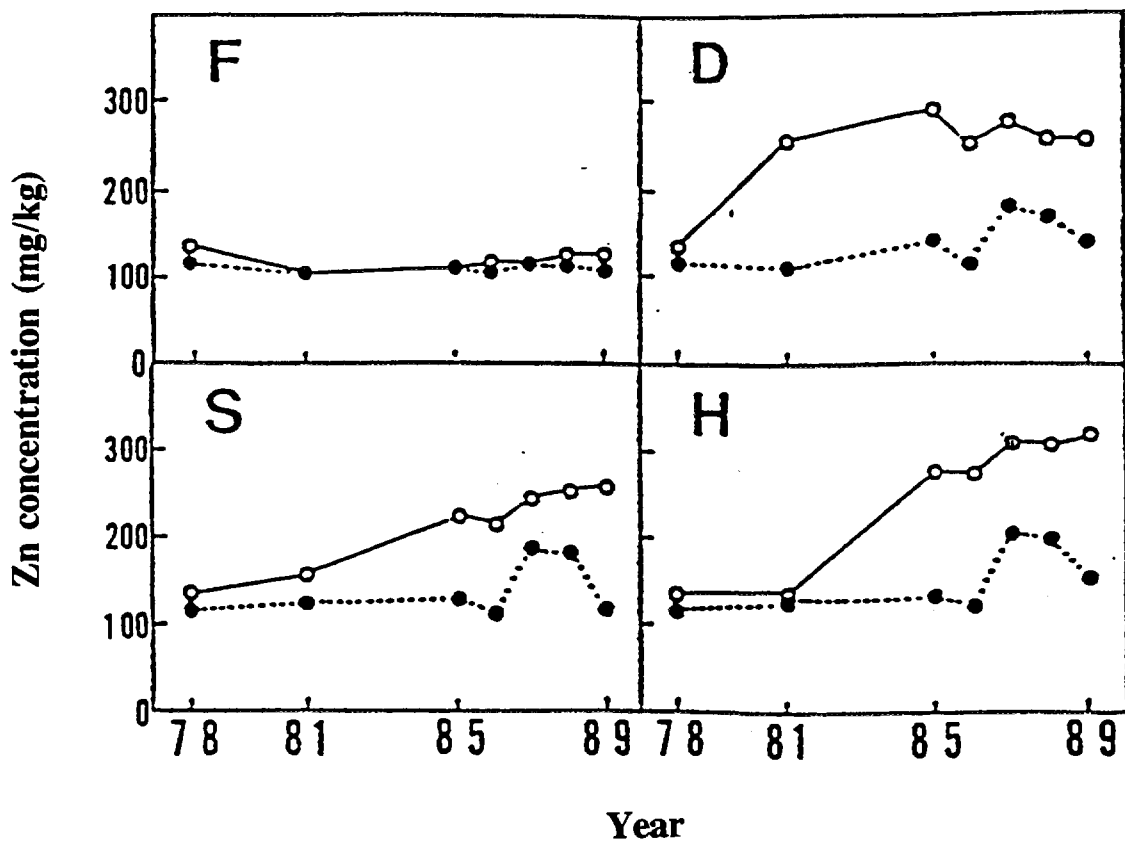


FIG. 4. Concentration of total zinc in surface soil (○) and sub-soil (●).
(F: Fertilizer D: Dried sludge H: Rice-husk compost S: Sawdust compost)

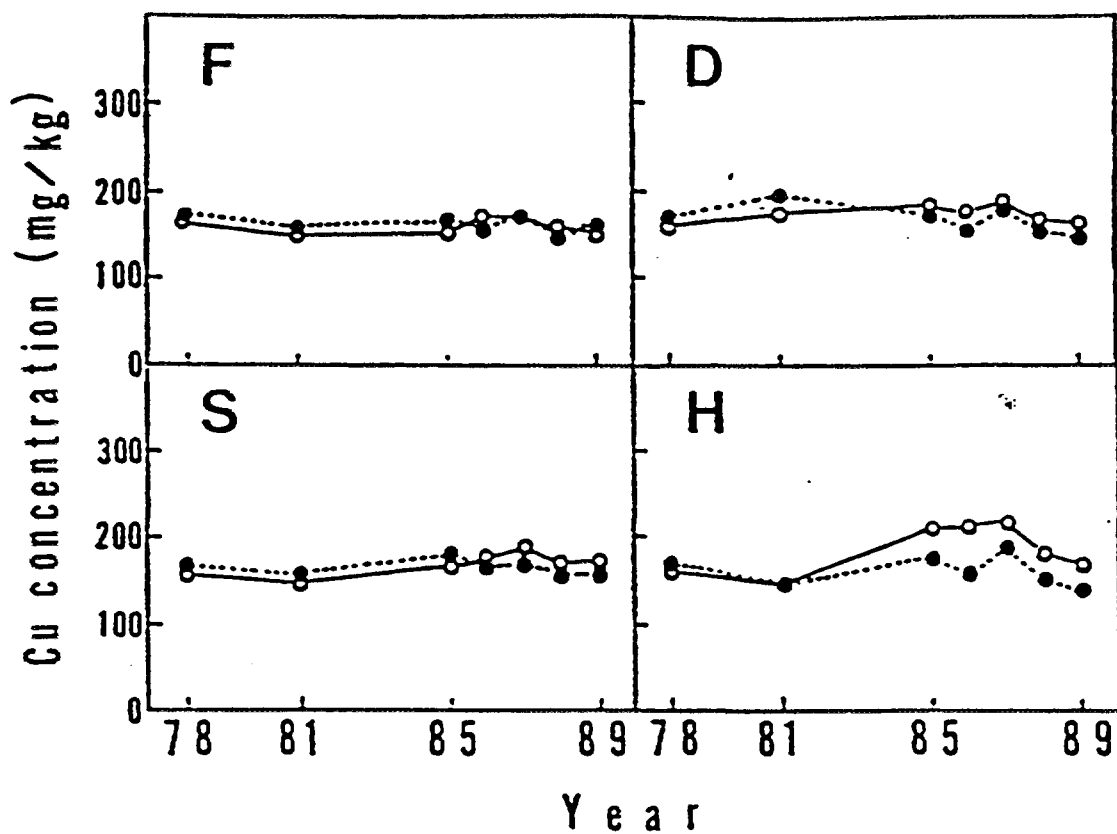


FIG. 5. Concentration of total copper in surface soil (○) and sub-soil (●).
(F: Fertilizer D: Dried sludge H: Rice-husk compost S: Sawdust compost)

8. BEHAVIOR OF HEAVY METALS IN SLUDGE-AMENDED SOIL

After adding nuclide-labeled heavy metals ^{54}Mn , ^{65}Zn , ^{109}Cd , ^{203}Hg , and ^{210}Pb , to soil, the amounts extractable with DTPA, 0.1N HCl, and 1N HNO_3 were little higher than from unamended soil, with no significant change after 3 months [7]. With this steady state, there were significant correlations between DTPA- and HCl-extractable heavy metals in soil and in plants, for applied and total heavy metals. These results indicate that equilibrium is established in sludge among the various chemical forms of heavy metals, as occurs in native soil.

From the above experiments and other field studies that have shown similar trends, guidelines have been drawn up to limit application, so that total calculated quantities of Zn in sludge and soil remain below recommended values.

9. EFFECT OF SEWAGE SLUDGE AND SEWAGE-SLUDGE COMPOST ON CROP PRODUCTION AND SOIL FERTILITY

Several field experiments have been conducted to investigate the effects of sewage sludge and sewage-sludge compost on various crops. In general they were similar to the effects of other organic fertilizers, such as farmyard manure and common compost.

9.1. Flocculant and toxic organic compounds

Various kinds of chemical flocculants are used to accelerate dewatering of sludge. Mixtures of lime and ferric chloride are popular, and sludges so treated contain more than 10% CaO and about 4% Fe. Field trials indicate that successive application of this lime-sludge to sandy soil reduces crop growth and yields due to increased soil pH. For this reason, lime-sludge and its composting products should be used for neutralizing soil acidity rather than organic fertilizer. From this standpoint, Japanese fertilizer law classifies sludge according to the CaO content; sludges with more than 25% alkalinity (CaO+MgO) are distinguished from others as "lime-treated fertilizers". The quantity of lime-sludge that can be applied may be restricted for some soils because of the likelihood of elevated pH.

Polyacrylamide compounds are popular as organic flocculants. Although the monomer is reported to be toxic to plants, no adverse effects on growth have been reported.

There is little information about effects of toxic organic compounds in sludge. The major organic compounds are polychlorinated derivatives, such as PCBs, pesticides, and herbicides. Their concentrations in sludge are likely to be too low to present major environmental risk in Japan.

9.2. Nitrogen and phosphorus

Sludge and sludge compost not only supply nutrients to crops but they may also increase and sustain soil fertility. Major benefits can be attributed to supplying N, which is found in substantial amounts in sludge. However, excessive application of N is accompanied by detrimental side effects on crop production and the environment. It is therefore advisable to adjust sludge application to supply sufficient but not a surfeit of N for crop requirements.

Sludge also has a relatively high P content. Phosphorus is efficiently used by crops, but again, excessive application of sludge may accelerate water eutrophication. Phosphorus content in Japanese soils is generally high because of continuous application of fertilizers for many years.

TABLE XII. INCREASES IN ZINC AND COPPER IN SOIL FROM APPLIED SEWAGE-SLUDGE COMPOST

Year	Zinc		Copper	
	Surface	Subsoil	Surface	Subsoil
	(mg/kg dry soil)			
1978	3.5	0.6	1.0	-
1979	12.8	2.3	2.8	0.1
1980	16.5	5.1	3.6	1.0
1981	20.0	4.6	4.5	0.4
1982	20.2	5.2	5.9	0.4
1983	26.3	12.3	7.8	1.2
1984	28.0	12.3	8.5	0.5
1985	29.4	12.9	10.6	0.9
1986	31.1	11.0	12.3	0.9
1987	31.0	11.9	13.7	1.5

10. QUALITY STANDARDS FOR SEWAGE SLUDGE AND SEWAGE-SLUDGE COMPOST

Variability in the quality of sewage sludge or sewage-sludge compost is rather large owing to differences of source, treatment methods, additives used, fermentation method, etc. However, as demand and commercial production increase, it becomes necessary to demonstrate product quality in terms of C, N, P, Cu and Zn contents, pH etc., as information for farmers. Table XIII shows recommended quality standards for sewage-sludge fertilizer and sewage-sludge compost. Certification tags have made farmers aware of the importance of quality in sewage products.

Most local governments have recommended standards for application of sewage-sludge compost to crops in diverse soil conditions. Taking into consideration these recommended values, tentative national-standard quantities for application to crops were prepared by the Association for Utilization of Sewage Sludge in 1994, as shown in Table XIV. These standard quantities were calculated on the basis of several criteria: (a) the total Zn content should be kept below 120 mg/kg, (b) the surface soil Zn content is less than 60 mg/kg, (c) Zinc and N content of sewage sludge compost are 1100 mg/kg and 3.6%, respectively, and (d) a third of basic applied chemical fertilizer is to be replaced with effective sludge N. The total applicable sludge compost for 10 years was calculated as 10 t/ha for the litorol, 8 t/ha for the alluvial soil, and 5 t/ha for the andosol. In this calculation, the apparent specific gravity values were 1.2, 1.0 and 0.6, respectively, and the surface soil depth was 15 cm.

11. CONCLUSIONS

The use of sewage sludge and sewage-sludge compost in Japan is gradually increasing. They are used not only on arable and pasture lands, but also on golf courses and parks, as shown in Fig. 6. There is now a need for better quality control of these organic fertilizers, to foster public acceptance. At a time when environmental preservation is a major issue, greater emphasis will have to be placed on providing hygienically acceptable sludge and compost with minimum contamination from pathogenic organisms and heavy metals, so that the benefits as fertilizer, increasing and sustaining soil fertility and crop production, will not be compromised.

TABLE XIII. MINIMUM QUALITY STANDARDS FOR
SEWAGE SLUDGE AND COMPOSTED SEWAGE SLUDGE

	Sewage-sludge fertilizer	Sewage-sludge compost
C:N ratio	< 10	< 20
Organic matter	> 35 %	> 35 %
Total N	> 2 %	> 1.5 %
Total P	> 2 %	> 2 %
Alkalinity	< 25 %	< 25 %
Moisture	< 30 %	< 50 %
pH	-	< 8.5
Cu	< 600 mg/kg	< 600 mg/kg
Zn	< 1,800 mg/kg	< 1,800 mg/kg
Seedling test	pass	pass

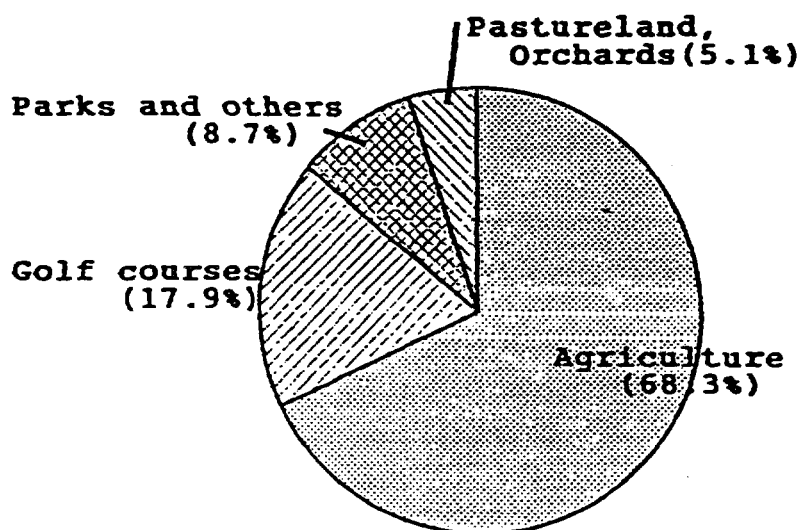


FIG. 6. Uses of sewage sludge as fertilizer in Japan (1990).

TABLE XIV. STANDARD QUANTITIES OF SEWAGE-SLUDGE
COMPOST FOR APPLICATION TO CROPS ON THREE SOIL TYPES

	Litosol	Alluvial soil	Andosol
	(dry matter t/ha/year)		
Rice	1.0 - 1.5	0.5 - 1.5	0.8 - 1.5
Barley	2.0 - 4.0	2.0 - 4.0	2.0 - 4.0
Wheat	2.0 - 4.0	3.0 - 4.0	2.0 - 4.0
Potato	2.0 - 3.0	3.0 - 3.8	2.5 - 3.8
Sweet potato	1.0 - 3.0	0.5 - 1.0	0.5 - 1.0
Soya bean	1.0 - 1.5	1.0	1.0
Groundnut	1.0 - 1.5	1.0	1.0
Rape	5.0	5.0	3.0 - 5.0
Cabbage	2.5 - 4.5	3.5 - 6.5	3.5 - 6.5
Chinese cabbage	3.0 - 5.0	3.0 - 5.0	3.0 - 5.0
Small turnip	3.8 - 6.0	3.8 - 5.0	3.0 - 5.0
Carrot	1.5 - 2.0	2.0 - 3.0	2.0 - 3.0
Radish	2.5 - 4.0	2.5 - 4.0	2.5 - 4.0
Onion	2.0 - 4.0	4.0 - 5.0	4.0 - 5.0
Sweet corn	5.0 - 7.5	7.5	5.0
Green soya bean	1.2 - 2.5	1.2	1.2
Corn	3.0 - 5.0	3.0 - 5.0	3.0 - 5.0
Sorghum	2.5	2.5 - 5.0	2.5 - 5.0
Italian ryegrass	2.5 - 3.0	2.0 - 3.0	2.5
Timothy	2.0 - 3.0	2.0 - 3.0	2.5 - 4.0
Tea	2.0	2.0	2.0 - 5.0
Orchards	2.0	2.0 - 3.0	3.0

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USE OF SEWAGE SLUDGE AS A FERTILIZER FOR INCREASING SOIL FERTILITY AND CROP PRODUCTION

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Abstract

The high nutrient and organic-matter contents of sewage sludge make it a useful soil amendment for farmers. In this study at four locations in Bavaria, the application of sewage sludge produced corn yields that were similar to or better than those produced by an equal application (in terms of N) of chemical fertilizer. High rates of sludge (800 m³/ha) further improved crop yields, although such are impractical for farmers' fields. Residual beneficial effects of sewage-sludge application were seen also in terms of subsequent yields of barley. Application of sludge also improved biological and physical properties of the soils. More long-term studies are needed to better understand how sewage sludge contributes to the improvement of soil fertility and crop yields.

1. INTRODUCTION

The treatment of domestic and industrial wastes in sewage plants produces large amounts of sludge. Containing organic matter, and macro- and micro-nutrients, this product has been long used in agriculture and horticulture to improve soil fertility. Sewage sludges of disparate origins, e.g. household and industrial, may differ greatly in composition, making it necessary to check for harmful substances. In Germany, a 1992 ordinance dictates acceptable levels of heavy metals and organic chemicals in sewage sludge as well as in soil to which it is applied [1]. About 40% of sewage sludge is applied to agricultural land, and there are limitations to the amounts that can be used; for example, it can no longer be applied in water-shed areas, public land or parks [2].

2. FIELD-TRIAL METHODS AND SEWAGE-SLUDGE APPLICATION

The fertility of a soil depends on several factors, of which biological, chemical and physical influences interact. Therefore the effects of sewage sludge on plant growth must be studied under diverse climatic and soil conditions.

Plant yields in sludge-treated plots were compared against chemical-fertilizer controls, on four soil types in Bavaria. The amounts of sewage sludge applied varied during a 3-year rotation period, from 130 m³/ha every year, 400 m³/ha once in the rotation, to 800 m³/ha once as an overdose. This high rate was for experimental purposes only to provide sludge in excess, and would not be practical for farmers' fields. All applications were made in the autumn.

To determine if γ -radiation changes the properties of sewage sludge, and influences the availability of nutrients to plants it was radiated with a dosage of 3 kGy. Because the sludge K-content was low, K fertilizer was applied at the recommended rate. The crop rotation consisted of corn, wheat and spring barley. The characteristics of the soils and the sewage sludge are shown in Tables I and II.

The activities of soil enzymes, dehydrogenase, alkaline phosphatase, protease, and catalase, were determined using standard techniques [5, 6].

3. RESULTS OF THE SEWAGE-SLUDGE FIELD TRIALS

The yields of corn differed with soil type and location (Table III). At Strassfeld, Neuriss and Baumannshof, the 130 m³/ha treatment produced grain yields similar or superior¹ to those obtained with NPK fertilizer. The 400 m³/ha treatment produced grain yields higher than with chemical fertilizer at Strassfeld, Neuriss and Neuhof. The trends in straw yields were similar to those of the grain, although the yield differences among the treatments were higher for straw than for grain. Radiation of the sludge resulted in slight reductions in grain yields at Strassfeld, Neuriss, and Neuhof. The 800 m³/ha rate increased total yields at Strassfeld, Neuriss, and Baumannshof (Table III, Fig. 1).

In the second year of the crop rotation, grain yields of wheat with 130 m³/ha did not reach those with the chemical-fertilizer treatment (Table IV). Also, the residual effects of 400 m³/ha produced inferior yields, as did 800 m³/ha with the exception of Strassfeld. The trends in wheat straw yield were different from those in grain yield [3].

Spring barley was planted in the third year of the rotation. Higher grain yields were observed with the sewage-sludge application rate of 130 m³/ha at all four locations compared to the fertilizer treatment (Table V). In contrast, the 400 m³/ha treatment failed to equal the fertilizer-control yield at any location; this applied also with 800 m³/ha at Neuriss and Baumannshof. The effects of sludge on the barley straw were similar to those on the grain, and yields of grain and straw were generally comparable [4].

4. EFFECT OF SEWAGE SLUDGE ON SOIL FERTILITY

Sewage-sludge application increased the activity of soil microorganisms, as measured by enzyme assay (Table VI; the Baumannshof data showed inconsistencies, and are not included for comparison). Phosphatase, protease and catalase activities increased with sewage-sludge rate, whereas there was no trend in dehydrogenase activity. Differences in the enzyme activities occurred among the soil types. Tests at the end of the 3-year rotation showed microbial activity still increasing. The 800 m³/ha treatment produced the highest activities, except for dehydrogenase. Irradiation of the sewage sludge had no effect on the enzyme activities (data not shown) [5].

Changes in physical properties resulted from sewage-sludge application, but in several cases the trends were not consistent from soil to soil (Table VII); for example, field capacity was increased by 41 % at Neuriss but decreased by 9 % at Strassfeld. Clearly, soil type is important when studying the effects of sewage sludge, therefore field trials should be done across sites in order to find the most suitable rates for different soils [6].

5. CONCLUSIONS

As a source of nutrients and organic matter, sewage sludge is becoming increasingly important to farmers [2]. In this work at four locations in Bavaria, sewage sludge application gave corn yields similar to those obtained with the equivalent N-rate applied as chemical fertilizer. A rate of 130 m³/ha was sufficient for this purpose, and 800 m³/ha produced even higher yields [7]. Residual beneficial

¹Editor's note: The results are described as trends, not in terms of statistical significance.

effects of sewage-sludge were seen in the third year of the crop rotation (but not in the second year), and they varied depending on the location and the amount applied. Sludge improved biological as well as physical properties of the soil.

More long-term experiments are needed to improve our understanding of the effects of sewage sludge on soil fertility and crop yields, to contribute to the development of sustainable agricultural practices.

TABLE I. CHARACTERISTICS OF THE EXPERIMENTAL SOILS

	Strassfeld	Neuhof	Baumannshof	Neuriss
Soil type	Brown Earth	Humic Loam	Humic Sand	Sandy Loam
pH	6.4	6.7	5.1	7.1
Total N (ppm)	1,410	1,500	2,550	2,420
Cadmium	0.33	0.41	0.49	0.45
Copper	67	56	130	54
Zinc	220	27	200	350
Lead	9.9	9.6	3.6	14.2
Rainfall (mm/year)	850	764	764	905

TABLE II. CHEMICAL ANALYSIS OF SEWAGE SLUDGE FROM THE GEISELBULLACH PLANT (GERMANY)

Geiselbullach sewage sludge			
	(%)		(mg/kg dry matter)
(pH 7.3)		Copper	382
Dry matter	3.0	Zinc	3,241
Organic matter	56.5	Manganese	228
Total nitrogen	7.7	Cobalt	5.9
NH ₄ amount	4.3	Iron	7,150
Phosphorus	3.2	Lead	163
Potassium	0.48	Cadmium	12.5
Calcium	6.6	Chromium	63
Magnesium	0.94	Nickel	128

TABLE III. CORN YIELDS WITH VARIOUS APPLICATIONS OF SEWAGE SLUDGE (FIRST YEAR)

	Strassfeld	Neuriss	Neuhof	Baumannshof
	(t/ha)			
<hr/>				
Grain				
NPK ^a	4.09	5.61	3.14	4.28
130 (m ³ /ha)	4.43	4.28	2.84	4.75
400	5.29	6.45	3.95	4.26
800	5.74	6.69	3.29	5.11
Untreated sludge average	5.15	5.80	3.36	4.71
Irradiated sludge average	4.85	5.42	3.29	4.91
Straw				
NPK	6.84	5.32	6.59	4.00
130 (m ³ /ha)	4.23	2.86	5.32	5.04
400	7.08	5.81	6.37	4.52
800	7.90	7.41	6.07	5.89
Untreated sludge average	6.40	5.36	5.92	5.15
Irradiated sludge average	5.48	5.18	5.61	5.13
<hr/>				
Relative total yield	(Total yield with NPK = 100)			
130 (m ³ /ha)	79.2	65.3	83.7	118
400	113	112	106	106
800	125	129	96.2	133
Untreated sludge average	116	117	95.3	119
Irradiated sludge average	103	106	91.4	121

^aApplied as 160-160-240.

TABLE IV. WHEAT YIELDS WITH VARIOUS APPLICATIONS OF SEWAGE SLUDGE (SECOND YEAR)

	Strassfeld	Neuriss	Neuhof	Baumannshof
	(t/ha)			
<hr/>				
Wheat grain				
NPK ^a	3.35	3.42	3.85	3.23
130 (m ³ /ha)	3.19	2.40	3.05	2.96
400	2.77	2.47	2.48	2.22
800	3.56	2.84	3.47	2.79
Untreated sludge average	3.17	2.57	3.02	2.66
Irradiated sludge average	2.97	2.61	3.14	2.86
Wheat straw				
NPK	2.09	2.80	3.45	4.97
130 (m ³ /ha)	2.14	2.98	2.50	5.16
400	1.74	2.04	2.30	3.57
800	2.11	2.19	3.08	4.13
Untreated sludge average	2.00	2.40	2.63	4.29
Irradiated sludge average	2.03	2.53	2.77	4.49
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Relative total yield	(Total yield with NPK = 100)			
130 (m ³ /ha)	97.9	86.3	96.0	98.3
400	83.0	72.4	65.4	70.0
800	104	80.7	89.6	83.8
Untreated sludge average	95.0	79.8	77.0	84.0
Irradiated sludge average	91.8	82.6	80.9	88.8

^aApplied as 100-120-180.

TABLE V. BARLEY YIELDS WITH VARIOUS APPLICATIONS OF SEWAGE SLUDGE (THIRD YEAR)

	Strassfeld	Neuriss	Neuhof	Baumannshof
	(t/ha)			
<hr/>				
Grain				
NPK ^a	5.50	2.43	3.80	2.40
130 (m ³ /ha)	6.02	2.51	4.65	3.08
400	5.18	2.28	3.33	2.05
800	6.28	2.17	4.02	2.34
Untreated sludge				
average	5.83	2.32	3.40	2.49
Irradiated sludge				
average	5.94	2.37	3.96	2.47
Straw				
NPK	5.04	3.53	3.89	3.70
130 (m ³ /ha)	5.68	3.59	4.67	4.99
400	4.61	2.89	3.40	2.44
800	5.68	2.73	4.04	3.32
Untreated sludge				
average	5.32	3.07	4.04	3.59
Irradiated sludge				
average	5.39	3.12	3.94	3.31
<hr/>				
Relative total yield	(Total yield with NPK = 100)			
130 (m ³ /ha)	117	61.0	93.1	80.8
400	97.8	51.6	67.3	44.9
800	120	49.0	80.6	56.6
Untreated sludge				
average	106	90.4	104	99.6
Irradiated sludge				
average	108	92.1	103	94.8

^aApplied as 40-100-150

TABLE VI. RELATIVE EFFECTS OF SEWAGE-SLUDGE APPLICATION ON SOIL-ENZYME ACTIVITIES

Enzyme and sludge rate	Strassfeld	Neuriss	Neuhof	Average irradiated
(Relative activity with NPK = 100)				
Dehydrogenase				
130 (m ³ /ha)	123 ^a	106	117	110
400	115	115	116	115
800	112	104	105	113
Alkaline phosphatase				
130 (m ³ /ha)	131	107	110	114
400	138	140	117	122
800	170	139	119	142
Protease				
130 (m ³ /ha)	163	125	125	135
400	175	154	146	159
800	233	175	170	190
Catalase				
130 (m ³ /ha)	99	108	115	107
400	135	148	136	144
800	237	208	201	190

^aAverage values for spring and autumn.

TABLE VII. RELATIVE EFFECTS OF 800 m³/ha SEWAGE SLUDGE ON SOIL PHYSICAL PROPERTIES.

	Strassfeld	Neuriss	Neuhof	Baumannshof
	(Relative to NPK = 100)			
Total pore volume (%)	90.4	91.4	104	97.7
Air pores (%)	57.0	64.0	57.0	85.0
Field moisture (%)	104	102	113	111
Effective field capacity (%)	91.1	141	126	106
Aggregate stability 6-2 mm (%)	108	111	119	154
Cation exchange capacity (mequiv/100g soil)	114	110	97.0	167
Ca (mequiv/100g soil)	117	103	148	260
Mg (mequiv/100g soil)	175	125	106	408

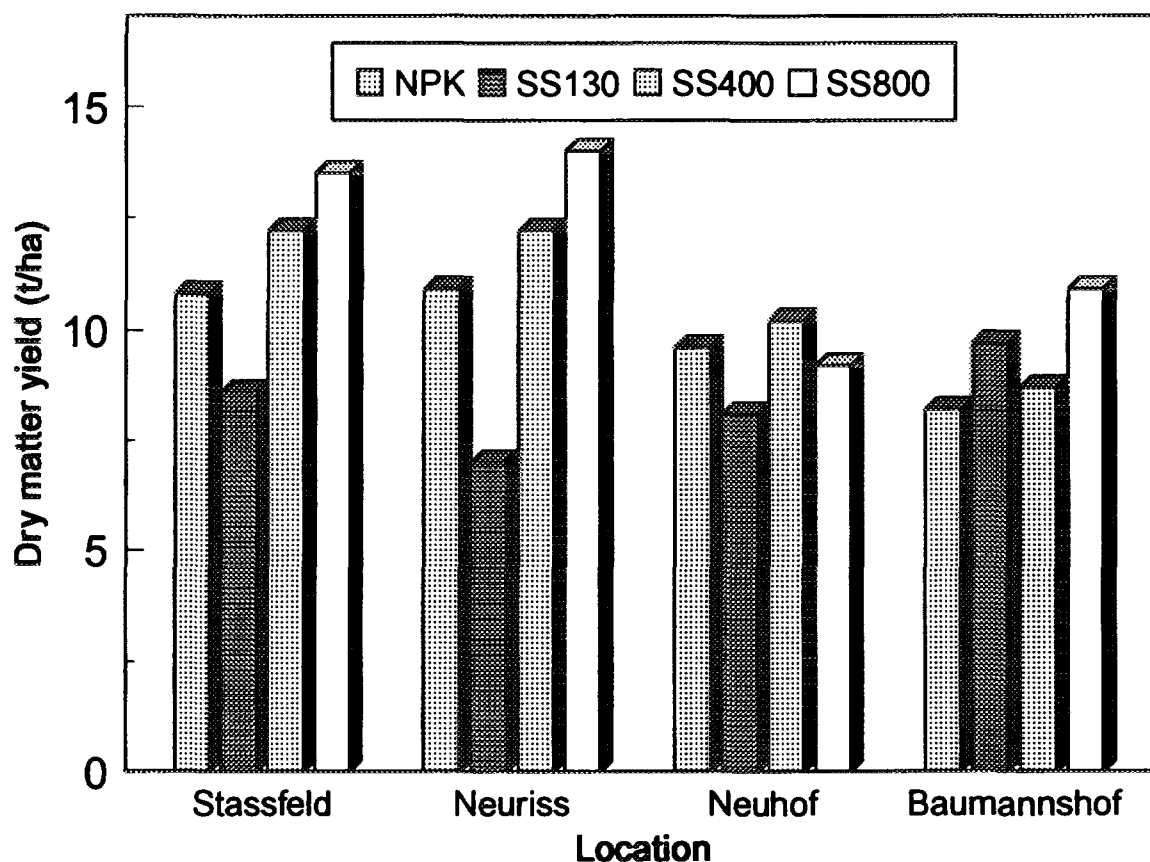


FIG. 1. Total dry matter yields of corn with various applications of sewage sludge (see Table III for details of NPK and sewage-sludge (SS) treatments).

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ASSESSMENT OF HEAVY METAL POLLUTION WITH APPLICATIONS OF SEWAGE SLUDGE AND CITY COMPOST FOR MAXIMIZING CROP YIELDS

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Abstract

ASSESSMENT OF HEAVY-METAL POLLUTION WITH APPLICATIONS OF SEWAGE SLUDGE AND CITY COMPOST FOR MAXIMIZING CROP YIELDS.

Land application of municipal sewage sludge and city compost as organic manures make it imperative to assess heavy-metal pollution in soils and crops. Greenhouse experiments, conducted on maize in a vertisol and an ultisol amended with various doses of dry sewage sludge and city compost from Mumbai, indicated significant increases in dry matter-yields only in the vertisol. Significantly higher concentrations of Zn, Cu, Co, Pb, Ni and Cd were obtained in plants grown in the amended ultisol, but not in the amended vertisol. As Cd is the most toxic, experiments were conducted with four contrasting soils amended with varying doses of Cd-enriched sewage sludge and city compost. Results showed significant reductions in dry-matter yields of maize shoots at the higher rates of sludge or compost in the ultisol and an alfisol, but with no significant effects in the vertisol or an entisol. The levels of Cd and Zn were significantly elevated in plants in all four soil types. There were negative residual effects from the sludge and compost amendments: dry-matter yields of a succeeding maize crop were decreased in the ultisol and alfisol. Experiments with soils amended with sludge enriched with either Cd or Zn at 80 mg kg⁻¹ indicated significant reductions in dry matter in all soils with Cd, but not with Zn. The results demonstrate that sewage sludges and city composts may be effectively used for maximizing crop yields, especially in vertisols and entisols. However, caution has to be exercised when using sludges containing even relatively low levels of Cd, or high levels of Zn, depending upon soil type.

1. INTRODUCTION

Integrated nutrient management offers the opportunity to not only maximize but also sustain crop productivity. The approach encompasses the complementary use of all available organic and biological sources of plant nutrients, along with chemical fertilizers. Among these are farmyard manure, composts, crop residues, green manures, blue-green algae, and recyclable wastes such as sewage sludge, biogas slurry, industrial wastewater, press-mud and fly ash. Sewage sludge is a nutrient-rich, largely organic by-product of municipal wastewater treatment, which has to be removed and disposed of by ocean-dumping, incineration, land-filling or utilization in agriculture and horticulture. Land application of municipal sewage sludge is practised throughout the world. High levels of N, P, and of organic matter make it excellent as fertilizer and soil conditioner [1, 2]. Whether applications are made at increasing rates per hectare or repeatedly in consecutive years [3-6], beneficial effects are well documented in terms of crop-yield improvement, increased soil organic matter content and cation-exchange capacity, improved water-holding capacity, and general fertility [7-10].

However, sewage sludge and city compost, besides providing macro-and micro-nutrients, also contain heavy metals, such as Cd, Cr, Ni, Pb, Co and Hg, in amounts beyond those normally

encountered in soils. A limiting factor, therefore, is the excessive accumulation of heavy metals in soil and resultant phytotoxicity [11-13]. Hence, fertility benefits must be balanced against the potential hazards of metal contamination through repeated heavy dressings over time.

Guidelines for applying sewage sludge, developed in Western countries, are based on N application rates, pH, cation-exchange capacity, or on crop responses determined within a short time following sludge application, with major concern over Cd uptake [14, 15]. Limits for maximum loading rates of specific toxic elements like Cd have also been prescribed [14]. The Zn-equivalent concept, which is the sum of $\text{Zn} + 2\text{Cu} + 8\text{Ni}$ ($\mu\text{g g}^{-1}$ soil) was developed to monitor maximum allowable metal concentrations (not to exceed $250 \mu\text{g g}^{-1}$) in soils [16]. Several reviewers have summarized metal uptake by a range of crops, and heavy-metal phytotoxicity has been demonstrated with plants grown in solution culture [17-19], in greenhouse pot experiments [13, 20-24] and in the field [13, 25, 26].

Plant availability of Pb and Cr is low, but their entry into the food chain can occur by direct ingestion of sludge by grazing animals [27]. Cadmium may pose a health problem since plants can accumulate it to levels toxic to animals or humans, although not to the plants [27]. High levels of Cd are encountered in many sludge-amended soils [28] and in soils near Zn smelters [29] that can affect plant growth and dry matter yield adversely [19, 30, 31]. Plant uptake is controlled, in part, by sludge Cd chemistry, specifically sludge Cd content [32], soil pH and soil cation-exchange capacity [7-10]. Cadmium accumulates in the kidneys, liver, pancreas and thyroid of humans and animals, and it has been associated with hypertension, emphysema, chronic bronchitis and even death in extreme circumstances [11, 33].

Although there is insufficient sewage sludge and city compost available to make a significant impact on total fertilizer needs in our country, low cost and availability make it an attractive alternative in areas near sewage-treatment plants. The composition of sludges from Ahmedabad, Delhi, Jaipur, Kolhapur, Madras, Nagpur and Vijayawada were summarized recently, and the ranges of values for the major nutrients were as follows: N, 0.82-2.3%; P_2O_5 , 0.84-2.1%; K_2O , 0.53-1.7%; and for organic matter, 27-55% [34]. Their heavy-metal contents, total and available (in brackets) in mg kg^{-1} were as follows: Cu, 194-535 (17.2-50.3); Zn, 833-2146 (70-216); Mn, 176-465 (1.3-26.5); Cd, 0.6-8.3 (0.1-1.4); Cr, 17-185; Ni, 11-815 (0.3-52.2) and Pb 14-77 (1.8-8.3). Little work has been done in our country to evaluate the fertilizer value and heavy-metal contributions of sewage sludges and city composts for different soil/crop combinations.

This paper reports pot-culture studies on the effects of a sewage sludge and a city compost from Mumbai on plant growth, and an assessment of the heavy-metal pollution of soil and plant. As Cd is one of the most toxic elements and Zn is chemically and geochemically related to it, their accumulation in soils and plants were separately examined.

2. MATERIALS AND METHODS

Four contrasting soils, an ultisol from Phondaghat, a vertisol from Hatkanangale, an entisol from Mahad, all in Maharashtra, and an alfisol from Chittoor, Andhra Pradesh, were selected. Their physicochemical properties are shown in Table I, and the concentrations of micronutrients and heavy metals in Table II. Total heavy-metal determinations were made by extracting the soils with 2 *M*

TABLE I. SOIL CHARACTERISTICS

	Ultisol laterite	Alfisol red	Entisol alluvial	Vertisol black
pH (1:2.5)	5.1	6.4	6.6	8.2
Moisture equivalent (%)	30.0	18.0	34.0	35.0
CEC (meq 100 g ⁻¹)	10.5	13.0	31.6	60.7
Organic C (%)	1.4	0.12	1.36	1.32
Free CaCO ₃ (%)	1.00	0.50	3.00	6.75
Texture	Sandy loam	Sandy loam	Silt loam	Clay loam

HNO₃ (soil:acid 1:10) in a boiling-water bath for 2 h [35]; this represents 75 to 80% of the metals that would be extractable with hydrofluoric acid. Plant-available metals were determined by extracting 10 g of soil with 20 mL of a solution of 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M CaCl₂, and 0.01 M triethanolamine (TEA), pH 7.3, in a rotary evaporator for 2 h [36].

The soils were separately amended with sewage sludge from the Dadar Municipal Sewage Plant, Mumbai, and with city compost from the Bombay Organic Manures Co. Ltd., Devnar, Mumbai. The concentrations of micronutrients and heavy metals are in Table III. In the first experiment, these materials were separately applied to one kg of two soil types, namely the ultisol and the vertisol, at 0, 56, 112, 224 and 448 t ha⁻¹. The pots were kept at field capacity for a week, after which time basal nutrients of N, P₂O₅, K₂O were applied at 60:40:60 kg ha⁻¹; two maize (*Zea mays* L.) plants were grown in each pot for eight weeks.

In order to assess Cd accumulation by maize, these soils were amended with Cd-enriched sewage sludge or city compost. The enrichment procedure consisted of preparing a slurry of the sewage sludge or compost with a solution of 3CdSO₄·2H₂O (300 µg Cd g⁻¹ sludge or compost) and subsequent air drying. The sieved soils were treated with doses of 25, 50 and 100 g Cd-enriched sludge or compost per kg soil, representing 56, 112 and 224 t ha⁻¹, respectively. The Cd concentration in these treatments amounted to 7.5, 15.0 and 30.0 mg kg⁻¹ soil. Two maize plants were grown for six weeks as described above. Residual effects were evaluated by allowing the soils to dry for a month followed by thorough mixing, maintenance of field capacity for 15 days, and then growing two maize plants for 30 days.

Sewage sludges of various Cd or Zn concentrations were applied at the agronomic rate of 44.8 t ha⁻¹ to the four soil types, to obtain levels of 5, 10, 20, 40 and 80 mg Cd or Zn kg⁻¹ (ppm) amended soil. The enrichment procedure and plant-growth conditions were as described above. Two maize plants were grown for six weeks.

TABLE II. CONCENTRATIONS OF MICRONUTRIENTS AND HEAVY METALS IN FOUR SOILS EXTRACTED WITH 2M HNO₃ AND DIETHYLENETRIAMINEPENTACETIC ACID (DTPA)

	Ultisol		Vertisol		Alfisol		Entisol	
	HNO ₃	DTPA	HNO ₃	DTPA	HNO ₃	DTPA	HNO ₃	DTPA
	(µg g ⁻¹ dry wt.)							
Fe	28,400	38.9	27,900	1.7	11,845	7.0	49,500	41
Mn	318	71.6	1,085	4.9	272	32	1,212	292
Cu	74	6.8	107	4.9	8.5	1.3	117	13
Zn	44	1.34	54	0.9	8.0	0.6	92	3.0
Co	17.2	0.43	29.5	0.17	11.0	0.5	48	2.5
Pb	12.7	0.44	13.5	0.42	10.0	0.63	16	0.32
Ni	27.2	0.14	35.9	0.06	10.0	0.25	46	1.4
Cd	0.3	0.01	0.05	0.02	0.25	0.02	0.9	0.06
Cr	24.3	trace	22.0	trace	19.0	0.02	57	0.02

All treatments were replicated four times. After harvest, plant shoots were dried at 70°C, weighed and wet-ashed using a 5:1 HNO₃:HClO₄ acid mixture. The concentration of the heavy metals in the clear-acid extracts were determined using a Perkin-Elmer Model 380 Atomic absorption spectrophotometer equipped with a D₂-arc background corrector. The data were statistically analysed adopting Duncan's multiple range test.

3. RESULTS AND DISCUSSION

The ultisol was less fertile than the vertisol (Fig 1). In the vertisol, significantly higher yields were obtained with sludge and compost amendments. In the ultisol, responses were not significant, and there was a decreasing yield trend with increasing compost rate. Even at the very high application rates of 224 and 448 t ha⁻¹ (levels in excess of those allowed by Western regulations and representing worst-case situations), no visual toxicity symptoms were exhibited by the maize. It is possible that the

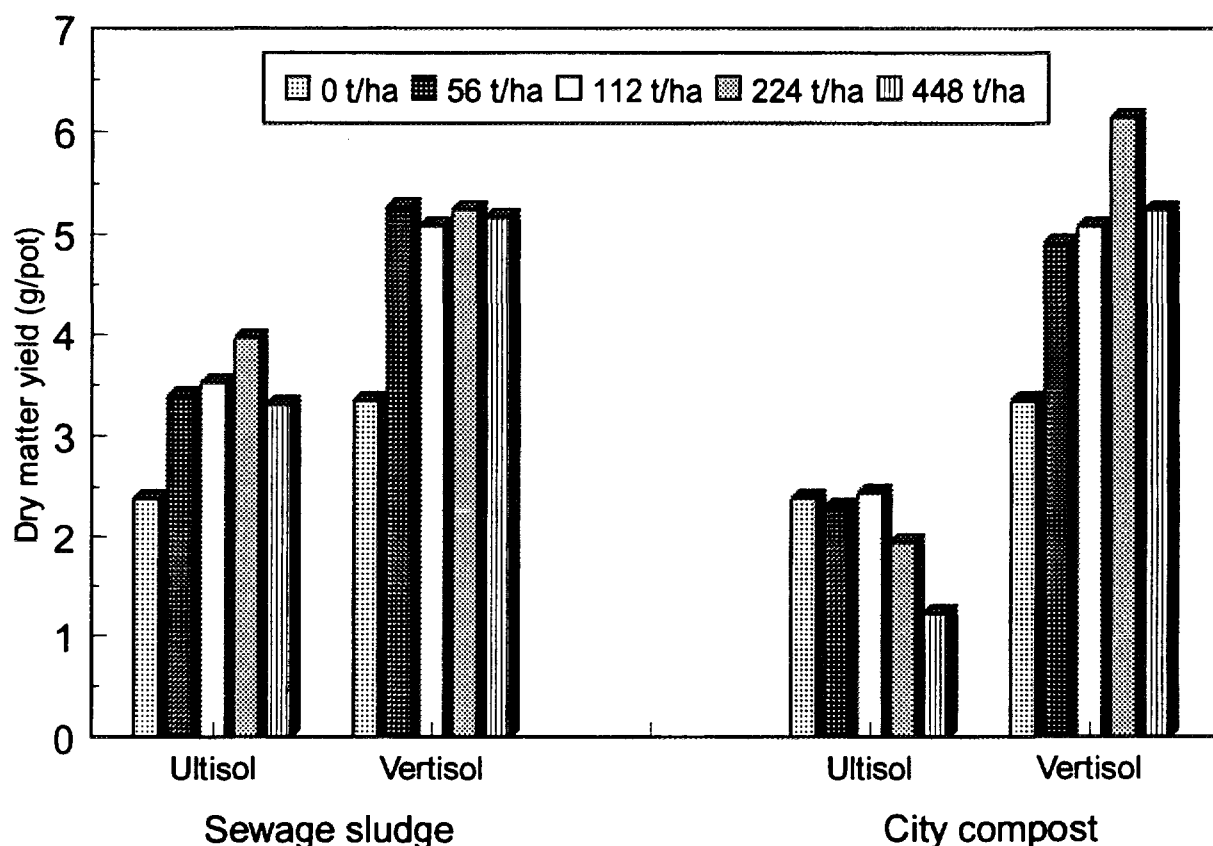


FIG. 1. Dry matter yields of maize grown on two soils amended with sewage sludge and city compost. (Bars denote LSD values, $P < 0.05$)

short duration of this experiment (8 weeks) was a contributory factor; a longer period of organic-matter mineralization might reveal a positive effect in the ultisol, at least with the low application, 56 t ha⁻¹. These data show that although beneficial effects are not obtained in all soils, these organic fertilizers can significantly improve yields, as indicated in earlier studies [3, 4, 6, 8].

The micronutrient (Fe, Mn, Cu, Zn) and heavy-metal (Co, Pb, Ni, Cd, Cr) concentrations in plant shoots grown on sludge-amended soils are shown in Table IV. In the ultisol, there were decreases in the Fe and Mn concentrations with sludge amendment; whereas, significantly higher concentrations of Cu and Zn were obtained with the higher rates of sludge. In the vertisol, there were no significant changes in the Fe, Mn and Cu concentrations, whereas Zn concentration in the plants increased with increasing rates of sludge. It is noteworthy that higher plant levels of Co, Pb, Ni and Cd were obtained at higher doses of sludge application in the ultisol, whereas, there were no similar trends in the vertisol. The Cr concentration in plants was not affected by sludge amendments in either soil type.

The compost-amendment data, (Table V) show trends similar to those with sludge amendment, mainly reduction in Fe and Mn and enhancement in Cu and Zn concentrations in plants grown on the ultisol. There was no significant variation in the Fe, Mn and Cu contents, but increased Zn, in plants grown in the vertisol. Addition of city compost also increased Ni, Pb, and Cd plant contents in the ultisol, whereas in the vertisol increased plant levels of Co and reduced levels of Ni were observed. The levels of these metals attained in plants are comparable to those reported by Maclean et al. [37]. Thus, a clear soil-specificity existed for plant uptake of the metals supplied in sludge and compost.

TABLE III. CONCENTRATIONS OF MICRONUTRIENTS AND HEAVY METALS IN SEWAGE SLUDGE AND CITY COMPOST EXTRACTED WITH 2 M HNO₃ AND DIETHYLENETRIAMINE-PENTAACETIC ACID (DTPA)

	Sewage sludge		City compost	
	HNO ₃	DTPA	HNO ₃	DTPA
	(μg g ⁻¹ dry weight)			
Fe	14,650	42	1,575	106
Mn	378	6.0	622	45
Cu	600	108	435	83
Zn	1,190	132	922	253
Co	11	0.54	15	0.47
Pb	129	0.94	246	47
Ni	65	47	48	3.0
Cd	3.0	0.72	1.0	0.78
Cr	137	0.14	51	0.09
	(%)			
N	2.0		1.2	
P ₂ O ₅	1.39		0.34	
K ₂ O	0.37		0.60	
Organic C	15.0		10.4	
C:N	7.00		8.67	
pH (1:2.5)	6.2		7.7	

Earlier studies [7-10] have shown that metals in sewage sludge differ in their availability to crops depending upon soil pH and organic-matter content, and cation-exchange capacity. The lower pH and cation-exchange capacity of the ultisol in this study must have contributed to greater accumulation of Cu, Zn, Pb, Ni and Cd. The restricted uptake of Fe and Mn with sludge and compost must have resulted from conversion of the Fe and Mn to insoluble forms by the high levels of organic matter.

Data on Cd toxicity are presented in Tables VI and VII. Significant reductions in the dry matter yields of both crops of maize occurred at the higher rates of Cd-enriched sludge in the ultisol and alfisol (Table VI); however, in the vertisol, only the second crop was adversely affected, and no significant effects were observed in the entisol. In the compost-amended soils (Table VII), significant losses in yield were observed also in the ultisol and alfisol, but only with the second crop.

Significantly larger accumulations of Cd were observed in the shoots of both crops in all four soils amended with the Cd-enriched sludge (Table VI) or city compost (Table VII). Moreover, the highest levels of accumulation, at any particular Cd level, occurred in the ultisol and the alfisol, which

TABLE IV. CONCENTRATION OF MICRONUTRIENTS AND HEAVY METALS IN MAIZE SHOOTS GROWN ON TWO SOILS AMENDED WITH SEWAGE SLUDGE

Soil and sludge rate	Fe	Mn	Cu	Zn	Co	Pb	Ni	Cd	Cr
(μg g ⁻¹ dry shoot)									
Ultisol									
0	331b ^a	245c	5.8a	41a	3.7a	11.8a	1.2a	2.3a	0.9a
56 (t ha ⁻¹)	129a	46a	5.6a	57a	12.0d	4.3a	8.7b	2.9ab	1.3a
112	150a	55a	7.7ab	122b	9.0bc	35.8c	11.4c	3.3b	1.1a
224	103a	49a	6.8a	123b	9.9cd	36.8c	10.1bc	4.6c	0.8a
448	111a	85a	11.4b	168c	7.1b	22.1b	11.8c	4.5c	1.0a
Vertisol									
0	67a	60b	8.3a	21a	3.8a	27.3ab	23.4c	2.0a	0.9a
56 (t ha ⁻¹)	64a	63b	13.9a	59b	5.5ab	41.8c	17.9abc	2.3ab	0.5a
112	65a	62b	8.4a	92c	6.3b	38.8bc	22.4bc	2.6b	0.9a
224	76a	64b	10.0a	110c	5.5ab	34.6abc	15.7ab	2.1a	0.6a
448	68a	39a	8.9a	146d	5.1ab	24.0a	14.0a	2.4ab	0.8a

^aNumbers within columns followed by the same letter are not significantly different by Duncan's Multiple Range Test ($P < 0.05$).

may explain the depression of yields in these two soils types. Although the Cd accumulated by the unaffected plants in the entisol and vertisol did not reach toxic levels, contamination of fodder and food is possible. The residual effects of the sludge and compost in terms of depressed plant yields and high Cd levels in the succeeding maize crop demonstrate continued availability to plants. These data are consistent with earlier reports of decreased availability of Cd to plant shoots in soils of higher pH and high cation exchange capacity [38-42].

Simulated sewage sludges containing varying levels of either Cd or Zn were evaluated by applying sludge at a uniform agronomic rate to the four soils with maize as the test crop. Sludge addition without Cd enrichment significantly enhanced the dry-matter yields of shoots only in the vertisol (Table VIII). Addition of sludge with increasing levels of Cd resulted in progressive yield reduction in the vertisol, entisol and alfisol, but not in the ultisol in which yield potential was already low. Significant negative correlations were obtained between soil Cd concentration and dry matter yield (Table IX). Further, plant Cd contents increased with Cd supply in all four soils, indicating that yield depression was due to Cd accumulation in plant tissue (Table VIII). There were positive

TABLE V. CONCENTRATIONS OF MICRONUTRIENTS AND HEAVY METALS IN MAIZE SHOOTS GROWN ON TWO SOILS AMENDED WITH CITY COMPOST

Soil and compost rate	Fe	Mn	Cu	Zn	Co	Pb	Ni	Cd	Cr
	(μg g ⁻¹ dry shoot)								
Ultisol									
0	331b ^a	245d	5.8a	41a	3.7a	11.8a	1.2a	2.3a	0.9a
56 (t ha ⁻¹)	81a	48a	6.8a	50a	5.0a	11.5a	9.7c	1.9b	1.3a
112	124a	73b	8.3a	61a	4.4a	27.7b	5.5b	1.6b	0.9a
224	136a	110c	7.9a	91b	8.6a	21.8b		2.4a	0.9a
448		131c	12.0b	125c				2.7a	0.4a
Vertisol									
0	67a	60b	8.3b	21a	3.8ab	27.3a	23.4b	2.0a	0.9a
56 (t ha ⁻¹)	62a	40a	3.6a	47b	3.4a	20.6a	12.0a	2.8b	0.8a
112	93b	45a	6.0ab	63b	6.4b	27.5a	11.8a	2.6b	0.5a
224	60a	50ab	5.2ab	60b	9.4c	22.1a	12.1a	2.4ab	1.0a
448	96b	51ab	13.3c	105c	9.5c	29.2a	10.8a	2.6b	1.1a

^aNumbers within columns followed by the same letter are not significantly different by Duncan's Multiple Range Test ($P < 0.05$).

correlations between soil Cd level and plant Cd content for all four soil types (Table IX). In general, the Cd contents of maize grown on the alfisol and ultisol were greater than for the vertisol and entisol, possibly due to higher pH and cation-exchange capacity as discussed above.

As mentioned above, the addition of unamended sludge resulted in the enhancement of dry matter yield only in the vertisol (Table VIII, Fig. 2). Zn-enriched sludge amendments did not further affect yield in the vertisol, whereas in the alfisol and ultisol 5 ppm Zn produced significant yield enhancement. A significant yield reduction was observed at 80 ppm in the entisol. The Zn content of the maize shoots was significantly enhanced with sludge application (without enrichment) in all soils except the ultisol (Fig. 2). Progressive enhancement in Zn uptake occurred as the added Zn level increased from 5 to 80 ppm, with positive correlations for all soils (Table X). Negative correlations were obtained between added Zn and dry-matter yield in the vertisol and entisol, whereas a positive correlation was observed in the alfisol (Table X), showing that high levels of Zn in sludge will depress plant yields in some soils.

TABLE VI. YIELDS AND CADMIUM CONTENT OF MAIZE GROWN ON FOUR SOILS AMENDED WITH CADMIUM-ENRICHED SEWAGE SLUDGE

Crop and cadmium level	Dry matter yield				Cadmium content			
	Ultisol	Alfisol	Entisol	Vertisol	Ultisol	Alfisol	Entisol	Vertisol
	(g pot ⁻¹)				(μg g ⁻¹ dry shoot)			
First crop								
0	0.81a ^a	1.14a	1.18a	1.09ab				
7.5 (ppm)	0.88a	1.04a	1.27a	0.95a	43.8a	56.4a	15.8a	19.8a
15.0	0.90a	0.58b	1.10a	1.25ab	66.7b	63.4ab	34.5b	29.0b
30.0	0.40b	0.29c	1.17a	1.40b	92.7c	74.3b	64.7c	32.9b
Second crop								
0	1.08a	1.32a	0.93a	1.14a				
7.5 (ppm)	0.75b	0.65b	0.95a	1.02ab	63.1a	55.5a	12.5a	16.2a
15.0	0.62c	0.74b	0.93a	1.04ab	56.2a	92.7b	26.6b	37.3b
30.0	0.61c	0.66b	0.96a	0.71b	78.7b	101.9b	48.3c	55.8c

^aNumbers within columns followed by the same letter are not significantly different by Duncan's Multiple Range Test ($P < 0.05$).

4. CONCLUSIONS

In general, the results demonstrate that sewage sludges and city composts may be effective as organic fertilizers for maximizing crop yields. However, depending upon soil type, caution has to be exercised with sludges containing even relatively low levels of Cd, or high levels of Zn. Little work has been done under field conditions, and research is needed to establish guidelines for safe application of these materials to Indian soils. The guidelines should take into account crop requirements for N and P, the heavy-metal levels in the organic amendment and in the native soil, pH and cation-exchange capacity of the soil, and overall sludge chemistry in soils. The effects of repeated application over long periods (5 years and more) should be evaluated and ameliorative measures, such as application of lime or fly ash, should be considered so as to maintain sludge-amended soils at a pH of around 6.5. Further, chemical speciation of heavy metals in sludge-amended soils has to be studied in order to evaluate availability to plants in order to develop methods of restricting entry into the human food chain. Therefore, future research should be aimed not only at evaluation of sewage sludges and city composts as effective and economical fertilizer sources, but also to establish guidelines to limit their application to soils based on phytotoxic effects, maximum allowable metal concentrations, and metal build-up in soils.

TABLE VII. YIELDS AND CADMIUM CONTENT OF MAIZE GROWN ON FOUR SOILS AMENDED WITH CADMIUM-ENRICHED CITY COMPOST

Crop and cadmium level	Dry matter yield				Cadmium content			
	Ultisol	Alfisol	Entisol	Vertisol	Ultisol	Alfisol	Entisol	Vertisol
	(g pot ⁻¹)				(μg g ⁻¹ dry shoot)			
First crop								
0	0.79a ^a	0.83a	0.84a	0.87a				
7.5 (ppm)	0.59b	0.92b	1.09a	1.26b	55.7a	56.8ab	15.9a	22.0a
15.0	0.67ab	0.88a	1.10a	0.71a	72.1a	72.9ab	37.2b	27.8a
30.0	0.72ab	0.55a	0.95a	0.83a	82.1a	90.5b	64.5c	50.3b
Second Crop								
0	0.51a	0.75a	0.91a	0.64a				
7.5 (ppm)	0.40ab	0.66ab	0.85a	0.54ab	36.4a	42.4a	16.1a	27.1a
15.0	0.38ab	0.55ab	0.77a	0.44b	69.8b	75.8b	24.4b	39.3ab
30.0	0.26b	0.37b	0.82a	0.47ab	108c	108c	52.4c	55.1b

^aNumbers within columns followed by different letters are significantly different by Duncan's Multiple Range Test ($P < 0.05$).

TABLE VIII. YIELDS AND CADMIUM CONTENT OF MAIZE GROWN ON FOUR SOILS AMENDED WITH CADMIUM-ENRICHED SEWAGE SLUDGE

Treatment	Dry matter yield				Cadmium content			
	Vertisol	Alfisol	Entisol	Ultisol	Vertisol	Alfisol	Entisol	Ultisol
	(g pot ⁻¹)				(μg g ⁻¹ dry shoot)			
No amendment	5.65a ^a	7.68c	14.5cd	3.64a				
Sludge alone	10.45c	8.20c	11.7c	3.73ab				
Sludge								
+ 5 ppm Cd	10.9c	5.05b	16.0d	5.50b	12.0a	3.6a	20.5a	27.9a
+10	10.4c	4.50b	12.8cd	5.10ab	14.8a	8.9a	57.5b	37.1a
+20	9.24bc	4.96b	11.1bc	4.96ab	22.1b	16.3b	71.9b	53.3b
+40	7.75b	3.65ab	7.92b	4.61ab	36.1c	22.1b	118c	75.4c
+80	4.87a	2.35a	4.42a	4.93ab	42.3c	35.5c	128c	100d

^aNumbers within columns followed by different letters are significantly different by Duncan's Multiple Range Test ($P < 0.05$).

TABLE IX. RELATIONSHIPS BETWEEN ADDED CADMIUM, MAIZE YIELD, AND MAIZE CADMIUM-CONTENT

Soil	x vs y_1^a		x vs y_2	
	Correlation coefficient	Regression equation	Correlation coefficient	Regression equation
Vertisol	- 0.988**	$y_1 = 10.86 - 0.075x$	0.923**	$y_2 = 8.71 + 0.484x$
Entisol	- 0.816*	$y_1 = 6.15 - 0.053x$	0.975**	$y_2 = 3.40 + 0.426x$
Alfisol	- 0.913*	$y_1 = 13.80 - 0.122x$	0.889*	$y_2 = 26.7 + 1.51x$
Ultisol	NS ^b	-	0.936**	$y_2 = 20.33 + 1.11x$

^ax = $\mu\text{g Cd g}^{-1}$ soil y_1 = dry matter in g $y_2 = \mu\text{g Cd g}^{-1}$ dry matter.

*Significant at $P < 0.05$.

**at $P < 0.01$.

^bNot significant.

TABLE X. RELATIONSHIPS BETWEEN ADDED ZINC, MAIZE YIELD, AND MAIZE ZINC-CONTENT

Soil	x vs y_1^a		x vs y_2	
	Correlation coefficient	Regression equation	Correlation coefficient	Regression equation
Vertisol	-0.821**	$y_1 = 0.79 - 0.036x$	0.982***	$y_2 = 38.73 + 0.63x$
Entisol	-0.782*	$y_1 = 6.99 - 0.033x$	0.938***	$y_2 = 49.00 + 0.31x$
Alfisol	0.834**	$y_1 = 13.69 + 0.059x$	0.984***	$y_2 = 90.53 + 1.42x$
Ultisol	NS ^b	-	0.950***	$y_2 = 71.60 + 0.71x$

^ax = $\mu\text{g Zn g}^{-1}$ soil y_1 = dry matter in g $y_2 = \mu\text{g Zn g}^{-1}$ dry matter.

*Significant at $P < 0.10$.

**at $P < 0.05$.

***at $P < 0.01$.

^bNot significant.

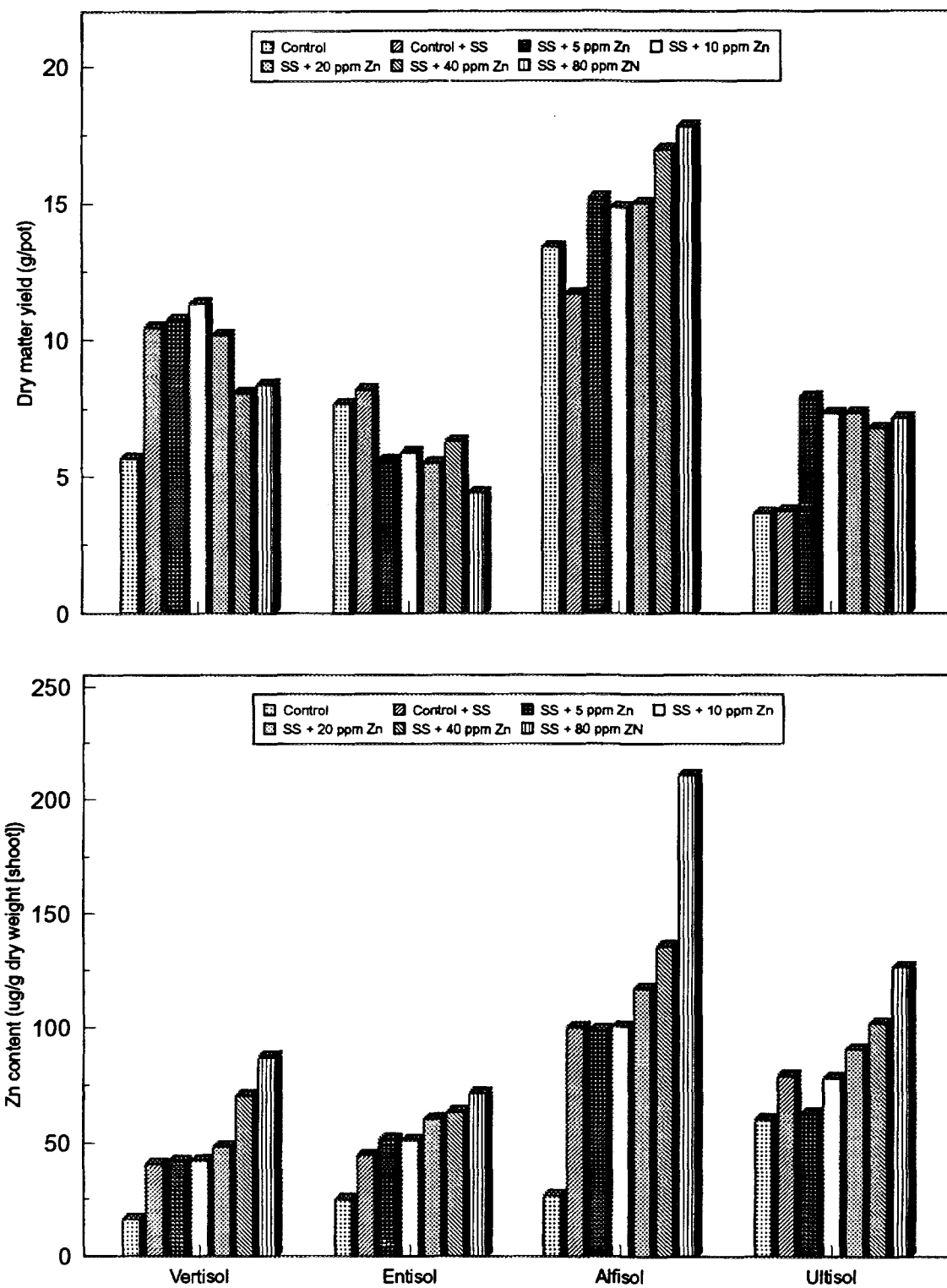


FIG. 2. Dry matter yields and zinc content of maize grown on four soils amended with zinc-enriched sewage sludge. (Bars denote LSD values, $P < 0.05$)

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EVALUATION OF HEAVY METAL CONTENT IN IRRADIATED SLUDGE, CHICKEN MANURE AND FERTILIZED SOIL IN INDONESIA

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Abstract

The contents of heavy metals, Hg, Cd, Cr, Cu, Ni, Pb, Zn and Co, were determined in two irradiated sludges, chicken manure and fertilized soil. Sludge I was collected from a treatment plant in Jakarta city, Sludge II from a sludge reservoir in a Jakarta suburb, chicken manure was obtained from a farm south of Jakarta, and the soil had been treated with phosphate fertilizer since 1967. The sludges and chicken manure were collected during the rainy and dry seasons, and the heavy-metal contents were determined by atomic-absorption spectrometry and neutron-activation analysis. The results obtained are compared with data from Canada, and are discussed in terms of permissible limits in the environment.

1. INTRODUCTION

The disposal of sewage is becoming a major problem in industrialized and developing countries because of increasing volumes of sludge and treated municipal wastewater (sewage effluent). Health risks and increasing concern for the environment call for alternatives in waste management. One of the most readily available methods of utilizing and disposing of these wastes is by application to crop land. However, with increasing industrialization and modernization, heavy metals and other toxic materials now contaminate municipal sewage materials, and it is becoming increasingly apparent that land application must be restricted to levels that will prevent ground- and surface-water pollution and accumulation of toxic substances in the environment [1]. Sewage sludge contains xenobiotic chemicals and heavy metals that can accumulate in the soil and then be taken up by crops, which, in turn, may become toxic to humans. The levels of these toxic substances in a sludge depend very much on its origin.

Due to free-radical formation, the radiolysis of sludge may alter the form and distribution of heavy metals contained therein. It is known that metals in sludge are generally present as mineral particulates and colloids, due to cation exchange, sorption, precipitation as carbonates, phosphates and sulphides, complex formation and chelation. Irradiation produces high-energy excitation and ionization of molecules, lethal penetration of cell tissue and the formation of free radicals that create strong oxidation conditions in the sludge matrix [2, 3].

In Indonesia, sewage sludge and chicken manure are being used to provide nutrients for crops and animal feed. To ensure safety, toxic substances must be kept at acceptable levels. At present, there is no specific regulation governing the use of sludge or chicken manure as fertilizer in Indonesia.

This report examines the heavy metals in two irradiated sewage sludges collected from the city of Jakarta and its suburbs, and also in chicken manure, phosphate fertilizer (triple super phosphate [TSP]) and fertilized soil. The concentrations of heavy metals, determined by atomic absorption spectrometry and neutron activation analysis, are shown in Table I [4, 5, 6, 7].

TABLE I. HEAVY METAL CONCENTRATIONS IN SEWAGE SLUDGE, CHICKEN MANURE, PHOSPHATE FERTILIZER AND FERTILIZED SOIL

Sample	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Co
	(ppm)							
Sludge I	2.50 ^a ±0.10	1.52 ±0.40	13.4 ±1.1	100 ±10.0	14.2 ±10.0	18.0 ±12.0	630 ±20.0	20.0 ±0.02
Sludge II	1.35 ±0.09	0.88 ±0.20	10.4 ±0.30	50.0 ±2.0	14.4 ±0.4	12.8 ±1.2	450 ±60.0	24.4 ±2.4
Chicken manure	0.03 ±0.01	0.51 ±0.88	0.06 ±0.08	30.0 ±2.0	15.7 ±1.3	0.01 ±0.01	250 ±10.0	ND ^b
P fertilizer	0.09 ±0.01	8.4 ±5.8	0.27 ±0.13	10.2 ±5.5	15.4 ±7.9	4.6 ±1.4	240 ±100	2.51 ±1.7
Fertilized soil	-	2.76 ±0.10	86.9 ±33.9	21.3 ±5.5	22.0 ±2.0	29.9 ±3.3	22.2 ±1.06	50.9 ±44.2
Permissible conc. in soil	-	1.00	250	2- 100	3- 1000	2- 2000	10- 100	1- 13

^aMean ± standard deviation (n = 5).

^bNot detected.

1.1. Cadmium

There is no evidence of an essential role of this element in plant growth. Cd is readily absorbed and consequently is detectable in most plants. Soil contamination with Cd is believed to be a serious health risk. The concentration of Cd in top soil is high in the vicinity of Pb and Zn mines (2-144 ppm) [8]. Sewage sludge and phosphate fertilizer are also important sources of Cd. The maximum permissible rate of Cd addition to soil depends on the soil pH. At high pH, Cd exhibits higher mobility than in acid environments. The background value of Cd in soils is usually between

0.07 and 1.10 ppm, and should not exceed 1.5 ppm [8]. Cd content in the sludge collected from the treatment plant in Jakarta city (Sludge I) was 1.52 ppm and 0.88 ppm in the sludge reservoir in a Jakarta suburb (Sludge II). The mean concentrations of Cd were 1.20 ppm in the sludge, 0.51 ppm in chicken manure, 8.37 ppm in phosphate fertilizer, and 2.76 ppm in fertilized soil. The sludge and chicken-manure levels were lower than those reported for sludges Canada (Table II). The risk of high absorption of this metal by plants can be controlled by using a low amount of sludge in the soil-sludge mixture.

1.2. Copper

Copper is very soluble and its ions are released in acid environments. Therefore, it is among the more mobile of the heavy metals. Contamination of soil results from utilization of Cu-containing fertilizer in agriculture or from municipal wastes or industrial emissions. Another possible source is the corrosion of Cu alloys (electric wires, pipes etc.).

The addition of Cu to cultivated soils through fertilizer, chemicals and waste has recently been extensively investigated. The most important aspect of Cu contamination is its accumulation in surface soils. The threshold value of 100 ppm Cu has been exceeded in several cases [8]. In root tissue, Cu is found in complexed forms, although it is most likely to be taken up in dissociated forms. In this investigation the concentrations of Cu in Sludge I, Sludge II, chicken manure and fertilized soil were 100, 50, 30 and 21 ppm, respectively. Although the Cu levels in the sludges and chicken manure were higher than in the phosphate fertilizer (10 ppm), they were generally lower than those reported for soil and sludges in Canada (Table II).

TABLE II. HEAVY-METAL CONCENTRATIONS IN SOIL AND SLUDGES IN CANADA [2]

Sample	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Co
	(ppm)							
Soil	0.01- 0.3	0.0- 0.7	3- 3000	2- 100	10- 1000	2- 200	10- 300	-
Sludge	0.1- 50	3- 3000	40- 8800	200- 800	20- 5300	120- 300	700- 4900	- -
Sewage sludge	-	<0.5	24	335	9.7	88	151	1.7

1.3. Lead

The natural Pb content of soil originates from the parent rock. All soils are likely to contain it, especially in the top horizon. There are much data available in the literature on soil Pb, but it can be difficult to separate background levels from anthropogenic amounts in surface soil. Davies [9] stated that 70 ppm is an upper background limit for Pb in normal soils.

Lead is not an essential element, although it is found in all plants. Some species tolerate high levels, whereas others show retarded growth at 10 ppm in solution-culture studies. The concentrations in Sludge I, Sludge II, chicken manure and fertilized soil were 10.0, 12.8, 0.01, and 19.9 ppm respectively - i.e. higher in the sludges than in phosphate fertilizer (5 ppm) but lower than reported by Chuaqui et al. [2] (Table II). The levels of soil Pb that are toxic to plants, not easy to predict, generally range from 100 to 500 ppm [8].

1.4. Mercury

The concentrations of Hg in Sludge I, Sludge II, chicken manure and phosphate fertilizer were 2.5, 1.35, 0.03 and 0.09 ppm, respectively. Levels were higher in the sludges than in phosphate fertilizer, but generally lower than levels found in soils and sludges in Canada (Table II). The accumulation of Hg in soil is controlled mainly by organic-complex formation and by precipitate formation. Mobility of Hg requires dissolution and biological degradation of organo-mercury compounds.

Sewage sludge and other wastes, and phosphate fertilizer are possible sources of Hg contamination in soil. The behaviour of Hg in soil is of interest since its ready bioavailability creates an important health hazard. It is readily taken up from solution culture and transported within plants. The affinity that protein sulphydryl groups have for Hg apparently is the key disrupting metabolic process. Toxic effects in young barley were observed at Hg levels of 0.01 ppm and a concentration of 3 ppm was severely toxic [10]. Volatilized elemental Hg and methylated derivatives are known to be very toxic for plants.

1.5. Chromium

The determination of total Cr (Cr^{+3} and Cr^{+6}) concentrations in the samples are shown in Table I. The sludge levels were higher than those of phosphate fertilizer and chicken manure, but again lower than those obtained by Chuaqui et al. [2] (Table II).

Chromium may accumulate in surface soil due to pollution from industrial wastes and municipal sewage sludge. The Cr added to soils is usually accumulated in a thin surface layer. There is no evidence of an essential role of Cr in plant metabolism, although low concentrations in soil may give positive effects on plant growth [11]. The Cr content in plants is controlled mainly by its soluble content in the soil, and although most soils contain significant amounts, availability to plants is often limited. The rate of uptake depends on several factors. Usually, roots and leaves retain more Cr than does grain. Anderson et al. [12] reported toxicity in oats with a Cr content of 49 ppm when grown in a soil containing of 634 ppm. Turner and Rust [13] observed symptoms of toxicity with as little as 0.5 ppm Cr in nutrient culture, and 60 ppm in soil culture. The toxicity of Cr depends on its oxidation state and on the presence of readily-available forms.

1.6. Nickel

Nickel content was 14 ppm in Sludges I and II, 16 ppm in phosphate fertilizer, 16 ppm in chicken manure, and 22 ppm in fertilized soil. Soil treatments such as addition of lime, phosphate or organic matter are known to decrease availability of Ni to plants. The beneficial effects of Ni on plant growth indicate that it has an essential function in plants [14]. Generally, the range of excessive or toxic amounts of Ni in most plant species is from 10-100 ppm [8].

1.7. Zinc

Zinc is easily adsorbed by mineral and organic components of most soil types, with background levels normally in the range 17 to 25 ppm [8]. The processes involved in Zn adsorption are not completely understood; in acid conditions it is controlled by cation-exchange sites, and in alkaline conditions by chemisorption and organic ligands. Soil organic matter is known to be capable of binding Zn in stable forms, therefore accumulation in organic soil horizons and in some peats is common. Soluble organic complexes of Zn that occur in municipal sewage sludges are mobile in soil and available to plants, and therefore can create environmental problems.

In plants, Zn plays a role in the metabolism of carbohydrates, proteins and phosphates, and in the formation of auxins, RNA and ribosomes. There is evidence that Zn influences the permeability of membranes, and that it stabilizes the cellular components of higher plants and micro-organisms. The levels of Zn in descending order were, sludges > phosphate fertilizer > chicken manure; they were generally lower than those recorded by Chuaqui et al. [a] (Table II).

1.8. Cobalt

Cobalt occurs in two states Co^{+2} and Co^{+3} , and may also exist as a complex anion $\text{Co}(\text{OH})_3$. During weathering, it is relatively mobile in oxidizing acid environments, but does not migrate in the soluble phase. Its mobility is related to the kind of organic matter in the soil. Cobalt concentrations usually range from 3 to 15 ppm. It can be taken up through the cuticle into the leaf; therefore foliar application in solution is effective in the correction of Co deficiency.

In legumes, Co deficiency inhibits the formation of leghaemoglobin and hence N_2 fixation. When taken up in excess by roots, it moves in the transpiration stream resulting in an enrichment at leaf margins and tips: common toxicity symptoms are white necrotic foliar margins and tips. Kitagishi et al. [15] reported that the addition of 25 and 50 ppm of Co to the soil was toxic to rice plants. The Co content in Sludge I, Sludge II, chicken manure, phosphate fertilizer and fertilized soil are 20, 24, undetectable, 2.5, and 51 ppm, respectively. The concentrations of Co in the sludges were higher than those in the chicken manure, the phosphate fertilizer, and the soil (Table 1).

2. CONCLUSIONS

Except for Ni, the heavy-metal levels in the sludges were higher than in chicken manure. And the heavy-metal contents in the sludges were lower than those reported in Canada by Chuaqui et al. [2], although similar to those reported by Bates et al. [3]. The concentrations in the fertilized soils in Indonesia are still within permissible levels [16], except for Cd. Based on the data presented, sewage sludges can be safely used to increase and sustain soil fertility and crop production in Indonesia.

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POTENTIAL HARMFUL EFFECTS ON AGRICULTURAL ENVIRONMENTS OF SEWAGE SLUDGE UTILIZATION AS A FERTILIZER

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Abstract

There can be harmful effects of sewage-sludge utilization in agriculture. However, these can be overcome by treatment of the sludge and by appropriate farm-management practices. Sewage sludge is of increasing potential importance to farmers because of its value as a fertilizer. But some compounds in sludge can be harmful for plants, animals and man. Heavy metals may be taken up by plants, and the higher the content in the soil, the greater the uptake. There are substantial differences in heavy-metal accumulation and tolerance among plant species. With respect to pathogens (for example *Salmonella*) in sludge, recent developments in decontamination processes can provide greater guarantee of preservation of the environment. Gamma-radiation treatment at a dose of 3 kGy has been proven effective. The use of sewage sludge in agriculture is attractive from the economical and environmental points of view. It is therefore important that farmers are provided not only with more information about the nutrient effects, but also about risks, if any, of leaching of heavy metals and microbial contamination to groundwater. To achieve this, there must be close co-operation between farmers and the authorities responsible for disposal of sewage sludge.

1. INTRODUCTION

In 1989, the Ministry of Agriculture of the Federal Republic of Germany announced that cultivation of arable land should deliver unpolluted agricultural products of high nutritional quality. An ordinance established limits for microbial pathogens and heavy metals in sewage sludge, to eliminate risk of soil contamination and danger to public health.

Within a co-ordinated program organized by the Federal Ministry of Research and Technology, nine German institutes dealing with soil science, plant production and soil biology worked together for several years, investigating the effects of long-term sewage-sludge application. The behaviour of heavy metals was followed in 14 field trials and pot experiments over 4 years, using 13 plant species. The results of these experiments are summarized here.

2. HARMFUL EFFECTS OF SEWAGE SLUDGE APPLIED TO SOIL

Before sewage sludge can be applied to agricultural soil, determination of heavy-metal content is necessary. Soil analyses have to be repeated after 10 years, and sewage-sludge analyses twice a year. The guidelines of the German sewage-sludge ordinance are in Table I. By taking into account the natural concentrations of heavy metals in the soil in conjunction with the amounts of sewage sludge added (5 t dry matter/3 years/ha), uptake by plants and other losses, it is possible to calculate the time required to reach limits set by law, as shown in Table II. The time period over which sewage sludge can be applied before limits are reached can be hundreds of years. It must be mentioned that during this time the soil is not considered to be contaminated, and the farmer continues to produce crops without concern over safety and quality. The land area on which sewage sludge is used in Germany is relatively small. Even if all sewage sludge in Germany were used in agriculture, it would cover only 7% of the arable land.

Sludge also contains organic pollutants, such as the polychlorinated biphenyls (PCBs), dioxins and furanes depending on the origin of the sewage [1]. At present there are no limits set for the levels of such organic chemicals in soil. Many trials have indicated that uptake of xenobiotic compounds by plants is small. But such investigations are plagued by difficulties, with results dependent on many and varied factors. In one case, a farmer applied sewage sludge for more than 30 years, with little effect on the soil and no dioxins or furanes found in food or milk. Another farmer with similar conditions showed increased concentrations of dioxin and furane in milk by a factor of three, and of PCBs by a factor of 2.3; these values were confirmed by hay analyses. These results indicate that farm-management methods are important. Because organic pollutants are increasingly important these days, it is necessary to monitor their accumulation in soil/plant/animal systems.

3. HARMFUL EFFECTS OF SEWAGE SLUDGE ON PLANTS

Heavy metals and organic pollutants are not readily translocated in soil. Concentrations may increase due to sewage-sludge application and they may be taken up by plants. In 1986, the German authorities (Bundesgesundheitsamt) fixed tolerance limits for agricultural and horticultural crops in order to assess heavy-metal problems with respect to some elements (Figs. 1 and 2).

The experiments showed that heavy metals are taken up by plants, depending on soil conditions, concentration in the soil, plant species and variety, and fertilization. The concentrations in plants differed from year to year and were negatively correlated with rainfall [2]. A relatively high pH and uniform rainfall-distribution minimized uptake.

No vegetable species showed high uptake of all heavy metals, and in no case did accumulation reach toxic levels. Celery is more sensitive to chromium and copper whereas carrot takes up more cadmium, chromium and copper (Table III, Fig. 1), and leeks use more chromium, copper and zinc. Different plant species accumulated heavy metals to different extents [2].

Because it is considered to be the most critical element, the impact only of cadmium is considered in detail here. Large species differences were found for cadmium uptake (Fig. 1). The relative affinity of some plant species for Cd differed according to whether the range of concentrations was 0.0-0.3 ppm or up to 7.0-7.5 ppm, although clear trends were found in wheat, oats, gather salad and celery. It is likely that some vegetable species reacted more to diverse soil conditions than to different heavy-metal contamination. For cadmium, a maximum of 10% of the amount applied was taken up in a 10-year rotation, and for zinc the figure was 15%. The other heavy metals showed very low levels of uptake.

The total content of a substance in soil can seldom be used as a criterion for estimating its biological or agricultural significance. The total amount in soil is distributed among soluble, exchangeable and complexed forms, as well as more-stable solid forms. Extraction with aqua regia overestimates the availability of heavy metals to plants. For cadmium, zinc and nickel, extraction with neutral salts (0.1N CaCl_2 or 1M NH_4NO_3) is more indicative. The following concentrations in soil can be considered as the tolerance limits for cadmium depending on the method of extraction [3]:

- Aqua regia extraction - 0.7 ppm
- Complex salt extraction - 0.23 ppm
- CaCl_2 extraction - 0.13 ppm

4. HARMFUL EFFECTS OF SEWAGE SLUDGE ON MAN AND ANIMALS

Sewage sludge may contain pathogens, therefore for safe reutilization in agriculture disinfection is necessary [4]. The conventional methods are, heat-treatment (pasteurization), composting and lime treatment, however, digested sewage sludge may still contain, for example, *Salmonella*, which can survive for long periods outside its native environment (Table IV), up to 350 days in dried plants, and up to 500 days in soil. Neither aerobic stabilization nor anaerobic digestion significantly reduced *Salmonella* contamination (Table IV). *Salmonella* infections have increased in Germany during the last 10 years [5, 6].

Salmonella was present in more than 80% of sewage-sludge samples tested from Switzerland, where increases of such infections in cattle were found during the grazing period from July to October. In epidemiological investigations, 13,877 samples confirmed the relationship between food poisoning and sewage-sludge use [6]. Therefore, application of sludge to grassland has been forbidden in Germany. Another problem is infection by *Taenia saginata*, a tapeworm causing disease in man and dogs. There is a report of a farmer using untreated sewage sludge on his farm, resulting in widespread distribution of the parasite with subsequent economical losses.

A new technique for sludge disinfection is radiation, with γ -rays or accelerated electrons. The first plant for γ -irradiation of sewage sludge has been in operation since 1973 in Geiselbullach, near Munich, Germany. Experiments there have shown that a γ -ray dosage of 3 kGy is sufficient to make sludge hygienically safe [7].

Another problem with the use of sewage sludge is transfer of heavy metals from amended soil to plant, and in turn to animal and man. Feeding experiments with naturally contaminated food stuff and with heavy metals have demonstrated accumulation in the kidney and liver, less so in muscle. No heavy metals were found in milk, therefore muscle and milk can be considered as filters for pollutants in animals [8].

Pigs fed with wheat grown in soil highly contaminated with cadmium (cadmium content 1.28 mg/kg dry grain) showed accumulation in the liver and the kidney (Table V). The cadmium content in muscle also increased in relation to total uptake, but the differences were not statistically significant. The excretion of cadmium by faeces was about 80% (71-88%) of the amount ingested. Feeding experiments with cattle and sheep showed similar results [3]. In all of the feeding experiments, no changes in weight were found even with highly contaminated fodder.

Besides heavy metals, pollution with organic chemicals is an important aspect to be considered for animals [1]. Experiments with fodder plants grown on sludge-fertilized soil showed indications of higher content of organic pollutants in milk; dioxin was detected and likely came from the contaminated soil through grazing, although uptake of chlorinated compounds through roots is low.

5. EFFECTS OF SEWAGE-SLUDGE APPLICATION ON LEACHING OF HEAVY METALS TO GROUND WATER.

Ground water can be contaminated with pathogenic organisms as well as chemical pollutants. Application of municipal wastes and agricultural chemicals to soil are two of the most important sources of such contamination. Surface waters in lakes or rivers have similarly become contaminated, often through direct discharge of municipal, industrial and agricultural aqueous effluents. Many of the pollutants are highly hazardous to man and, in a number of cases, they have been found to exceed legally permitted concentration limits. However, the extent of contamination can vary depending on

the source and the soil type [9]. In a field trial conducted in Germany with highly contaminated sewage sludge, surprisingly there was no leaching of heavy metals to the subsoil; the levels detected were below the legal limits set for drinking water (Table VI). The results showed that very little, if any, of the heavy metals leached to the ground water.

TABLE I. MAXIMUM ACCEPTABLE LEVELS OF POLLUTANTS IN SEWAGE SLUDGE AND SOILS IN GERMANY

Pollutant	Sewage sludge	Soil
	(ppm in dry matter)	
Lead	900	100
Cadmium	10 (5) ^a	1.5 (1)
Chromium	100	-
Copper	800	60
Nickel	1200	50
Mercury	8	1
Zinc	2500 (2000)	200 (150)
PCBs ^b	0.2	-
Dioxins/Furanes	0.0001	-
AOX ^c	500	-

^aValues in parenthesis refer to light soils, pH <6.0.

^bPolychlorinated biphenyls, per component.

^cOrganic halogen compounds.

TABLE II. HEAVY-METAL CONTENTS AND BALANCE IN SOIL TO A TILLAGE DEPTH OF 20 cm

	Cadmium	Lead	Zinc
Average concentration in soil (ppm)	0.33	26.6	71
Yearly addition from 1.67 t/ha sludge (ppm)	5	252	240
Yearly loss (g/ha)	1	63	140
Uptake by plants (g/ha/year)	2	8	200
Time to reach the limit in soil (years)	877	723	165

TABLE III. CHANGES IN HEAVY-METAL CONCENTRATIONS IN CARROTS GROWN OVER SEVERAL YEARS ON THE SAME SOIL

	Pb	Cd	Cr	Cu	Ni	Zn
	(mg/kg dry matter)					
1979	0.23	0.43	0.98	3.4	0.67	37
1980	1.68	0.35	0.19	3.0	0.67	19
1981	1.30	0.37	0.60	4.0	1.13	24
1985	2.90	0.54	0.14	3.3	1.02	18
1986	4.23	0.83	1.33	4.0	1.53	32
1987	0.34	0.26	0.21	3.3	0.56	26

TABLE IV. LEVEL OF CONTAMINATION OF DIFFERENT SEWAGE SLUDGES BY *SALMONELLA*

Sewage sludge type	Sample number per material	Samples containing <i>Salmonella</i>	Percentage
Untreated	49	45	92
Aerobically stabilised	25	25	78
Digested	138	113	82
Total sewage sludge	219	183	84

TABLE V. CADMIUM UPTAKE, AND CONCENTRATION IN THE ORGANS OF PIGS

	Animal group		
	I ^a	II ^a	III ^b
Average total cadmium uptake (mg)	58	208	327
Muscle (ppm)	0.0034	0.0044	0.0051
Liver	0.104	0.226	0.334
Kidney	0.41	1.02	2.19

^aTwelve animals.

^bTen animals.

**TABLE VI. CONCENTRATIONS OF HEAVY METALS LEACHING
FROM A HIGHLY CONTAMINATED SOIL pH 6.6 COMPARED
WITH DRINKING-WATER STANDARDS**

	In soil	In leaching water	Maximum acceptable in drinking water
	(mg/kg)	(ppm)	
Pb	1431	0.0008	0.04
Cd	47	0.0005	0.0005
Cr	279	0.003	0.05
Cu	367	0.052	-
Ni	78	0.01	0.05
Zn	1865	0.02	-
Mn	427	0.0014	-

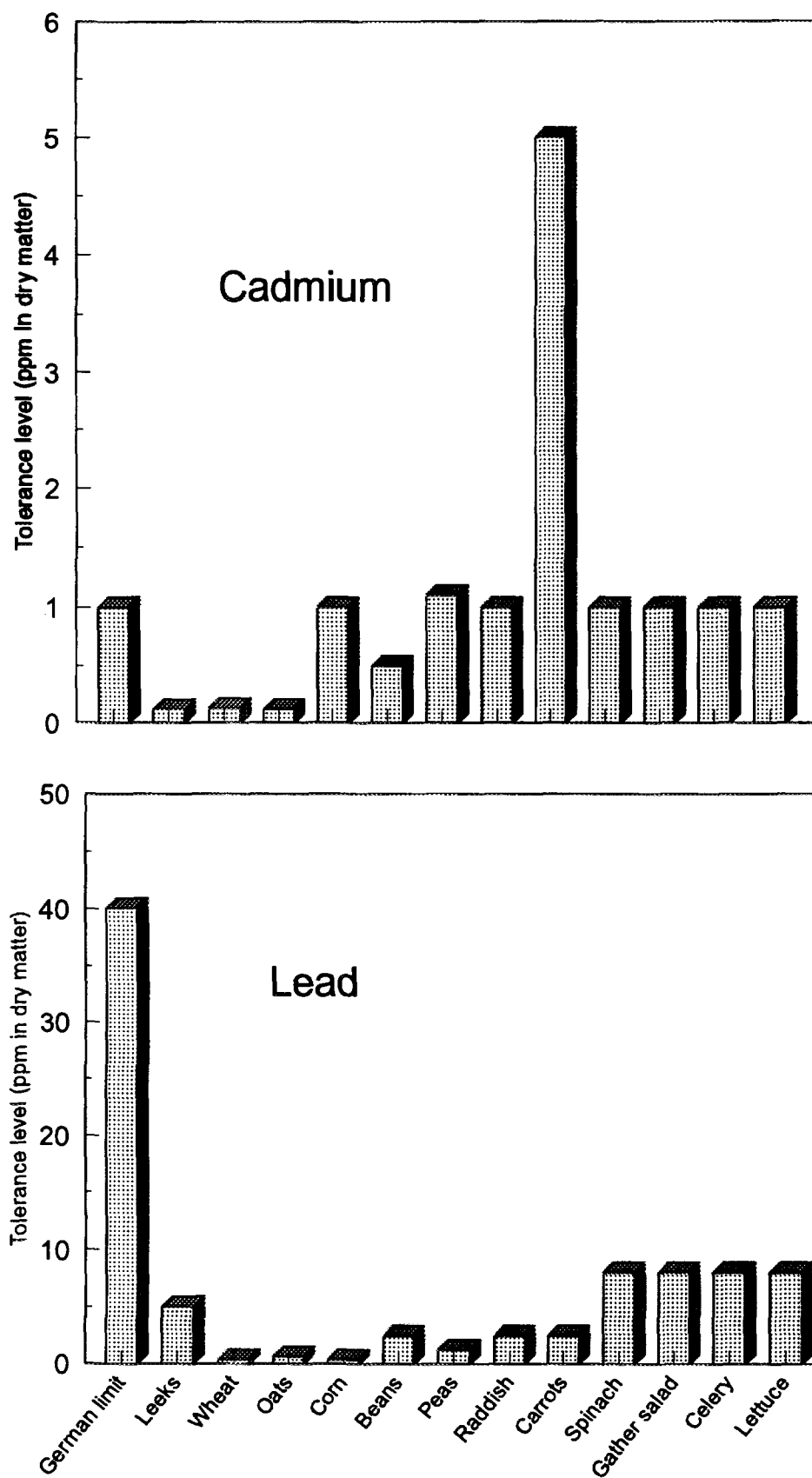


FIG. 1. Differences in crop species for heavy-metal tolerance - cadmium and lead

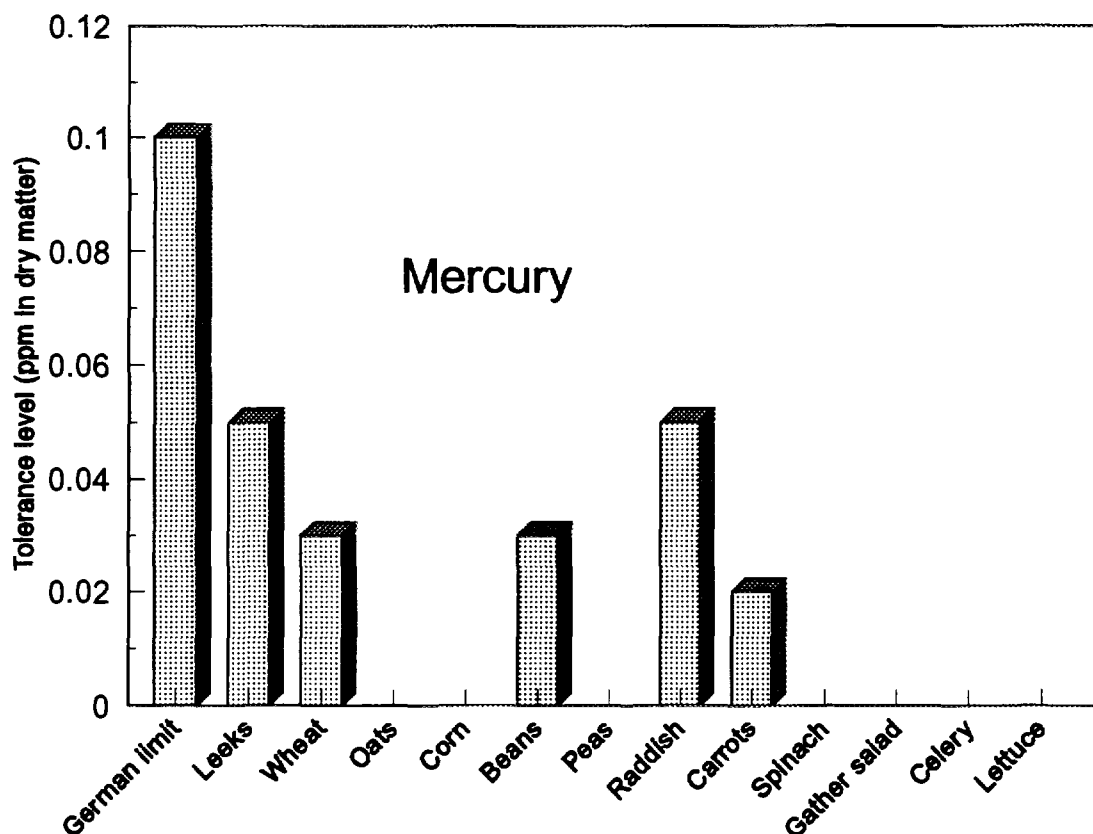


FIG. 2. Differences in crop species for heavy-metal tolerance - mercury

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SEWAGE SLUDGE DISPOSAL IN AUSTRIA

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Abstract

Sewerage systems serve about 70% of the Austrian population, producing 6 million m³ of sewage sludge per year with a dry matter content of 4-5%. At present about 52% of this sludge is disposed of in land fills, 33% is incinerated, and only about 15% is used in agriculture. Although agricultural utilization is becoming increasingly important, several problems, especially those related to public opinion, need to be resolved before increased use will be possible. In this paper, wastewater treatment and sewage-sludge production in Austria, and problems associated with sludge disposal are discussed.

1. INTRODUCTION

One of the most effective treatments for municipal wastewater is the activated sludge system: purification by microorganisms. The residue, along with the solid matter that originates from human metabolism, is sewage sludge. Currently there is no convenient means of disposal of sludge, it is a major problem for every treatment plant in Austria. As long as we are unable to find economically and ecologically rational solutions for sludge disposal, the problem of wastewater treatment remains to be solved. Preserving water quality is important even for a privileged country like Austria, situated as it is in an alpine region with relatively high precipitation. At present, the principal demand for drinking water is met by the Alpine sources, but with increasing population it is becoming necessary to use ground and surface waters. Therefore, wastewater treatment is of increasing importance for safeguarding these alternative water resources.

2. SEWAGE TREATMENT

2.1. Collection system

A little more than 70% of the Austrian population (about 5.6 million people) is served by a sewerage system. There are two different types of collection system:

- combined sewer system
- separate sewer system.

In a combined sewer system, storm water and sewage are collected together. In Austria, treatment plants are usually designed for a through-put of twice the dry-weather-flow (DWF). Surplus flow is diverted to the receiving stream by storm-water discharge systems. The discharge system type (overflow or retention tank) depends on the quality of the receiving stream. The initial, highly polluted flush water can be stored in a retention tank, and only subsequent less-polluted run-off water discharges into surface water. Thereafter, the content of the storage tank flows to the treatment plant. This means that pollutants from surface deposition, e.g. heavy metals, can reach the treatment plant and will be concentrated in the sludge. There are no data available on the magnitude of this effect, but investigations are currently in progress.

In separate sewerage systems, storm-water run-off is collected in a separate sewer and discharged directly into the receiving stream. Only wastewater flows to the treatment plant. This decreases the probability that pollutants from surface deposition will reach the treatment plant.

There is no current information available about the spread of these two collection systems in Austria, but in 1970 about 95 % of the population was served by the combined system. Since then, the number of autonomous sewerage systems also increased sharply.

2.2. Wastewater treatment

About 70% of wastewater is treated with biological systems: activated sludge systems, trickling filters, and rotating disc filters. This means that about 20 million population equivalents (PE) are treated in municipal and industrial plants. Since 1990, new wastewater-treatment regulations have been in force in Austria [1, 2]. Along with carbon removal, additional elimination of nitrogen and phosphorus is required. Due to a need for cost effectiveness and to abide by legal strictures, the multistage activated sludge system is now in most common use. An overview of recent technological developments is shown in Table I.

2.3. Sewage sludge

2.3.1. Sewage-sludge production

The treatment technology affects how much sewage sludge is produced. Teller et al. [3] estimated quantities produced by various treatment systems (Table II). In comparison to singular carbon removal, additional nitrification/denitrification diminishes the specific production of sewage sludge due to lower growth rates of nitrifying and denitrifying microorganisms.

TABLE I. DEVELOPMENTS IN MUNICIPAL SEWAGE TREATMENT

Rank	Regulative demands	Technology	Necessary facilities
1	Carbon removal	Biological degradation (oxidation theoretically to CO_2)	One aeration tank
2	Additional ammonia removal	Biological oxidation of NH_4 to NO_3	One long-term aeration tank (nitrification)
3	Additional nitrogen removal	Biological reduction of NO_3 to $\text{N}_2/\text{N}_2\text{O}$	Two tanks: nitrification and denitrification tank
4	Additional phosphorus removal	Luxury biomass uptake with respect to the energy metabolism and/or chemical precipitation	Three tanks: anaerobic tank and/or precipitation station, nitrification and denitrification tank

TABLE II. ANNUAL SPECIFIC SEWAGE-SLUDGE PRODUCTION
(DRY SOLID MATTER PER POPULATION EQUIVALENT) [3]

Treatment system	Sewage sludge production (kg/PE/yr)
C-removal	+ 12
N-removal:	
Nitrification, denitrification	- 2
P-removal:	
Simultaneous precipitation	+ 6
(flocculation and filtration)	(+ 5)
Total production	16
Primary sludge (primary settling tank)	15

In Austria, an annual sewage sludge amount of 6 million m³ with 4-5% dry solid matter (DSM) is produced. This means that about 300,000 tons DSM have to be disposed of every year. With a water content of 70% this amounts to a total of about 900,000 tons/yr.

2.3.2. *Nutrients and pollutants*

When considering agricultural utilization, it must be borne in mind that sewage sludge consists of water, solid matter, precipitation products, nutrients, microelements, heavy metals and organic pollutants. The ranges of these constituents, set out in Table III, are based on long-term investigations in different provinces [4].

2.3.3. *Sewage-sludge disposal*

Currently, most of Austria's sewage sludge is deposited in landfills (52%), and only 15% is utilized in agriculture. The amount incinerated is relatively high (33%) because all of capital city Vienna's sewage sludge is so treated at a central plant.

2.4. **Future outlook**

Up to an 85% increase in wastewater disposal is expected in the next several years. Treatment plants will be upgraded for more complete removal of nitrogen and phosphorus, which will further increase sewage-sludge production. The implementation of a phosphorus-precipitation step alone will increase production by between 15 and 20%.

It is expected that sludge production will double in the medium term [5]. On the other hand, disposal in landfill sites will be sharply restricted in future, by limiting the maximum permissible content of organic substances to approximately 5%. A pre-treatment by e.g. incineration will therefore be necessary. A 10-year transitional phase is scheduled. However, it is not expected that the necessary incineration capacity will then be available, and so a large increase in agricultural utilization is likely in the near future.

TABLE III. SEWAGE SLUDGE CONSTITUENTS [4]

Parameter	Unit	Range		Most frequent value	Limits for Lower Austria Class III (Class II)
		From	To		
Dry solid matter	%	0.2	99.8	7.9	
Organic substance	(% DSM ^a)	1.5	91.3	5.4	
Nitrogen		0.3	38.5	3.9	
P ₂ O ₅		0.2	24.2	3.0	
K ₂ O		0.04	6.5	0.6	
CaO		0.06	65.4	8.1	
Copper	(mg/kg)	12	4310	190	500 (300)
Zinc		18	14370	1320	2000 (1500)
Lead		5	19150	145	400 (100)
Chromium		5	97600	64	500 (50)
Nickel		2	1840	37	100 (25)
Arsenic		0.1	54	4	
Mercury		0.01	460	2	8 (2)
Cadmium		0.1	285	3	8 (2)
AOX ^b	(mg/kg)	78	1000	200	500
PAH ^c (3,4 BP)	(µg/kg)	n.n.	7700	260	
PCB ^d (6 Cong.)		60	1836	570	1200
PCDD ^e		25	2670		100

^aDry solid matter.^bAdsorbed organic halogens.^cPolycyclic aromatic^dPolychlorinated biphenyls.^ePolychlorinated dibenzo-p-dioxin.

hydrocarbons

3. TREATMENT SYSTEMS AND SLUDGE QUALITY

The amount of sludge produced and its quality depend on the wastewater- and sludge-treatment systems. In this section, the relationship between phosphorus removal/sludge stabilization and sludge amount/nutrient content will be described. The data are from investigations on two treatment- plant systems conducted by the Department of Sanitary Water Management, Technical University of Vienna [6].

3.1. Specific sludge production

Sewage sludge can be viewed as a mixture of organic and inorganic substances. The organic matter consists mainly of products of human metabolism and microorganisms from the activated sludge system. The inorganic component consists of the wastewater and additives for precipitation and sludge stabilization, e.g. lime.

Specific sludge production per PE depends on the treatment system (Table IV). The average can be estimated at 20 kg DSM/PE/yr. The organic solid component constitutes about 50% of the total dry matter.

3.2. Specific nutrient content

The specific nutrient content of sewage sludge also depends on the composition of the wastewater and on the treatment system (Table V). The average specific nutrient content (per PE and year) is approximately 7.5 kg organic matter, 0.5 kg nitrogen and 0.5 kg phosphorus.

4. UTILIZATION OF SEWAGE SLUDGE

As previously described, sludge utilization is becoming increasingly important in Austria [5]. However, public opinion and official agricultural policy are at odds with this trend: sewage sludge is considered to be a poison. Consequently, work has to be done to remove this prejudice. One step in this direction is to decrease the concentration of pollutants by introducing new legal restrictions. Another, in parallel, is a program to find out where pollutants originate and eliminate them, and to demonstrate the advantages of sludge utilization in pilot projects.

TABLE IV. RANGE OF SPECIFIC DRY SLUDGE PRODUCTION PER POPULATION EQUIVALENT AND YEAR

Sludge-treatment system	Wastewater-treatment system	Specific sludge production (kg/PE/yr)
Extended stabilization	Conventional system	15 - 20
	Additional P-removal	20 - 25
Simultaneous aerobic stabilization	Conventional system	20 - 25
	Additional P-removal	25 - 30

TABLE V. RANGE OF SPECIFIC NUTRIENT CONTENT PER POPULATION EQUIVALENT AND YEAR [6]

Sludge-treatment system	Nutrient	Specific nutrient content (kg/PE/yr)
Extended stabilization	Organic matter	5.5 - 7.5
	Nitrogen	0.4 - 0.5
	Phosphorus	0.4 - 0.5
Simultaneous aerobic stabilization	Organic matter	7.5 - 11
	Nitrogen	0.5 - 0.8
	Phosphorus	0.4 - 0.5

4.1. Austrian regulations

In Austria, sewage-sludge utilization is regulated by provincial soil-protection laws [6]. The maximum concentrations for pollutants in soil and sewage sludge, and permissible application rates per ha are defined. The permissible rates range from 1.25 to 5.0 tons DSM/ha/yr. Some provinces, such as Carinthia, Salzburg, Tyrol and Vienna, have not yet introduced any such regulations, and there is on-going discussion as to whether or not to institute a general ban on sludge utilization in agriculture. The limits differ little among the provinces, and are generally lower than those set by the European Union (Tables VI and VII). Burgenland and Lower Austria have set two Quality Classes (Table VII). No soil analysis is necessary in Burgenland when the sludge quality is within that of Class 1. In Lower Austria, Class III limits will apply until the year 2004 at the latest, from which time Quality Class II will be enforced for agricultural use.

4.2. Model of lower Austria

The province of Lower Austria has tried to increase sewage-sludge utilization for many years, but without much success. Since 1993, efforts have been made to improve sludge quality, the main thrust of which is a change from the philosophy of disposal to a philosophy consistent with sustainable development. The chief aspects of this program are:

- A new sewage-sludge utilization regulation.
- Measures to improve sludge quality.
- Establishment of a "liability fund" to ensure against unknown risks.
- Institution of several pilot projects.

The new regulation sets higher limits for heavy metals and new limits for organic pollutants, and introduces three classes of sludge quality. Quality Class III, with higher limits, will be permitted only for the next ten years. Then, Class II will be enforced, and eventually target Class I. Quality Class I is defined in terms of usual regional soil qualities. To reach Class II limits, most treatment plants in Lower Austria will have to decrease the concentrations of pollutants. Therefore, effluent analysis will be needed and appropriate technologies installed. These are being worked out.

4.3. The Mödling pilot project

The catchment area of the wastewater treatment plant in Mödling consists of eight communities with a total population of 50,000. It encompasses rural communities, settlement districts, and commercial and industrial zones, producing typical municipal wastewater.

The Mödling plant was built to take a load of 100,000 PE. Its technological capacity for nitrification, denitrification, biological phosphorus-elimination and phosphorus-precipitation concurs with the Water Regulation Act (Wasserrechtsgesetznovelle) of 1990. The wastewater flows to the treatment plant through two main sewers in Brunn and Mödling. The Brunn sewer belongs to the combined system, whereas the Mödling is separate.

Technically, it is an activated sludge plant with two anaerobic tanks for biological phosphorus elimination, two connected activated sludge tanks with simultaneous denitrification, and three final clarification basins. Additionally, it is possible to precipitate phosphorus at the outflow of the activated sludge tanks. Pre-dewatering is carried out in rotary drum strainers with added polymers, and further dewatering is achieved with chamber-type filter presses and addition of ferric chloride and polymers.

Sewage sludge is stabilized usually by low aeration during denitrification following standard methodologies. During the simultaneous aerobic stabilization, the average oxygen concentration in the activated sludge tank is 0.5 mg L^{-1} . In practice at Mödling the transformation rates are insufficient to guarantee sludge-stabilization, which has led to considerable stench and problems in the course of handling.

TABLE VI. SOIL LIMITS (mg/kg) FOR SEWAGE-SLUDGE UTILIZATION

	EU ^a	Bgld ^b	Ktn ^c	NOE ^d	OOE ^e	Sbg ^f	Styria	Tyrol	Vbg ^g
Mercury	1-1.5	1.5	- ^h	1.0	1.0	-	2.0	-	2.0
Cadmium	1-3	2.0	-	1.5 (1) ^j	1.0	-	2.0	-	3.0
Nickel	30-75	60	-	50	60	-	60	-	60
Cobalt	-	-	-	-	-	-	50	-	-
Chromium	-	100	-	100	100	-	100	-	100
Copper	50-140	100	-	60	100	-	100	-	100
Lead	50-300	100	-	100	100	-	100	-	100
Zinc	150-300	300	-	200	300	-	300	-	300

^aEuropean Union.

^bBurgenland.

^cCarinthia.

^dLower Austria.

^eUpper Austria.

^fSalzburg.

^gVorarlberg.

^hLimit not yet defined.

^jWhere pH < 6

TABLE VII. SEWAGE-SLUDGE LIMITS FOR AGRICULTURAL UTILIZATION

	Units	EU ^a	Bgld ^b		NOE ^c		OOE ^d	Styria	Vbg ^e
			Class 1	Class 2	Class II	Cls. III			
Mercury	(mg/kg)	16 - 25	2	10	2	8	7	10	10
Cadmium		20 - 40	2	10	2	8	5	10	10
Nickel		300 - 400	60	100	25	100	80	100	100
Cobalt					25	100		100	100
Molybdenum								20	
Lead		750 - 1200	100	500	100	400	400	500	500
Copper		1000 - 1750	100	500	300	500	400	500	500
Chromium			100	500	50	500	400	500	500
Zinc		2500 - 4000	1000	2000	1500	2000	1600	2000	2000
AOX ^f	(mg/kg)				500	500	500		
PCB ^g per congener	(µg/kg)				each 200	each 200	each 200		
PCDD/F ^h	(ngTE ⁱ /kg)				100	100	100		
Hygienic conditions (for grasslands only):									
<i>Enterobacteriaceae</i> (1/g FM ^k)					1000	1000			
<i>Salmonella</i>					0	0			
Nematodes					0	0			

^aEuropean Union.^bBurgenland.^cLower Austria.^dUpper Austria.^eVorarlberg.^fAdsorbed organic halogens.^gPolychlorinated biphenyls.^hPolychlorinated dibenzo-p-dioxin and -furane.ⁱToxicity equivalent.^kFresh matter.

Toxic substances found in Lower Austrian Quality Class III sewage sludge in the last two years are summarized in Table VIII. According to the existing legal standards, this sludge can be applied to agricultural land. However, the production of Quality Class III sludge will be permitted only until the year 2004, and thereafter it must concur with the more rigorous criteria of Quality Class II (Table VII). For this reason, a comprehensive programme entitled "Agricultural Application of Sewage Sludge" is being developed (Fig. 1). A detailed system analysis of the catchment area will be made, with comprehensive and precise investigations of the sewage. Pilot compostings of sludge are being set up, and the effects of sludge and compost compared with commercial fertilizers in

TABLE VIII. HEAVY METALS AND TOXIC ORGANIC SUBSTANCES IN QUALITY CLASS III SEWAGE SLUDGE FROM THE WASTEWATER-TREATMENT PLANT IN MÖDLING (100,000 POPULATION EQUIVALENTS)

Parameter	Unit	n	Average value	Standard variance	Minimum	Maximum
Zinc	(mg/kg)	14	1139	185	815	1450
Copper		14	253	47	161	324
Chromium		14	77	11	61	102
Lead		14	128	30	73	185
Nickel		14	36.0	9.3	23.3	53.0
Cobalt		14	4.2	1.1	2.3	6.2
Cadmium		14	5.7	4.0	2.4	16.9
Mercury		14	2.4	0.8	1.0	4.2
AOX ^a	(mg/kg)	6	338	119	173	470
PCB ^b :						
PCB 101	(µg/kg)	6	14	6	5	21
HxCB 138		6	36	16	12	55
HxCB 153		6	38	17	14	61
HpCB 180		6	33	18	14	58
TriCB 28		5	17	10	1	26
TeCB 52		4	20	20	1	48
Total-PCB		6	201	106	95	401
PCDD/F ^c	(ng TE ^d /kg)	6	6.9	3.8	2.9	11.9

^aAdsorbed organic halogens.

^bPolychlorinated biphenyls.

^cPolychlorinated dibenzo-p-dioxin and -furane.

^dToxicity equivalent.

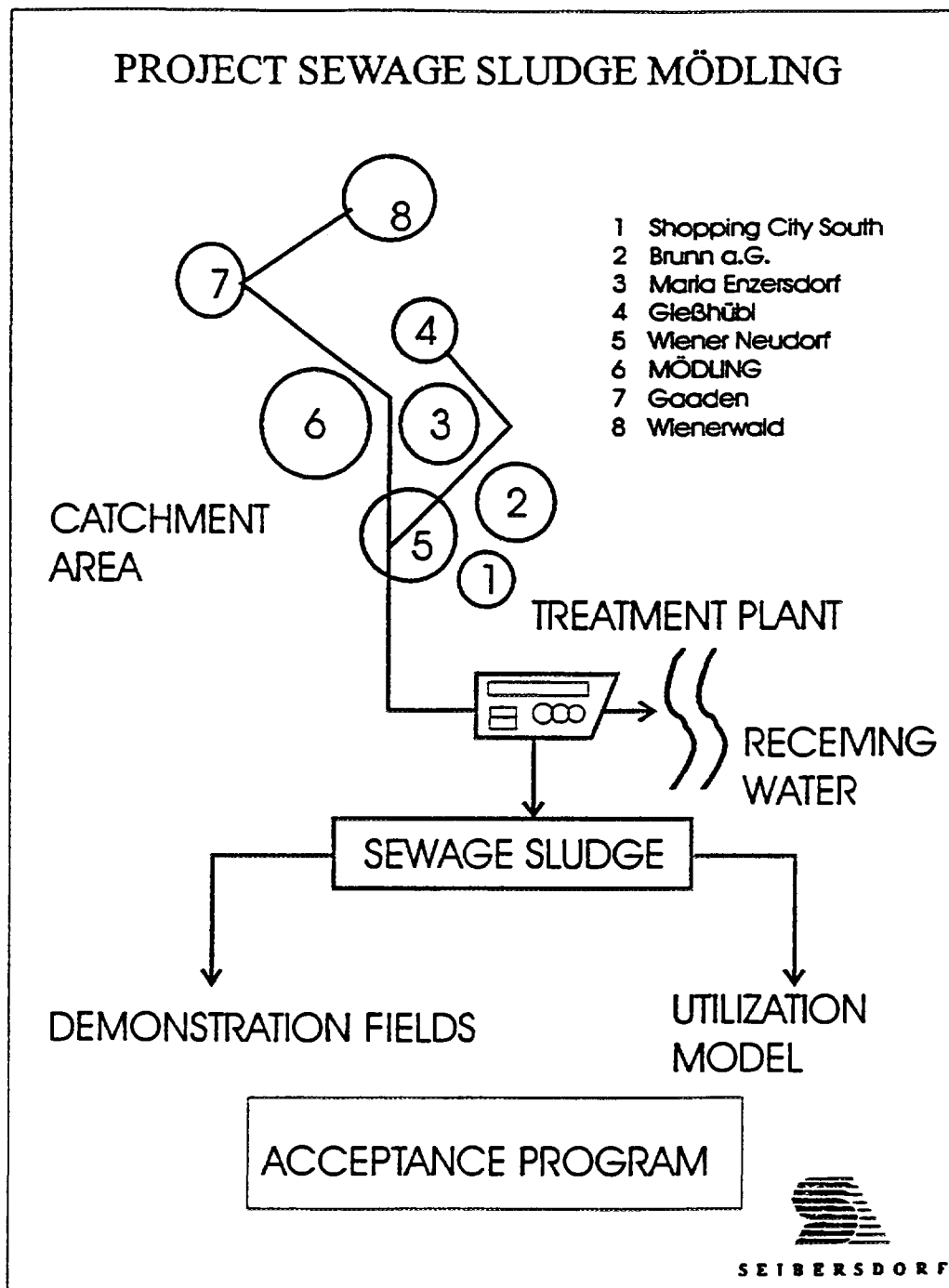


FIG. 1. Sewage-sludge pilot project in Mödling.

demonstration trials. Information will be disseminated, for example listing toxic substances that must not be added to wastewater, to improve public consciousness of problems, and to foster acceptance by target groups of disposal/utilization on agricultural land. Some aspects of the development of technical and public relations components of the project are described below.

4.3.1. Composting

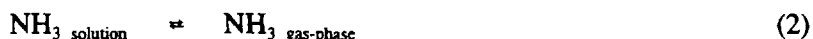
Through composting, the organic substances in sewage sludge are transformed into a stable, plant-friendly, humus-like substance. The benefits from compost lie, on the one hand, in improving

soil structure, bringing stabilization of texture, better aeration, and improved moisture-holding capacity. On the other hand it decreases nutrient loss, prevents nutrient leaching, improves nutrient availability to plants, and has phyto-sanitary properties. In general, composting sewage sludge improves soil qualities and hygienic conditions.

Up to now, two composting experiments have been carried out. As expected, composting decreased the nutrient content of the sludge. Although the total amount of nitrogen remained the same, its chemical form was changed. The ratio of nitrate to ammonium exceeded 2, which is particularly appropriate for agricultural application. The most important nutrients, nitrogen phosphorus and potassium were present in the proportions 1 : 2 : 0.3.

The concentrations of toxic substances in a compost depend on their respective concentrations in the prior sludge. In general there are only insignificant changes in heavy-metal concentrations in the transformation from sludge to compost. At the beginning of the process their concentrations decrease due to overall increase in mass as a consequence of the addition of a substantial amount of straw. Later, however, because of decay, this effect almost disappears. Investigations of hygienic aspects show significant decreases in counts of reference *Enterobacteriaceae* microbes during composting.

In the second experiment, we attempted to further improve the hygienic state of the compost by optimizing temperature changes with time. Substantial ammonia emissions occurred, and the experiment had to be abandoned so as not to expose neighbouring residents. There were several possible reasons for these emissions. The Mödling treatment plant produces a sludge that is not fully stabilized. In the course of further decomposition, there is a rapid transformation of organic substances accompanied by an increase in temperature (Fig. 2). Moreover, the concentration of ammonium in this sewage sludge is high at 1.6%, well above the average of 0.75%. Under these conditions, the following chemical reactions can take place:



According to Equation (1) ammonium is in dissociative equilibrium with ammonia, through an ammonium hydroxide intermediate. The equilibrium can be shifted by change of pH or by alteration of temperature. In the course of the heating that accompanies decomposition, ammonia is emitted; the more rapid the temperature rise, the more intensive is the emission of ammonia. The process is amplified by the rapid microbial transformations that occur with the high organic content of the non-stabilized sludge. Equation (2) shows the prevailing liquid/gas equilibrium. When the amount of the gas phase decreases as a consequence of aeration, equilibrium is restored by additional release of ammonia from the liquid phase. Moreover, aeration brings about a reduction of the carbon dioxide in the decomposing organic material, in accordance with Equation (3), this causes a shift in equilibrium and transformation of ammonium carbonate to ammonium hydroxide. In turn, this increases the release of ammonia according to Equation (1). Therefore, the measures taken to improve hygiene conflict with the requirements for reducing stench and ammonia emission, making necessary a closed system with aeration for future composting.

4.3.2. Public-relations work

Initial opinion-surveys in the communities of the catchment area revealed no public or political interest in the topics of wastewater treatment and sewage-sludge disposal. The most important organ of communication is the community newspaper issued by the municipal administration. Other local methods of communications possibilities are seldom used and are of little account (Fig. 3).

Pilot Composting Mödling 1994

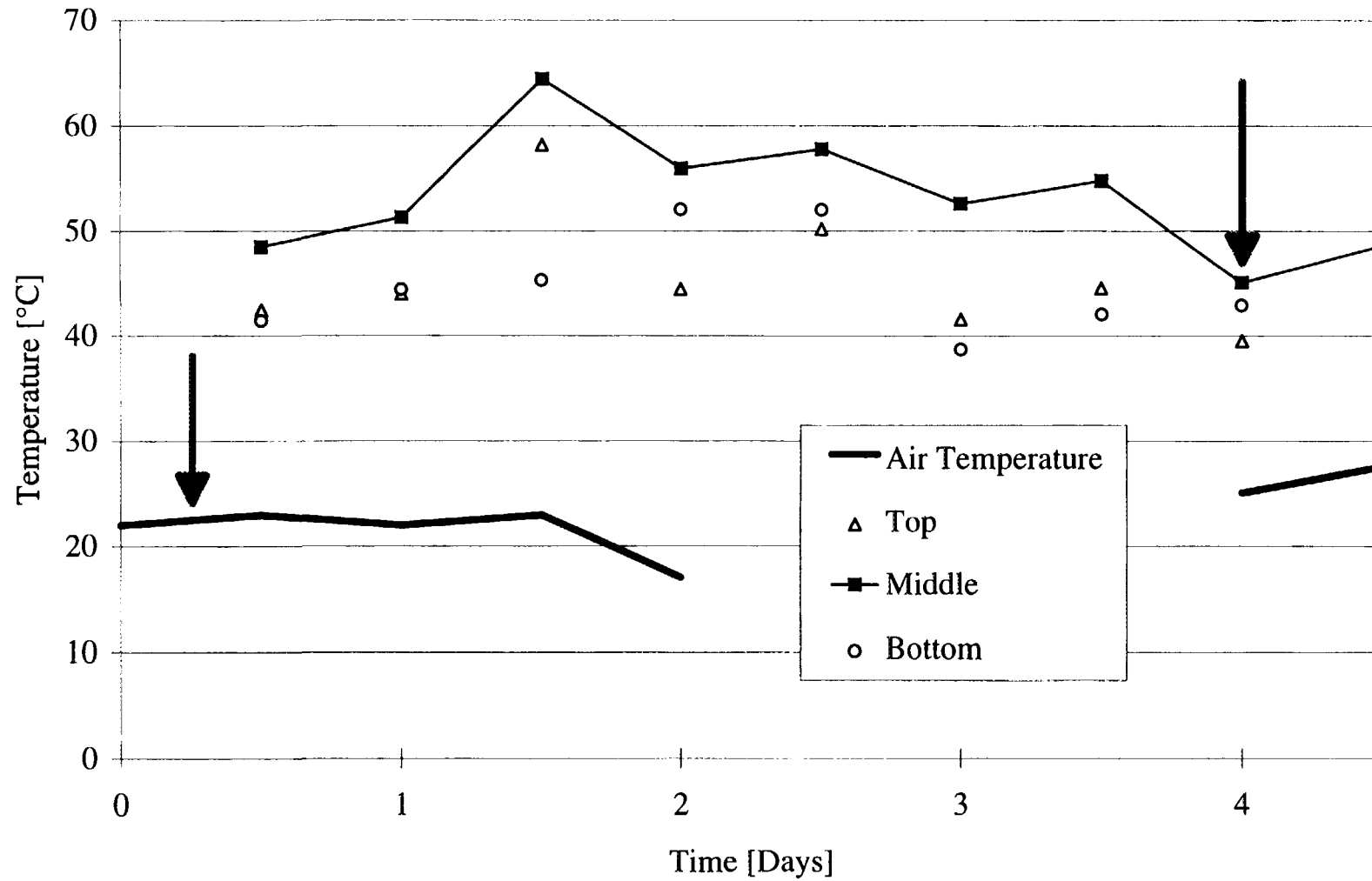


FIG. 2. Temperature as a function of time of composting (aeration introduced at arrows).

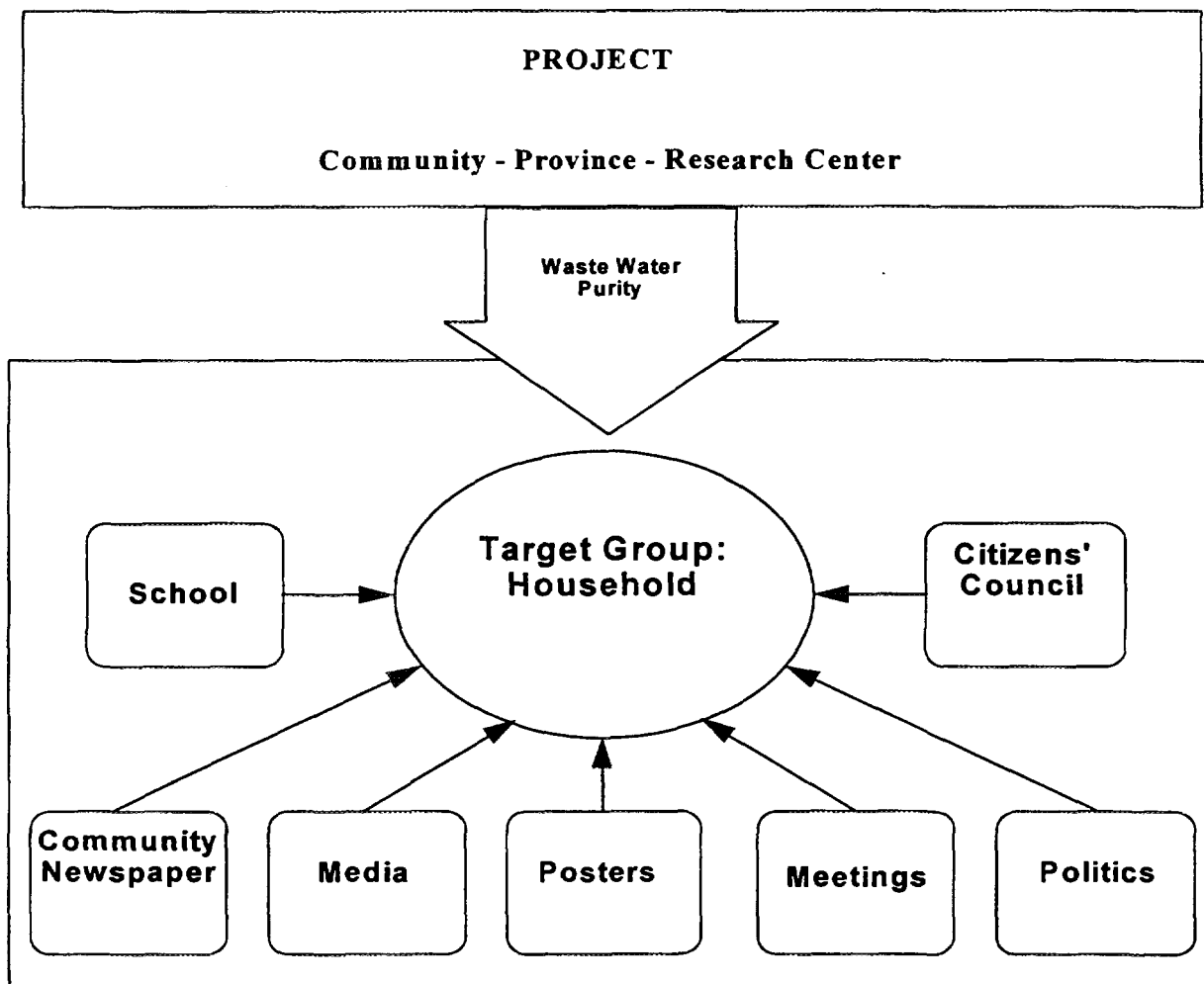


FIG. 3. An example of a target group: a household.

The municipal newspapers in the catchment area are of various types. Some offer exclusively service news, and only in the town of Mödling does the newspaper provide a platform for discussion. In the present case, there have been continual reports on the sewage-sludge project, and the citizens are now accustomed to reading "something related to sewage sludge." However, although it is thus possible to improve public awareness, it is more difficult to achieve improvement in wastewater quality. Therefore a long-term strategy was devised, utilizing the school system. A survey of textbooks for primary and secondary schools (ages 6 to 14 years) showed that the subjects of drinking-water quality and wastewater are touched upon only occasionally and then very restrictively. For this reason a teacher-oriented instruction brochure was published, directed principally at primary schools (ages 9 to 11 years) and dealing with water in general and with special reference to the impact of residual substances in wastewater. The test-period recently came to an end, and positive responses have led to the preparation of a province-wide edition.

Agricultural sludge utilization requires a measure of mutual understanding and confidence between farmers and sewage-treatment plants. Such confidence must be rebuilt to reverse past misunderstandings. An essential precondition lies not only in improving, but also maintaining the quality of the sewage sludge. By the enforcement of legal restrictions, significant improvements are

possible through technology. But, so-called background pollution can be reduced only by long-term educational work. Developing public consciousness of problems inherent in the preservation of water, the treatment of wastewater, and the disposal/utilization of sewage sludge is rather similar to doing so for recycling. Just as recycling has been successfully brought to public attention so can an awareness of wastewater. The Lower Austria model as well as the Mödling project are steps in the right direction, with positive responses from farmers. Ultimate success, however, will depend both on future detailed work and on the introduction of meaningful technical measures in the sewage-sludge processing.

Sewage sludge is a fertilizer and a soil conditioner. From the point of view of recycling and acceptable economies in agriculture, it must be applied continuously, like other commercial fertilizers. However, the disposal of biologically degradable substances has become a concern for present and future generations. The transition period of 10 years must therefore be used to develop alternative models acceptable to municipal councils and farmers, and, more importantly, with benefit for the environment.

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LAND APPLICATION OF SEWAGE SLUDGE: PATHOGEN ISSUES

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Abstract

Diseases transmitted via the faecal-oral exposure route cause severe gastroenteric disorders, and large numbers of causative organisms are discharged with the faecal matter of infected individuals. For this reason, pathogenic bacteria, viruses, protozoa, or helminths, are always found in sewage sludge. If not properly treated for use in agriculture, sludge can be a source of pathogenic contamination. Radiation is an attractive method to reduce the numbers of microorganisms in sewage sludge. Routine examination for pathogens is not practised nor recommended because complicated and costly procedures are involved. Instead, an indicator organism is usually assayed and enumerated. In this paper, methods are discussed for the investigation of pathogens in sewage sludge.

1. INTRODUCTION

Diseases of sanitary significance are transmitted via the faecal-oral exposure route by which causative agents are orally ingested, rapidly multiply in the intestinal tract causing severe gastroenteric disorders, and are discharged in large numbers with the faecal matter. Even after an infected individual has recovered from the illness, he/she may be a carrier of the pathogen for a long time. For this reason, pathogens - bacteria, viruses, protozoa, or helminths - are always found in domestic sewage and solid residuals of the treatment process, the sewage sludge. If these pathogens are not adequately separated, properly treated and disposed of, sewage and sewage sludge often become the sources of disease. With the frequency and volume of international travel nowadays, pathogens causing outbreaks of disease in one part of the world may appear in the wastewater of another part of the world in a very short time-span.

The pathogens found in domestic sewage and sewage sludge are numerous (Table I). The types present vary from community to community depending on prevalence of particular diseases among residents, population density, nature of the wastewater collection system, and season.

2. DETECTION AND ENUMERATION OF PATHOGENS

No single procedure is available to isolate, identify, and enumerate all pathogens simultaneously. To estimate the disease-causing potential of a sample, each pathogenic species must first be separated and identity confirmed using biochemical and/or microscopic techniques, and then enumerated. Microbiological Examination in Standard Methods for the Examination of Water and Wastewater, Part 9000 [1] outlines general procedures used by the water and wastewater profession

TABLE I. PATHOGENS IN SEWAGE AND SLUDGE

Group	Pathogen	Disease
Bacteria	<i>Salmonella</i> (> 1700 strains)	Typhoid fever, salmonellosis
	<i>Shigella</i> spp. (4 strains)	Bacillary dysentery
	Enteropathogenic <i>E. coli</i>	Gastroenteritis
	<i>Yersinia enterocolitica</i>	Gastroenteritis
	<i>Campylobacter jejuni</i>	Gastroenteritis
	<i>Vibrio cholerae</i>	Cholera
	<i>Leptospira</i>	Weill's disease
Protozoa	<i>Entamoeba histolytica</i>	Dysentery, colonoid ulceration
	<i>Giardia lamblia</i>	Diarrhea
	<i>Balantidium coli</i>	Diarrhea, colonoid ulceration
	<i>Cryptosporidium</i> spp.	Cryptosporosis
Helminths	<i>Ascaris lumbricoides</i>	Ascariasis (round worm)
	<i>Ancylostoma duodenale</i>	(Hook worm)
	<i>Necator americanus</i>	(Hook worm)
	<i>Taenia saginata</i>	Taeniasis (Tape worm)
Virus	Enteroviruses (strains)	
	Poliovirus (3)	Meningitis, paralysis, fever
	Echovirus (31)	Meningitis, diarrhea, rash
	Hepatitis Type A	Infectious hepatitis
	Coxsackivirus (33)	Meningitis, respiratory disease
	Norwalk virus	Diarrhea, vomiting, fever
	Calicivirus	Gastroenteritis
	Astrovirus	Gastroenteritis
	Reovirus (3)	Respiratory disease
	Rotavirus (2)	Diarrhea, vomiting
	Adenovirus (40)	Respiratory disease

for assaying the pathogens listed in Table I. Routine examination of water and wastewater for pathogens, however, is not practised nor recommended, because such examinations involve complicated procedures, require trained and experienced personnel and specialized laboratory facilities, and they are time consuming and costly.

Instead, an indicator organism is assayed and enumerated. Indicator organisms and pathogens inhabit the intestinal tract of warm-blooded animals and both types are present in faecal discharge. The ideal indicator organism has the following characteristics.

- It is present when pathogens are present, for example in sewage sludge, and always absent when pathogens are absent.
- Its density in the medium has a direct and constant relationship to pathogen densities.

- It is unable to reproduce in the media it contaminates.
- It survives in the foreign environment for at least as long as the pathogens.

As the indicator organism may be detected, isolated, and enumerated by simple, rapid, and economical assay-procedures, it is used routinely to indicate recent contamination by faecal discharge from warm-blooded animals, potential presence of pathogens, and efficiencies of water- and wastewater-treatment processes.

Faecal coliforms are most commonly used as indicator organisms. They are present in the gut and faeces of warm-blooded animals in large numbers, and are capable of producing gas from lactose in suitable culturing media at $44.5 \pm 0.2^\circ\text{C}$. Coliforms from other sources often are not capable of producing gas under these conditions, therefore this criterion is used to isolate the faecal component of the group. The survival characteristics of faecal coliforms and of some bacterial pathogens are similar in a water environment and during disinfection, whereas viruses, protozoon cysts, and helminth ova usually are more resistant to adverse conditions and frequently have greater longevity. Although direct and constant relationships between densities of faecal coliforms and pathogens do not always hold, experience has established the significance of coliform group density as a measurement of contamination and, therefore, of sanitary quality of water and wastewater.

With sewage sludge and sludge-treated soils, solids interfere with microbial determinations and it is essential that they are removed before assay. Procedures for handling high-solid-content samples are by no means standardized. Samples of low pathogen density are especially difficult, as the volume of sample required for a meaningful determination may be large.

3. PATHOGEN SURVIVAL

3.1. Irradiated sewage sludge

Experiments in irradiating sewage sludge were first done more than 40 years ago. Radiation technology has steadily advanced and has found application in disinfecting medical equipment and food, but it has not been widely adopted for wastewater treatment. The process involves exposing the material to γ -radiation to reduce its pathogen density. Cesium-137 and cobalt-60 are commonly used and are logical sources for such purposes. Alternatively, accelerated electrons may be employed for disinfection of sewage sludge.

Gamma radiation induces ionization in biological tissues resulting in the production of free radicals that cause denaturation of cell protoplasm. Membranes and cell walls may also be damaged, causing lysis. Most pathogens are single-cell organisms that are inactivated when cell protoplasm is damaged. In sewage sludge, pathogens account for a minute fraction of the mass, and are scattered throughout the entire volume of material. Unless every pathogen is exposed to the radiation and the absorbed dosage is adequate, the inactivation will not be effective. Mathematically, the reduction of pathogens in sewage sludge by radiation is a function of the absorbed dose and may be described by a first-order reaction equation.

The dosage of ionized radiation required for inactivation appears to vary with pathogen type and the moisture content of the sewage sludge. *Salmonella* species have D_{10} values as low as 0.25 kGy in sewage sludge (Table II; D_{10} refers to the radiation dose (kGy) required for a 90% reduction in organism density). However, the absorbed dosage would rise to almost 1 kGy for dried sludge if a 90% reduction of density were needed.

Greater ionizing radiation doses are required to inactivate parasite ova and viruses. Early investigators used as much as 10 kGy absorbed dosage to ensure inactivation of naturally occurring

TABLE II. RADIATION ABSORBED DOSAGE FOR INACTIVATION OF SELECTED BACTERIA IN SEWAGE SLUDGE [2]

Organism	Liquid (2-10% solids) (kGy)	Composted (40% solids) (kGy)	Dried (90% solids) (kGy)
Coliform group	0.2-0.3 ^a	0.2-0.3	0.15-3.5
<i>Salmonella</i> spp.	0.25-0.5	0.3	0.35-0.8
Faecal <i>Streptococcus</i>	1.2-1.5	1.2-1.5	0.7-3.6
<i>Mycobacter</i>	1.6-3.0	-	-

^aD₁₀ values: absorbed dose required for each 90% reduction in bacterial counts.

Ascaris ova in the filter cake of anaerobically digested sludge and in composted sludge [2]. The required dosage for an effective reduction of *Ascaris* ova is probably considerably less than 10 kGy. Other investigations showed that 1-1.5 kGy absorbed dose resulted in at least two orders of magnitude reduction in *Ascaris* ova in sewage sludge [3]. Horak [4] found that the viability of *Ascaris* ova started to decrease at a radiation absorbed dose of 0.5 kGy and no viable ova were observed at dose > 1.1 kGy. Although viruses are susceptible to adverse conditions in the environment such as high temperature, desiccation, and the presence of small amounts of ammonia (such as in anaerobically digested sludge), they have relatively high resistance to inactivation by ionizing radiation. Data in the literature reported a D₁₀ of 2.5 kGy for inactivation of viruses in sewage sludge. Due to the difficulty of recovering viruses from sewage sludge, such inactivation studies always involve tracking a large amount of virus that has been artificially introduced into the medium being investigated. The actual dose required to reduce a small amount of viruses in sewage sludge to an acceptable level probably is lower. In the opinion of radiation scientists, 3-5 kGy of ionized radiation is adequate to completely inactivate pathogens in sewage sludge [5].

3.2. Sludge-treated soils

The soil is a hostile environment for pathogens that inhabit the intestinal tract of warm-blooded animals. They fail to multiply and rapidly die off due to adverse conditions and microbial antagonism. Generally, unfavorable conditions for survival of pathogens in soils are: desiccation, high ambient temperature, acidic pH, and low organic matter content. Published data show die-off rate constants (number of days for log₁₀ reduction in organism density) for indicator organisms, bacterial pathogens, and viruses, ranging from 0.04 to < 10 [6]. At these rates, pathogens introduced in sewage sludge may be reduced to non-detectable levels in a 100- to 150-day crop-growing season (Table III) [7]. Few data are available on survival of protozoon cysts and helminth ova. For sludge deposited on the soil surface and not incorporated, a 30-day period is considered adequate to eliminate the hazards of transmitting parasitic diseases [8]. Because of their ability to resist adverse environmental conditions, cysts and ova incorporated into the soil may survive for extended periods of time (Table III).

Radiation reduces pathogen density in sewage sludge significantly, if not altogether. Any remaining pathogens would be expected to be weakened and to die off rapidly in the soil.

TABLE III. REPORTED PATHOGEN SURVIVAL TIME IN SOILS [7]

Organism	Time (days)
Coliform Group	38
Faecal <i>Streptococcus</i>	26 - 77
<i>Salmonellae</i> spp.	15 - > 180
<i>Salmonella typhi</i>	1 - 120
<i>Entamoeba histolytica</i> cysts	6 - 8
<i>Ascaris</i> ova	up to 7 years
Hook larvae	42
Enterovirus	8 - 175

4. PROTOCOLS FOR PATHOGEN-SURVIVAL INVESTIGATIONS

The effectiveness of ionizing radiation for disinfecting sewage sludge was demonstrated in the IAEA Co-ordinated Research Programme (CRP) (E3-40.03) on Radiation Treatment of Sewage Sludge for Safe Reutilization (May 1983 - July 1990). As for pathogen survival in the current CRP (D1-50.04) on The Use of Irradiated Sewage Sludge to Increase Soil Fertility, Crop Yields and to Preserve the Environment, initiated in July 1995, the objectives should be limited to:

- Compare the pathogen characteristics of irradiated and non-irradiated sewage sludges used in field experiments.
- Demonstrate that no pathogen accumulated in soil through repeated applications of irradiated sewage sludge.

Pathogen assays, however, require specialized laboratory facilities and a trained technician. As none of the participants of the current CRP has experience or is equipped to undertake pathogen determination, this part of the study should be kept to a minimum and be as simple as possible. Instead of attempting comprehensive pathogen determinations, participants should utilize local facilities where exist the necessary capability and expertise. Usually, public-health groups in universities (medical schools) and hospitals have access to laboratories that routinely perform pathogen assays. Participants should seek expert advice if they plan to conduct this phase of the work in their own laboratories.

4.1. Sampling procedures

Each participant is required to determine the density of faecal coliforms and *Ascaris* ova in sewage sludge to be applied to soil. The requirements are outlined as follows.

4.1.1. Sewage sludge

Because sewage sludge undergoes further changes following radiation, samples should not be obtained immediately following the irradiation process. Instead, samples should be obtained at the time of application to the experimental plots. One sample should be taken from the material going to each

experimental plot. As non-irradiated sewage sludge is also used in the experiment, comparable non-irradiated samples should be obtained. According to the previously agreed experimental design, there will be a total of 40 samples (note: the number of samples will vary depending on the number of treatments used) accounting for four replications of:

- control (no sewage sludge + ^{15}N labeled fertilizer at locally recommended rate, 1% a.e.),
- sewage sludge, 50% of recommended N rate
- sewage sludge, 100% of recommended N rate,
- sewage sludge, 150% of recommended N rate, and
- sewage sludge, 200% of recommended N rate for both irradiated sludge and non-irradiated sludge treatments.

Each sample should consist of approximately 500 g (in dry weight equivalent) if the material is in solid form or 500 mL if the material is in liquid form obtained from a composite of random grab samples. Samples should be refrigerated or stored in ice-packed coolers immediately and the pathogen determination should begin as soon as the samples are received at the laboratory. Noticeable changes in organism density and types have been reported in unrefrigerated samples, especially when the ambient temperature is $> 13^{\circ}\text{C}$. Samples of field moisture content are used in pathogen determination and no drying is needed. During the sampling, extraordinary caution should be exercised to prevent cross-contamination between irradiated and non-irradiated sludges (do not use the same sampling tool for irradiated and non-irradiated sludges, or sample the irradiated sludges first; transport and store irradiated and non-irradiated sludge samples separately; alert the personnel involved in handling samples and in determining pathogens of the need for separating these samples). It is also advisable that the sample taker should avoid direct contact with any sewage sludge and wash hands after handling the samples.

The pathogen determination for sewage sludges will be done only once during the entire 5-year experimental period.

4.1.2. Sludge-treated soils

Soil from plots receiving irradiated and non-irradiated sewage sludge will be sampled after the last crop of the experiment is harvested. This one-time sampling will involve only the experimental plots corresponding to the sewage-sludge sampling. The soil will be sampled from the surface to the depth of sludge incorporation.

The general procedures outlined in the previous section for obtaining and handling the sludge samples should be followed for soil sampling.

5. PATHOGEN ASSAYS

All of the samples used for pathogen analysis should be sieved to pass through a 2-mm screen to insure homogeneity of the sub-samples drawn for the determinations.

5.1. Faecal coliforms

The faecal coliform determination starts with an aliquot of approximately 64 g (dry weight equivalent) of sludge solids or 64 mL of liquid sludge. Each aliquot will be mixed and divided into quarters. One of the quarters will be selected for further sample subdivision and the remainder may be discarded. The sludge aliquot will be divided in this manner three times until approximately 1 g (dry weight equivalent) or 1 mL of sample is obtained.

The sample (1 g or 1 mL) is then diluted to a volume of 100 mL using sterile water, and appropriate series dilutions made for faecal coliform determinations. To avoid complications in filtering and developing a bacterial colony from high-solid suspensions, the multiple-tube fermentation technique should be used for the assay. The procedures for preparing the culture media, incubation, and enumeration may be found in Multiple-tube Fermentation Technique for the Coliform Group (Part 9221) in the Standard Methods for the Examination of Water and Wastewater [1]. The detection limit of this procedure is approximately 2 MPN per 1 g or 1 mL of sewage sludge. (MPN stands for most probable number, in this case of faecal coliforms, in a given unit of sample; it is a statistically derived estimation of cell density.) The data should be adjusted according to moisture content of the sludge and reported as MPN of faecal coliform per g sludge or soil dry weight.

5.2. *Ascaris ova*

This part of the assay starts with 320 g (dry weight equivalent) of solid sludge or 320 mL of liquid sludge. Using the previously described quartering technique, the material is divided three times to obtain a sample of approximately 5 g or 5 mL. If the sample is liquid, it is centrifuged at 2000 rpm for 5 min and the supernate discarded. The *Ascaris ova* will be recovered from the solids through successive flotation (the ova will float on the surface) using saturated NaNO₃ solution (density = 1.38g/mL). The recovered ova will then be incubated in Petri dishes with saline containing 0.8% formaldehyde for a period of 8 weeks. At the end of the incubation, viable ova (those able to embryonate) will be counted. The detectability of this procedure is approximately 0.2 ova /g or /mL.

Standardized procedures for isolation and enumeration of helminth ova in sewage and sewage sludge are not available. Textbooks on helminthology should be consulted for specifics in procedures for identifying ova and judging embryonation.

6. RECOMMENDATIONS

The results of pathogen determinations are procedure-dependent. For consistency of data and comparisons between sites, it is advisable that all participants follow the same general procedures and make only minor modifications to suit special local conditions. There are no data in the technical literature on pathogens in irradiated sludge-treated soils. It is possible that data from this CRP on "The Use of Irradiated Sewage Sludge to Increase Soil Fertility, Crop Yields and to Preserve the Environment" may be pooled and published in the future.

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SUMMARY AND CONCLUSIONS

The utilization and disposal of sewage sludge is a serious problem in many countries due to rapid urbanization. One solution is its use as an organic fertilizer for agriculture and horticulture. Sewage sludge has components essential for crop growth: macronutrients N, P, K, micronutrients Zn, Fe, Cu, Mn, trace elements, and considerable amounts of organic matter. However, it may also contain pathogenic organisms, heavy metals and other toxic materials from industry. Because of health risks, application of sewage sludge to agricultural lands is restricted. Health hazards posed by pathogens and helminths can be mitigated by the use of irradiation as a pre-treatment. There are sufficient technical data available at present for gamma treatment of sludges, permitting its application on the demonstration or commercial scale, but gaps in our knowledge still exist, especially for the practical application of electron beam technology.

Two Consultants meetings were held during the same week in December 1994 to address the problems of irradiation of sewage sludge and wastewater, and to investigate their use in agriculture.

1. CONSULTANTS MEETING ON IRRADIATION TREATMENT OF WATER, WASTEWATER AND SLUDGES

Sewage, wastewater and other aqueous effluents are usually contaminated with pathogenic microorganisms and protozoan parasites of human, animal or other origin, as well as with non-biodegradable (refractory) organic compounds originating from industrial or agricultural applications (herbicides, insecticides, fungicides, etc.). These contaminated solutions may percolate through certain soils and/or soil fissures into groundwater or be discharged, in principle after some remediating treatment, into surface-water reservoirs (lakes or rivers).

Studies in recent years have demonstrated the effectiveness of ionizing radiation as such, or in combination with other agents (ozone, heat, UV, etc.) in decomposing refractory organic compounds in aqueous solutions, and in effectively removing or inactivating pathogenic microorganisms and protozoan parasites.

The last Research Co-ordination meeting (RCM) of the Co-ordinated Research Programme (CRP) on Radiation Treatment of Sewage Sludge for Safe Reutilization, finalized in 1991, concluded that the biocidal effects of penetrating ionizing radiation doses constitute a reliable and quantifiable method of disinfecting sewage of the naturally high numbers of pathogenic bacteria, viruses and protozoa, as well as of moulds, and eggs and larvae of parasites. Radiation-induced physico-chemical changes in the sludge solids seem to improve settling and flocculation rate, while the radiation pre-treatment of sludge accelerates subsequent composting by eight- to ten-fold, and eliminates foul odor. It was also concluded that technology-scale experience with irradiated sludge has established its safe utilization as fertilizer, and soil conditioner.

In that CRP, radiation was characterized as a practical techno-economic alternative in the available wastewater treatment scenario, while an important combination treatment — oxy-radiation — has been demonstrated on a pilot scale, enabling reduction of the dose by one third.

The present Consultants meeting was convened in order to advise the Agency in regard to a new CRP aimed at complementing the former CRP by focusing on the irradiation treatment of water, wastewater and sludges, with particular emphasis on the effects of radiation and of combined treatments on the refractory organic pollutants. The overall objective of the meeting was to review the status of the technology of radiation processing of

water, wastewater and sludges, to evaluate the scientific and technological data gaps that require closing in order to facilitate industrial implementation, and to assess the present status of knowledge on possible combination treatments, and their potential application in this field.

Five experts from Austria, Germany, Italy and the Russian Federation, as well as staff members of the Industrial Applications and Chemistry section attended the meeting. Also present were two observers from Chile and the United States of America, who participated in the discussions.

The overall objectives outlined for the recommended programme are:

- a) For ground and surface water, to consider:
 - the influence of natural solutes on radiation-induced decomposition of refractory substances, particularly of atrazine;
 - the effects of ionizing radiation on colorants and other pollutants, particularly halogenated aromatics;
 - the mass balance of products formed, particularly of eventually harmful ones;
 - dose rate effects and other parameters concerned with electron beam treatment, including conveying logistics to, under and from the beam;
 - dosimetric systems and procedures and dose distribution in the case of electron beam treatment (in the case of non-turbulent flow);
 - the beam utilization factor (in the case of turbulent flow);
 - the possibility of addition of small quantities of chlorine, for prophylactic purposes (depot effect).
- b) For municipal and rural sludges, to consider:
 - dose rate effects and other parameters concerned with electron beam treatment, including conveying logistics to, under and from the beam;
 - dosimetric systems, procedures and dose distribution for electron beam treatment;
 - the possible combination of ionizing radiation with subsequent composting or other types of biological stabilization;
 - effects of radiation on pathogenic organisms and microorganisms specific to a particular country.
- c) For wastewater from industry and sewage-treatment plants, to consider the same items as for ground and surface water, but to investigate the possibly synergistic or contributing effects of oxygen and ozone on pathogens, rather than the prophylactic effect of chlorine.
- d) For sludges and wastewater, to co-ordinate the research efforts with those of the parallel CRP of RIFA, which would center on the applicability of these effluents on crop yields and environmental aspects.

2. CONSULTANTS MEETING ON RADIATION PROCESSING OF SEWAGE SLUDGE AND ITS USE TO INCREASE CROP YIELDS, AND TO PRESERVE THE ENVIRONMENT

Land application of municipal sewage sludge is practised throughout the world at various levels. Beneficial effects include increases in crop yields, soil organic matter, cation exchange

capacity, water-holding capacity and fertility. The high levels of N, P and micronutrients in sewage sludge make it an excellent fertilizer. In addition, the high organic matter levels can counteract harmful effects on soil structure. However, a factor limiting the use of sewage sludge is excessive accumulation of heavy metals in soils and resultant phytotoxicity. Hence, fertility benefits must be balanced against the potential hazards of metal contamination due to repeated applications of heavy dressings over long periods.

At present, information is limited on availability of nutrients from sewage sludges to crops, benefits as an organic amendment to soil, and harmful effects of heavy metals on crop growth. Isotope and radiation techniques could provide a valuable tool in attempts to find answers to some of these questions. The Consultants meeting on Radiation Processing of Sewage Sludge and its Use to Increase Crop Yields, and to Preserve the Environment was attended by participants from Austria, Germany, India, Indonesia and Japan, and staff members of the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture, and of the Soils Unit of the FAO/IAEA Agriculture and Biotechnology Laboratory in Seibersdorf. The consultant from the USA did not attend for unavoidable reasons.

The overall objective of the meeting was to review the current status and future trends of the application of nuclear techniques in the use of sewage sludge in agriculture including: radiation processing of sewage sludge by γ irradiation, electron beam radiation and other alternative methods; application of sewage sludge as fertilizer for increasing soil fertility and crop production; heavy metal (Cd, Cu, Ni, Pb and Zn) contamination of agricultural soils; potential harmful effects of sewage sludge utilization as fertilizer on the agricultural environment, and; to provide a critical evaluation of the topics to be investigated using nuclear and related techniques. Conclusions and recommendations made by the consultants are given below.

The overall objectives outlined for the recommended programme are:

- a) To assess sewage sludge, especially irradiated sludge, for its utility as a fertilizer for increased crop production. Evaluate N and P uptake from the sludge under different soil and climatic conditions taking into account N and P losses, using ^{15}N and ^{32}P isotope techniques.
- b) To assess the role of sewage sludge as an organic matter amendment to improve soil fertility, using neutron probes and gamma-density probes, and isotopes such as ^{14}C , ^{13}C and ^{15}N .
- c) To evaluate possible environmental contamination by:
 - pathogens
 - heavy metals
 - organic pollutants.
- d) Close co-operation should be established with other organizations that are involved in irradiation and utilization of sewage sludge in agriculture.
- e) Reference laboratories and standard materials must be identified for the analysis of nutrients, heavy metals and organic pollutants.
- f) In collaboration with the Austrian Research Centre, backup research should be conducted in support of this programme.
- g) The findings of this programme should be published and made available as widely as possible.

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OPENING STATEMENT

S. Machi

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On behalf of the Director General of the International Atomic Energy Agency, I have great pleasure in welcoming you to the Consultants Meeting on "Irradiation Treatment of Water, Wastewater and Sludges" organized by the Industrial Applications and Chemistry Section of the Division of Physical and Chemical Sciences, and the Consultants Meeting on "Radiation Processing of Sewage Sludge and its Use to Increase Crop Yields, and to Preserve the Environment" organized by the Soil Fertility, Irrigation and Crop Production Section of the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture. The meetings were convened to obtain advice and guidance in the planning of two Co-ordinated Research Programmes on radiation processing of sewage sludge and wastewater, and their use in agriculture. This is a unique event where two Divisions of the IAEA have combined to solve a problem of common interest - that of the recycling of waste materials.

The application of nuclear technologies has contributed to industrial efficiency, energy conservation, and environmental protection for many years. Industrial applications of radiation processing are widespread in many countries, and growing in others. In Japan, for example, 280 electron-beam accelerators were in use for industrial purposes and for research and development in 1995. In many developing countries, radiation technologies are being increasingly applied, often with IAEA support, for the benefit of mankind. Some areas of key interest are: (1) production and upgrading of polymers, (2) sterilization of medical products and pharmaceuticals, (3) cleaning of flue gases, (4) food irradiation (5) cleaning of water, and (6) disinfection of sewage sludge.

Wastes have been used by mankind since antiquity. However, methods for systematic collection and disposal did not evolve until late last century. Since then, land application has been a common practice for disposal of municipal wastes, especially wastewater and residues resulting from treatment of waste material. Many large urban centres around the world have applied their waste material to land for years. Noted examples are the "sewage farms" in Paris, Berlin and Melbourne. Early promoters of this practice advocated the use of soil as a "treatment" medium and wastewater as a source of plant nutrients, in contrast to the customary "direct" discharge into a surface water body. While land application was a cost-effective process, the systems became plagued with both hydraulic and solid contaminants, and other operational difficulties. Consequently, pollution became a major problem. The advances in wastewater-treatment technology in recent years have reduced the pollution potential of treated effluent to a considerable extent, however the contamination of potable water with bacterial and chemical pollutants, and the disposal of sewage sludge, remain significant problems.

Pollution of land, water and air is now a widespread growing concern of global proportions. Increased awareness of potential health hazards from insufficient or inappropriate waste handling methods has stimulated the search for more effective waste-treatment alternatives. Of particular concern are wastes that present problems in two areas: (i) those containing potentially infectious microorganisms (i.e. sewage sludge, biomedical wastes, and wastewater) and (ii) those contaminated

with toxic chemicals, particularly those originating from industrial and municipal effluents. Conventional methods for disinfection are heat treatment (pasteurization), composting and lime treatment. A more attractive technique for sludge disinfection is irradiation. The first practical plant for gamma irradiation of sewage sludge became operational in 1973 in Geisebullach (near Munich) in Germany. Since then, other countries such as the USA, Japan, India and Argentina have embarked on radiation processing of wastes on various scales. The basic types of irradiation systems that are currently used (or studied) in waste-treatment operations include gamma rays and electron beam.

The IAEA has been involved in studies of radiation processing of sewage sludge for several years. A Co-ordinated Research Programme on "Radiation Treatment of Sewage Sludge for Safe Reutilization" was implemented from 1986-1990, involving participants from Canada, Germany, India, Indonesia, Italy, Japan, and the USA. The findings of this Co-ordinated Research Programme will be of great value for the implementation of new programmes in this field.

The consultants meeting on "Irradiation Treatment of Water, Wastewater and Sedges" will deal with the use of ionizing radiation, either alone, or in combination with synergistic agents, such as ozone, heat, and electrical discharges, as effective decontaminating agents for aqueous environmental pollutants and for potable water. The meeting on "Radiation Processing of Sewage Sludge and its Use to Increase Crop Yields, and to Preserve the Environment" will deal with the use of isotope and radiation techniques as a tool to find ways of utilizing sewage sludge to increase and sustain soil fertility and crop production in an environmentally friendly manner. The initiation of these studies is timely in view of the dire need to find ways to integrate nutrient-management practices involving organic fertilizers into cropping systems so that the need for expensive commercial fertilizer inputs may be reduced, while decreasing harmful effects on the environment.

I understand that we have here with us today the world's leading authorities in sewage sludge and wastewater studies from Austria, Germany, India, Indonesia, Italy, Japan, Russia, United Kingdom and the United States of America. May I wish you success in your meetings and an enjoyable stay in the beautiful city of Vienna.

LIST OF PARTICIPANTS

IAEA Consultants meeting on Irradiation Treatment of Water, Wastewater and Sludges, 5–7 December 1994

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