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DOE/FDA/EPA Workshop on Methylmercury and Human Health

March 22-23, 1994
Bethesda Marriott, Bethesda, Maryland

A Cooperative Effort By:

Office of Fossil Energy
U.S. Department of Energy
Washington, DC 20585

Center for Food Safety and Applied Nutrition
U.S. Food and Drug Administration
Washington, DC 20204

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

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Workshop on Methylmercury and Human Health

Editors:
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J. Cicmanec, and S. Durkee

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DISCLAIMER

FOREWORD

An Interagency Working Group has been established by the Office of Fossil Energy, U.S. Department of Energy, the Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, and the Office of Research and Development, U.S. Environmental Protection Agency. The purpose of this Working Group is to promote dialogue among agencies that are interested in the potential health and environmental risks presented by mercury, especially methylmercury. To help achieve this objective, regularly scheduled meetings are held in an informal setting to discuss a broad range of topics, including, but not limited to:

- Coordination of ongoing and planned research
- Conduit for announcement and early review of new findings
- Data sharing
- Identification of research needs
- Cosponsoring of new studies
- Hosting of workshops
- Interagency exchange of personnel

This report represents a product of the Interagency Working Group. Although each Federal organization has a different mission, all are joined by two strong bonds. First, all three organizations are interested in protecting public health. Second, the three organizations wish to ensure that the best science on methylmercury is available to each organization. These areas of common interest provide a focal point for interagency cooperation. This report is one example of this cooperation.

Lowell Miller

Dr. C. Lowell Miller
Director, Office of Clean Coal Technology
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Mr. Thomas J. Billy
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ABSTRACT

In the U.S., the general population is exposed to methylmercury (MeHg) principally through the consumption of fish. There is continuing discussion about the sources of this form of mercury (Hg), the magnitudes and trends in exposures to consumers, and the significance of the sources and their contributions to human health. In response to these discussions, the U.S. Department of Energy, the U.S. Food and Drug Administration, and the U.S. Environmental Protection Agency cosponsored a two-day workshop to discuss data and methods available for characterizing the risk to human health presented by MeHg. This workshop was attended by 45 individuals representing various Federal and state organizations and interested stakeholders. The agenda covered the following topic: Agency interests; probabilistic approach to risk assessment; emission sources; atmospheric transport; biogeochemical cycling; exposure assessment; health effects of MeHg; and, research needs. To facilitate the discussions at this workshop, the cosponsoring organizations commissioned brief background papers to overview each of the highlighted topics. Each paper was presented in a plenary type session, followed by an in-depth discussion of the paper. The following points were raised. The speciation properties of Hg in an atmospheric plume and their rates of change and deposition are poorly known. An immediate cessation of Hg emissions from anthropogenic sources may not result in appreciable short-term changes in fish MeHg levels due to continuing deposition of Hg from the atmosphere and release from soils and sediments. Most older fish consumption data used for exposure assessments are now considered inaccurate. Few of the existing surveys collected fish consumption and hair or blood Hg levels at the same time. There are few studies available to characterize the sensitivity of the fetus to MeHg exposures; and, the MeHg epidemiological studies nearing completion in the Faroe and Seychelles Islands may be using different measurement protocols, which may make interstudy comparisons difficult. Based on these concerns, various research needs were identified and discussed, including the need to develop inventories of natural and anthropogenic sources of emissions, estimates of regional air quality impacts from multiple sources, characterizations of the spatial and temporal trends of Hg in various biogeochemical repositories, food fish consumption surveys targeted to sensitive populations and paired with appropriate biomarkers, and characterizations of maternal and fetal developmental effects. The list of identified research needs can serve as a focal point for future interagency cooperation.

ACKNOWLEDGMENTS

This workshop was jointly sponsored by the Office of Fossil Energy, U.S. Department of Energy (DOE); the Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration (FDA); and, the Office of Research and Development, U.S. Environmental Protection Agency (EPA). The Federal agency representatives who planned and hosted the workshop were: Lawrence Saroff (DOE), Michael Bolger (FDA), John Cicmanec (EPA), and Stan Durkee (EPA). Paul Moskowitz (Brookhaven National Laboratory - BNL) assisted in the planning for this workshop and acted as the workshop facilitator. Michael DePhillips (BNL) provided logistical and technical support in the planning for the workshop and preparation of this report. We thank Michael for these extended efforts.

The workshop sponsors acknowledge the enthusiastic and cooperative support provided by all of the workshop participants. We especially thank the invited speakers who addressed the following topics:

- Fred Lipfert, Brookhaven National Laboratory, Risk Assessment
- Winston Chow, Electric Power Research Institute, Emission Sources
- Jack Shannon, Argonne National Laboratory, Atmospheric Transport
- William Fitzgerald, University of Connecticut, Biogeochemical Cycling
- Greg Cramer, FDA, Exposure Assessment
- Thomas Clarkson, University of Rochester, Dose Response

Finally, note that the materials presented in this report do not necessarily reflect the opinions or endorsements of any participating organization or individual.

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1. SUMMARY

On March 22-23, 1994, a two-day workshop was held on "Methylmercury and Human Health." The meeting was jointly sponsored by the Office of Fossil Energy, U.S. Department of Energy (DOE); the Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration (FDA); and, the Office of Research and Development, U.S. Environmental Protection Agency (EPA). This workshop was attended by 45 individuals representing various Federal agencies (e.g., National Institute for Environmental Health Sciences), state governments (e.g., California Environmental Protection Agency), and interested stakeholders (e.g., Environmental Defense Fund, National Fisheries Institute and Electric Power Research Institute - EPRI).

The purpose of this workshop was to initiate dialogue among experts regarding relevant data and methods that could be used to evaluate hazards and risks to human health from natural and anthropogenic sources of methylmercury (MeHg). The following is a brief summary of the speakers papers, and topics discussed.

- Agency Interests: DOE is interested in characterizing mercury (Hg) emissions from fossil-fuel fired power plants and determining the degree of risk they may present to environment and health. FDA establishes standards and advisories for MeHg levels in fish. EPA is required by the Clean Air Act Amendments of 1990 to report to Congress on the health and environmental effects of Hg emissions of anthropogenic origin. The report must also cover control technologies and their costs.

- Risk Assessment: Fred Lipfert (Brookhaven National Laboratory) discussed approaches and data that may be appropriate to evaluate the background and incremental health risks from a point source of Hg.

- Emission Sources: Winston Chow (EPRI) discussed the EPRI/DOE measurement program for air toxics from fossil fuel sources, especially coal-fired power plants.

- Atmospheric Transport: Jack Shannon (Argonne National Laboratory) presented an overview of a long-range transport study being conducted in the Great Lakes region. A model developed for the acid rain program is being used to model Hg deposition patterns.

- Biogeochemical Cycling: William Fitzgerald (University of Connecticut) described spatial and temporal variations in different forms of Hg in various environmental compartments. This presentation was augmented by a brief overview given by Donald Porcella (EPRI), who described the EPRI model for Hg cycling in terrestrial and aquatic systems.

- Exposure Assessment: Greg Cramer (FDA) described various surveys conducted by the FDA and others that quantify fish consumption and MeHg levels in fish. From these studies, he constructed estimates of the past and current exposure levels to MeHg in the U.S. population.

- Dose Response: Thomas Clarkson (University of Rochester) overviewed the findings of existing human and animal studies. He noted that most available human data used in dose-response analyses are based on acute, high-level exposures, while chronic low-level exposures are currently of concern.

- Research Needs: Paul Moskowitz (Brookhaven National Laboratory) summarized the results of a questionnaire distributed to the participants. Key research needs in each issue area were defined.

At the workshop, extended discussions were held following the presentation of each issue paper. Many important points were raised in these discussions. Examples include:

- Model results need to be compared with real data.

- The speciation properties of Hg in an atmospheric plume from a point source and their rates of change and deposition are poorly known.

- An immediate cessation of Hg emissions from anthropogenic sources may not result in appreciable short-term changes in fish MeHg levels due to continuing deposition, as well as the continuing release of Hg from soils and sediments.

- Most of the fish consumption data used for exposure assessments are based on surveys that are now considered inaccurate. Few of the existing surveys collected fish consumption and hair or blood Hg levels at the same time.

- There is concern about applying dose-response information derived from acute poisoning incidents to low-level chronic intakes.

- There are only a few studies available to characterize the sensitivity of the fetus to MeHg exposure. The ongoing epidemiological studies nearing completion in the Faroe and Seychelles Islands should more accurately characterize these dose-response relationships. These studies, however, are using different measurement protocols, which may make interstudy comparisons difficult.

From these discussions, a list of parallel research needs was developed. The identified research can serve as focal points for future interagency cooperation.

2. INTRODUCTION

In the U.S., the general population is exposed to methylmecury (MeHg) principally through the consumption of fish. There is continuing discussion about the sources of this mercury (Hg), the magnitude and trends in exposures to consumers, and their health significance. The forums for these discussions extend from the scientific literature to the U.S. Congress. Much is at stake as measured in both human and economic terms. In this context, there are various stakeholders representing different interests. This is true in both the private and public sectors. In the Federal government, the U.S. Department of Energy (DOE), the U.S. Food and Drug Administration (FDA), and the U.S. Environmental Protection Agency (EPA) each has different responsibilities with respect to this issue. In a highly summarized overview: DOE is interested in characterizing Hg emissions from fossil fuel sources and the risks they may present; FDA establishes guidelines or standards for MeHg levels in fish; and, EPA is investigating potential MeHg risks associated with stack emissions from industrial sources and the need to implement emission controls for electricity generating plants as required by the Clean Air Act Amendments of 1990. Although each Federal organization has a different mission, they are joined by two strong bonds. First, all three organizations are interested in protecting public health. Second, all three organizations wish to ensure that the decision process regarding these potential risks and control options be based on the best available scientific information. These areas of common interest provide a focal point for interagency cooperation.

In this context, a two-day workshop was held on "Methylmercury and Human Health" in Bethesda, Maryland. The meeting was jointly sponsored by the Office of Fossil Energy, DOE; Center for Food Safety and Applied Nutrition, FDA; and, the Office of Research and Development, EPA. This workshop was attended by 45 individuals (Table 1 and Appendix A) representing various Federal agencies (e.g., National Institute for Environmental Health), state governments, (e.g., California Environmental Protection Agency) and interested stakeholders (e.g., National Fisheries Institute).

The purpose of this workshop was to initiate dialogue among experts regarding data and methods that could be used to evaluate hazards and risks to human health from natural and anthropogenic sources of methylmercury. At the workshop, discussion was directed to the following issues:

1. Hg emissions (from coal, incinerators, other point sources, and nonpoint sources)
   - statistics of total and reactive Hg emissions (can we describe the whole U.S.?)
   - functional dependencies (e.g., Cl^-)
   - chemical speciation
   - geographic variability in Hg and Cl^-
   - efficacy of controls in removing Hg compounds

2. Transport and deposition
   - is the reactive Hg chemically stable out to 50-100 km?

- dry deposition velocities
- what is the appropriate wet scavenging model?
- seasonal dependencies
- time and space scales (do we need a meso-scale model?)

3. Aquatic processes and uptake by organisms
   - time scales (need to consider seasonal factors?)
   - need to consider overland transport (need data to prove the point)
   - roles of pH and DOC; need to consider joint distributions
   - within and between fish species variations in Hg and uptake rates
   - reliability of data on baseline Hg in fish

4. Human exposures to MeHg
   - types/results of monitoring and modeling data
   - are there trends?
   - available surveys and appropriate uses of data
   - data on recreational and subsistence catches
   - reliability of data
   - data on consumption by pregnant females
   - which species to track (besides tuna)

5. Dose-response (health effects)
   - interpretation of Iraqi and body burden Hg data
   - epidemiological studies of fish eaters (new and old)
   - how to simulate the averaging that takes place during approach to equilibrium body burden (do we need nested Monte Carlo?)
   - interpretation of small deltas over existing background levels of health endpoints
   - endpoints for prenatal/child developmental effects
   - dealing with uncertainties

6. Risk assessment
   - safety assessment (a yes-or-no answer) versus risk analysis (the quantitative discription of risk at different levels of exposure).
   - need to understand baseline and incremental effects
   - need to study subsistence populations separately
   - importance of form of dose/response model
   - interpretation of small deltas over existing background levels of health endpoints
   - how important are the precise shapes of input probability distributions?

To facilitate the discussions at this workshop, the cosponsoring organizations commissioned brief background papers to overview each of the highlighted topics. Each paper was presented in a plenary type session, followed by a detailed discussion of the paper. The specific agenda for the workshop and the invited papers and speakers are outlined in Table 2.

This report presents these papers and a summary of the discussion that followed each presentation. The cosponsoring organizations hope that these discussions will lead to a clearer understanding of the limitations of existing data and methods available for characterizing the risks presented by MeHg to human health. As a sidebar to these basic discussions, important research needs were also identified and discussed. These are outlined in the final chapter to this report.

Table 1. List of Participants

NAME	AFFILIATION
Maths Berlin	University of Lund, Sweden
Mike Bolger	U.S. Food and Drug Administration
Tom Brown	U.S. Department of Energy
Thomas Burbacher	University of Washington
Rick Canady	Agency for Toxic Substances and Disease Registry
Clark Carrington	U.S. Food and Drug Administration
Jason Ching	U.S. Environmental Protection Agency
Winston Chow	Electric Power Research Institute
John Cicmanec	U.S. Environmental Protection Agency
Thomas Clarkson	University of Rochester
Christopher Cox	University of Rochester
Gregory Cramer	U.S. Food and Drug Administration
Peter Defur	Environmental Defense Fund
Michael DePhillips	Brookhaven National Laboratory
Stan Durkee	U.S. Environmental Protection Agency
Earl Evans	U.S. Department of Energy
Anna Fan	California Environmental Protection Agency
William Fitzgerald	University of Connecticut
Robert Goyer	National Institutes of Health
Betty Hackley	National Marine Fisheries Service
Dale Hattis	Clark University
Rick Hoffman	U.S. Environmental Protection Agency
John Jansen	Southern Company Services, Inc.
Carol Kimmel	U.S. Environmental Protection Agency
Leonard Levin	Electric Power Research Institute
Christina Lewis	U.S. Food and Drug Administration
Fred Lipfert	Brookhaven National Laboratory
Gayle Miller	Centers for Disease Control and Prevention
Bruce Mintz	U.S. Environmental Protection Agency
Paul Moskowitz	Brookhaven National Laboratory
Gary Myers	University of Rochester
Donald Porcella	Electric Power Research Institute
Lawrence Saroff	U.S. Department of Energy
Chuck Schmidt	U.S. Department of Energy
Christian Seigneur	ENSR Consulting and Engineering
Jack Shannon	Argonne National Laboratory
Pamela Shubat	Minnesota Department of Public Health
Robert Sills	Michigan Department of Natural Resources
Thomas Snyder	Argonne National Laboratory
Mark Stack	Oak Ridge National Laboratory
Alan Stern	New Jersey Department of Environmental Protection and Energy
Lee Weddig	National Fisheries Institute
Chris Whipple	ICF-Kaiser Engineers, Inc.
Roberta White	Boston University
Ronald Wyzga	Electric Power Research Institute

Table 2. Workshop Agenda

MARCH 22		
9:00-9:10 AM	*WELCOME*	*P. MOSKOWITZ*
9:10-9:20 AM	*DOE INTERESTS*	*L. SAROFF*
9:20-9:30 AM	*FDA INTERESTS*	*M. BOLGER*
9:30-9:40 AM	*EPA INTERESTS*	*J. CICMANEC*
10:00-12:00 AM	*RISK ASSESSMENT*	*F. LIPFERT*
1:00-2:00 PM	*Hg EMISSIONS*	*W. CHOW*
2:00-3:00 PM	*ATMOSPHERIC TRANSPORT*	*J. SHANNON*
3:30-5:00 PM	*AQUATIC PROCESSES*	*W. FITZGERALD*
MARCH 23		
8:30-10:00 AM	*EXPOSURE ASSESSMENT*	*G. CRAMER*
10:30 -12:00 PM	*DOSE-RESPONSE*	*T. CLARKSON*
1:00-2:00 PM	*DOSE-RESPONSE CONTINUED*	*T. CLARKSON*
2:00-2:30 PM	*OPEN DISCUSSION*	*ALL*
2:30-3:30 PM	*RESEARCH NEEDS*	*P. MOSKOWITZ*

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3. RISK ASSESSMENT

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INTRODUCTION

Traditionally, the risk assessment process involves three distinct phases: identification of risks, characterization of risks, and management of risks. The specific health risks of methylmercury (MeHg) have been previously identified through the excellent biomedical foundation that followed the unfortunate poisoning incidents of past decades. In this report, we interpret risk "characterization" in the probabilistic sense: to define the frequency distributions of health risks based on the distributions of the causal factors that determine those risks. The question of risk management is deliberately postponed pending judgments as to the severity of the risks that emerge from the characterization phase.

In support of this workshop, this report describes an approach to a probabilistic assessment of the health risks associated with mercury emissions from a hypothetical coal-fired power plant. The approach draws on the extant knowledge and data in each of the important steps in the chain from emissions to health effects, recognizing that both global background levels and local source increments must be considered, because of the non-linear nature of the dose-response functions. Many of these elements are quite technically complex, and in some cases a "black-box" approach must be taken. We recommend the use of data (i.e., measurements) wherever possible, so as to reduce the width of the confidence limits that would result from the use of uncertain models. In a probabilistic assessment, realism is desired rather than conservatism; the user can then apply his own desired level of conservatism by choosing an appropriate level of acceptable risk.

Atmospheric and aquatic processes must be considered on two separate scales: local (up to ~100 km from a source), and global. Hg emitted from a source that is not deposited locally is assumed to enter the global Hg pool. The main MeHg exposure pathway is through ingestion of seafood. It must be recognized that the general public has a wide range of fish consumption patterns, mainly comprising a variety of species, and that appropriate data on baseline mercury levels and bioconcentration factors may not always be available. Freshwater species are affected by both global and local Hg deposition; marine species are only affected by global Hg deposition. Further, the health effects of MeHg are keyed to equilibrium levels of blood Hg, not to the acute effects of individual doses. The process of reaching equilibrium greatly diminishes the importance of individual doses, so that the frequency distribution of equilibrium body burdens is considerably narrower than the distribution of individual doses (i.e., fish meals). One must realize that, given the practical upper limits on the MeHg content of fish taken from waters contaminated only by airborne Hg deposition, that a high MeHg dose can only be obtained by consuming fish more often. Thus, the confidence limits for the equilibrium dose will become narrower as the frequency of consumption and absolute levels of dose increase.

For an assessment of MeHg health effects, it may be useful to define three separate (but aggregated) sources of dietary Hg: canned tuna fish, marine shellfish and fin fish, and freshwater game fish. We estimate wet and dry deposition of Hg from the coal combustion source in terms of the increment with respect to existing background levels, which are based on extant measurements. The incremental Hg in local fish is assumed to be proportional to the incremental total Hg deposition. Alternative dose-response models are derived from the published epidemiological data on specific neurological responses; adult paresthesia was used as the initial end point of concern, but the methodology applies to any endpoint with a quasi-continuous dose-response characteristic. The probabilistic methods used in the assessment must specifically incorporate the uncertainties in the dose terms, but also in the dose-response functions. In general, the parameters describing a dose-response function are linked; for example, the slope, intercept, and background prevalence levels are all correlated in a logistic dose-response function DRF, so that only one of them can be considered as independent with respect to the representation of uncertainties.

In probabilistic risk assessment, it is important to recognize the different sources of heterogeneity or uncertainty, especially for MeHg, since the focus is more likely to be on extreme rather than central values of risk. Confidence limits become widened as a result of (bona fide) heterogeneity in the dose term; there are real differences in fish consumption patterns and in the MeHg content of seafood. However, confidence limits are also widened because of ignorance; this rubric includes measurement errors, variance arising from small samples, lack of knowledge about physical processes and the parameters which describe them, and lack of knowledge about the "true" functional forms of dose-response functions. A complete assessment will attempt to partition the overall spread in the distribution of risks to these component causes.

In this recommended assessment approach, two estimates of incremental health risks are made: one for the baseline levels of Hg in fish, and one for the sum of baseline and contributions from coal burning. This allows measured data on "background" Hg deposition and fish Hg content to be used as "anchor" points, which reduces the overall uncertainty considerably in comparison to what would result from trying to predict these quantities from first principles. The estimated levels of risk are then compared with the background prevalence rates of the health endpoints in question, to provide context.

In this paper, we provide capsule critical reviews of some of the extant assessments of MeHg health risks and then go on to provide more detail about the recommended assessment approach. We include a discussion of some of the problems of representing dose-response data with appropriate mathematical functions and some examples of the propagation of variance through components of a risk assessment model.

PREVIOUS ASSESSMENTS OF METHYLMERCURY HEALTH EFFECTS

Previous assessments of the health risks of mercury have been of two general types: assessment of the baseline risks due to all sources of atmospheric mercury, and assessment of the incremental effects of emissions from specific sources or types of sources. In the recommended assessment approach, a good understanding of the baseline is a prerequisite for considering the incremental risks. Virtually all studies agree that the average health risks from MeHg are quite small; what may be at issue are the estimates of extreme values, which must be derived from probabilistic considerations. Probabilistic methods have come into use for such purposes only relatively recently. Some of the previous assessment efforts have been rather simplistic when viewed in that light, but are included in this section for completeness and perspective.

Assessment Methods

There are perhaps two basic methods of risk assessment that have been used in these studies. The more comprehensive analyses compare methylmercury doses to those leading to actual observed neurological responses or to mathematical models of those responses. The major poisoning incidents mentioned above are often the source of such dose-response data. The other analyses rely on dose thresholds or "no observed adverse effect" levels (NOAELs) that have been established by various regulatory or advisory agencies, such as the U.S. Food and Drug Administration (FDA), the U.S. Environmental Protection Agency (EPA), or the World Health Organization (WHO). Unfortunately, whether or not a given study finds an adverse effect can depend on the study design, sample sizes, and errors in dose estimation. In all cases, it is necessary to estimate the distribution of MeHg doses to the various populations being considered. In most general populations, the average doses of MeHg are well below the steady-state levels at which neurological responses might be expected, so that the adequacy of the assessment depends on the methods by which extreme cases are considered and the levels of realism incorporated in the assumptions used. Note that the reference dose concept does not distinguish between a single massive dose and a steady consumption rate of randomly varying individual doses.

Assessments of Baseline Risks

The National Academy of Sciences (NAS) Study, "Seafood Safety." The Institute of Medicine of the NAS prepared a comprehensive account of many of the risks involved in eating seafood, including natural toxins, organic pollutants, and trace metals including mercury (Ahmed, 1991). Their methodology included individual variability in

MeHg uptake and metabolic half-life and was based on mathematical models of the responses to the Iraqi grain poisoning incident (Marsh et al., 1987; Bakir et al., 1973). The objective of this analysis was to estimate the actual risks entailed at the regulatory thresholds most often used, with and without a safety factor of 10. Although the report presented data on seafood consumption and mercury contamination levels, it did not go on to combine the two distributions in order to estimate the actual population risks. The report concluded, nevertheless "risks that may be significant include reproductive effects from polychlorinated biphenyls (PCBs) and methylmercury... and, possibly, parkinsonism in the elderly from long-term mercury exposure."

The 1986 FDA Analysis. The NAS study described above criticized a previous FDA effort by Tollefson and Cordle (1986) for its reliance on acceptable daily intake levels (ADIs) rather than on dose-response functions, and on its failure to consider a wide range of fish species (the latter criticism seems unjustified since consumption and mercury data were provided for 6 species and mercury data for another 20 or so). Tollefson and Cordle concluded "The majority of fish consumers in the United States could easily double their intake and still remain below the ADI." They went on to defend the FDA action level of 1 μg/g Hg in fish as providing adequate protection for adults and children.

The 1993 FDA Risk Assessment. The FDA (C. Carrington, personal communication, August 1993) is developing a spreadsheet-based probabilistic model to assess the health risks from mercury in tuna fish. This model samples from discrete distributions of mercury in tuna and tuna consumption levels, develops equilibrium blood Hg levels for a number of individuals, adds background blood Hg levels, and then evaluates their risks based on the Iraqi poisoning data. We have only fragmentary information about this model, but it appears that the fish consumption data are based on only the tuna-consuming portion of the population, with a mean consumption rate of 31 g/d. The endpoint in question here is the transfer of effects of maternal consumption of MeHg to fetal and child development. Details and results from this model have not yet been published.

National Institute of Environmental Health Sciences (NIEHS). NIEHS was requested by Congress to "...determine the threshold level of mercury exposure below which adverse human health effects are not expected to occur." The preliminary draft of this report discusses the available dose-response information and provides some fish consumption data and exposure estimates for methylmercury. The report discusses the thresholds apparent in the poison data but observes that "...the hockey-stick dose-response model may only reflect the limitations of the available data." The report evaluates the available data on fish consumption and their uncertainties, including subgroups of high fish consumers, but makes no estimates of population exposures to MeHg. To satisfy the Congressional mandate, the NIEHS report cites the "tolerable" doses or fish concentrations previously derived by the FDA, EPA, and WHO.

The New Jersey Baseline Risk Assessment. The most recent general assessment of baseline risks is that of Stern (1993), who used the data on Iraqi mothers and children, as analyzed by Marsh et al. (1987) to estimate the risks entailed in the current U.S. EPA reference dose (0.3 μg/day per kg of body weight). Stern also discusses other relevant epidemiological studies of MeHg and neurological symptoms. He concluded that the reference dose should be reduced to 0.07 μg/kg/day to preclude effects on fetal development.

Stern used data on mercury content of various marine species taken from the 1978 survey by Hall et al. and them combined with consumption data from a nationwide survey from 1982-87, in a probabilistic analysis. The average mercury concentration, weighted by percentage of the catch, was 0.11 μg/g, with a maximum of 1.0 μg/g. This algorithm implicitly assumes that the variability in the MeHg concentration of the fish eaten in various amounts comes from variations by species, rather than variations within species due to age, weight, length, etc., and ignores typical consumption patterns involving a mixture of species. The maximum consumption rate considered was 227 g/d, with an average of 32 g/d (slightly more than 1 meal per week), based on an unpublished FDA document. These consumption rates pertain only to that segment of the population that consumes fish on a regular basis, which Stern estimated to be about 85% (based on surveys). On this basis, he estimated that 3% of the (fish-eating) 70 kg adults exceeded the present EPA reference dose, and that 23% of the 62 kg females exceeded the recommended lower standard for fetal effects.

Risk Assessments for Mercury Sources

New Jersey Municipal Solid Waste Incinerators. In 1992, the New Jersey Task Force on Mercury Emissions Standard Setting released an analysis of six specific incinerators for which mercury emission rates had been determined. Their method of analysis was to predict downwind air concentrations using standard dispersion models, estimate wet and dry deposition rates and run-off, and then to estimate rates of Hg accumulation in aquatic sediments and subsequent bioaccumulation in fish. In order to estimate the incremental MeHg dose, estimates were made of the amount of locally-caught fish consumed, which was taken as equal to the national average for all types of fish. The consumption value used (32 g/d) was obtained from an internal FDA publication. These doses were then compared to the reference dose. Such an assessment approach does not actually estimate health risks *per se*, since dose-response information underlying the reference dose levels is not considered.

The New Jersey analysis used the maximum annual average air concentrations from each incinerator as a starting point, and applied these values to hypothetical lakes, assuming that all of the mercury was emitted as soluble $HgCl_2$. These concentration increments were about the same as the existing ambient mercury background. This mercury was assumed to be deposited wet and dry into the watershed, where it accumulated in lake sediments for 20 years. The bioconcentration factor used was based on sediment Hg concentrations and was chosen to be representative of New Jersey lakes, but no consideration was given to the implied fish species involved and their actual rates of consumption by humans (the basic data were obtained from northern Minnesota lakes). The resulting fish MeHg concentrations due to the incremental effects of incinerators ranged from 0.7 to 2.68 mg/kg, while the baseline concentrations due to all other mercury sources averaged only 0.11 mg/kg, with a maximum of 1.0 mg/kg.

Consumption rates of these locally-caught fish were assumed to be the same as the U.S. average for all types of fish, adjusted downward to reflect absence of fishing during the winter, to yield a figure of 24 g/d/person. The overall conclusions of the New Jersey assessment were that the current EPA reference dose should be reduced, and that emissions from existing incinerators may cause "significant increase in the ingestion of methylmercury."

Power Plant Risk Analysis. Constantinou et al. (1993) presented a power plant risk analysis for mercury with both deterministic and probabilistic elements. They considered a range of exposure pathways, including inhalation, drinking water, and ingestion of plants and fish. Ingestion of fish was found to be the most important pathway in their deterministic (worst case) analysis. The endpoint of this analysis was the fraction of the reference dose implied by the incremental effects of a single power plant, which they identified as the "hazard index." Inorganic and organic mercury hazards were combined in this analysis. The modeling inputs for the deterministic analysis featured "conservative" assumptions for the point estimates that might be suitable for a regulatory perspective. The probabilistic analysis used distributions of parameters from the literature, which may or may nor encompass the deterministic point estimates (personal communication, E. Constantinou, April 1994). The power plant was assumed to have emissions controls, and the modeling incorporated the actual positions of lakes within its near-field impact area.

For the deterministic analysis, the total hazard index due to the plant was estimated to be about 0.09; for the probabilistic analysis, the expected (i.e., mean) value was 0.0014 with a GSD of about 4.5. The deterministic value fell at about the 99th percentile of the probabilistic dose distribution. This analysis provides a good example of the expansion of uncertainty that can occur in a chain calculation involving many individually uncertain inputs.

New York State Methodology for Estimating Externalities. Rowe et al. (1993) proposed a methodology for estimating health effects of coal combustion, for application to New York power plants. The Hg emission rates cited are about twice the national average, according to the most recent EPRI data (D. Porcella, personal communication, 1993). They assume all Hg is emitted in soluble form ($HgCl_2$). All deposition is concentrated in one catchment area (watershed). Much of the analytical methodology follows the New Jersey model described above for incinerators. The mechanism for making Hg available for bioconcentration by fish is through uptake by sediments during the plant's lifetime (60 y), for release to the water column. The bioconcentration factors (BCF) used are keyed to sediment Hg concentrations. A single BCF is used for all fish species; no account is taken of chemical or geomorphic factors associated with the lake or watershed. The model considers background levels of MeHg in fish and in humans, but assumes a national average seafood consumption rate of 32 g/d (no source cited). A parametric approach was taken to the ingestion of locally-impacted freshwater fish: 1 meal/mo, 4 meals/mo, and 10 meals/mo. Data from the Iraqi grain poisoning accident were used to develop dose-response functions for adult paresthesia and retardation in children through placental transfer. In addition, the EPA "lowest observed adverse effect levels" (LOAELs) were used to set thresholds of no effect.

This model is applied to three specific New York lakes, and it is noted that small lakes may concentrate the Hg emissions to a greater extent, but that the population exposed to the fish in such a lake will be small, a compensating factor. This methodology appears to be reasonably well grounded in terms of its basic relationships, but it may not produce credible estimates of upper percentile risks unless probabilistic techniques are incorporated.

Summary of Previous Mercury Risk Assessments

The extant assessments of mercury risks are based on data assembled from a wide range of sources and disciplines; a common methodology has not yet evolved. Taking full advantage of the benefits of hindsight, we can suggest that improved accuracy and relevance might result from incorporating the following features:

1. Use of probabilistic rather than deterministic methods.

2. Disaggregation of the total seafood diet into separate components for which distributions of mercury contents and rates of consumption can be estimated.

3. Identifying particular dietary components that might be sensitive to power plant impacts.

4. Considering equilibrium body burdens rather than instantaneous blood levels of Hg.

5. Incorporating the dose-response functions for the endpoints of interest directly into the assessment, including the associated uncertainties.

6. For site-specific applications, using area-averaged deposition to the water bodies in the vicinity of the sources.

PROPOSED PROTOCOLS FOR PROBABILISTIC ASSESSMENT OF MEHG HEALTH RISKS

Assessment of Baseline Risks

The medical literature indicates that MeHg health effects are controlled by the body burden of MeHg at or near equilibrium (or after a peak occurrence, for transient responses). This burden is expressed as mg of MeHg per kg of body weight; probabilistically, this metric can be generated by dividing the distribution of MeHg levels by the distribution of body mass. In the absence of other information, independence of these two factors may be assumed, and the distribution of body mass of the U.S. population is available from published tables. Note that if it were desired to evaluate transient risks from single fish meals, a two-step process could be envisioned, in which a distribution of single meal doses is added to the distribution of equilibrium body burdens. These combined distributions would then be used as input to the appropriate dose-response functions (described below). Note that this approach does not require the use of blood or hair concentrations of MeHg *per se*, however useful these data may be in a clinical setting.

The distribution of equilibrium body burdens is obtained by combining the distributions of daily dose (MeHg concentration x consumption rate) and of MeHg half-life. Strictly speaking, this requires a nested probabilistic (Monte Carlo) analysis: each individual in the population is assumed to consume random doses of MeHg and to attain a quasi steady-state Hg level after about 5 half-lives. The distribution of individuals is then estimated, based on the distributions of body mass and of half lives of MeHg. However, we have attempted to accomplish this result in a single step, by synthesizing the averaging process inherent in the approach to body-burden equilibrium and using closed-form mathematical expressions to represent the reduction in spread of the confidence limits over time (Figure 1). This approach is computationally efficient, and we believe any inherent inaccuracies to be small when compared to other sources of uncertainty in the assessment.

The distribution of daily doses is derived from the sum of the distributions for tuna, for marine shell and fin fish, and for freshwater fish. In each case, the distribution of MeHg content is multiplied by the distribution of the consumption rate. The (high) extremes of these distributions are taken to represent subsistence fish-eating populations.

Assessment of Incremental Risks from Local Sources

There are two important interfaces which govern transfers of Hg between airborne emissions and fish: the interface between the atmospheric and the surface water compartments, and the transfer from water column to fish, by way of storage, methylation, and release from sediments. In the first instance, we use simplified aerometric relationships to estimate the total deposition and run-off into a waterbody.

We then use a distribution of incremental deposition over existing (measured) background as the airborne dose metric. For a specific rather than hypothetical or generic risk assessment, this modeling could be made as comprehensive as appropriate. However, we use the "black box" approach for the aquatic and methylation processes, for the following reasons:

1. Research has shown the importance of the specific characteristics of the watershed and lake in terms of the uptake of deposited Hg. Factors such as lake pH and dissolved organic carbon (DOC) and the terrain and ground cover of the watershed may all be important, but descriptive data are not available for a general case. A joint frequency distribution would be needed for a probablistic analysis.

2. Bioaccumulation of MeHg varies by fish species and size. Since most people would be expected to consume a range of sizes and species, there is little to be gained by incorporating this level of detail in the assessment. Instead, we rely on the distributions of measured MeHg levels by broad classes of fish as in the baseline risk assessment, and simply estimate the increases due to local Hg deposition as a straight linear proportion with the incremental Hg deposition. Empirical data indicate that the within-species variation in MeHg in a given lake is about the same as the between-lake variation averaged over all species.

3. There are substantial uncertainties associated with the physico-chemical models for these processes, which arise from ignorance of process details and their associated parameters. Uncertainty also arise from heterogeneity over space and time. By using appropriately averaged (measured) data for baseline Hg deposition and fish Hg content, these uncertainties can be precluded from unduly influencing the precision of the final answers. However, there may also be a loss in the specificity of the risk predictions. A detailed analysis of the roles of individual uncertainty elements would be required to optimize this risk assessment design process.

It remains to determine the sensitivity of the overall uncertainty of the risk assessment to these various simplifying assumptions. This is a necessary step prior to recommending additional detailed research on any of the many links of the assessment chain.

DOSE-RESPONSE FUNCTIONS

Quantifying the types and severity of health responses expected at given MeHg dose levels is the domain of the clinician or epidemiologist. However, the task of transforming such data into the mathematical expressions required for risk analysis often falls to the data analyst, as does consideration of the associated uncertainties. The requirements of this task include:

1. Selecting a dose metric that is compatible with the goals of the risk analysis and the available dose data.

2. Expressing the functional relationship accurately, with minimum uncertainty. This requires accurate dose data, among the other requirements of curve-fitting.

3. Considering the ramifications of extrapolating the relationship beyond the range of the original data, especially for low doses.

DOSE METRICS FOR METHYLMERCURY

The basic response data from the 1971-72 Iraqi grain poisoning incident (Bakir et al., 1973) have been expressed in several ways:

1. In terms of blood Hg concentrations, as determined about 2 months after the incident.

2. In terms of the amount or rates of bread consumed.

3. As a function of estimated maximum Hg concentrations in scalp hair.

4. In terms of estimated (maximum) body burdens of MeHg.

In selecting a dose metric, we must consider that the basic physiology of mercury poisoning points to body burden as the fundamental determinant of response, but blood and/or hair Hg levels have the advantage of being direct measurements and thus they may be less subject to error. Unfortunately, in this instance, the blood data were obtained substantially after the appearance of symptoms and the cessation of MeHg intake, and direct measurements of hair levels were not made for all patients. MeHg consumption rate is not a direct determinant of response, since response also depends on the body weight and half-life of MeHg for that individual. Thus, an error-free indication of dose is simply not available for this incident.

Given this situation, we recommend the dose-metric that is most compatible with the framework of the risk assessment, which is body burden. This metric is defined for the assessment in terms of the total MeHg at equilibrium (which is derived from the daily dose), divided by body mass. Distributions of both of these parameters are available for the assessment. Use of either the measured Iraqi blood or the estimated hair MeHg levels would entail additional assumptions and additional assessment calculations. However, we are forced to assume an equivalence between the steady-state situation represented by the assessment and the dynamic situation that was the Iraqi incident. Differences in the linearity of the observed decay rates of blood Hg suggest that this may be a source of uncertainty.

Additional ambiguity arises from the lack of precise definition of some of the neurological endpoints used by Bakir et al. Paresthesia is perhaps the mildest of the adult symptoms of MeHg poisoning and is thus a logical choice for our assessment; however, none of literature describing this poisoning incident specifies whether this symptom was considered as a transient or a chronic condition in evaluating patients.

If transient paresthesia is a valid health concern, then the risk assessment should consider the probability of acute MeHg excursions above the equilibrium steady state, due, for example, to consuming an occasional high-Hg fish meal.

Functional Relationships

Figure 2 is a plot of the Iraqi dose-response data (Bakir et al., 1973). The data are represented here as "hockey-stick" functions, i.e., a horizontal line representing the background prevalence rate, valid up to some dose level (the threshold value), and an upward slope from this point representing the rate of change of prevalence with dose. Three parameters are required to define this function: a slope, an intercept, and a background prevalence rate. Only two are independent; for a given dataset, the slope and intercept are correlated (r = -1).

Figure 3 shows how several other functional forms might be used to represent the same data for paresthesia. In this plot, the dataset has been augmented by adding the observations of Al-Mufti et al. (1976) and adjusting for the delayed determinations of blood Hg in the data of Bakir et al. The logistic function is favored by some biometricians, since it provides a non-zero risk estimate at low doses and is only asymptotic to 100% prevalence at high doses. Logistic regression also accounts for the absolute numbers of observations, rather than just a prevalence rate. However, the logistic function also admits a background prevalence rate; operationally, this value is subtracted from each observation before the logistic equation is derived. Figure 4 shows how the background assumption affects the regression fits, when expressed in logit coordinates. Although there are also 3 parameters involved here (slope, intercept, and background), only one is independent.

We used the @RISK package to generate expected values and 95th percentiles for logistic and hockey-stick functions for these data over an arbitrary range of body burdens. Through trial and error, we determined that a background rate of about 0.045 fit the logistic equation best (minimum chi-square), as shown in Figure 5. However, because of the linkage between background rate and slope (Figure 6), we also determined that the uncertainty in slope due to lack of fit would dominate the uncertainty in the background prevalence rate. We linked slope, intercept, and background prevalence in generating the confidence limits shown in Figure 7; the fitting procedure allowed different intercepts for the two constituent data sets used, which amounts to a larger uncertainty for the intercept. This made only a small difference in the confidence limit.

Figure 7 shows that the dose-response function alone contributes an uncertainty of about a factor of 5 at the lowest dose considered; however, this narrows to a about a factor of 2 near the threshold body burden of about 1 mg/kg. The corresponding data for a hockey-stick DRF are shown in Figure 8; however, by definition, this function estimates zero additional risk for values below the threshold. The uncertainty in predicted risk is somewhat less at the low end of the hockey stick function than for the logistic DRF.

Another consideration is that of the form of expression of "excess" risk, in the presence of appreciable background levels of the endpoint in question. Background plays a role in the parameterization of the logistic model; the ratio of risk due to MeHg to the background level is thus a logical parameter. Figure 9 displays the DRF confidence limits in this format.

Consideration of these two functional forms allows two choices for the estimated risk at low doses: zero, with no margin of uncertainty (given this model choice), or a wide range of small but finite values. This outcome requires additional information in order to allow a rational choice, such as the physiological considerations that pertain to the existence of thresholds.

WHY IS PROBABILISTIC RISK ASSESSMENT NEEDED?

As is the case with most assessments of the risks of hazardous materials, the main interest in the risks of MeHg is in the extremes of the distributions. In our current society, the average risks entailed through exposure to most environmental agents pose no particular hazard; if this were not the case, action would have been taken long ago to reduce such risks.

Sources of Variability

There are three typical sources of variability that enter into a probabilistic risk assessment. Heterogeneity exists in the human population and in the fish population. It is manifested as a range of fish-eating habits, body weights, and mercury half-lives in humans, and in a range of mercury concentrations in fish. If the entire distribution of mercury emission sources were under consideration, they would also exhibit considerable heterogeneity, through a range of stack heights, emission rates, and the meteorological factors that typify a geographic location.

Stochastic variability reflects the natural dynamics of certain factors, especially those meteorological factors that control transport, dispersion, and deposition. These effects can be minimized by considering long-term average deposition, for example. We label the uncertainties arising from lack of knowledge about certain processes, chemical reactions, etc. as the ignorance contribution to the overall variance.

Research is needed to reduce these effects. Finally, measurement errors contribute variance. These contributions include sampling errors and instrument errors. Additional measurements and laboratory intercomparisons can help here.

Propapagation of Variance

A probabilistic risk assessment is intended to produce a frequency distribution of predicted risks as its ultimate output, based on the distributions of a number of input parameters, including those representing the uncertainties of physical constants and of the parameters controlling environmental processes and transfers. Each arithmetic operation combining inputs increases the variance of the outputs. An alternative to the probabilistic approach that has been used in the past is to identify "high," "medium," and "low" values for each parameter, and then to work through the model with the appropriate combinations to derive three point estimates, which are then also labeled as "high," "medium," and "low." This approach takes no account of the (remote) probability that all "high" factors can occur simultaneously, and thus its applicability is uncertain. In the following section, we provide some examples of the errors that can occur through this practice. We used the program @RISK (Palisades, Corporation, 1988) to generate 95th percentiles of various combined distributions; these values are compared to the result obtained by performing the same arithmetic operations on the 95th percentile of each individual input distribution. All distributions were scaled to a mean of zero; the standard deviations of D1, D2, and D3 were 1, 2, and 3, respectively.

For example, the variance of a sum is given by the sum of the variances of the addends. This is also the case with subtractions. As a result, the variance of the least certain term will dominate the variance of the end result; addition or subtraction of factors with tight confidence limits will not seriously degrade the final confidence limits. Adding the extreme values of each factor will thus be an overestimate, as shown in Figure 10. Note that the probabilistic estimates of the 95th percentiles of all operations involving D3 are not much greater then the 95th percentile of D3 alone (4.93).

When two distributions are multiplied, the variances of both factors contribute to the variance of the product, and in some cases, the point estimates are reasonable (Figure 11). However, with division (Figure 12), the absoluet magnitudes of the terms matter, in addition to the standard deviations. When the variance is large compared to the mean, such that values near zero can occur frequently in the divisor, the distribution of the quotients may be unstable. In Figure 12, this case shows much larger 95th percentiles than thencase with mean values of 10, and the effect of additional variance in the divisor is reversed. Suffice it to say, that careful attention must be given to formulae which involve division by small and variable numbers. Note that it is not immediately obvious how to synthesize such a result using point estimates; the quotient of the high-value dividend with the low-value divisor in this example is negative, for example.

The uncertainties inherent in the dose-response functions (discussed above) also contribute to the overall variance and may be the largest source of variance for which improvements might be sought. This source of variance also includes the uncertainties arising from the selection of alternative functional forms to represent a given dataset.

How Can Systems Analysis Improve the Overall Risk Estimates?

An analysis of the components of variance can provide important guidance for future research, by identifying those elements whose uncertainties have the largest effects on the distribution of predicted risks. As an example, take the methylmercury dose per unit of body weight, which involves three factors: fish Hg concentration, fish consumption rate, and body mass. Since (presumably) only heterogeneity controls the variance of body mass and there are no near-zero values, we must look to the other two factors for improvements. The results of Figure 11 suggest that improvements should be sought in both of them, although narrowing the range of either one will help. With respect to the summation of the terms for different sea foods that comprise the overall dose, improvements should be sought in the one with the largest (absolute) variance.

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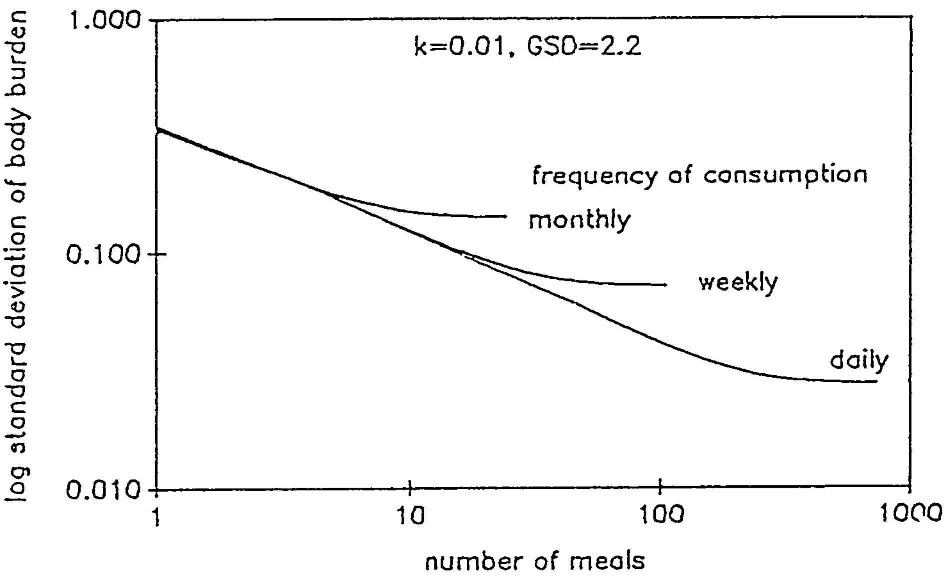

Figure 1. Reduction in the standard deviation of body burden as a function of number of fish meals consumed in the time to reach equilibrium as a function of meal frequency.

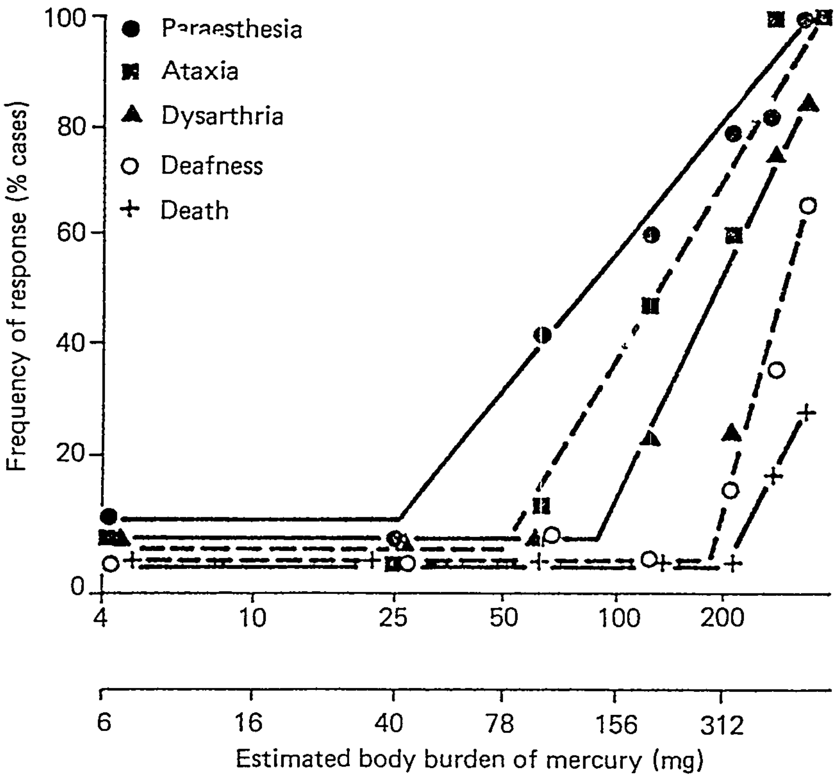

Figure 2. Dose-response plots for the 1971-72 Iraqi grain poisoning incident. Source: Bakir et al., 1973.

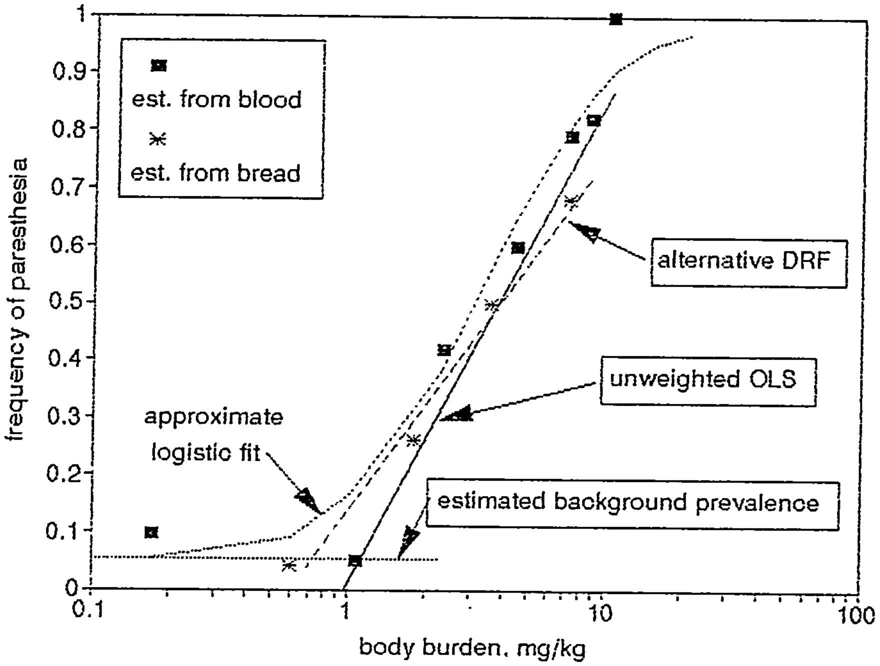

Figure 3. Alternative representations of the paresthesia response data from the 1971-72 Iraqi poisoning incident.

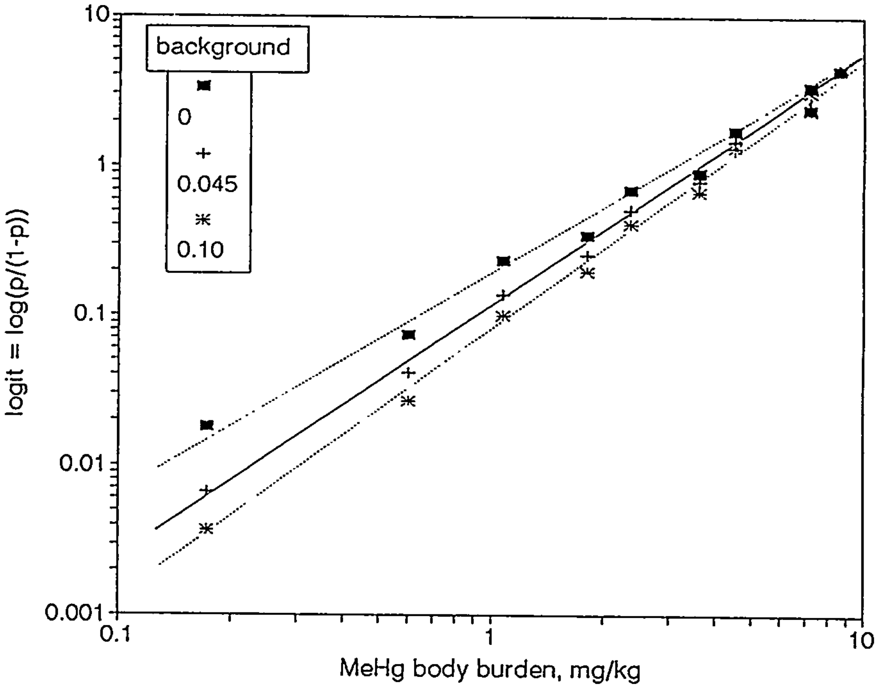

Figure 4. Effect of varying assumptions for background prevalence of paresthesia on logistic model fits.

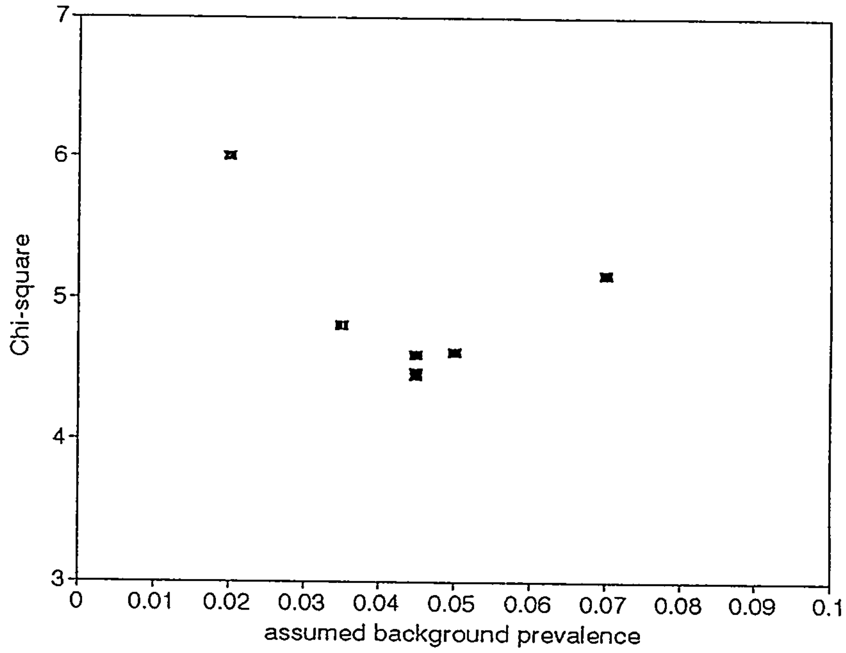

Figure 5. Chi-square results from logistic regressions using various assumed background prevalence rates for paresthesia.

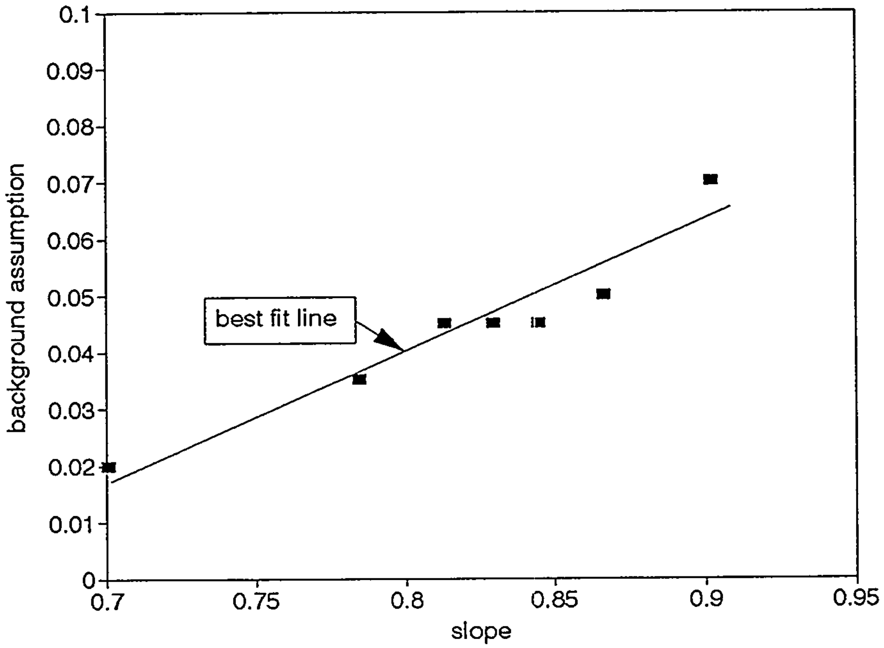

Figure 6. Relationship between background assumption and regression slope (in logistic coordinates).

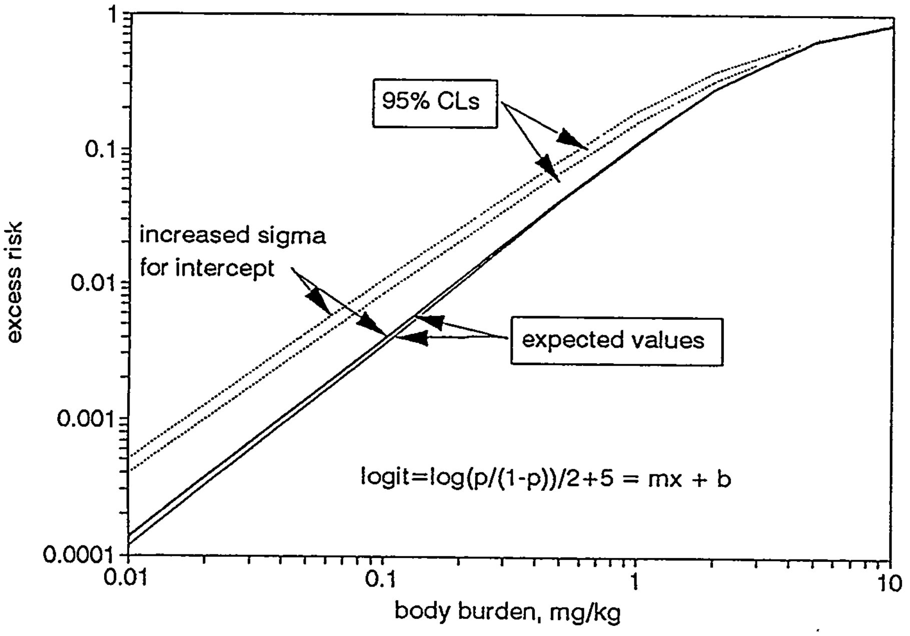

Figure 7. 95% confidence limits for logistic fit to the Iraqi paresthesia response data.

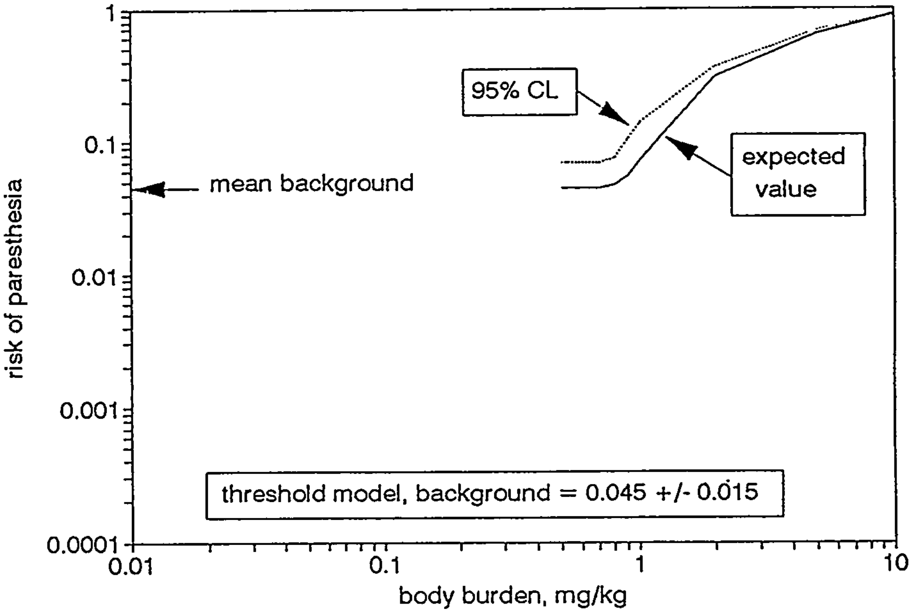

Figure 8. 95% confidence limits for a hockey stick fit to the Iraqi paresthesia response data.

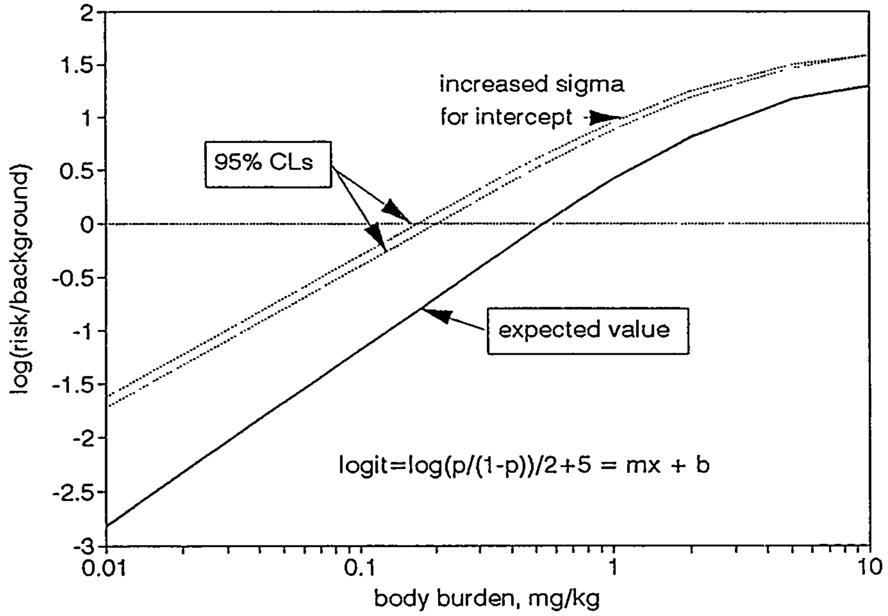

Figure 9. 95% confidence limits for logistic fit to the Iraqi paresthesia response data, expressed in terms of the ratio of excess risk/background risk.

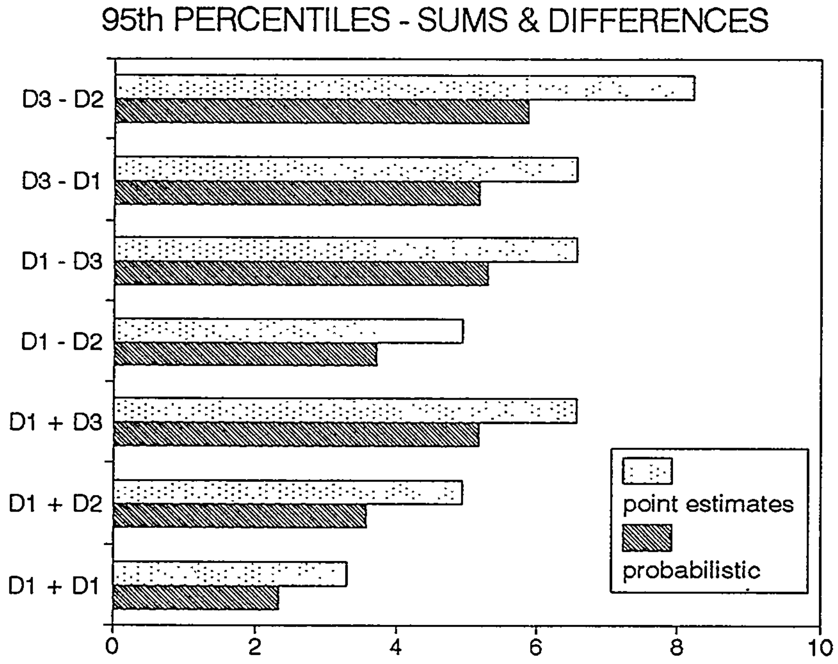

Figure 10. Comparison of point and probabilistic estimates of the sums and differences of various statistical distributions (D1, D2, and D3) with means of zero and standard deviations of 1, 2, and 3, respectively.

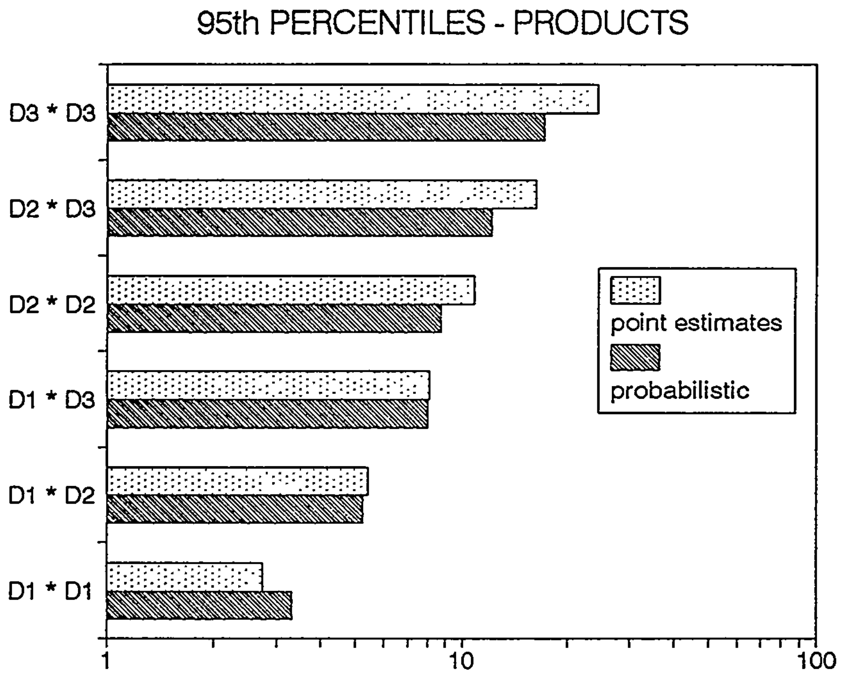

Figure 11. As in Figure 10, for products (note log scale).

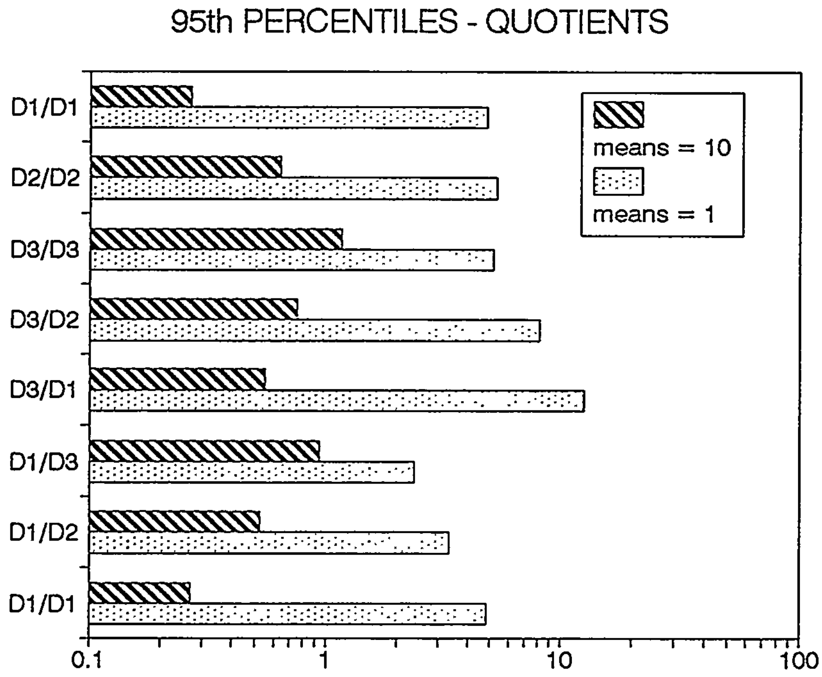

Figure 12. As in Figure 10, for quotients (note log scale).

WORKSHOP DISCUSSION

Suggested improvements to the BNL study included: 1) reframing the observed parameters; 2) validating the exposure and dose-response models, and 3) evaluating appropriateness of a hockey stick dose-response model. Several participants voiced the need to include regional deposition in addition to the already estimated local and global deposition. One participant also suggested that it would be important to compare the model used in the assessment with real data (e.g., compare against body burden measurements in a real population). Also voiced was the need to compare the model with other potential models to provide an estimate of uncertainty arising from model selection.

There was some concern that one shouldn't accept the result of a hockey stick model by default. Hockey stick analyses are not sensitive to variations in susceptibility among individuals. It was suggested that a better choice would be a probit model which could find non-zero risks realized at very low dose levels.

There was a general consensus that there is a need for more extensive and updated seafood consumption data. Among three existing food consumption sources (i.e., Hall, EPA, and a new FDA survey) there is large scatter. There is a need for an additional survey. Also, old analytical data may not be reliable due to changes in methodology. Data on consumption of freshwater species are very limited.

Another participant voiced the need for a further understanding of end-points and of mechanisms of sensitivity at a cellular level. There is evidence that cells exhibit resistance to Hg, suggesting a threshold of effect. This prompted the question of what is the population distribution of these defensive capabilities (e.g., age, genetic, heterogeneity, etc.). There was a suggestion that there is a need for further understanding of end points. Dose and time of exposure are both important determinants of response, which suggests that it may be important to model fetal exposure.

Finally, concern was expressed about the high correlation between MeHg in people and fish consumption. Similarly, fish also may contain other contaminants. Fish is an excellent source of quality protein, and if contaminant limits are set that reduce consumption, this may result in an overall adverse health effect. This question was echoed by other participants, but fell into a category of risk management which was deemed outside the scope of the discussion.

4. MERCURY EMISSIONS FROM ELECTRIC GENERATING STATIONS

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PREFACE

Under the new 1990 Clean Air Act Amendments, the U.S. EPA must evaluate emissions, available control technologies, and risks to public health from electric utility steam generating stations for 189 listed hazardous air pollutants. In response, EPRI has instituted the PISCES (Power Plant Integrated Systems: Chemical Emissions Studies) research program to improve the understanding of chemical emissions from power plants. Its focus is to create an industry database on mercury and other trace chemical emissions, to define methods for measuring these substances including techniques to speciate selected elements, to establish the capabilities of existing and emerging environmental technologies for controlling chemicals, if warranted, and to conduct field sampling campaigns at pilot-and full-scale power plants to ascertain process trace chemical data absent from the literature. The ultimate aim of the current effort is to characterize industry emission profiles and produce information and tools for utilities to assess emission risks and evaluate alternative control options. This paper provides some interpretations from the PISCES literature database for mercury, presents some preliminary field testing results from EPRI's research to date, and identifies critical needs for mercury in both data and fundamental knowledge.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has historically regulated air toxics (hazardous air pollutants) under the Clean Air Act since 1972. By 1990, however, EPA established emission standards for only 8 hazardous air pollutants (arsenic, asbestos, benzene, beryllium, mercury, radionuclides, coke oven emissions and vinyl chloride). While the U.S. electric utility industry was not defined as a source category requiring regulation for any of the eight chemicals, the 1990 Clean Air Act Amendments required a new evaluation of the electric utility industry emissions of hazardous air pollutants (Public Law 101-549, 1990).

The new law greatly expanded EPA's rulemaking authority over hazardous (toxic) air pollutants. It contains a list of 189 chemicals, including mercury, that would be subject to control. It requires sources, with exception of utility sources, that emit 10 tons or more per year of any one pollutant, or 25 tons or more per year of any combination, to apply Maximum Achievable Control Technology (MACT). Although not clearly defined, MACT is the maximum degree of reduction of hazardous pollutants that the Administrator determines is achievable. Consideration would be given to the cost and feasibility of control, energy impacts, and environmental factors. After applying MACT, a residual risk analysis will need to be performed to determine if additional controls are warranted.

Of the five studies mandated by the new law, two address mercury and directly affect electric utility operations: a 3-year study to address the hazards to public health associated with emissions from fossil-fuel power plants (after compliance with the acid rain provisions of the new law); and, a 4-year evaluation of mercury emissions, their effect on human health and the environment, and the availability and cost of potential control technology. EPA is directed to regulate the utility industry for air toxics only if its electric utility study -- now scheduled for completion by November 1995 -- indicates that such regulation is necessary and appropriate.

In previous risk assessments, EPA used available air toxic emissions factors from the literature (Radian Corporation, 1989). However, the values used are of uncertain quality with many acknowledged limitations. Variations in trace element levels in coal, the design and operating parameters of boilers and control devices, and uncertainty in sampling and analytical methodologies for detecting trace pollutants all contribute to the uncertainty. More recent analyses of these data and data gathered since completion of the earlier EPA risk studies generally support lower emission factors than those recommended in the EPA report (especially for chromium, manganese, and nickel).

This paper describes several key EPRI activities relating to mercury and provides some preliminary insights from EPRI's research to date.

EPRI AIR TOXICS EMISSIONS RESEARCH

To help the electric utility industry better understand emissions of potentially toxic chemicals from fossil fuel power plants, EPRI initiated the PISCES (Power Plant Integrated Systems: Chemical Emissions Study) project in mid-1988. PISCES is multimedia in perspective; that is, the study evaluates the presence and fate of chemicals in air, water and solid waste discharges (Chow et. al., 1992). This approach is being taken so that the effects of controls on air emissions, for example, can be assessed with full knowledge of the impacts on other plant process streams (i.e., solids and wastewaters).

The project involves the collection and review of existing data regarding the source, distribution, and fate of mercury and other chemicals in both conventional and advanced fossil-fuel fired power systems. It consists of several major products and activities including: a relational database of information gathered from the literature and other sources; a probabilistic power plant systems computer model to track the pathways of chemical substances and quantify emissions; a field monitoring program to measure emissions of mercury and some 21 other chemicals in utility flue gas at plants employing a variety of emission control technologies; a series of emission control technology reference guides; measurement methods validation and a set of guidelines for measuring trace chemicals in utility process and discharge streams. This effort is closely coupled with the development of trace chemical emissions control technologies and comprehensive, multimedia risk assessments.

Other EPRI air toxics research currently underway or planned, although not described in this paper, includes an evaluation of potential health effects (e.g., arsenic, mercury, and nickel) associated with utility emissions; a comprehensive study of mercury cycling and ecosystem impacts; and, an investigation of the atmospheric transformations of selected chemical species such as mercury.

A Database

An early phase of the PISCES project was to create an industry emissions database based on available literature information collected for conventional coal-, oil-, and gas-fired power plants. Over 500 chemicals were identified in power plant process streams. Approximately 80 of these 500 were selected for additional data search on regulatory limits and health effects. In general, more and better data tend to be available for inorganic species in liquid and solid process streams than for air toxics. Further, lesser amounts of data are available for inorganic species in gaseous process streams and organic species in all media. In fact, the quantity of data altogether for trace chemicals in internal power plant streams are quite sparse. Data on mercury on conventional power generation systems was virtually nonexistent. However, with this database vehicle, one can organize the data to explore relationships between mercury and other chemicals, process streams, and one or more systems or plant components.

An example of information derived from the interim database is shown in Figures 13 and 14, depicting the concentration of mercury in various fuels and fly ashes. These curves represent the probability of finding mercury less than a specific concentration for four fuels. Based on data in the PISCES database, the fuel with the highest variability is oil.

Given sufficient data in the PISCES database, first order predictions of air quality control technology performance for air toxics removals, for mercury for instance, could reasonably be attained. However, the major issue is the lack of fundamental data about these technologies for chemical species of concern. Although the number of available data points for plant emissions of various chemical species is quite large, the number of paired data sets -- inlet and outlet -- on any given control device is sparse. This led to a Field Chemical Emission Monitoring (FCEM) program in association with EPRI member companies and the U.S. DOE.

About Mercury

During the debates on the air toxics provisions of the Clean Air Act Amendments one chemical have received significant attention -- mercury. Mercury, however, is emitted in relatively small quantities from conventional electric generation facilities. Uncontrolled emissions from a typical 500 MW coal-fired power plant would be about 500 pounds per year. Actual emissions are less given that currently available environmental control technology does remove some mercury. Utility emissions of mercury are relatively small; that is, the annual contribution from U.S. fossil-fuel fired electric utility boilers represents roughly 1 or 2 percent of the 6 million kilograms global mercury budget and less than 2 percent or so of global anthropogenic emissions [Porcella, private communications; Nriagu, et. al., (1988). The following discussion is a summary of the state-of-knowledge regarding the emissions and control of mercury.

Mercury levels in U.S. coals vary from about 0.01 to 8 ppm (Radian Corp., 1988; Smith, I., 1987). Typical values, however, are about 0.24 ppm for Appalachian coals, 0.14 ppm for Interior Eastern coals, and 0.21 ppm for Illinois Basin coals (Coal Conversion Systems Technical Data Book, 1982). However, more recent measurements of mercury point to a much lower average value in the range of 0.1 ppm for a broad range of U.S. coals fired in power plant boilers. This may be due to coal washing, a practice by coal suppliers to reduce ash content, before the fuel is fired. The washing may reduce the raw coal concentrations of mercury as well as other heavy metals. Mercury reductions between 20-30% have been reported (Clarke and Sloss, 1992). The dominant form of mercury (divalent or elemental) emitted is uncertain. Speciation properties of mercury found in coal combustion flue gases may be dependent on the chlorine concentration in the coal and therefore the HCl concentrations in flue gas. Hence, we must first develop a validated methods for measuring mercury species and then define whether chloride content indeed influences mercury emissions.

The literature is quite confusing regarding mercury emissions from coal-fired power plants. First, it is not always clear whether the measured mercury was total, vapor phase, or that condensed on particulates. Secondly, the sampling and analytical methods used may have been unreliable. Finally, most early data available on mercury removal are from the municipal waste incinerator industry where mercury concentrations are higher by several orders of magnitude than in utility flue gas.

Literature reviews by IEA Coal Research (Clarke and Sloss, 1992; Smith, I., 1987) showed mercury removals ranging from 10% to 50% through fabric filters or ESP's. These references also reported that FGD systems removal spans a large range, from 30 to 80%. In contrast, the EPRI PISCES literature database indicates about 20 to 90% removal for cold-side ESPs (5 data points) and 85 to 90% for fabric filters (3 data points). The reasons for these large ranges may be (1) the sampling and analytical variability, (2) the unburnt carbon carryover due to loss on ignition during combustion, (3) the speciation form of the mercury, and/or perhaps even the chlorine concentration in fossil fuels.

Measuring For Mercury and Other Elements

The PISCES FCEM program began in May 1990 with the collection of data on 22 chemicals (Table 3). Emissions and discharges are being measured for several control technologies, including cold-side ESPs, fabric filters (conventional and pulse-jet), low-NOx burners, postcombustion NOx systems, spray dry FGD, and wet lime/limestone FGD. Plant mass balances are being performed for each metal and inorganic chemical to define their sources, pathways, and the way they partition in the plant system. Therefore, all appropriate liquid and solid waste streams are sampled in addition to the flue gas. A variety of coal-types and combustion systems are included in the program. Bituminous, subbituminous, and lignite coals are included. Combustion sources include wall-, tangential-, and cyclone-fired boilers and fluidized bed systems. Also, oil- and gas-fired boiler and combustion turbine emissions are being examined for a smaller subset of air toxics.

The acquisition of new, better quality data from current utility operations, using improved sampling and analytical procedures (Table 4), is intended to upgrade the database and provide performance information for the future production of control technology engineering reference guides. Evaluating potentially toxic emissions is critically dependent on the ability to sample and measure these chemical species, especially when a vast majority of those listed in the new Clean Air Act Amendments only appear in trace amounts in plant process streams. This is particularly appropos for mercury. Mercury physically appears in flue gas in both gaseous and condensed forms. To exacerbate matters, the species (vis a vis chemical oxidation state) of mercury is a key determinant for its pathway towards possible methylation in the environment and also for the effectiveness by which various air quality control devices can remove this trace element from flue gas streams prior to emission. Without the requisite understanding of a method's capabilities and limitations, misleading results are not only possible, but highly probable.

Mercury removal has been difficult to accurately determine since it is present in such low concentrations in the clean flue gas (less than 1 $\mu g/Nm^3$). Because of this, EPRI and EPA has jointly sponsored field validation test of a full-scale power plant stack gas for mercury concentrations. The methods compared for mercury determination included: (1) EPA's multi-metals Method 29, (2) EPA's Method 101, -- both methods are based on potassium permanganate oxidation and the samples analyzed by cold vapor atomic absorption, (3) the iodated carbon sorbent method using cold vapor atomic fluorescence analysis, (4) the carbon impregnated filter element using x-ray flourescence, and (5) the neutron activated analysis of a carbon sorbent sample. Results of this study will be reported in later this Spring. However, preliminary indications are that the comparisons have been reasonably good for mercury at average flue gas concentrations of about 1.5 μg/Nm^3. EPRI continues to evaluate these sampling and analytical procedures for mercury at selected test sites.

In addition to measuring for total mercury, EPRI (as well as DOE) has tried to measure for mercury species with varying degrees of success. Two methods have been used for this purpose: EPA's Method 29 and Frontier-Geoscience's Mercury Speciation Method. While not designed for this purpose, EPA's Method 29 has been used on occasions by DEO to distinguish between elemental and oxidized forms of mercury by analyzing the tandem sets of impingers separately. The oxidized forms of mercury are captured by the nitric acid/peroxide impingers, while elemental mercury is captured in the permanganate impingers. EPRI has complemented the use of EPA's Method 29 for speciating mercury with that of the method used by Frontier-Geosciences. That method relies upon a potassium chloride/soda lime traps to detain oxidized mercury followed closely by iodated carbon for capturing elemental mercury. Thus far, speciation results by Method 29 for a limit set of comparative tests appear to agree well with those from simultaneous measurements using Frontier-Geosciences' solid sorbent trap method.

However, the methods offered by Frontier-Geosciences was taken one step further. During the course of EPRI's field testing for hazardous air pollutants, samples were gathered at selected sites by Frontier-Geosciences and tested for monomethyl mercury. These early flue gas test results seemed to show some monomethyl mercury present in stack gas (up to 15%). The methylmercury was determined from the potassium chloride/soda lime samples following methylene chloride extraction, using aqueous phase ethylation, cryogenic GC separation, and cold-vapor atomic fluorescence detection. But recent studies have uncovered an artifact in this approach which overestimates the amount of monomethylmercury found. The speculation is that divalent mercury and sulfite (S+4) collected on the solid potassium/soda lime sorbent, when digested with an acetic acid solution, will form monomethylmercury on the high pH surface of the dissolving soda lime. Monomethylmercury forms due to the release of methyl groups during the degradation of the acetic acid in conjunction with the oxidation of the sulfite. Work is being actively pursued to resolve this question.

Field Measurement Results

Preliminary data from EPRI's field monitoring study are now becoming available. Comparing the PISCES FCEM test results to information in the literature database, one can reaffirm our common understanding of the fate of certain classes of chemical species within the power plant. For example, both available literature data and FCEM results for mercury indicates that most of this volatile element remains in the flue gas following an ESP (Figure 15). However, noteworthy are the much lower new mercury values of between 0.1 to 0.2 ppm measured for the FCEM coals, in contrast to the more variable historical literature data.

Electrostatic Precipitator (ESP) - controlled coal-fired power plants represent the largest segment of the industry tested under EPRI's PISCES and DOE's air toxics field sampling programs. Early test results have demonstrated the tremendous capacity of particulate collection devices to reduce many heavy metals from flue gas streams. A number of metals such as arsenic, nickel, chromium, lead, cadmium can be removed by an average of better than 90%. Figure 4 illustrates this point for arsenic and chromium. With very limited results (4 early sites), the removal performance from fabric filters are quite encouraging, indicating reductions over 99% for metals such as arsenic.

Much of the reductions are attributable to the metals condensation onto particulate material as combustion gas temperatures drop from 1260°C (2300°F) in the boilers to 121°C-149°C (250°F-300°F) inlet to the cold-side particulate capture devices. This suggests that improved removals of combustion and post-combustion particulates and aerosols coupled with lower temperatures would significantly reduce flue gas concentrations of many of the heavy metals. The question is will this also hold true for mercury and selenium which are more volatile. [Future test data will be carefully examined to confirm these hypotheses.] Note in these same results the relatively low reduction characteristics (15-30%) for mercury. However, the results are still confounding. A few data points have indicated higher removals (up to about 60%) by ESP's (again, Figure 16). One theory suggests that unburnt carbon carryover due to loss of ignition (LOI) may be adsorbing the element. This is a subject for follow-up research.

Early PISCES results were also compared between different combinations of technologies represented by the tests sites. The best trace metals reduction properties, with above 95% reductions, were achieved with fabric filters and the combination of particulate controls with a flue gas desulfurization process, whether wet or dry systems. The exceptions may be the volatile elements such as mercury where the physicochemical behavior is not well understood. Mercury removals appear to be reasonable with scrubbers; but further confirmation awaits.

Based on very limited mercury studies around a 4-MW pilot unit consisting of a cold-side ESP plus wet limestone FGD combination treating bituminous coal gas, both oxidized, and elemental-mercury were found. Two observations are notable. First, the dominant form of mercury in the combustion flue gas was the oxidized form (at approximately 60% of the total mercury); and, second, the combination pilot ESP and wet FGD captured all of the oxidized mercury, leaving a third of the elemental mercury behind in the emitted flue gas (Figure 17). There is the matter of whether and to what extent any methylmercury is present. Early methylmercury findings are questionable.

Material balance for variety of key elements has been excellent, mostly within the 70-130% desired interval, mercury balances were mixed. 100% closure represents a complete material balance. Most of the older mercury emissions data reported in the literature are suspect given the difficulties in mercury sampling and analysis. Since mercury amalgamates with many metals, it is ubiquitous in many laboratories and thus contaminates samples. It does appear that the more recently reported data using better sampling techniques and analytical methods are reducing some of this uncertainty.

Difficulties in learning to use both EPA's Method 29 and the Solid Iodated Carbon trap techniques was an issue. For instance, even results from early PISCES field sampling of mercury were unspectacular. Mercury recovery from the EPA multi-metals sampling train were a meager 30 to 40%. Material balances were reporting less than 50% closure at the early test sites (Figure 18). However, with experience improvements to the sampling and analytical procedures, and frequent cross-comparisons with alternative mercury measurement methods, the accuracy and reproducibility of mercury determinations improved dramatically for flue gas, sluice water, flyash, and coal samples. Recent material balances for mercury around the power plant site are now much closer to complete closure. They are now within the 70-130% acceptance interval around the 100% closure mark. Several of the early test sites have since been re-tested to obtain more useful mercury measurements. However, these results from the FCEM program points to the need for further improvements in mercury sampling and analysis aimed at fuels and other solid particles.

To date, EPRI has sampled at over two dozen conventional power plant sites. In addition, the U.S. Department of Energy-Pittsburgh Energy Technology Center (DOE-PETC) conducted a complementary program in 1993 at approximately 8 more locations. DOE-PETC sampled for nearly the same suite chemicals and followed a similar sampling and analytical protocol as EPRI's FCEM Program. DOE-PETC's work, however, was expanded to also include radionuclides and collected additional samples for particle size distribution studies.

Other Mercury Studies

Several papers have reported that mercury can be removed from municipal waste incinerator flue gas through use of chemical additives. Joy Technologies (Donnelly, and Felsvang, 1989) reported that use of an additive in a spray dryer system improved mercury removal as did operation at lower exit gas temperatures. Joy's data show that a spray dry/baghouse combination operating on a municipal waste incinerator removed 69% of the total mercury without the additive and from 91% to 95% with the additive. The spray dry/ESP combination removed from 27% to 66% of total mercury without the additive and from 78% to 86% with the additive. The higher removals were observed at the lower exit gas temperatures. Although the additive was not specified, it is assumed to be activated carbon. Use of activated carbon has been reported by others with similar results (Teller, et. al., 1989; Volland, 1991, Guest, et. al., 1991; Riley, et. al., 1991).

More recent EPRI exploratory tests were conducted with activated carbon injection just upstream of a 1-MW pilot pulse jet fabric filter system at a low sulfur subbituminous coal-fired power plant (Chang and Owens, 1993). Inlet mercury concentrations ranged from 2 to 8 µg/Nm^3. When activated carbon was injected at a ratio of 4000 parts of carbon per part of mercury in the flue gas, where most of the flyash has been removed by a reverse-gas fabric filter upstream, mercury removals of better than 90% was observed (Figure 19) at temperatures of 121°C (250°F). The coal contained low chlorine concentrations and the measured ratio of ionic to elemental mercury was about 75/25. In the same EPRI study, mercury rich activated carbon was sampled for desorption effects over a four week period. No significant mercury re-volatization was detected. Without carbon injection, the pilot fabric filter mercury removal efficiency dropped to 30 to 50%. And yet, the dependability of activated carbon is still elusive. Another recent activated carbon test by the University of North Dakota energy and Environmental Research Center yielded significantly lower vapor phase mercury removals at similar carbon injection ratios.

Because the technique of using sorbents, such as activated carbon, is promising, additional research is underway by the electric utility industry and U.S. government agencies to establish their properties and better define their applications.

CONCLUSIONS

Future PISCES efforts will involve both laboratory development as well as field evaluation studies of specific methods for measuring mercury species and other important chemicals in fuels and flue gas. Besides mercury, improved sampling techniques for benzene and speciation of important trace elements such as arsenic and chromium would also be of particular interest.

Electric utility flue gas emissions are generally well controlled and will be even more so after complying with the acid rain provisions in the 1990 Clean Air Act Amendments. However, the new Clean Air Act Amendments require several detailed studies of the risks associated with the combustion of fossil fuels. Based on these studies, the U.S. EPA will make a determination as to whether further controls beyond the acid rain provisions are necessary.

As for mercury, on-going studies by EPRI, U.S. DOE and others will continue to provide information on mercury and its species to assist in EPA's evaluation. These studies, including emissions characterization and the quality of emission measurements, understanding mercury cycling in the environment and producing accurate risk models will provide valuable input to the assessment of health risks and the EPA's studies. With these continuing efforts to acquire better quality mercury data and specific information on the forms which impacts health risk, the Federal agencies and industry will be in an improved position to make a positive technical contribution to the hazardous air pollutants debate.

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Table 3. FCEM Target Analytes

INORGANICS			ORGANICS
Arsenic	Barium	Beryllium	Benzene
Cadmium	Chlorine/HCl	Chromium	Toluene
Cobalt	Copper	Fluorine/HF	Formaldehyde
Lead	Manganese	Mercury	PAHs
Molybdenum	Nickel	Phosphorous / phosphate	Dioxins / Furans
Selenium	Vanadium		

Table 4. FCEM Chemical Detection Limits

Substance	Sampling Method	Analytical Method	Detection Limit (ug/Nm3)
Arsenic	Multi-metals	GFAAS	0.12
Cadmium	Multi-metals	GFAAS	0.04
Chromium	Multi-metals	ICP-AES	0.4
Mercury	Multi-metals	CVAAS	0.07
HCl	Anions	IC	12
Benzene	VOST	GC/MS 8240	0.25
Formaldehyde	Aldehydes	HPLC	0.5
PAH's	Modified Method 5	HRGC/MS 8270	0.001

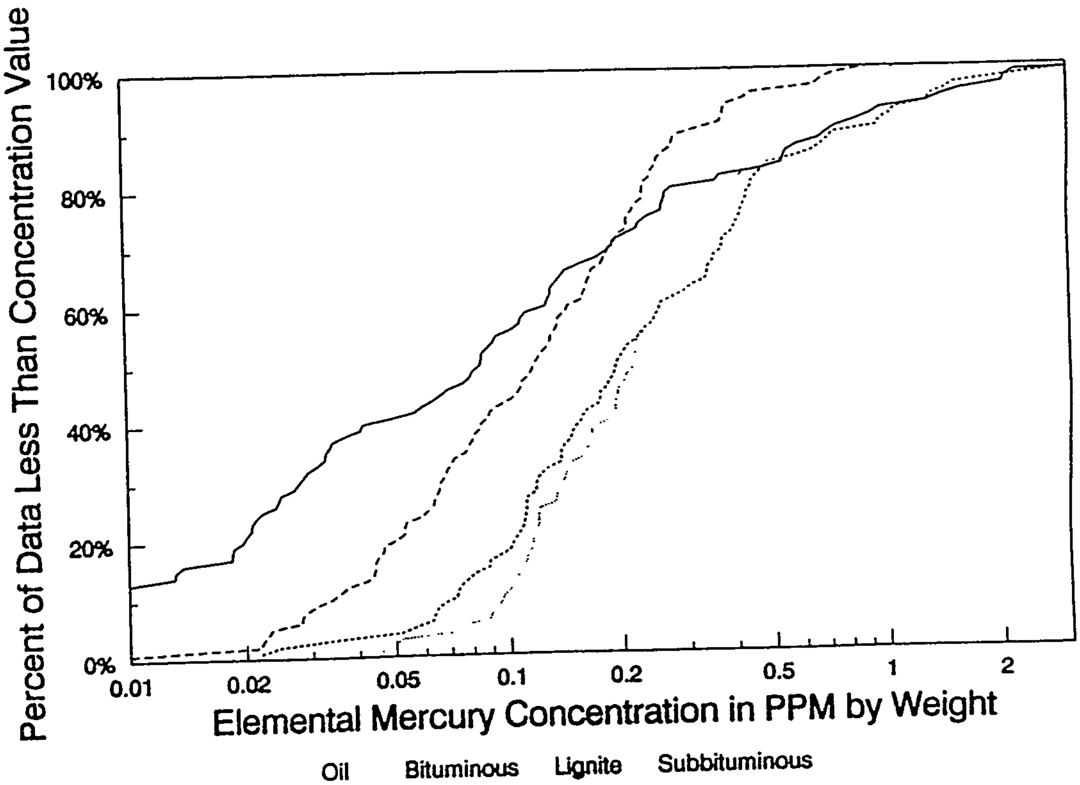

Figure 13. Mercury concentration in fuels.

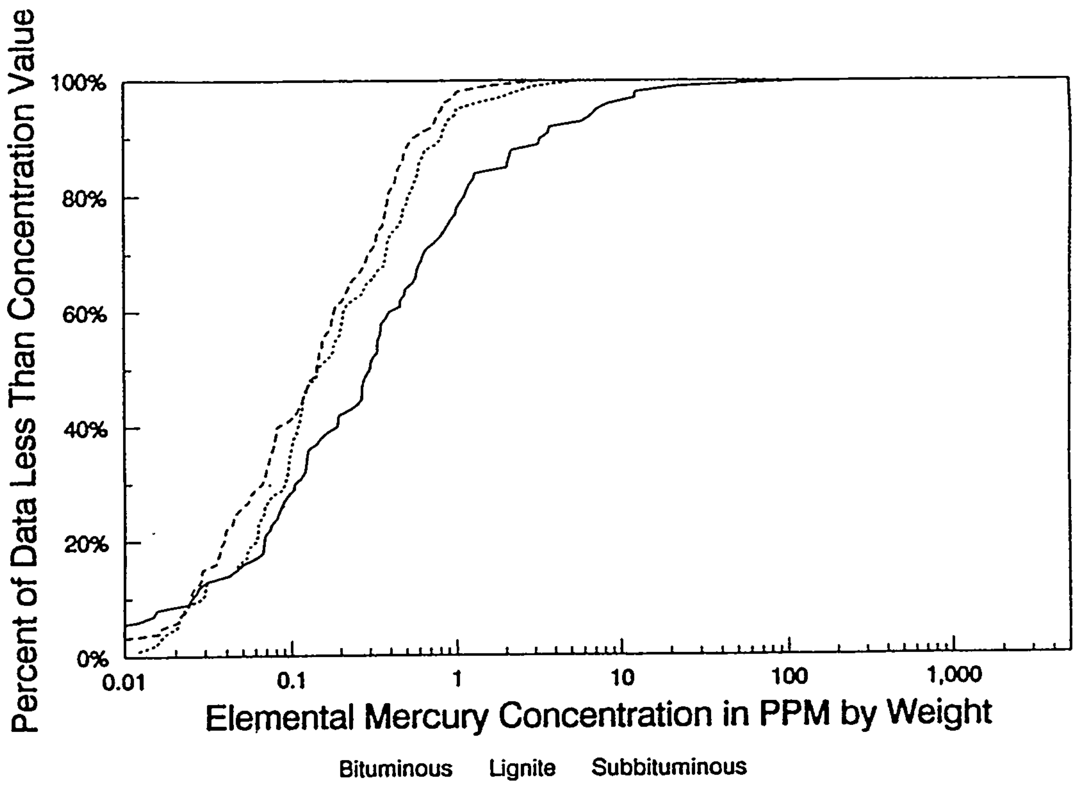

Figure 14. Mercury concentration in fly ash.

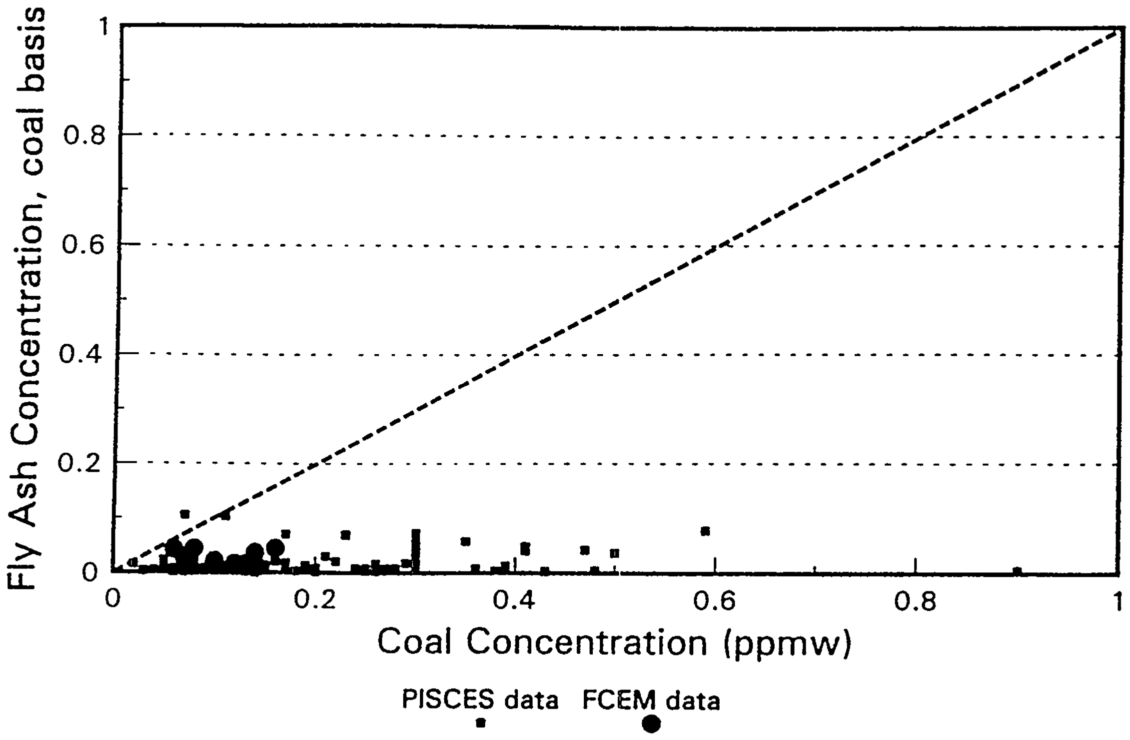

Figure 15. Mercury literature and FCEM values.

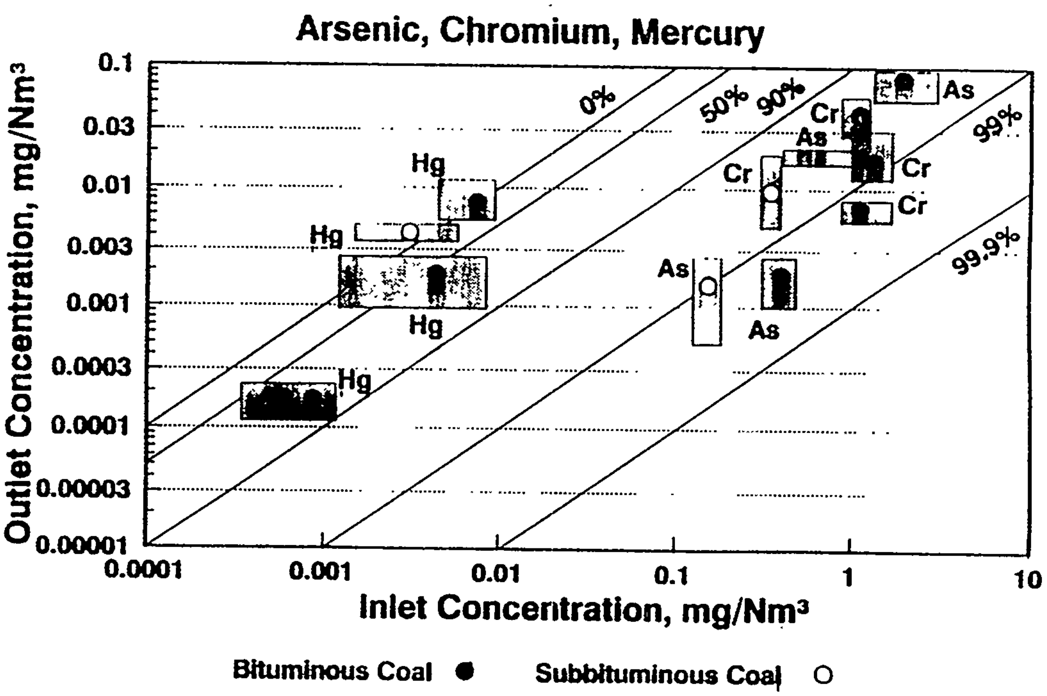

Figure 16. ESP removal efficiency: 4 test sites.

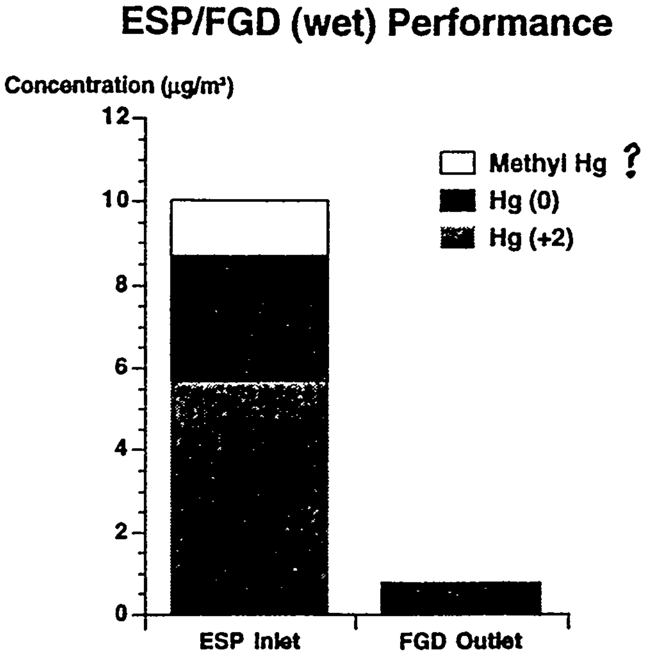

Figure 17. Mercury emissions speciation.

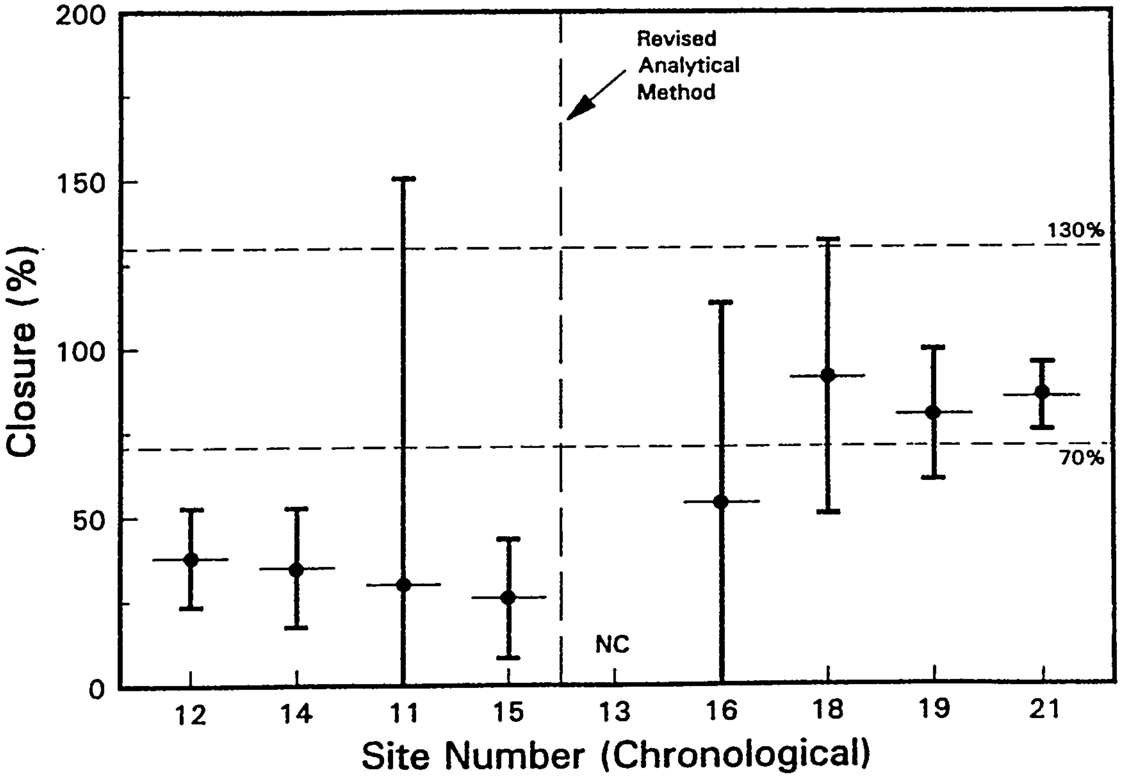

Figure 18. Mercury recovery from the EPA multi-metals sampling train.

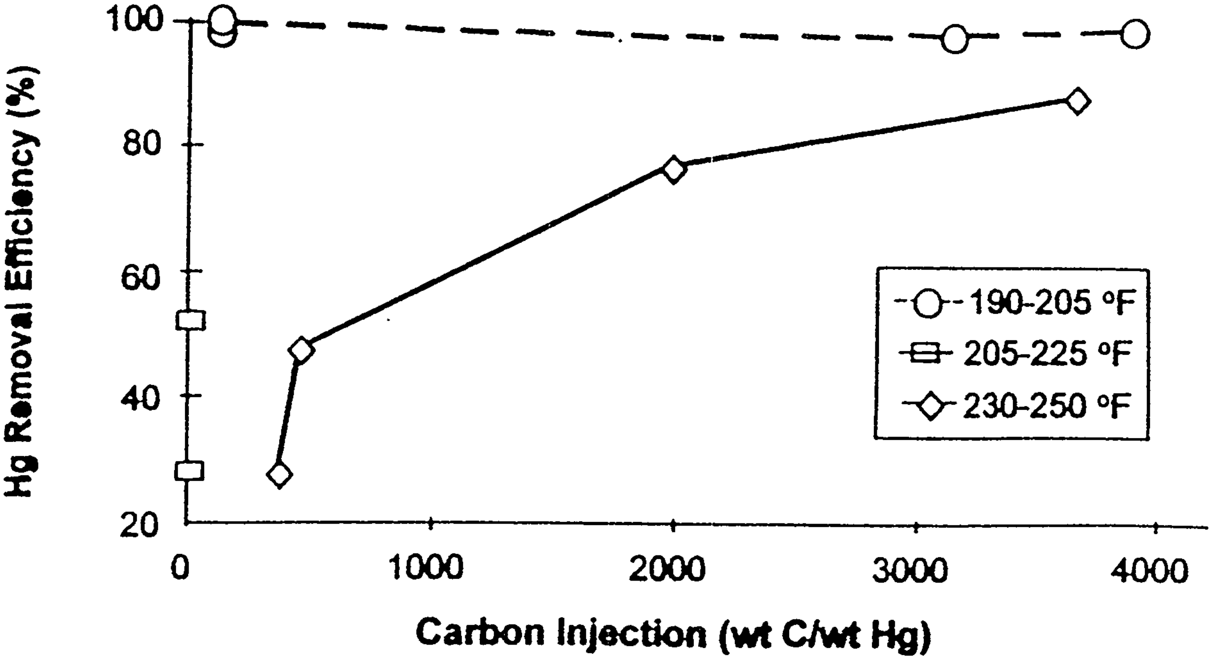

Figure 19. Mercury removal vs. temperature.

WORKSHOP DISCUSSION

There was general consensus on the importance of considering speciation when measuring Hg emissions from fossil fuel sources. Speciation is important for estimating where the Hg will deposit (e.g., Hg^{++} would deposit locally within 50 km and Hg^0 would be part of the regional and global problem). Other important factors put forth by participants that should be considered are: stack height, particle size, ambient air quality, and precipitation rate.

A question arose regarding the significance of removing Hg through coal washing. The speaker indicated that information is available showing that coal washing may result in a 50% reduction in Hg. This prompted a question of whether this has been verified by mass balance calculating at coal-cleaning plants. The response indicated that DOE is presently evaluating a coal-cleaning plant.

One participant asked about the need for developing spatially disaggregated emission inventories. There is presently disagreement between existing EPA and EPRI inventories.

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5. MODELING ATMOSPHERIC CONCENTRATIONS AND DEPOSITION OF Hg

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INTRODUCTION

The deleterious effects on ecosystems of mercury pollution are well established and fish advisories are in effect for many lakes in North America. Because methylation and other transformation processes in ecosystems can alter the original speciation of deposited Hg, a decrease in atmospheric loading of Hg in all forms is highly desirable. The contribution to Hg deposition by emissions from current anthropogenic activities relative to the deposition contribution by emissions from natural processes must be estimated to establish what fraction of atmospheric loading to watersheds and ecosystems is at least potentially amenable to control actions. Additional modeling questions concern source-receptor relationships (SRR) for major point sources and for emissions aggregated over geopolitical regions or emission sectors, because of the usefulness of SRR in comparing effectiveness of alternate control strategies.

Modeling of atmospheric Hg is less advanced than that of some other widespread air pollution problems such as acid deposition. Nonetheless, several promising studies have been made for northern Europe (*e.g.*, Peterson and Iverfeldt, 1993) and North America (*e.g.*, Bloxam *et al.*, 1992). For this study of Hg deposition in eastern North America we extend modeling techniques used extensively and successfully during the last 15 years for concentrations and deposition of SO_X and NO_X over regional scales, with parameterization rates adjusted to suitable values for Hg transformation and removal.

MODEL

Although field investigation of key atmospheric processes of Hg reactions and removal has been limited, the processes are known to be complex (Munthe, 1993; Lindquist and Rodhe, 1985; Schroeder *et al.*, 1991). Diagnostic analysis with sophisticated Eulerian models can be very informative because of the potential for detailed treatment of Hg chemistry (Bloxam *et al.*, 1992), but such models are difficult to apply in policy assessment because of their extensive input data and computational requirements and their typical temporal limitation to episodes of only several days duration. However, detailed atmospheric Hg models make important contributions to emissions control policy analysis through development of improved parameterizations for simpler, more efficient models, such as the model described below.

For this study we use the framework of the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model. ASTRAP was originally developed to simulate long-range transport and deposition of SO_X and NO_X over North America (Shannon, 1981, 1985), but also has been applied with appropriate modifications to simulate deposition to the Great Lakes of toxaphene (Voldner and Schroeder, 1989), S and NO_X-N (Shannon and Voldner, 1992), and Pb (Voldner *et al.*, 1993). To extend the model to simulations of Hg concentrations and deposition, changes in the number of pollutant species treated and in their parameterized rates of transformation and removal must be made. The meteorological parameterizations, which are related primarily to average diurnal and seasonal patterns of vertical mixing, are independent of the pollutant of interest and need not be altered. We treat Hg as a three-species system; elemental Hg vapor (Hg^0), divalent Hg vapor (Hg-II), and particulate Hg (Hg-p), and allow a very slow net transformation of Hg^0 to Hg-p.

Briefly, ASTRAP is a long-term Lagrangian (trajectory) model applied over regional to continental scales. For each point in a grid of virtual sources covering all of the contiguous United States and the Canadian provinces an ASTRAP subprogram calculates seasonal mean trajectories and wet deposition "plumes." Horizontal dispersion is approximated by the spread of individual trajectories about the mean trajectory, rather than by diffusion about individual trajectories. The wet removal rate is a function of the half-power of the 6-hr precipitation; cumulative wet removal is a function of precipitation frequency. The calculations require regularly updated analyses of precipitation and mixed-layer wind fields across North America.

A second subprogram calculates dry deposition and the vertical profile of the one-dimensional concentration of each Hg species as a function of season, effective emission height, and plume age. Calculations require parameterized patterns of dry deposition velocities, chemical transformation rates, and vertical profiles of eddy diffusivity; the specified patterns vary diurnally and seasonally.

A third subprogram combines horizontal dispersion statistics from the first subprogram and vertical dispersion statistics from the second subprogram with an emission inventory to calculate seasonal average air concentrations and cumulative seasonal wet and dry deposition for the region of interest. Spatial resolution of gridded output is a modeling option, for which the resolution of the input emission and meteorological fields and the purpose of the model simulation should be taken into account.

The method of parameterization of dry deposition, *i.e.*, specified seasonal and diurnal variations in dry deposition velocity (v_d) for each Hg species, allows no horizontal variation of v_d except over the Great Lakes in postprocessing as discussed later. The v_d patterns used in these simulations (Figs. 20-22) are estimated subjectively, based on field studies of Lindberg *et al.* (1991, 1992) and Iverfeldt (1991) and on arguments made in other modeling studies (Bloxom *et al.*, 1992), and in estimates of the global Hg cycle (Fitzgerald, 1993). The field studies by Lindberg *et al.* over a forested area in the southern United States calculated Hg^{o} and Hg-p deposition velocities from modified Bowen ratio techniques. Their deposition velocities for Hg^{o}, while small, are still much larger than the values assumed or implied in calculation of global Hg budgets. Part of the difference may be because the field experiments were conducted over a specific surface, *i.e.*, a deciduous forest in hilly terrain. Another possible contributing factor is that in the field measurements vapor-phase Hg was dominated by Hg^{o} and subsequent v_d analyses assumed that vapor-phase Hg consisted entirely of Hg^{o}. If only 1% of the vapor-phase Hg was Hg-II, and typical values of v_d for Hg-II are two orders of magnitude larger than that for Hg^{o}, an assumption consistent with arguments of Munthe (1993), then the apparent v_d for Hg^{o} would be doubled. On the basis of the latter argument and because the model parameterizations of v_d are not surface specific except as described below for the Great Lakes, we have selected v_d parameterizations that when seasonally averaged are about 1/4 of the seasonal means from the Lindberg *et al.* studies. With the specified v_d patterns Hg-II is rapidly removed by dry processes, with the effective limitation being atmospheric resistance to vertical transfer; Hg-p is removed slowly as is typical of submicron particles; and, Hg^{o} is removed very inefficiently. Dry deposition is most efficient seasonally during summer, and most efficient diurnally during midday.

The treatment of Hg transformation in the model framework is problematic because of limited knowledge about atmospheric processes (Munthe, 1993) as well as limitations in the model structure. Gas-phase reactions are assumed to be unimportant. The main aqueous-phase reactions and transformations are thought to be oxidation of Hg^{o} by ozone to Hg-II; reduction of Hg-II by sulfite; and, adsorption of Hg-II to soot particles (Petersen, 1992; Petersen and Iverfeldt, 1993). The model framework cannot directly accomodate these processes; instead, the model simulates a slow net conversion of Hg^{o} to Hg-p. The Hg-p is subject to wet scavenging, but a portion of the Hg would be incorporated into the submicron particles that remain after cloud droplets evaporate. We have prescribed diurnal and seasonal variations about an average transformation rate of 0.05% hr^{-1} as shown in Figure 23.

Wet removal from the mixed layer in the model has two components: wet deposition to the surface (R_1) and (for Hg-II only) loss to the free troposphere by convective mixing assumed to be associated with precipitation systems (R_2). The parameterization assumes that concentrations of Hg-II in the free troposphere are negligible because of highly efficient wet removal, and thus vertical redistribution would serve to decrease mixed-layer concentrations. Redistribution to the free troposphere is not simulated for Hg^{o} and Hg-p because their much longer atmospheric residence times, particularly for Hg^{o}, should lead to similar concentrations within and above the mixed layer and thus convective mixing should have no significant effect. Hg-II exported to the free troposphere remains available for later wet removal, but is no longer available for dry deposition because of decoupling from the surface. All R_i values refer to fractions of the pollutant mass airborne at the beginning of the trajectory time step. The parameterization of a wet removal event is:

Where P is the precipitation rate (cm per 6 hr),

$R_1 = \mathrm{Min}\{a \cdot b(t) \cdot P^{0.5}, 0.5\}$ $\quad P \geq 0.1,$

$\quad a = 10,\ b(t) = 1$ $\quad$ (Hg-II)

$\quad a = 1,\ b(t) = 1$ $\quad$ (Hg-p)

$\quad a = 1,\ b(t) = 0.0005\ \mathrm{hr}^{-1}$ $\quad$ (Hg^{0})

$R_2 = \mathrm{Min}\{P^{0.5}, 0.5\}$ $\quad P \geq 0.1$ $\quad$ (Hg-II),

$R_2 = 0.0$ $\quad$ (Hg^{0}, Hg-p),

$R_1 = 0.0,\ R_2 = 0.0$ $\quad P < 0.1,$

Simulated wet removal is zero for precipitation amounts less than 0.1 cm per 6 hr because gridded precipitation analyses tend to have non-zero values more frequently than would an individual point because of multigauge averaging in the spatial analysis. Direct field data are sparse, but it has been argued that wet removal of Hg-II is very efficient, wet removal of Hg-p is fairly efficient, and wet removal of Hg^{0} is very inefficient (Munthe, 1993). The *b(t)* factor limits the wet removal process for initial emissions of Hg^{0} to the approximate fraction that has been transformed to particulate form.

ASTRAP has been exercised in a variety of applications over an extended time and thus has been modified periodically as the structure of input data sets has changed and as new information about key processes and their parameterizations has been learned. The most important change made in applying the model to the Great Lakes basin, which is about 1/3 water, is that the dry deposition field is adjusted after initial calculation to take into account the dramatically different annual patterns of dry deposition velocities over the large water bodies (Shannon and Voldner, 1992). (In normal application of ASTRAP in simulations over eastern North America, for which water surfaces are a relatively minor component, deposition velocity varies with species, time of day, and season, but not with horizontal location.) Because of the large thermal lag of the Lakes relative to the surrounding land, a strong atmospheric inversion over the Lakes is common during late spring and early summer, and an unstable atmospheric surface layer is common during late fall and early winter. Because atmospheric resistance is a limiting process for air/surface exchange in stable conditions, the proper seasonal dry deposition velocity pattern over the Lakes is almost opposite in phase to that expected over land surfaces. Our method of adjustment of the dry deposition field is to apply average seasonal deposition velocities specific to the Lakes to the seasonal average surface air concentrations calculated over the Lakes in initial model runs (Table 5).

Table 5. Average Dry Deposition Velocities (cm s^{-1}) in ASTRAP Simulations and in Postprocessing Model Results Over the Great Lakes

	WINTER	SPRING	SUMMER	AUTUMN	ANNUAL
LAND					
Hg^o	0.0016	0.006	0.013	0.0038	0.006
Hg-II	0.72	1.1	1.4	0.91	1.0
Hg-p	0.11	0.18	0.24	0.14	0.17
LAKES					
Hg^o	0.01	0.001	0.001	0.005	0.004
Hg-II	2.00	0.30	0.30	1.40	1.00
Hg-p	0.30	0.08	0.08	0.21	0.17

EMISSIONS INVENTORY

The annual anthropogenic emission inventory for Hg in this study consists of spatial distributions of near-surface and elevated emissions for Hg^o, Hg-II, and Hg-p. Although the emissions as used in this study are not attributed to particular source sectors, North American emissions are dominated by paint volatilization, coal-fired power plants, municipal incinerators and smelters (Bloxam *et al.*, 1992). The emission grid covers the United States and Canada east of about 95 deg W and is spatially detailed to Canadian Meteorological Centre (CMC) horizontal grid spacing, which is 127 km at 60 deg N and decreases with latitude to about 100 km at 30 deg N. The emission inventory is that used in exercise of a version of the ADOM model (Bloxam *et al.*, 1992) and should be considered an interim version. We have assumed that the emission rate is constant diurnally and seasonally. Our model results are quite sensitive to assumptions about the effective emission height of species with efficient dry removal, such as Hg-II. The initial effective emission height of Hg^o is of minor importance because of its long atmospheric residence time. The annual anthropogenic emission totals for Hg^o, Hg-II, and Hg-p are 270, 0.5, and 0.1 tonnes Hg, respectively, in the surface layer and 134, 77, and 10 tonnes aloft.

To make a preliminary estimate of the contributions to Hg air concentrations and deposition from emissions by natural processes we defined an arbitrary emission function over the United States and Canada that varied with season and latitude to approximate a temperature dependence. The maximum rates in the southern United States were approximately 8 ng Hg^o m^{-2} hr^{-1} during summer, 6 ng Hg^o m^{-2} hr^{-1} during spring and autumn, and 4 ng Hg^o m^{-2} hr^{-1} in winter, which are reasonably consistent with measurements of emissions over uncontaminated soils (Kim *et al.*, 1993). Integrating the natural emission function over the United States and Canada produces total emissions of 41, 130, 206, and 130 tonnes Hg^o for winter through autumn, respectively. The function does not consider the nature of the underlying surface.

As will be shown, our estimate of the total Hg^o concentration resulting from our arbitrary terrestrial emission function and from anthropogenic emissions is about one-half of the typical rural background level in the Great Lakes region. We believe that this is due largely to background levels of Hg^o that are transported into our region of interest from globally distributed sources. We have estimated the global background concentration for Hg^o not already accounted for to be 1.0 ng m^{-3}, and for consistency with our modeling approach have estimated the background concentration of Hg-p to be 0.01 ng m^{-3}. These values are lower than those usually found in remote areas (Lamborg *et al.*, 1993), because our modeling already includes an estimate of the concentrations and deposition resulting from emissions by natural processes over the United States and Canada. We can apply our removal parameterizations to estimate the additional wet and dry deposition associated with the global background.

METEOROLOGICAL DATA

The meteorological analyses used in these simulations are wind fields over North America and adjacent oceanic areas, updated four times daily, and 24-hr precipitation totals over the United States and Canada and updated twice daily for December 1988 through November 1989. The precipitation fields are processed to produce 12-hr precipitation totals, and extrapolated beyond the continent to allow simulation of wet deposition over oceanic areas. The wind fields are for the 1000-mb and 850-mb levels, and they are combined in a mean mixed-layer wind for model calculations. All analyses were produced at the Canadian Meteorological Centre. The spacing of the wind grid is 381 km, while the spacing of the precipitation grid is 127 km, both spacings applying at 60 deg N and decreasing with decreasing latitude. Because the model parameterization for wet removal is based on the 6-hr precipitation total, all of the 12-hr precipitation is assumed to fall in one of the two corresponding 6-hr periods.

RESULTS AND COMPARISON WITH OBSERVATIONS

Isopleths of modeled annual average concentration and cumulative deposition of Hg species over the Great Lakes basin are shown in Figures 5 for all sources, including the global background. The dry deposition field over the Lakes has been adjusted in postprocessing as discussed in an earlier section. Integration of the deposition fields over the Lakes results in the deposition budgets shown in Table 6.

High quality monitoring data for Hg air concentrations and deposition in North America are quite limited, although several current investigations will improve the database. Long-term monitoring values for air concentrations and wet deposition of Hg are compared in Table 7 with corresponding values from model simulations with 1989 meteorology. Model estimates of wet deposition show agreement within a factor of two, with a portion of the difference possibly due to the different periods of meteorology for observations and simulations. The model indicates generally higher dry deposition than the other estimate; this is largely due to model estimates of Hg-II dry deposition. The model estimate is for dry deposition of all Hg species to a terrestrial surface at that

Table 6. Hg Deposition Budget (kg Hg yr^{-1})

	Anthropogenic Emissions						Terrestrial emissions and global background	
	Hg^{o}		Hg-II		Hg-p			
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
LAKES								
SUPERIOR	29	22	87	146	42	19	73	166
MICHIGAN	25	71	220	583	67	46	65	130
HURON	36	45	207	228	87	41	63	131
ERIE	24	60	268	595	68	45	30	64
ONTARIO	18	26	210	499	52	29	23	43
Total	132	224	992	2051	316	180	254	534
LAND BASINS								
SUPERIOR	23	43	96	133	51	27	105	493
MICHIGAN	47	170	369	740	123	95	108	507
HURON	71	134	431	398	175	89	137	549
ERIE	56	205	589	1207	160	125	78	318
ONTARIO	58	109	607	978	167	95	75	275
Total	255	661	2092	3456	686	431	503	2142
GREAT LAKES BASIN	387	885	3084	5507	1002	611	757	2676

Table 7. Comparison of Model Results with Observations

	MODEL				OBS
	Anthropogenic emissions	Terrestrial emissions	Global background	Total	
Hg wet dep ($\mu g\ m^{-2}\ yr^{-1}$)					
[a]South Haven, MI	8.0	0.4	0.6	9.0	9.9
[a]Ann Arbor, MI	9.0	0.4	0.6	10.0	8.8
[a]Pellston, MI	3.8	0.4	0.6	4.8	6.2
[b]Wolf Lake, WI	2.6	0.3	0.5	3.4	6.8
Hg dry dep ($\mu g\ m^{-2}\ yr^{-1}$)					
[b]Wolf Lake, WI	4.5	1.4	2.4	7.3	3.5
Hg^{o} air conc. ($ng\ m^{-3}$)					
[b]Wolf Lake, WI	0.4	0.4	1.0	1.8	1.8
Hg-p air conc. ($ng\ m^{-3}$)					
[c]Wolf Lake, WI	0.007	0.006	0.01	0.023	0.02
[d]New York State Network	0.034	0.006	0.01	0.05	0.07

[a] Hoyer *et al.*, 1993

[b] Lamborg *et al.*, 1993

[c] Fitzgerald *et al.*, 1991

[d] Olmez *et al.*, 1992

location, while the "observation" is actually a combination of measured Hg-p atmospheric concentrations and modeled dry deposition velocity. Model estimates of atmospheric concentrations of Hg^o and Hg-p are similar to observations, once the global background is taken into account.

UNCERTAINTIES IN THE MODELING APPROACH

Emissions are always a potential source of uncertainty in modeling of atmospheric pollution, but here the uncertainties in the total amount and the spatial and temporal distribution of Hg emissions are further complicated by the importance of Hg speciation that arises from the vastly different removal rates for the principal emitted species, Hg^o and Hg-II. Because Hg-II is deposited so efficiently, knowledge of the effective emission heights of Hg-II sources also is important, as the dry deposition pattern for a surface source of Hg-II is greater in magnitude and shorter in distance scale than that of an elevated source, which may be decoupled from surface removal processes during stable nocturnal conditions.

Our parameterization of Hg^o dry deposition velocity is a compromise between the extremely inefficient rates assumed in global budget studies and the field measurements made over a hilly forest in the southern United States. Because the atmospheric burden of Hg is dominated by Hg^o, minor adjustments of the Hg^o dry deposition velocity can make a large difference in the Hg deposition budget. Our subjective estimation of the net transformation of Hg^o to Hg-p is arbitrary, but it does give us reasonable ratios of Hg-p to Hg^o. Because our parameterization of wet removal of Hg^o emissions is limited by the cumulative transformation rate, wet removal of Hg emitted as Hg^o is roughly proportional to our assumption about the effective net transformation rate.

Our simulations used meteorological analyses for 1989. Earlier studies of the climatological variability of wet deposition of S found the coefficient of variation of annual wet deposition outside major emission regions to be about 12-16 %, with year to year seasonal variation even greater (Shannon and Streets, 1986). The annual variability of dry deposition was somewhat less than that for wet deposition.

CONCLUSIONS

A highly parameterized model of long-range transport and deposition appears to give good results for an atmospheric Hg system consisting of elemental, divalent, and particulate Hg species. Model results are similar in magnitude to the few available long-term monitoring observations of Hg concentrations and wet deposition when a global background is taken into account. Wet and dry deposition directly to the Lakes of Hg emitted by current anthropogenic activities are estimated with the model and meteorology for 1989 to be 1.44 and 2.46 tonnes yr^{-1}, respectively. Deposition of Hg emitted by natural processes, with the emission field defined subjectively as a function of season and latitude (as a surrogate for surface temperature) is calculated to be 0.09 and 0.15 tonnes yr^{-1} for wet and dry, respectively. The contribution from the global background is estimated to be 0.15 and 0.39 tonnes Hg yr^{-1} for wet and dry deposition, respectively. Current anthropogenic emissions account for the dominant portion (83%) of loading to the Great Lakes largelyh because 16% of the anthropogenic emission inventory is in the efficiently depositing divalent form; Hg-II accounts for 65% of the total Hg deposition from all source.

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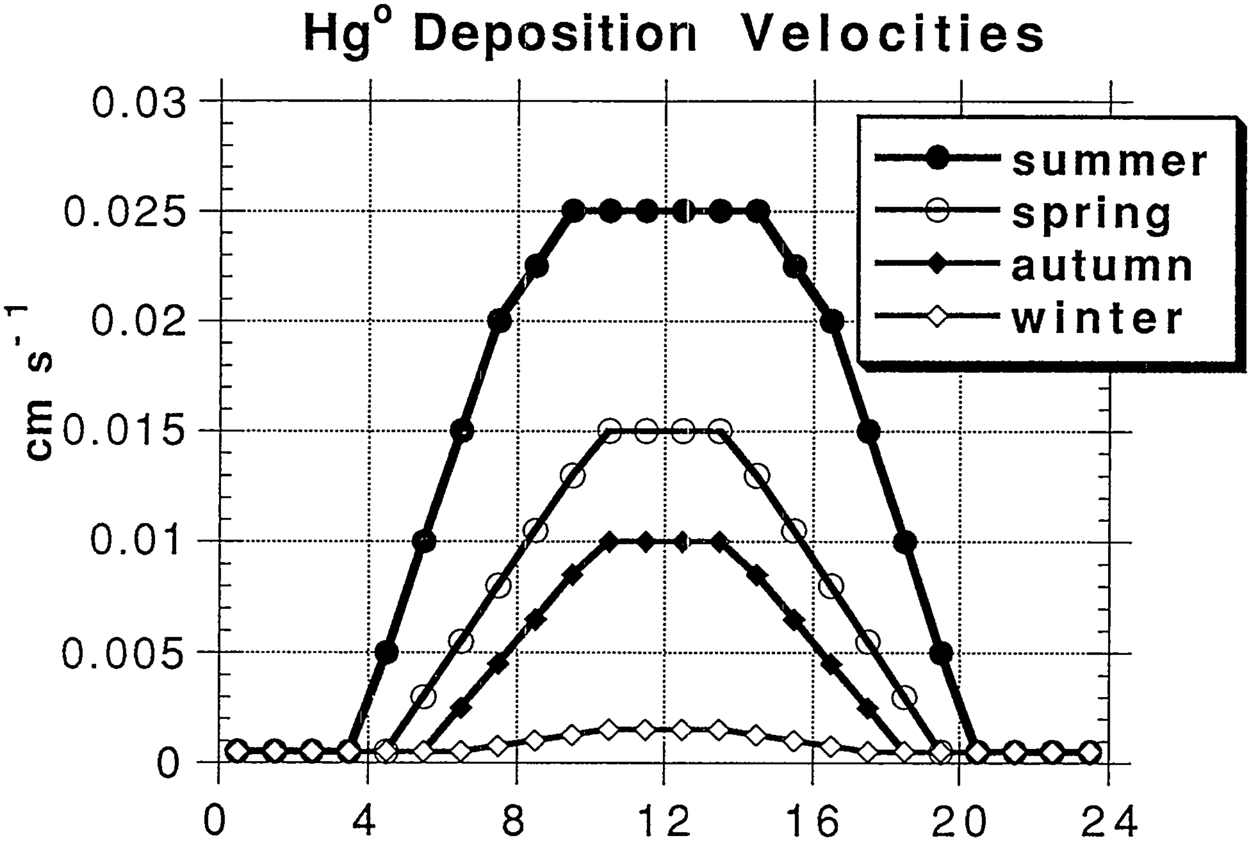


Figure 20. Model parameterization of seasonal and diurnal patterns of dry deposition velocity for Hg^0.

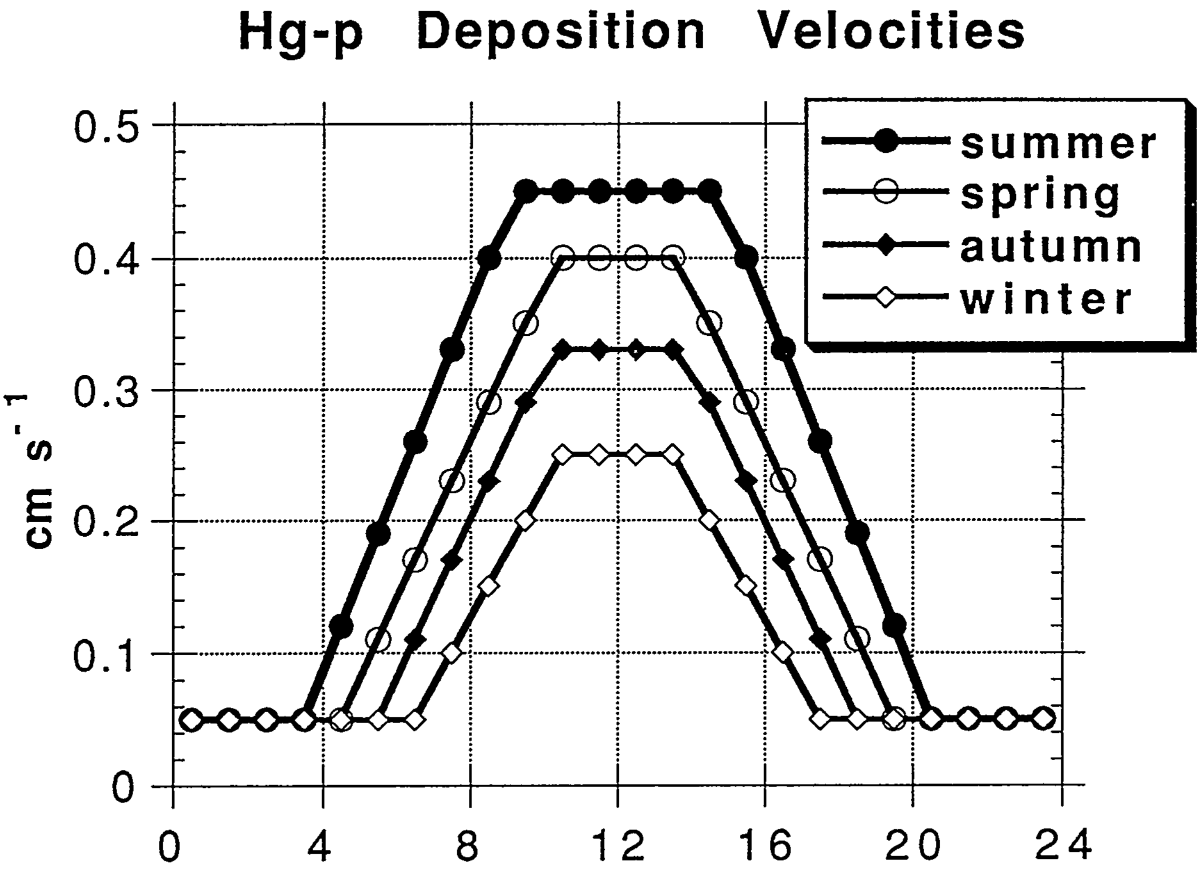


Figure 21. Model parameterizations of seasonal and diurnal patterns of dry deposition velocities for Hg-p.

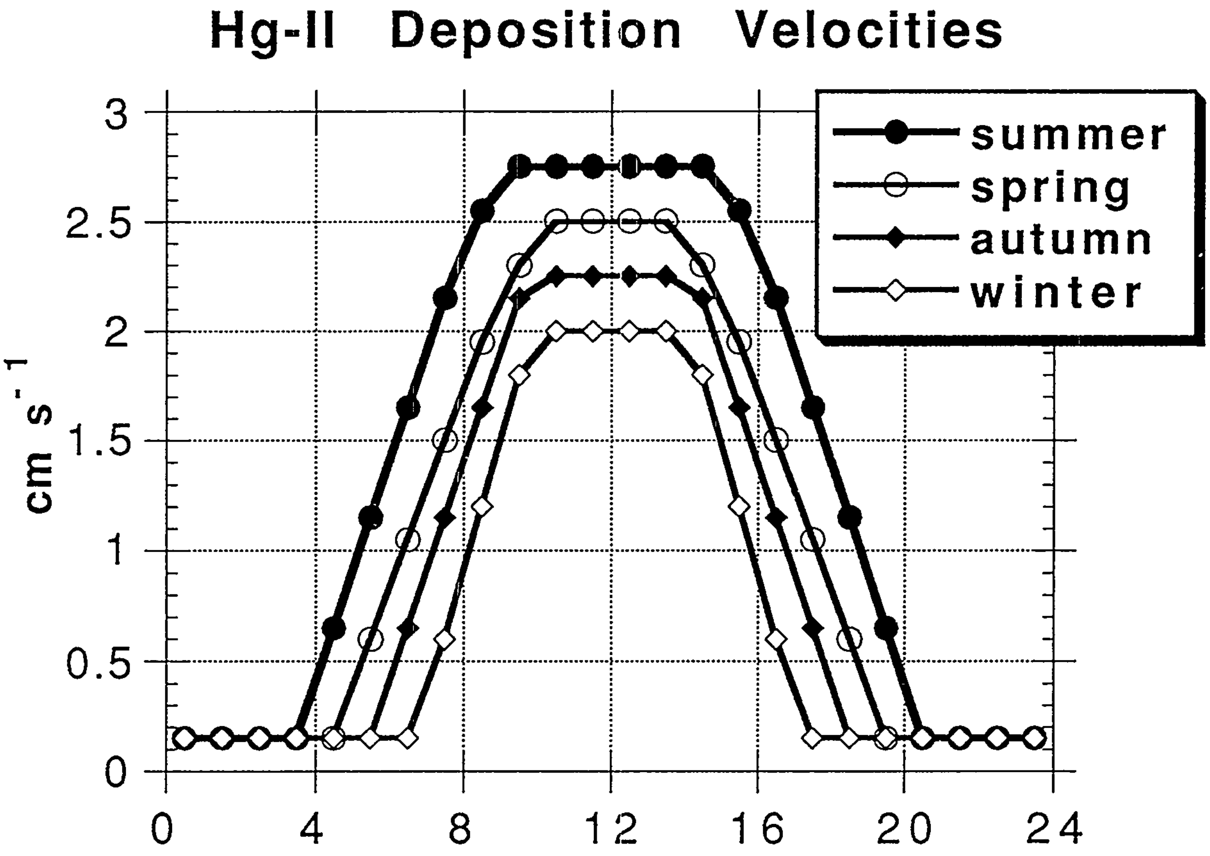


Figure 22. Model parameterizations of seasonal and diurnal patterns of dry deposition velocities for Hg-II.

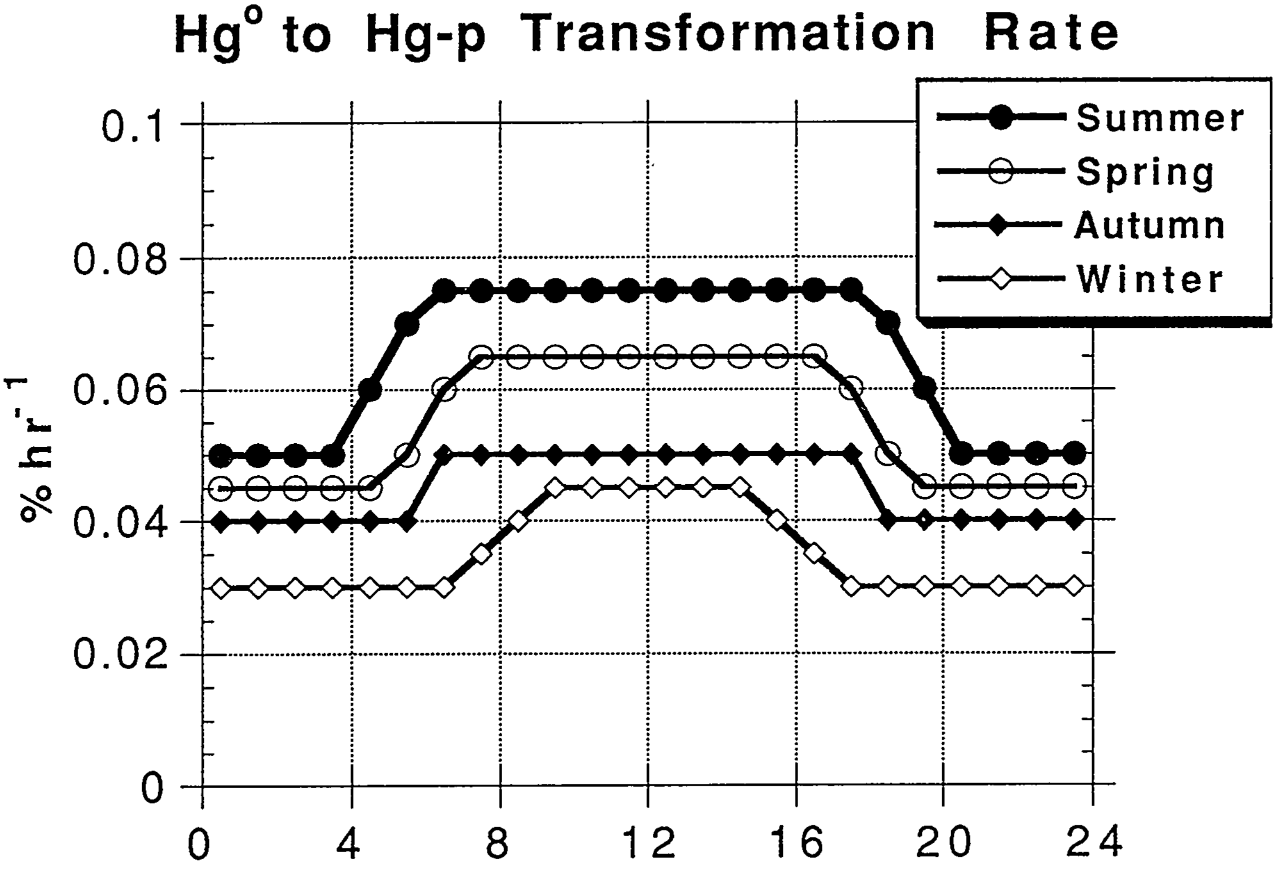
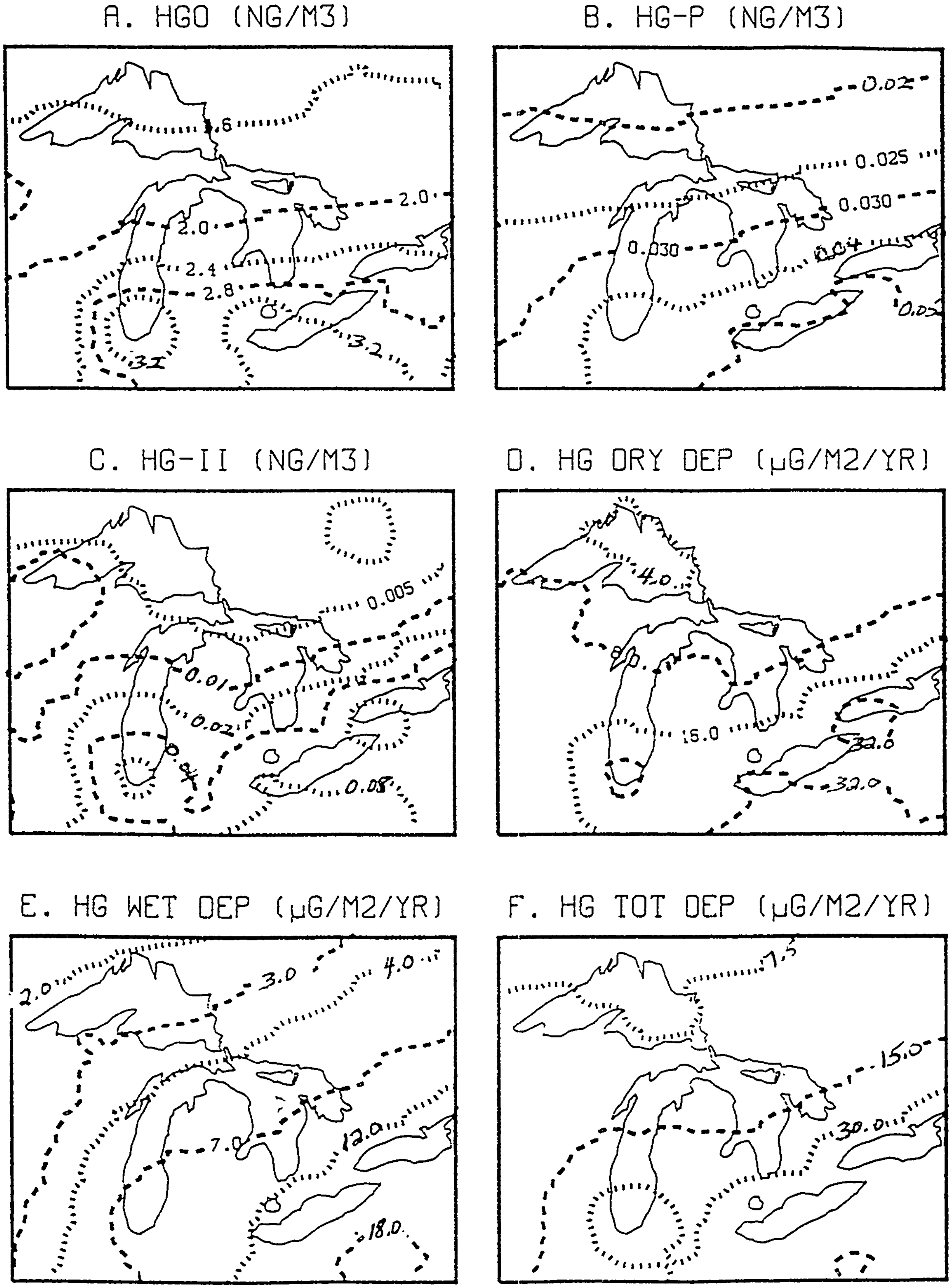


Figure 23. Model parameterizations of seasonal and diurnal patterns of the net rate of transformation of Hg^0 to Hg-p.


A. HGO (NG/M3)

B. HG-P (NG/M3)

C. HG-II (NG/M3)

D. HG DRY DEP (μG/M2/YR)

E. HG WET DEP (μG/M2/YR)

F. HG TOT DEP (μG/M2/YR)

Figure 24. ASTRAP simulations of annual average air concentrations and cumulative annual deposition resulting from all sources, including an assumed global background of 1.0 ng Hg^0 m^{-3} and 0.01 ng Hg-p m^{-3}

WORKSHOP DISCUSSION

The issue regarding the importance of assessing regional deposition was raised again. One participant suggested that regional deposition is a problem that involves both wet and dry deposition. It was pointed out that regional air quality is dependent on boundaries and sources. One method of study currently being used by Shannon is to analyze the entire U.S. by dividing it into about 100 - 200 km grids.

This discussion led to a question concerning whether there is a consensus on how wet deposition is modeled. The reply indicated that there was general, but, not a specific agreement. For example, Lagrangian models have similar approaches for parameterizing wet deposition; however, a Eulerian modeling approach would be different.

A question arose regarding procedures needed to model local concentrations within grid squares. The reply indicated that presently no attempt is being made to model concentrations at finer grid scales. It can, however, be done but is subject to great uncertainty. A subsequent discussion revealed that estimates of local deposition range from 5 to 100%. Also of concern was seasonal variation effects on emissions and deposition. Information on this topic is limited.

One participant suggested that it might be possible to get by with less atmospheric transport modeling by correlating coal consumption with MeHg levels in fish. This initiated a discussion of Hg trends in fish. Over the past 20 years, Hg has been increasing at a rate of about 1.7 to 5% per year in fish. Also, sediment cores indicate large increases beginning in the 1850s and again in the 1920s. Difficulties in using fish measurements that were pointed out include: 1) the totality of fish data is limited, 2) comparisons across lakes are difficult, and 3) multiple sources of Hg feed into freshwater bodies.

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6. GLOBAL BIOGEOCHEMICAL CYCLING OF MERCURY

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ENVIRONMENTAL AND HUMAN HEALTH CONSIDERATIONS

There is now much evidence documenting tissue concentrations of Hg in marine and freshwater fish that exceed local, national and international public health guidelines (e.g., Wiener, et al., 1990a; Eisler, 1981). Moreover, nearly all Hg in fish flesh (>95%) occurs as methylmercury [(MeHg) Westöö, 1966; Huckabee, et al., 1979; Grieb, et al., 1990]. Methylmercury compounds are considerably more lethal than elemental mercury and its inorganic salts. Further, human exposure to MeHg comes almost exclusively from consumption of fish and fish products, and prenatal life is more susceptible to brain damage than adults (Fitzgerald and Clarkson, 1991). This situation represents a serious human health concern as well as a significant economic threat to commercial and sport fishing industries. The presence of high MeHg concentrations in fish from many fresh and marine waters that are remote from localized pollution suggests a linkage to atmospherically-borne contamination. This coupling has been recognized and included in the US 1990 Clean Air Act Amendments which require an assessment of health risk to humans and wildlife caused by Hg emissions.

The current human-health and environmental concerns associated with elevated levels of Hg in freshwater and marine piscivorous fish have led to an expansion in research concerned with the global biogeochemical cycling of Hg and a refocusing of attention on Hg as a pollutant. Unfortunately, much Hg research and environmental assessments have been inaccurate because of carelessness, flawed techniques and contamination prone methodologies. Today, there is a heightened awareness of the need for accurate and broader measurements of mercury in nature, and for ultra trace-metal clean sampling and analytical protocols. Indeed, the amounts of mercury in air, ice and water are so extraordinarily minute (≤ pg/g) that the study of Hg in polar ice and snow, the atmosphere and in aqueous systems that an ultra-clean rigorously careful investigative approach is required for environmental studies of Hg (e.g., Vandal, et al., 1993; Fitzgerald, et al., 1993;1991; Mason and Fitzgerald, 1990; Gill and Fitzgerald, 1985). It is noteworthy, that while game fish (e.g., walleye and northern pike in freshwater; swordfish, tuna, and mako shark from seawater) often show MeHg levels > 1 ppm, the concentrations in water are commonly < 1ppt. An amplification of more than 10^6 has occurred.

Two international meetings dealing with Hg in the environment have taken place recently. The first was held in Gävle, Sweden (1990) and the other convened in

Monterey, California (1992). A third meeting is scheduled to take place in Vancouver, British Columbia during July 1994. New analytical and geochemical information is being communicated effectively, and knowledge of the biogeochemical cycling of Hg is growing. Increasingly, environmental Hg research is speciation and reaction oriented. For example, inorganic Hg [Hg(II)], elemental Hg [Hg^o] and alkylated Hg species (MeHg; dimethyl Hg [DMHg]) are being measured at pico to femtomolar levels in air, water, and precipitation. A new wave of exciting and important environmental Hg studies are beginning to yield coherent models for the principal species and reactions governing the behavior and fate of Hg in nature. Much needs to be done and critical research areas include: (1) establishing patterns of modern and historic Hg deposition to provide an essential foundation for detailed biogeochemical and ecological studies of Hg, (2) assessing the contributions of global versus local / regional Hg sources to terrestrial and oceanic regions, (3) identifying the reactions associated with cycling of elemental Hg (Hg^o) in the atmosphere and natural waters, (4) investigating the mechanisms leading to the post-depositional *in-situ* bacterial conversion of Hg species to methylated forms, and (5) relating human exposure to methylmercury with the levels of lowest effect. Here, I am focusing on the linkages between the Hg^o cycle, Hg speciation, atmospheric Hg dispersion/deposition, anthropogenic perturbations and the accumulation of MeHg in fish especially for regions (e.g., open ocean; lakes) that are remote from localized pollution.

ATMOSPHERIC Hg CYCLE

The prominence of atmospheric mobilization and depositional processes in the global biogeochemical cycling of Hg are well recognized and described in a variety of mass balance formulations for the global Hg cycle (e.g., Wollast et al., 1975; NAS, 1978; Slemr et al., 1981; Lindqvist and Rodhe, 1985; Fitzgerald, 1986, 1989; Nriagu, 1989; Fitzgerald and Clarkson, 1991; Lindqvist et al., 1991). Although the significance of the atmosphere appeared in early models, environmental assessments of source strengths for natural and anthropogenic processes were often in error because of the paucity of accurate information for critical aspects of the Hg cycle. It has become increasingly evident that human-related emissions of Hg to the air exceed natural inputs, with the principal sources being coal combustion, smelting and waste incineration (Nriagu and Pacyna, 1988). The major fluxes associated with the global atmospheric Hg cycle are summarized in a mass balance format in Table 8.

As illustrated in Table 8, recent estimates for annual amounts of Hg released into the atmosphere by human activities range between 2 and 4.5 x 10^9g, which represents about 30 to 75% of the total yearly input to the atmosphere from all sources (assuming annual Hg emissions are equivalent to yearly depositional estimates). The current estimate for total annual emissions of Hg to the atmosphere is in the 5 to 7.5 x 10^9 g range. Elemental Hg evasion from the oceans and other natural waters is a significant source of atmospheric Hg (ca.. 2 x 10^9g), and may account for approximately 30% of the annual fluxes of Hg. Indeed, *in situ* production and water-air transfer of Hg^o

exerts a major influence on the behavior and fate of Hg in the environment. Marine studies demonstrated that *in situ* synthesis of volatile Hg, which is principally Hg^{o} in the mixed layer (Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1991) and its subsequent evasion at the water-air interface were major features of the global Hg cycle (Fitzgerald, et.al., 1984; Fitzgerald, 1989; Iverfeldt, 1988). Most recently, fresh water investigations by Vandal et. al., (1991) in Wisconsin and Xiao, et al., (1991) in Sweden have shown a similar and important in-lake Hg^{o} cycle which yields significant Hg^{o} fluxes to the atmosphere. Our recent modeling suggests that anthropogenic interferences may even be larger because it is now apparent that volatile Hg^{o} emissions from terrestrial and marine systems (e.g., equatorial Pacific) include the recycling of a pollution derived component (Mason et al., 1994). The influence of the Hg^{o} cycle and its impact on the bacterial synthesis and trophic transfer of MeHg in natural waters is considered in the last section.

Other natural sources of Hg such as volcanic emanations, biological mobilization, and forest fires can contribute about 30 to 60% to the yearly emissions. The comparatively small estimate for the fluvial flux of Hg (0.2×10^{9}g) illustrates the preeminence of the atmosphere in the transfer of Hg from terrestrial sources to the marine environment. Finally, it must be stressed that this "budget" for the global atmospheric Hg cycle is derived from a limited amount of data. Much refinement is required for an accurate assessment of source strengths and the environmental impact associated with the important natural and human-related sources of Hg. For example, we suspect that significant atmospheric Hg emissions are occurring from the extensive use of Hg in the wide-spread, poorly regulated and environmentally hazardous "gold strip mining operations" such as those in South America (especially the Amazon basin) and Africa (Nriagu, 1993). We have limited knowledge of these activities and their emissions, which are both a local and global concern.

Atmospheric Hg Distribution

Most of the Hg species in the troposphere are in the vapor phase (Braman and Johnson, 1974; Fitzgerald and Gill, 1979; Fitzgerald et al., 1981; Slemr et. al., 1981), and consist almost entirely of elemental Hg (Hg^{o}) as demonstrated by Kim and Fitzgerald (1986). Improved trapping, separation, detection procedures developed by us (Bloom and Fitzgerald,1988) have refined the partitioning of the vapor phase. We showed that Hg^{o} accounts for $\geq$95% of the total vapor phase in a coastal/urban location on Long Island Sound. The remainder of the vapor phase was MeHg. Our open ocean investigations have revealed that $\geq$99% of the total Hg present in the near surface marine atmosphere is Hg^{o} (Mason et al., 1992). Moreover, our recent studies in mid-continental northcentral Wisconsin are showing a similar partitioning with the Hg^{o} fraction generally > 99% (Fitzgerald, et al., 1991;1993). Monomethyl Hg is much more soluble in water than Hg^{o}, and small quantities are present in terrestrial precipitation. The source of MeHg in the atmosphere is not known.

Elemental Hg concentrations in the marine boundary layer decrease between the northern and southern hemisphere over the Pacific and Atlantic Oceans (see Figure 25, for our Pacific data). This interhemispheric distributional pattern characterizes a trace atmospheric gas whose primary sources, on a unit area basis, are continental and may include anthropogenic sources. Trace gas modeling for Hg yielded an average tropospheric residence time of total gaseous Hg, assumed to be Hg^{o}, of about a year. Confirmation of this relatively long average residence time is provided from estimates of annual Hg deposition to the earth's surface using a steady state model for the global Hg cycle (Fitzgerald, 1986; Table 8). Thus, Hg^{o} from both natural and anthropogenic sources can be readily mixed intrahemispherically. Interhemispheric mixing will allow northern hemispheric emissions of Hg^{o} to be transported to the atmosphere of the southern hemisphere. Presumably, the broad dispersion of Hg has reduced some localized impact from human related emissions of Hg. Unfortunately, it may have led to the geographically large problem of elevated Hg concentrations in fresh and marine fish.

Atmospheric Hg Deposition

Anthropogenic interferences within the biogeochemical cycle of Hg present perplexing and challenging problems. We must be concerned not only with sources, chemical composition, physical state, and direct impact of Hg compounds to natural waters, but with the post-depositional *in situ* bacterial conversion of Hg species to more toxic forms, especially MeHg. The importance of atmospheric Hg deposition in the aquatic biogeochemistry of Hg has been demonstrated for seepage lakes as part of The Mercury in Temperate Lakes (MTL) Program in Wisconsin (Fitzgerald, et al., 1991; Wiener et al.,1990), and for drainage lakes as part of broadly based investigation in Sweden, Mercury in the Swedish Environment (Lindqvist et al., 1991). Both studies indicate that small increases in atmospheric depositional fluxes of Hg could yield enhanced Hg concentrations in fish as suggested by Fitzgerald and Watras, (1989). For example, the initial MTL studies showed that the estimated net annual accumulation of Hg in fish (ca. 0.06g) could be supplied by < 10% of the annual deposition [ca. 10 mg m^{-2} y^{-1} (ca. 66% wet)]. The mass balance which is summarized in Figure 26 for a model temperate seepage system, Little Rock Lake (LRL), suggests that increases in atmospheric Hg loading could lead directly to elevated levels in the fish stock. Conversely, reduction in atmospheric Hg input would result in smaller levels of MeHg in biota.

Further, and as summarized in Figure 27, atmospheric deposition of MeHg, is insufficient to account for the amounts of MeHg observed in biota. An in-lake synthesis of MeHg is required. These results agree with recent findings showing that MeHg can be produced by sulfate reducing bacteria in lake (Gilmour and Henry, 1991) and estuarine environments (Mason et al., 1993), as well as with experimental evidence for the in-situ production of alkylated Hg species in lake waters (MTL Program) and in surface waters of the open ocean (Mason and Fitzgerald, 1990). The relative importance of water column versus sedimentary production of MeHg is not resolved for seepage lakes. In drainage lakes, there is an additional supply of MeHg. This drainage flux of MeHg is derived from reactions occurring in the watershed especially wetlands and from the atmospheric deposition of MeHg to the catchment (Heyes et al; 1994; Rudd et al., 1994; Hultberg and Iverfeldt, 1994 in Abstracts for the International Hg Conference, Vancouver, July 10 to 14, 1994).

The inferences and hypotheses derived from the MTL studies have been confirmed in a mechanistic model of the biogeochemical cycling of Hg in lakes that was developed as part of the MTL program (Hudson et al., 1994). Major features of the model are illustrated in Figure 28. This simulation illustrates the principal species of Hg that participate in abiotic and biological reactions and interconversions that contribute to the bioconcentration of MeHg as it passes through the food chain. Chemical and physical speciation measurements of particulate matter and precipitation point to scavenging of atmospheric particulate Hg as the major source of reactive Hg in rain (Section 2.3). Gaseous Hg in lake water is principally Hg°, and the evasional fluxes of Hg° are significant. Moreover, we hypothesized (Fitzgerald, et al., 1991) that the *in-situ* production and efflux of Hg° could provide a potential buffering and/or amelioration role in aqueous systems. It would limit the amount of reactant Hg(II) available to methylate.

Many of the features of the fresh water model can be applied to the marine environment. Moreover, a preliminary mass balance for the world's oceans indicates that the annual accumulation of MeHg in fish can be supplied by < 10% of the Hg deposition from the atmosphere (Fitzgerald and Rolfhus, in preparation). Thus, only a small amount of the atmospheric Hg input must be converted to MeHg in order to account for the distribution of MeHg in oceanic biota. Much of the upper ocean production of MeHg occurs in the water column rather than in surficial sediments. This water column synthesis has been investigated, demonstrated and modelled by Mason and Fitzgerald (1990,1993) for the biologically productive equatorial Pacific Ocean.

Temporal Variations and Secular Trends in Hg Deposition: Anthropogenic Perturbations

Regional Scale Effects

The LRL Hg depositional results can be placed in a larger regional perspective. Firstly, in 1984, Bjorklund and co-workers reported that elevated Hg levels found in pike from southern and central Sweden appeared related to increases in atmospheric Hg deposition as derived from the temporal imprint preserved in the vertical distribution of Hg in lake sediments. For the rural north central Wisconsin MTL lake study region, Rada et al. (1989) presented evidence inferred from sediment cores suggesting that an increase in atmospheric Hg deposition of a factor of 3 to 4 has occurred since precolonial times. We determined that Hg deposition was ca. 11.5 mg m^{-2} y^{-1} (ca. 69% wet) during October 1988 to October 1990 for the north central Wisconsin MTL region (Fitzgerald et al., 1991; 1993). Recently, Swain et al., 1992 (Figure 29) using whole lake accumulation rates for Hg distribution estimated present atmospheric deposition at 12.5 mg m^{-2} yr^{-1}, and the preindustrial value is 3.7 mg m^{-2} yr^{-1} to the northern Wisconsin environs. This represents an increase of a factor 3.4, and their estimate for modern annual Hg deposition agrees most satisfactorily with our current measurements. An average enhancement factor of 3.7 was obtained by averaging the increase for each lake in the study. Although, there are potential artifacts, such as postdepositional migration, bioturbation, and sediment focusing, which can affect the determination of temporal deposition patterns using lake sediments, these estimates of substantial anthropogenic enhancement to the mid-continental Hg cycle in the northern hemisphere at approximately 2% yr^{-1} for the past 140 years are consistent with predictions on a global scale (Fitzgerald and Clarkson, 1991). For example, approximately two-thirds of the total world's production of Hg has taken place during this century, and anthropogenic releases of Hg to the environment have increased about 3-fold since 1900 (Andren and Nriagu, 1979). In addition, there have much greater increases in the world-wide use (>25) of fossil fuels (Trends, 91). Combustion of fossil fuels, especially coal, releases Hg to the atmosphere as Hg^{o}, ionic Hg and particulate Hg.

Particulate Hg Cycle

Localized Atmospheric Hg Deposition: Mid-continental North America.

The depositional results for Hg as established by the Little Rock Lake budget, and the whole lake experiments by Swain et al. yield a consistent estimate for mid-continental deposition of Hg to relatively pristine semi-remote seepage lakes in the mid-continental U.S. Further support is provided by Mierle (1990) who reported a mean wet depositional flux of 10.2 mg m^{-2} yr^{-1} for a site at the Dorset laboratory in Dorset, Ontario which is about 1000 km east of the LRL study. Similar results have been obtained at non-urban sites in Michigan (Hoyer et al., 1993). This agreement may be misleading and bears careful scrutiny because it suggests that the atmospheric contributions to the mid-continental North America are almost exclusively associated with the global Hg cycle. As noted, Hg^{o}, the principal form of Hg in the atmosphere, has a tropospheric residence time of the order of a year. It will be widely dispersed before oxidization and removal by precipitation or dry deposition. Primary particulate Hg emissions will contribute principally to local and regional deposition. Therefore, one should expect to find the influence of continental sources of particulate Hg in mid-continental Hg deposition. This local-regional particulate Hg would be superimposed on a increasing background of Hg deposition associated with the global cycling of Hg^{o}. Nater and Grigal (1992) have found such a pattern of regional Hg deposition in organic litter and surface mineral soil at forested sites along a 1000 km track from northwestern Minnesota to eastern Michigan.

Localized Atmospheric Hg Deposition: Nordic Countries.

The importance of local and regional atmospheric deposition is demonstrated by the extensive study of the tropospheric cycling of Hg over the Nordic countries (Iverfeldt, 1991). The results are presented in Table 9, for locations shown in Figure 30 that were chosen to examine south - north gradients of Hg in air and precipitation over a distance of approximately 1500 km, which is comparable to the range covered between northwestern Minnesota and eastern Michigan in the Nater and Grigal work. In general, average total Hg in precipitation increases from ca. 8 ng L^{-1} at the most northerly stations to ca. 40 ng L^{-1} at the most southerly site. The latitudinal depositional pattern is particularly pronounced in Norway where with the smallest Hg fluxes observed at the northern most stations of Överbygd and Jergul, at 5 and 3 $\mu g\ m^{-2}\ yr^{-1}$ respectively, and the largest, 35 $\mu g\ m^{-2}\ yr^{-1}$, at Birkenes, a port on the southern tip of Norway. The variations in annual deposition of Hg are related to the locality and annual wet deposition. For example, Kårvatn, in southeast Norway, with a large annual precipitation of 1430 mm yields a flux of 13 $\mu g\ m^{-2}\ yr^{-1}$ while Keldsnor, Denmark the southern most site in the network, with a comparable yearly flux of 17 $\mu g\ m^{-2}\ yr^{-1}$ has a annual rainfall that is a factor of 3 lower (430 mm). The depositional pattern for the Nordic study closely resembles the average range for the global depositional pattern of Hg as estimated from a limited data base by Fitzgerald, in 1986.

The importance of regional European sources to Hg deposition in the Nordic countries is evident. The highest levels of Hg in precipitation were associated with air mass trajectories from the south/southeast, mostly from eastern part of Europe. Moreover, episodic effects were evident where concentrations of total Hg in precipitation were >100 ng L^{-1} for southerly air trajectories and these high levels correlated with "exceptionally high concentrations" of soot, and sulfate as well as low pH. The Pb and Cd concentration were also about a order of magnitude greater (Iverfeldt et al., 1991). In earlier studies in Sweden, Brosset (1987) and Brosset and Iverfeldt (1989) had previously reported a strong correlation between Hg, soot and air trajectories from the eastern part of Europe. Recently, Xaio et al., 1991 reported a good correlation (r= 0.74) between the particulate Hg fraction and soot for air samples collected in the environs of Göteborg, Sweden.

Fortunately, recent studies indicate that the concentration and depositional of Hg are decreasing over the Nordic network (Iverfeldt et al., Abstracts for the International Hg Conference, Vancouver, July 10 to 14, 1994). Earlier investigations had linked the patterns of Hg in air and precipitation over Scandanvia to a strong anthropogenic emission sources in the former DDR (East Germany). Following reunification, most of the chlor-alkali plants (a major source) in the Halle-Leipseig-Bittefeld regions were closed. These results are significant because they demonstrate the coupling between source strengths for regional anthropogenic emissions of Hg, and their adverse influence on the regional atmospheric Hg signal in air and deposition which affects the production of MeHg in aquatic environments. Further, it is shows that when remedial steps are taken, there is a rapid decline in the direct anthropogenically enhanced input of Hg to the natural waters. This positive response must be emphasized, because the MTL Hg model predicts that a reduction in atmospheric inputs of Hg to an aquatic system will result in a lowering of the MeHg content of fish.

Drainage Lakes in Sweden: Hg Mass Balance

Mercury fluxes to and from a model lake in southern half of Sweden is illustrated in Figure 31, which has been adapted from Johansson et al. (1991). The lake area is 1 km^2 and the drainage area is 10 km^2, and this proportion is representative of the average ratio for Swedish lakes. Wet deposition of Hg is estimated at 20 $\mu g\ m^{-2}\ yr^{-1}$, about 2.5x the LRL value of 8 $\mu g\ m^{-2}\ yr^{-1}$ (Table 9). The main source of Hg to the lake is via atmospheric deposition. As summarized in Figure 37, about 5 to 30 % of the Hg input from the atmosphere (20 $\mu g\ m^{-2}\ yr^{-1}$) to the catchment will enter the lake through runoff and this waterborne flux (1 - 6 $\mu g\ m^{-2}\ yr^{-1}$) will represent between 25 and 75% of total input from wet deposition. The sediment accumulation will depend on size of the lake, it biological and chemical character, and on evasional losses (0.2 to 2 $\mu g\ m^{-2}\ yr^{-1}$) of Hg at the water surface (which are estimated to range from 10 to 100% of the direct wet deposition of Hg (2 $\mu g\ m^{-2}\ yr^{-1}$) to the lake).

There is broad agreement between the Swedish work and the results from the MTL program in Wisconsin. For example, simulation of the Hg flows into and out of a typical Swedish lake clearly demonstrates that 1) atmospheric Hg deposition is the preeminent source of Hg to a drainage lake, and 2) evasional fluxes of Hg^o are significant though the estimates require refinement. Two striking differences between the drainage and seepage lake modelling are (1) the significant portion of the Hg input that is stored in forest soils of the catchment, and (2) the additional supply of MeHg in drainage as a result of the capture of MeHg in deposition to the catchment and the biological mediated production of MeHg in the watershed (e.g., wetlands). On average, present atmospheric deposition is greater than the output of Hg in run-off waters by about a factor of 10. Thus, even if anthropogenic Hg inputs were to cease, modern Hg deposition that has accumulated in the soil would continue to be released to the lakes from the forest soils. Indeed, Johansson and co-workers indicate that 70 to 80% of the Hg in the catchment is anthropogenic (Lindqvist et al., 1991), and as a consequence, the watershed transport of Hg to the lakes will remain elevated for long periods of time, perhaps several centuries. As indicated, this situation is exacerbated by the increasing evidence for the production of MeHg in wetlands and its subsequent export (Rudd et al., Abstracts for the International Hg Conference, Vancouver, July 10 to 14, 1994).

Hg Speciation in Precipitation

An average scavenging ratio (i.e., concentration in rain/concentration in air) observed for mercury in rain collected in Wisconsin was 437 (Fitzgerald *et al.*, 1991), and this value is comparable to scavenging ratios found for metals such as lead (Maring *et al.* 1989, Church *et al.*, 1991). Although there are limitations to the scavenging ratio approach, it appears that atmospheric Hg wet deposition is analogous to other trace metals (*i.e.*, Pb, Cu, Zn) which exist as particles in the atmosphere (Maring *et al.* 1989, Buat-Menard 1986). Similar conclusions regarding the prominence of the atmospheric particulate Hg cycle in conveying Hg to natural waters were reached in Swedish work (Brosset 1987, Lindqvist *et al.* 1991, Iverfeldt 1991a). The influence of particulate Hg on the composition of Hg in precipitation is shown in Table 10 from Iverfeldt (1991a). He found an on average, >67% and >79% of the total mercury in precipitation was filterable at the 0.4 mm size range for two sites, Överbygd, Norway and Keldsnor, Denmark, respectively, in the Nordic Countries Network. The results also show that Hg is associated with large particles (> 10mm) as well as particles between 0.4 mm and 10 mm size classes.

Mercury speciation in precipitation from the MTL Wisconsin studies (Fitzgerald *et al.* 1991, 1993) is shown in Table 11, where measurements of total mercury (Hg_T), reactive mercury (Hg_R) and monomethyl mercury in wet deposition (snow and rain) from these mid-continental rural temperate lacustrine environs are summarized for a two year period (1989 and 1990). Details of the Hg speciation for rain are presented in Figure 32. Several general features are evident in the broad geochemical view provided by the average speciation results in Table 11. Firstly, the average Hg_T was similar for both years (52.5 ± 24.0 and 49.3 ± 20.8 pM) while the average Hg_R was higher during 1990 (41.0 ± 20.6 pM) than during 1989 (13.7 ± 10.6 pM). As noted by Fitzgerald, *et al.*, (1991), the difference between Hg_T and Hg_R is not due to MeHg, which is present in very small quantities (≤ ca. 1 pM; see Figure 32). Rather, the difference is due principally to strong Hg associations with organic substances that are destroyed by the powerful oxidant (BrCl) used in the determination of Hg_T.. We also suggest that this strongly bound Hg fraction is associated with atmospheric particulates containing organics which may have a significant sulfur content. This interpretation is part of a more general atmospheric particulate Hg scavenging hypothesis emphasizing the influence of atmospheric particulate Hg on the composition in rain. Support for this postulate comes from the scavenging ratio estimates, and the Iverfeldt (1991) work (Table 10) showing that the filterable or colloidal species dominate the Hg_T in rain.

There is a consensus that the principal source of Hg_R in precipitation is the oxidation and dissolution of atmospheric Hg^o, and two atmospheric reaction pathways have been postulated. The first argues that Hg_R is derived from a generalized atmospheric oxidation of Hg^o, using oxidants such as O_3 or OH radicals. This reaction may occur heterogeneously and involve Hg^o adsorbed to particles (Fitzgerald *et al.* 1991, 1992). Such a particle conversion hypothesis is supported by Hg(II) washout calculations, and from the direct physical and chemical analysis of rain showing most of the Hg is associated with particles (Iverfeldt *et al.* 1991a,b, Fitzgerald *et al.* 1992, Mason *et al.* 1992). Alternatively, the work of Iverfeldt and Lindqvist (1986) suggests that O_3 oxidation of Hg^o in clouds could be an important mechanism contributing to Hg_R in rain. The authors predicted an oxidation rate of 0.01 hr^{-1} (88 yr^{-1}) for conversion of Hg^o to Hg(II) in clouds, assuming 1 g m^{-3} of liquid water and 23 ppb O_3 (a value similar to observed background concentrations). In the absence of O_3, the reaction rate is three orders of magnitude slower. However, a residence time of Hg in the atmosphere of approximately 1 yr (Fitzgerald, 1989) based on the global cycle yields an overall conversion rate of approximately 1 yr^{-1}, assuming all the Hg in rain is derived from oxidation of Hg^{o}. This calculation represents a maximum conversion rate. Therefore, the reaction investigated by Iverfeldt and Lindqvist (1986), which has a substantially larger rate constant, should not be a predominant mechanism for the oxidation of Hg^{o} in the atmosphere if the reaction occurs at rates comparable to those found in the laboratory. Munthe and Lindqvist (1989) and Munthe (1991, 1992) modified this model by suggesting that rapid sulfite ($SO_3^{=}$) complexation of Hg^{2+} in cloud water would yield [$Hg(SO_3)_2^{=}$] with subsequent reduction of Hg^{2+} to Hg^{o}, thereby serving as a potential reverse reaction which limits the net amount of Hg^{o} solubilized. However, insufficient amounts of atmospheric sulfur species are available in the atmosphere over most of the earth's surface (i.e., oceans). Thus, alternative gas to particle conversion processes such as suggested in the other hypothesis must be providing pathways for formation of the Hg_R compounds found in rain.

Summary

Atmospheric deposition dominates the flux of Hg to lacustrine systems and the open ocean, and it appears that modest increases in atmospheric Hg loading could lead directly to enhanced levels of Hg in biota. The U.S. and Nordic studies of current and historical Hg deposition show broad agreement. Mid-latitudinal preindustrial depositional fluxes of total Hg were ca. 4 $\mu g\ m^{-2}\ yr^{-1}$, while present day annual fluxes may vary between ca. 10 $\mu g\ m^{-2}\ yr^{-1}$ in rural semi-remote regions to > ca. 25 $\mu g\ m^{-2}\ yr^{-1}$ in places where the presence of local/regional Hg sources is pronounced. The influence of anthropogenic activities on the total Hg cycling is evident, and site specific research must be conducted to assess the impact of human-related interferences in particular localities. However, the more important and subtle concerns are associated with the physical and chemical speciation of Hg deposition. For example, the presence of a significant regional particulate Hg cycle is found in specific chemical analysis of Hg in atmospheric particulate matter and precipitation. Fitzgerald et al., (1991 & 1992) and Iverfeldt, (1991, 1991a) have shown that significant portion of the total Hg in precipitation and in particulate matter is non-reactive to reduction with stannous chloride. Thus, a portion of the Hg_T observed in precipitation at Little Rock Lake and in comparable Swedish regions, is in a particulate form which is not derived from the oxidation of Hg^{o} in the atmosphere. Moreover, significant variability is evident in the deposition of Hg_R. Differences in Hg_R inputs may have profound effects on the Hg^{o} and MeHg cycle in natural waters. In addition, their appears to regional differences in the amounts of MeHg observed in precipitation. MeHg deposition is more significant in the Swedish environs than in rural north central Wisconsin. The source of MeHg in precipitation is not known.

TEMPORAL VARIATIONS AND SECULAR TRENDS IN HG^{o}: ANTHROPOGENIC PERTURBATIONS

Global Scale Considerations

Mercury uses associated with human endeavors will lead to a general, though variable, volatilization of Hg to the atmosphere. Identification of the sources for temporal variations in Hg^{o}, and the accurate determination of secular trends in the atmospheric Hg burden will provide a direct quantitative assessment of the scale to which anthropogenic processes are affecting the natural geochemical cycle. Further, this information will provide an essential refinement and constraint that is currently lacking in mass balance models of the present day Hg cycle. Indeed, in a recent paper based on non-synoptic data from 7 oceanographic cruises of short duration, Slemr and Langer (1992) concluded that annual atmospheric Hg increases of ca. 1.5% for the Northern Hemisphere and ca. 1.2% for the Southern Hemisphere had occurred for the period between 1977 and 1990. While the inferred increases do agree with expectations, the precision of measurement appears inadequate, and the experimental design does not account for short time scale variations of both a natural and anthropogenic origin. For example, in a two-month study, we found variations in atmospheric Hg over the northeast Pacific ocean that were comparable to the changes reported for the 13 year period in the Slemr and Langer work. Thus, the very important question of whether Hg is increasing in the atmosphere has not been properly addressed.

Atmospheric Hg Sampling Network, *AMNET*

There are two desirable approaches to resolving contemporary and historical patterns of Hg mobilization and deposition. One approach would focus on current atmospheric measurements and utilize a sampling and analytical strategy similar to the successful Atmospheric Lifetime Experiment Program (ALE). The ALE studies of contemporary temporal changes in the atmospheric concentrations of the freons, methyl chloroform and carbon tetrachloride show that 3 to 5 years of on-site continuous measurements are necessary to deal satisfactorily with questions of natural variability and to resolve the influence of pollution on constituents such as Hg^{o} in the atmosphere. In addition, measurements must be carried out in a network context. Stations should selected in both the northern and southern hemispheres. Critical information concerning the biogeochemical cycling of Hg and the role of anthropogenic inputs can be derived from the temporal and spatial variations in atmospheric Hg^{o}. Such a research program might be called AMNET or Atmospheric Hg Sampling Network and would be international in scope. As noted and following the ALE format, sampling stations would be in both hemispheres and at sites free from strong local pollution sources of Hg (e.g., remote islands). A precision and accuracy of $\geq$1% is required over a 3 to 5 year period. AMNET needs international support and cooperation to provide the high quality data necessary to constrain global models, to determine the influence of natural and anthropogenic sources on the global atmospheric Hg cycle, and to assess their effects on the biogeochemical activity of Hg in natural waters. The accurate resolution of the variability and secular trends in the atmospheric Hg burden can provide (1) a direct quantitative assessment of the scale to which anthropogenic processes are affecting the natural biogeochemical cycling of Hg, (2) an essential refinement and constraint that is currently lacking in mass balance models, (3) an enhanced knowledge of the behavior of Hg in the atmosphere, and (4) an accurate data base required for global circulation atmospheric chemical Hg models.

Polar Icesheet Studies of Modern and Historical Hg Deposition

Antarctica

Archives of Hg deposition provided by lake sediments, and ombrotrophic bogs have been used for regional depositional studies. Global scale changes require a broader geographic record such as the depositional record preserved in the polar icesheets in the Antarctic and Greenland. Icesheet records of Hg deposition offer a distinct and important scientific advantage by allowing modern trends in atmosphere Hg mobilization (and other constituents) to be placed and examined in the historical context of past depositional patterns. Unfortunately, investigations to determine the temporal history of Hg as preserved in polar icesheets of Greenland and the Antarctic have been inconclusive. Mercury concentrations reported in most previous studies of ice cores and snow from polar regions (Weiss et al., 1971; Applequist et al., 1978; Carr and Wilkniss, 1973; Herron et al., 1977; Murozumi et al., 1978) are greater than we observed in snow from the midcontinental MTL studies in Wisconsin (3.8pg g^{-1} to 8.2pg g^{-1}, Fitzgerald et al.,1991) and the variations over time lack a consistent geochemical explanation. Previous polar studies were probably flawed due to spurious Hg contamination and inadequate analytical sensitivity.

Recently, we determined the temporal variation in the Hg distribution over the past 34,000 years as recorded in the Dome C ice core from the Antarctic Plateau and recent snow blocks from four stations along a transect from the coast Vandal, et al., 1993. The results are most interesting and as shown in Figure 33, strikingly elevated Hg concentrations were present during the last glacial maximum (28ka BP). This historical pattern provides geological and oceanic scale evidence for the significance of the sea-air emissions associated with aquatic Hg^{o} cycle. A linkage and possible tracer of paleoproductivity is suggest because we have found much evidence for significant contemporary production and sea-air fluxes of elemental Hg in the biologically productive equatorial Pacific Ocean (Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1990). These findings are quite exciting, and with broad implications. Nevertheless, increases in marine Hg^{o} evasion and deposition could reflect not only higher oceanic productivity, but changes in surface dwelling biota, stronger winds, increased upwelling, and the more arid climate during the last glaciation. Modern air-sea exchange research of Hg^{o} production and emission in the Southern Ocean in concert with depositional investigations on the Antarctic continent would help to establish the relative importance of the potential sources.

Greenland

Determination of the modern and historical expression of the Hg cycle as preserved in polar ice cores will help address questions associated with its global behavior and activity. Information can be gained concerning the atmospheric movement and chemistry of Hg, its biogeochemical behavior and fate in marine and terrestrial systems, the accumulation of MeHg in biota, and with assessment of interferences from anthropogenic emissions on the natural Hg cycle. Of particular interest is the pattern of modern Hg deposition in the northern hemisphere. The anthropogenic depositional signal is of pressing value. The relationship of historical Hg deposition to climatic changes, alterations in oceanic productivity and circulation, and the sulfur cycle merit much examination. Northern hemispheric investigation in Greenland Icesheet will complement and significantly extend our work on the historical patterns of Hg deposition in the Dome C ice core over the past 34,000 years. The work should try to: 1. to accurately quantify the concentration of Hg and Hg species, MeHg, acid-labile Hg, and strongly bound Hg in snow cores and blocks from Greenland and to establish modern rates of Hg accumulation of these species in both hemispheres; 2. to assess the importance of seasonal variation in Hg accumulation and species especially as it relates to anthropogenic perturbations and natural patterns of Hg deposition to the Greenland icesheet; 3. to quantify the temporal distribution of Hg accumulation in Greenland as well as identify the important preindustrial Hg sources, and examine the relationship between oceanic emissions of Hg and volatile S that was discovered in the previous study of prehistoric Hg deposition in the Dome C ice core from Antarctica.

ATMOSPHERE-WATER COUPLING: MEHG AND HG^{o} CYCLING

As outlined, Hg^{o} cycling plays a central role in dispersing Hg at the Earth's surface and in affecting the synthesis and bioaccumlation of MeHg in aqueous systems. Production and evasion of Hg^{o} in natural waters is a major feature of the aquatic biogeochemical cycling of Hg. Aquatic Hg^{o} emissions are related to the availability and supply of reactive Hg [the Hg(II) substrate or reactant, Hg_R] and the atmosphere is usually the principal source. As part of the Hg(II) substrate/ reactant hypothesis, we proposed that the *in-situ* production and efflux of Hg^{o} could provide a potential buffering and/or amelioration role in aqueous systems. We hypothesized that in-lake biological and chemical production processes for Hg^{o} and MeHg compete with one another for reactant (Hg_R) which we suggest is labile Hg (II) species. Our lacustrine and oceanic investigations support this unifying physicochemical paradigm. Further, our studies place oceanic emissions of Hg^{o} at about 30% to 40% of the annual Hg flux to the atmosphere. Aquatic biological production of Hg^{o} appears to predominate over abiotic mechanisms, and water-air recycling of anthropogenically derived Hg is significant. This reemission can exacerbate adverse environmental effects. Preliminary modelling of this recycling component indicates that approximately

70% of current oceanic emissions are of anthropogenic origin, and atmospheric Hg° is increasing at ca. 0.6% yr^{-1} (Mason, et al., 1994).

The results from our preliminary modeling of the Hg cycle at the Earth's surface and the effects of anthropogenic influences on the cycle are summarized in Figures 34 and 35, which represent respectively the current and preidustrial global Hg. The importance of Hg° in controlling the production of MeHg is quite evident. Evasion of Hg° is balanced by total atmospheric deposition of Hg(II) or reactant to the oceans. The mechanisms by which Hg(II) is reduced to Hg° are poorly known. However, the reduction appears to be biological and involve µorganisms. In view of the significance of Hg° in affecting the speciation, behavior and fate of Hg in the environment, the Hg° cycle in the atmosphere and waters deserves much scrutiny.

There is a rapid equilibrium between the atmosphere and the surface ocean. When this phenomenon is coupled with the small sedimentation of Hg in the oceans, deposition on land becomes the ultimate sink for atmospheric Hg. Further, we predict that since the oceanic component is largely recycled, most of the anthropogenic Hg added to the system will be deposited on land and sequestered into surface soils. According to Lindqvist et al. (1991) surface soils contain ca. 5,000 Mmol of Hg. Thus, the model projects a Hg input at about 947Mmol which would represent about 15% of the total soil burden. As we have seen, Nater and Grigal (1992) estimates of the net increase in Hg in surface soils from the north central region of the USA were between 2 and 20%, and comparable to the model estimate. Mercury accumulating in soils is released slowly to terrestrial waters. The Swedish study (Lindqvist et al., 1991; Johansson et al., 1991, Aastrup et al., 1991) and the Swain et al. (1992) research suggest that < 30% of the atmospheric Hg deposition to a watershed reaches a lake.As the Swedish workers have stressed, the effects from the anthropogenic Hg loading will persist for a long period after a reduction in Hg emissions.

We estimate that atmospheric emissions have increased by about a factor of 4.4 over the last century as a consequence of human activities. Notice that the net increase in the atmospheric burden is a factor of three, due to the predicted rapid removal near of the source of Hg emissions in the form of particles and ionic species. As a consequence, 60% of the direct or recycled component is contributing to the Hg background in the atmosphere even though 77% of the present day inputs are directly or indirectly of anthropogenic origin (27 of the 35Mmol yr^{-1}). The 25 Mmol Hg in the atmosphere represents an average concentration of 1.6 ng m^{-3} which is comparable to the average concentration of Hg over the oceans (see Pacific data in Figure 28). Given this contemporary constraint, we predict that the preindustrial atmosphere contained 8 Mmol of Hg with an average concentration of 0.5 ng m^{-3}.

A rate of increase of atmospheric Hg can predicted by assuming that anthropogenic inputs have increased linearly over the last 100 years. Accordingly, 1000 Mmol were emitted anthropogenically during the 100 year period. Of those emissions, 17 Mmol are now in the atmosphere, 36 Mmol are in the surface ocean and the remaining 947 Mmol have accumulated in surface soils. As noted, 500 Mmol came from the rapidly recycled anthropogenic component and 447 Mmol via the atmospheric cycle. The prediction that the present rate of increase of Hg the atmosphere is about 0.16 Mmol yr^{-1} (i.e., 0.6% yr^{-1}) is testable and an experimental design has been outlined in Section 4.0.

Finally, the Hg° and MeHg cycles are intimately linked. Environmental studies of Hg must view the biogeochemistry of Hg as unit and avoid a unilateral focus on one aspect of the system. For example, human exposure to MeHg in fish is related to anthropogenic emissions of Hg, especially Hg°, atmospheric transport and deposition processes, and in situ biological interaction and chemical reactions that lead to Hg° production and recycling between water and air. Although, Hg(II) reduction and evasion removes Hg from the waters where it might be methylated, the recycling between surface waters and the atmosphere will prolong the impact of anthropoenically derived Hg on aquatic systems. Present day ocean contains enhanced Hg levels that promote increased methylation in the water column. Oceanic emissions reflect the presence of this increased burden. About 70 to 80% of today's emission of Hg are related to human activities. A substantial portion of the emissions are predited to be deposited locally. Regional deposition would reflect the presence of ionic and particulate Hg species in emissions. Elemental Hg emission would contribute to far field and more global effects. An 3X increase in the Hg burden in the atmosphere in ocean is predicted. Surface soils contain most of the pollution derived Hg released over the past 100 years. Current emissions are exacerbating the problem by adding to a seriously contaminated active reservoirs of surface soils, watersheds, the atmosphere, and the oceans. As most Hg deposited on the oceans is recycled to the atmosphere, the terrestrial environment becomes a principal sink. Mercury deposited on land mobilized slowly to enter the watershed and tributaries of fresh and coastal waters. The insidious consequence of the complex and interesting biogeochemical cycling of Hg is to lengthen the influence and active lifetime of anthropogenic Hg in regions where methylation can occur.

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Table 8. Global Atmospheric Mercury Budget

Source	Mercury flux (10^9 g/year)	Reference
Deposition		
	5-6	Fitzgerald, 1986
	6	Slemr et al., 1981
	7.5	Lindqvist et al., 1991
Emissions		
Anthropogenic	2	Watson, 1979
	3.6	Nriagu and Pacyna, 1988
	4.5	Lindqvist et al., 1991
Natural	2.5	Nriagu, 1989
	3	Lindqvist et al., 1991
Oceanic sources	2	Kim and Fitzgerald, 1986
Equatorial Pacific	0.2	
Volcanic	0.06	Fitzgerald, 1986
	0.6	Varekamp and Buseck, 1986
Other continental sources - Crustal degassing - Forest fires - Biological mobilization	1-2	Fitzgerald and Clarkson, 1991
Fluvial Hg input	0.2	Gill and Fitzgerald, 1987

Table 9. Atmospheric Wet Depostional Fluxes of Total Hg to Various Station in the Nordic Countries (after Iverfeldt, 1991)

Station	No.	Precipitation (mm)	Deposition Rate ($\mu g\ m^{-2} yr^{-1}$)
Keldsnor,DK	1	430	17
Aspvreten, S	2	520	10
Rorvik, S	3	770	27
Birkenes, N	4	1730	35
Tikkakoski, SF	5	720	11
Vindeln, S	6	650	7
Karvatn, N	7	1430	13
Overbygd, N	8	540	5
Jergul, N	9	340	3

Table 10. Particle Associated Hg as a Percent of the Total Hg Observed in Precipitation at Two Sites in the Nordic Countries Network (adapted from Iverfeldt, 1991)

Station	Average	> 10 um Range	SD	n	> 0.4 um Average	Range	SD	n
Keldsnor, DK	64	8-93	22	12	79	59-92	12	10
Overbygd, N	42	8-64	20	6	67	24-92	27	5

Table 11. Summary of the Average Concentration of Hg Species Observed in Wet Deposition from Northcentral Wisconsin

SAMPLE PERIOD	n*	Hg_R (pM)	TOTAL (pM)	MMHg (pM)
RAIN 1989	12	13.7 ± 10.6	52.5 ± 24.0	0.78 ± 0.34
RAIN 1990	9	41.0 ± 20.6	49.3 ± 20.8	0.37 ± 0.16
SNOW 88/89	6	17.5 ± 12	30.0 ± 4.5	0.24 ± 0.11
SNOW 89/90	3	8.0 ± 0.75	14.9 ± 3.9	0.52 ± 0.20

* n = number of deposition events sampled

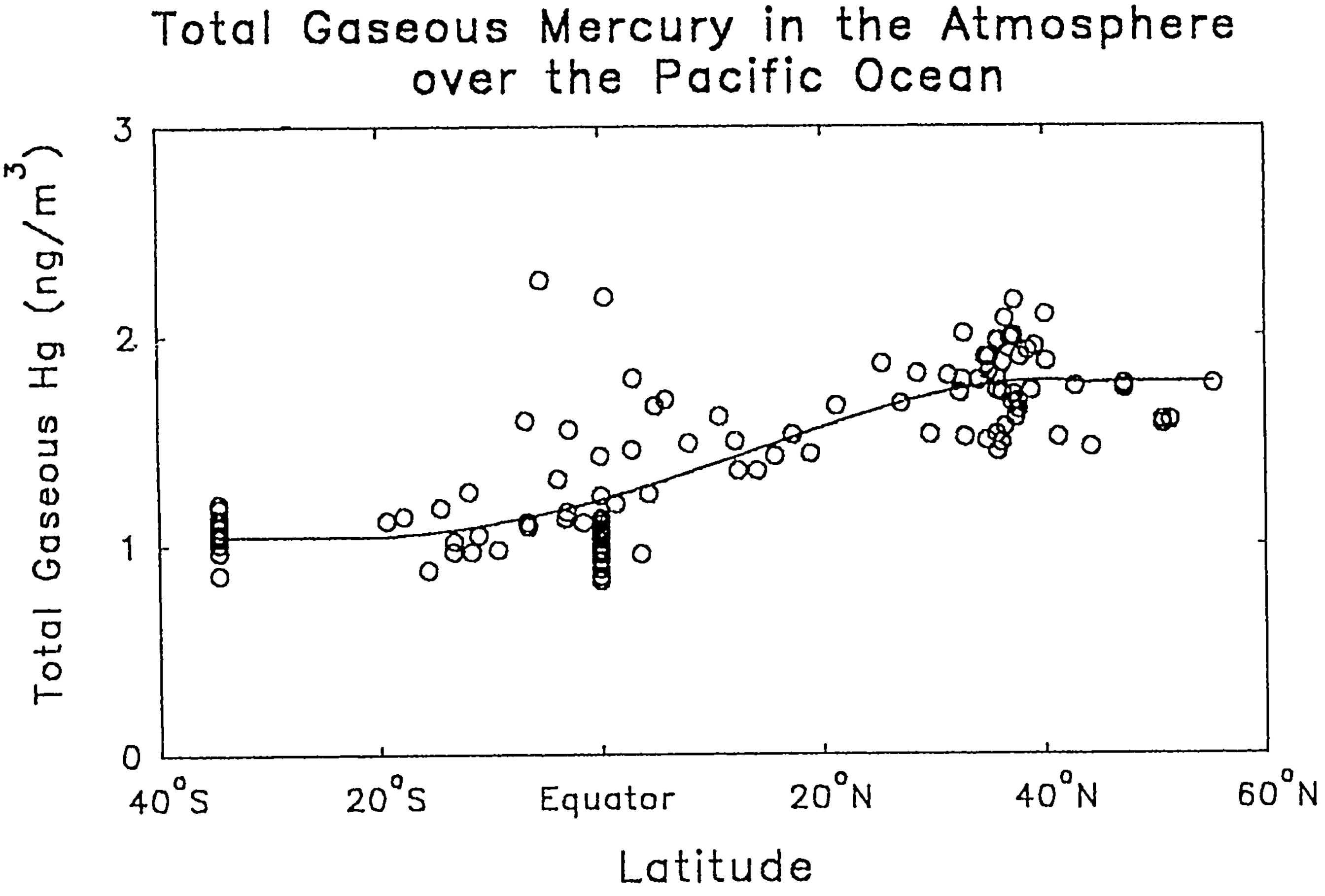

Figure 25. Latitudinal distribution of total gaseous Hg (TGM; ng m^{-3}) over the Pacific Ocean between 1980 and 1986. Adapted from Fitzgerald (1986).

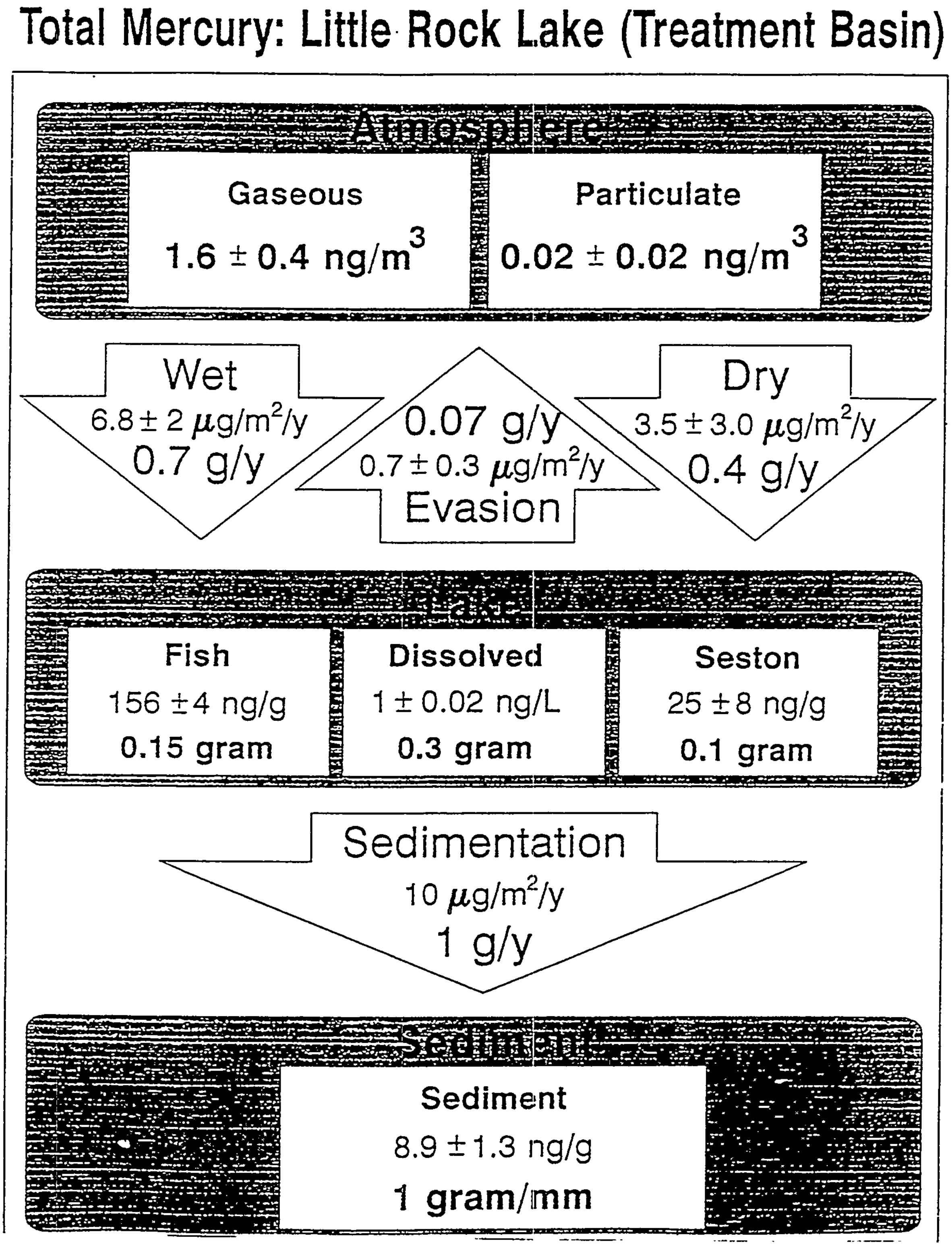

Figure 26. Mass balance model for Hg in the treatment basin of Little Rock Lake, Wisconsin (adapted from Fitzgerald et al., 1991 and based on work and preliminary budgets appearing in Wiener et al., 1990, Fitzgerald and Watras 1989, and to appear in Watras et al. 1994).

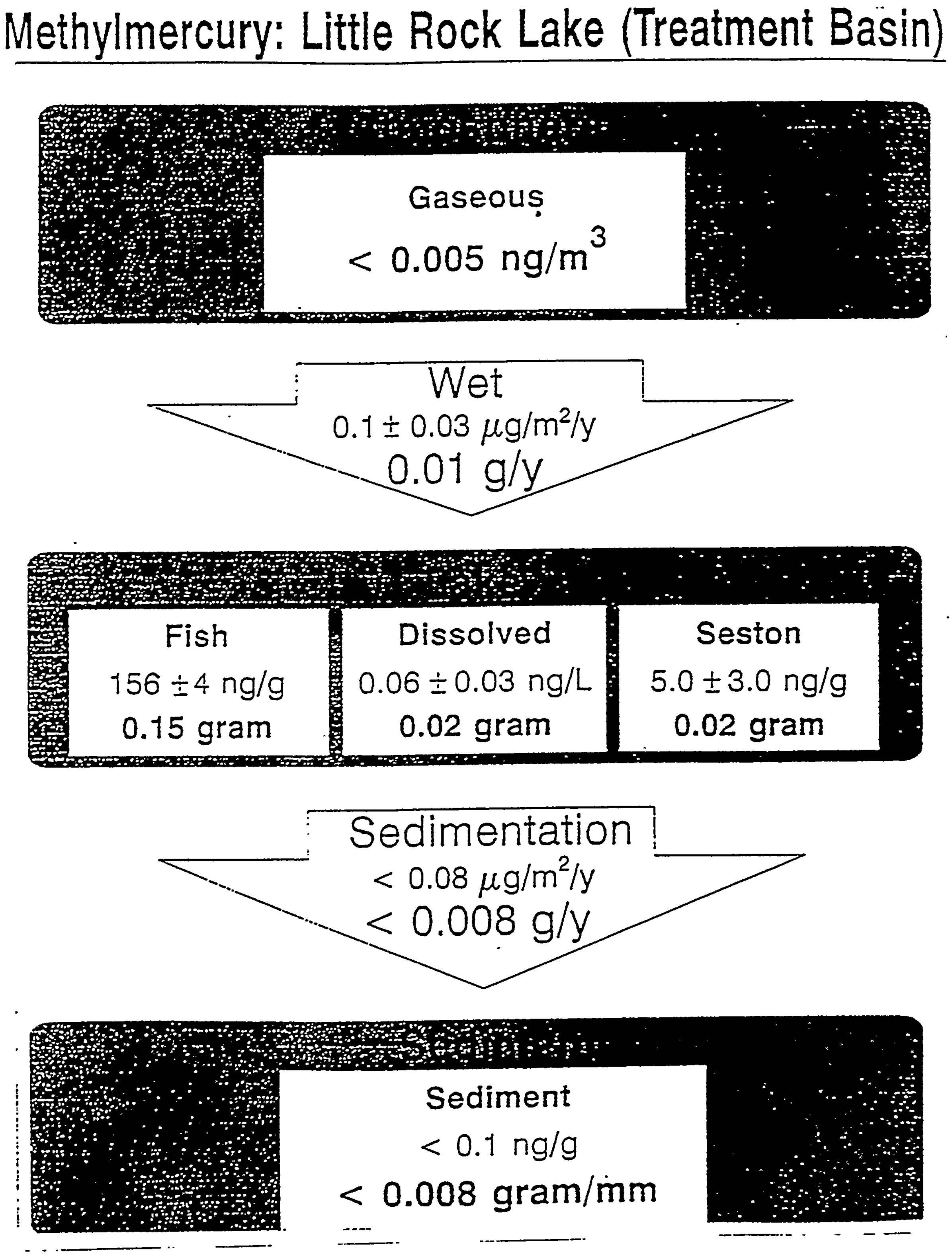

Figure 27. Mass balance model for monomethyl Hg in the treatment basin of Little Rock Lake, Wisconsin (adapted and based on work from Fitzgerald et al., 1991; Wiener et al 1990; Hurley et al., 1991 Bloom et al., 1991 and Watras et al. 1994).

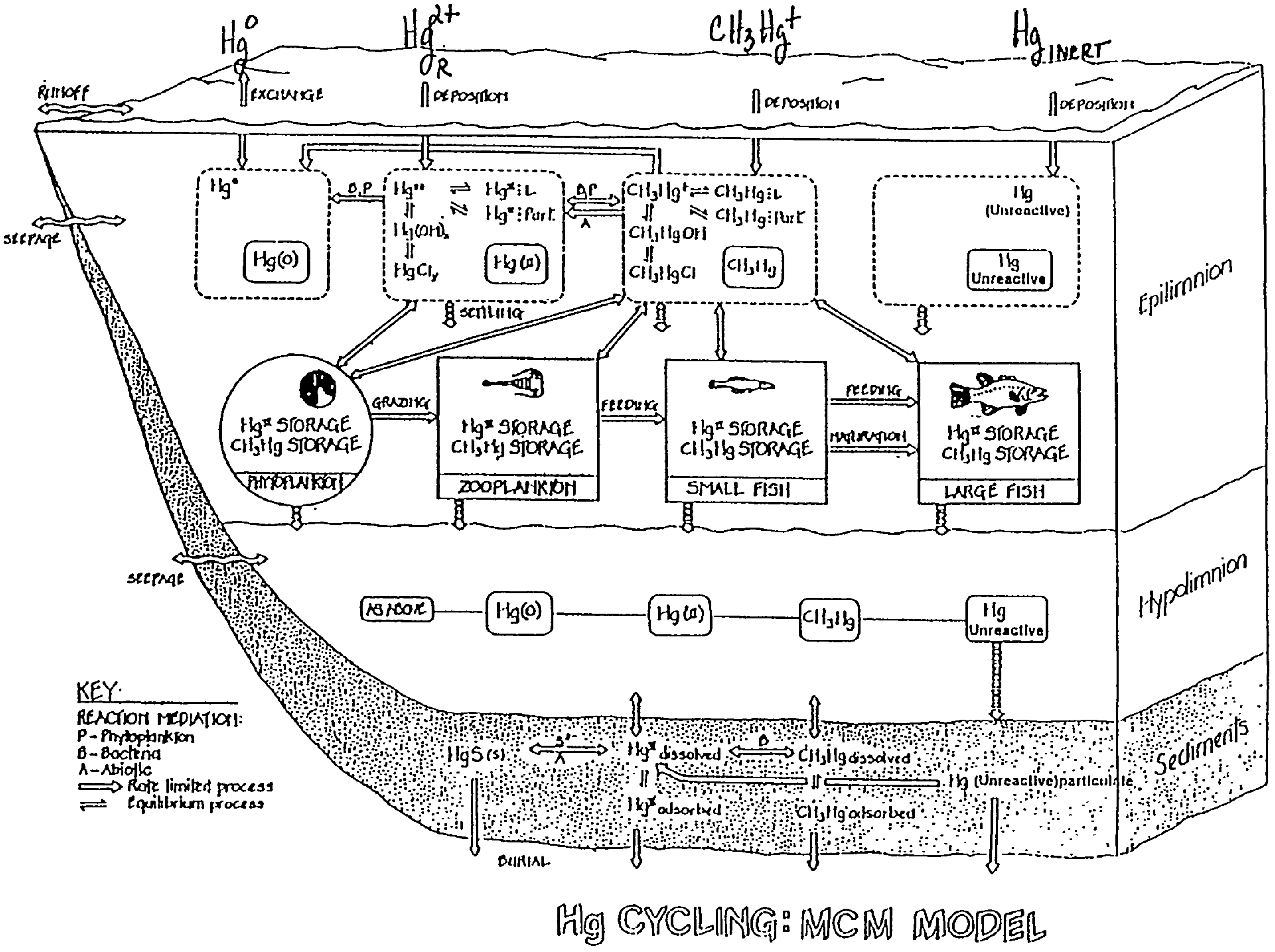

Figure 28. The major species, fluxes and reservoirs for the physical and biogeochemical cycling of Hg in the atmosphere and within lakes (adapted from Hudson et al., 1994).

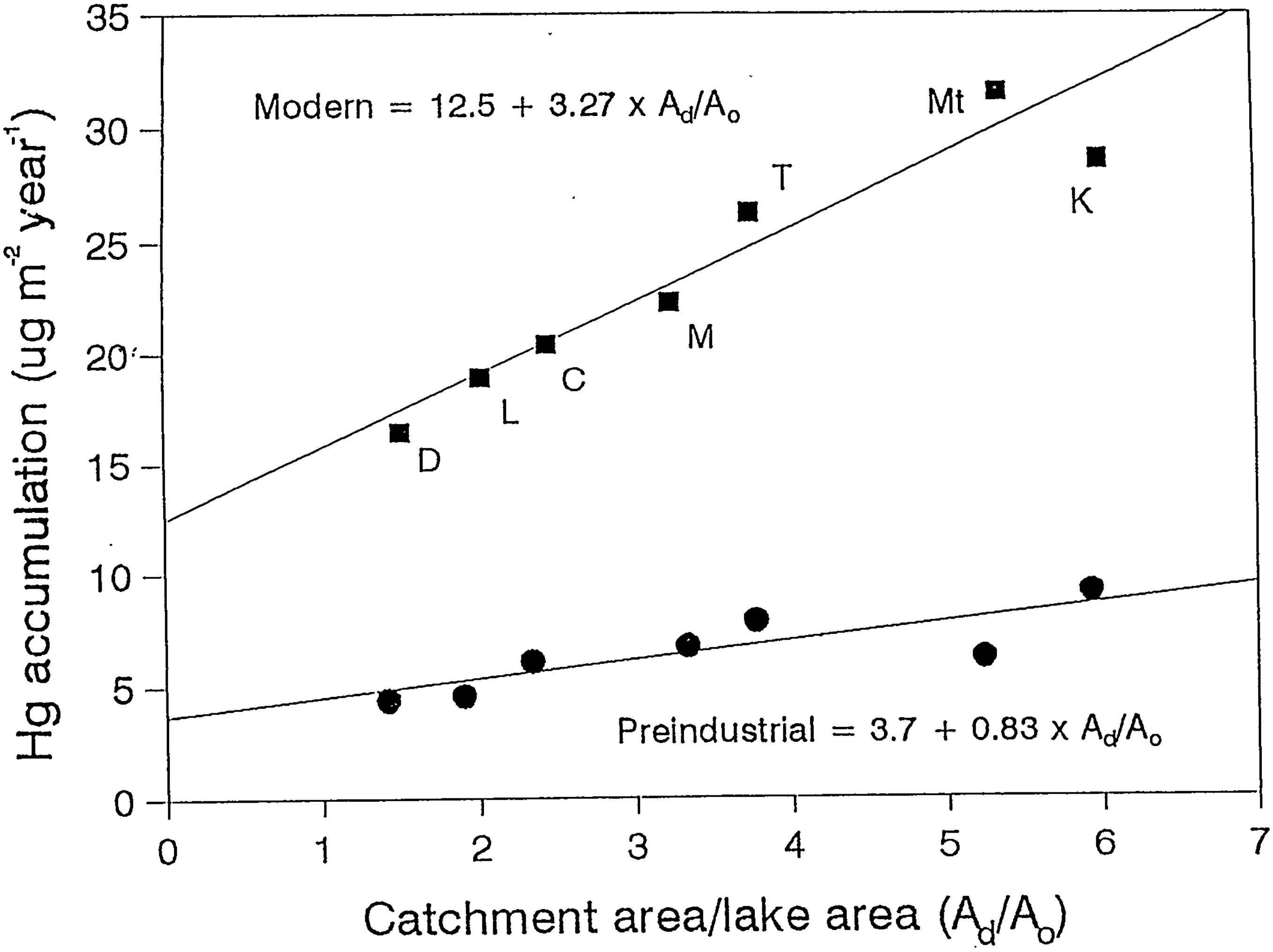

Figure 29. Whole basin accumulation rates for Hg (μg m^{-2} yr^{-1}) are plotted against the terrestrial catchment area to lake area ratio. Modern rates based on the past 10 years are indicated by the filled squares, while the preindustrial estimates (before ca. 1850) are indicated by the filled circles (adapted from Swain et al., 1992).

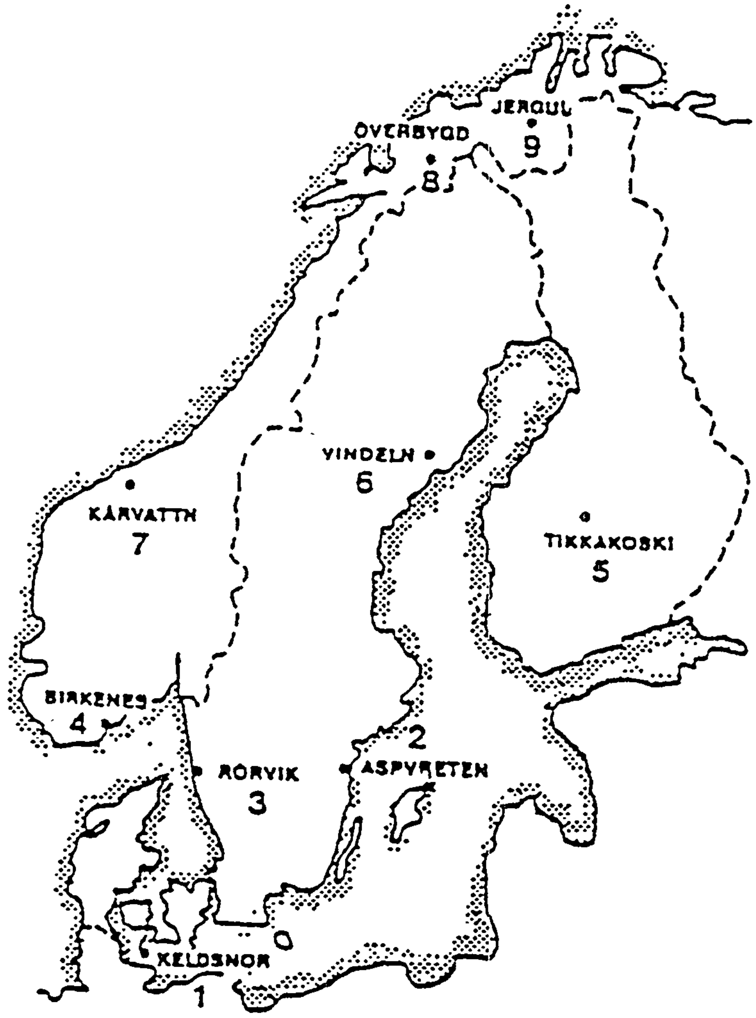

Figure 30. Stations in the Nordic network study of atmospheric Hg during 1985 to 1989 (from Iverfeldt, 1991).

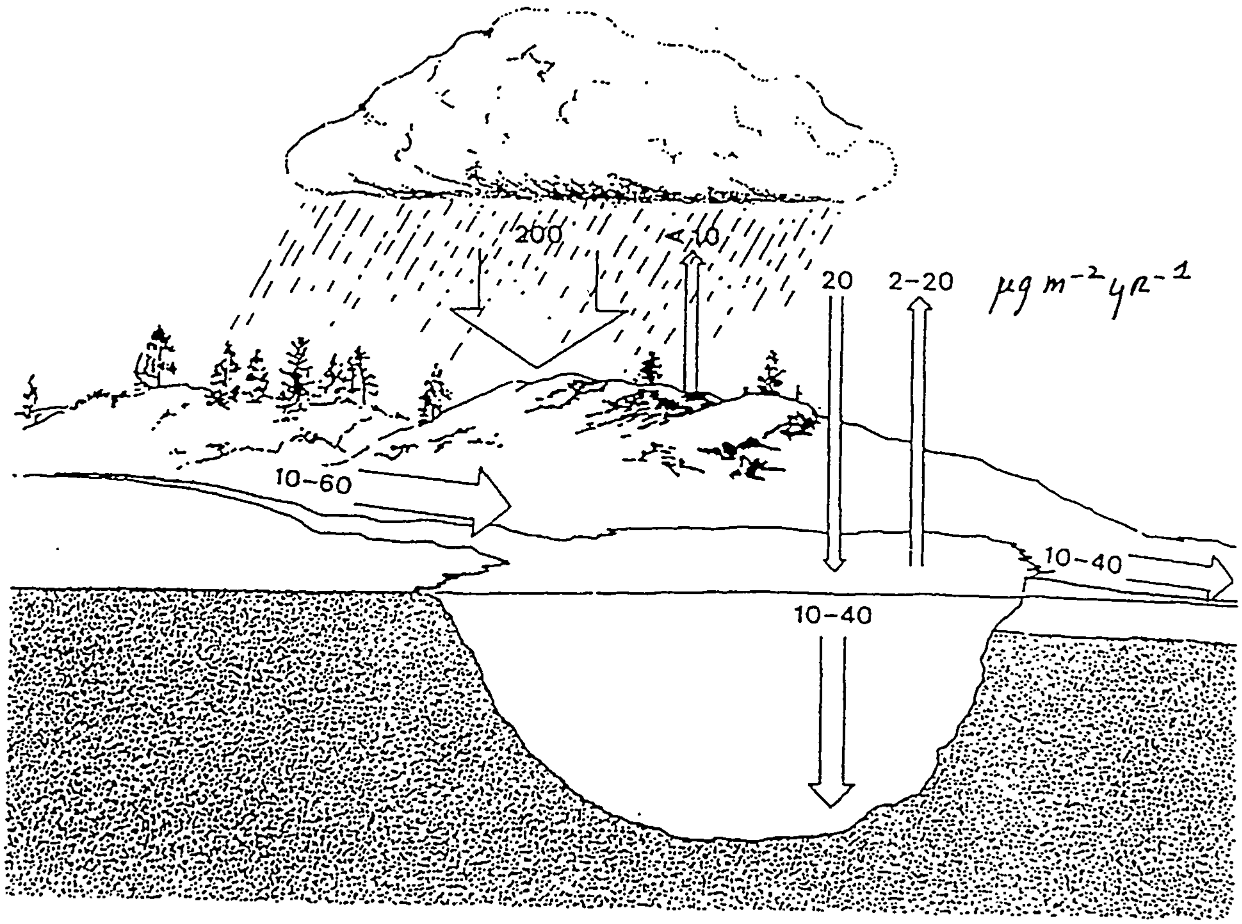

Figure 31. Flows of Hg in g yr^{-1} for typical southern Swedish lake with an area of 1 km^2 and a drainage area of 10 km^2. Atmospheric depositional fluxes of Hg are for precipitation and do not include dry deposition. Adapted from Johansson, et al., 1991, and Lindqvist et al., 1984.

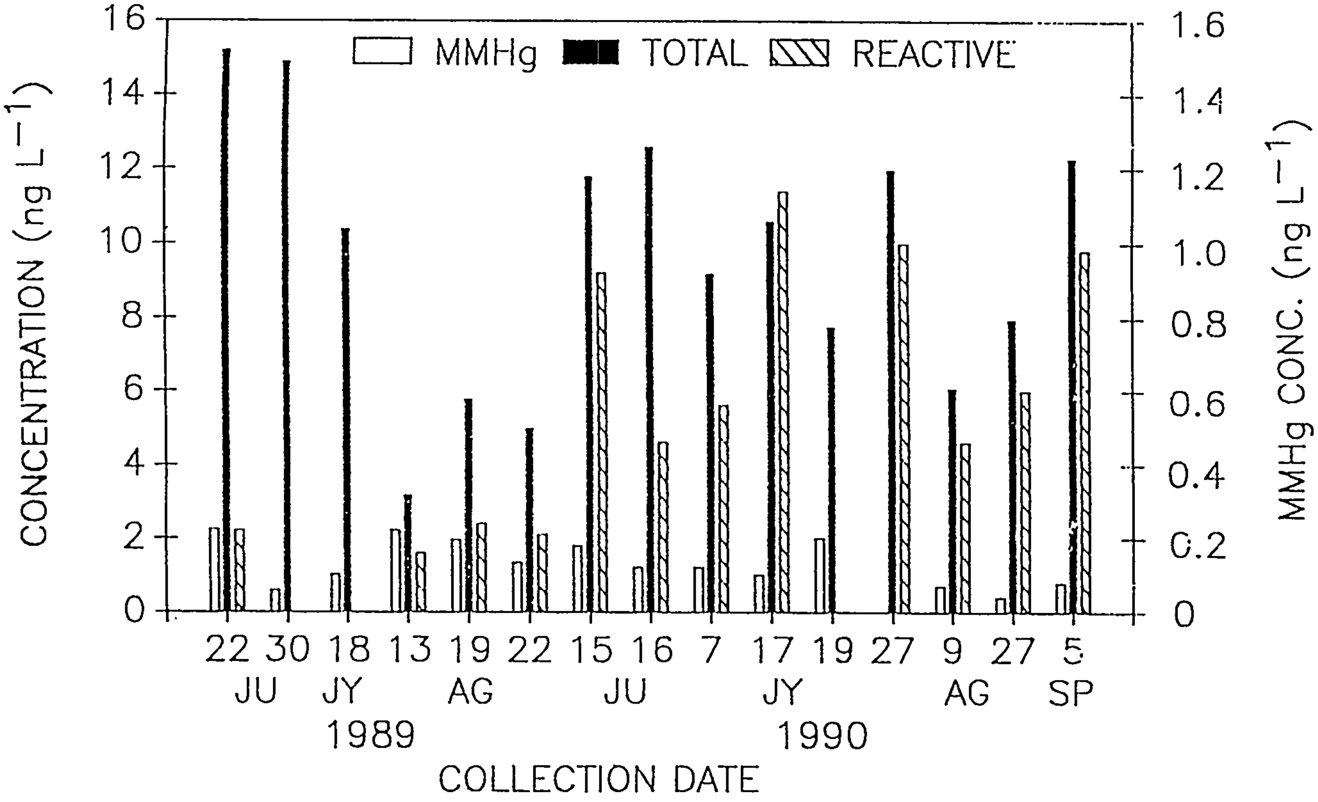

Figure 32. Total, reactive and methylmercury in rain collected in Wisconsin at Little Rock Lake Reference Basin, in 1989 and Max Lake in 1990, adapted from Fitzgerald et al., 1992 and Mason et al., 1991.

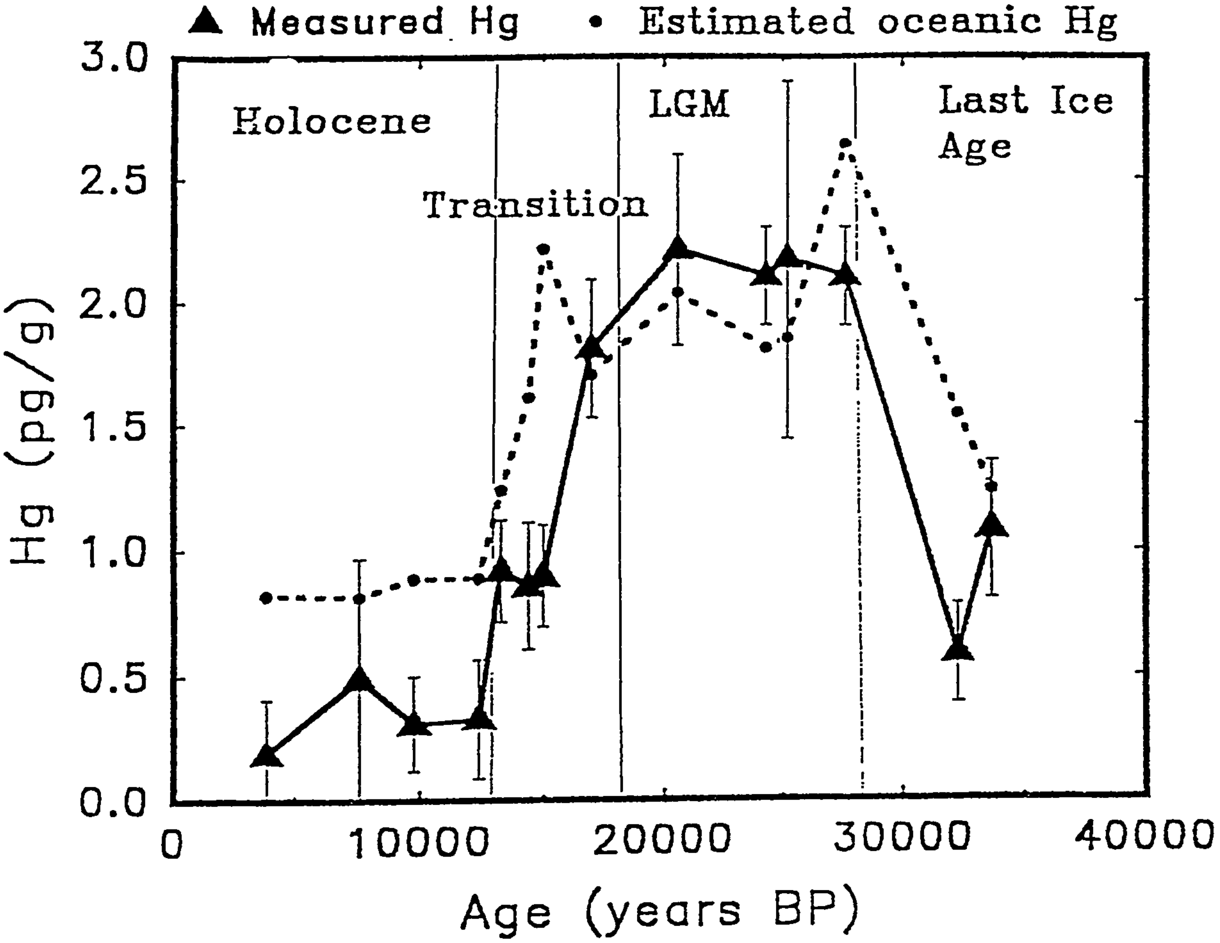

Figure 33. Mercury in the Dome C Ice Core (adapted from Vandal et al., 1993). Measured Hg concentrations are presented with error bars representative of the uncertainty associated with blank corrections. Mercury concentrations were 0.5 pg g^{-1} during the early part of the last ice age, 34 to 28 ka BP, and increased dramatically during the LGM (between 18,000 and 28,000 years BP) to 2.1 pg g^{-1}. Mercury concentrations in ice decreased during the glacial-interglacial transition period. The Hg values for Holocene ice, from 12 ka BP to present, were 0.4 pg g^{-1}. The predicted Hg contribution from oceanic gaseous emissions is presented and is remarkably close to the measured values indicating the oceans as the primary source of Hg to Dome C during pre-industrial times.

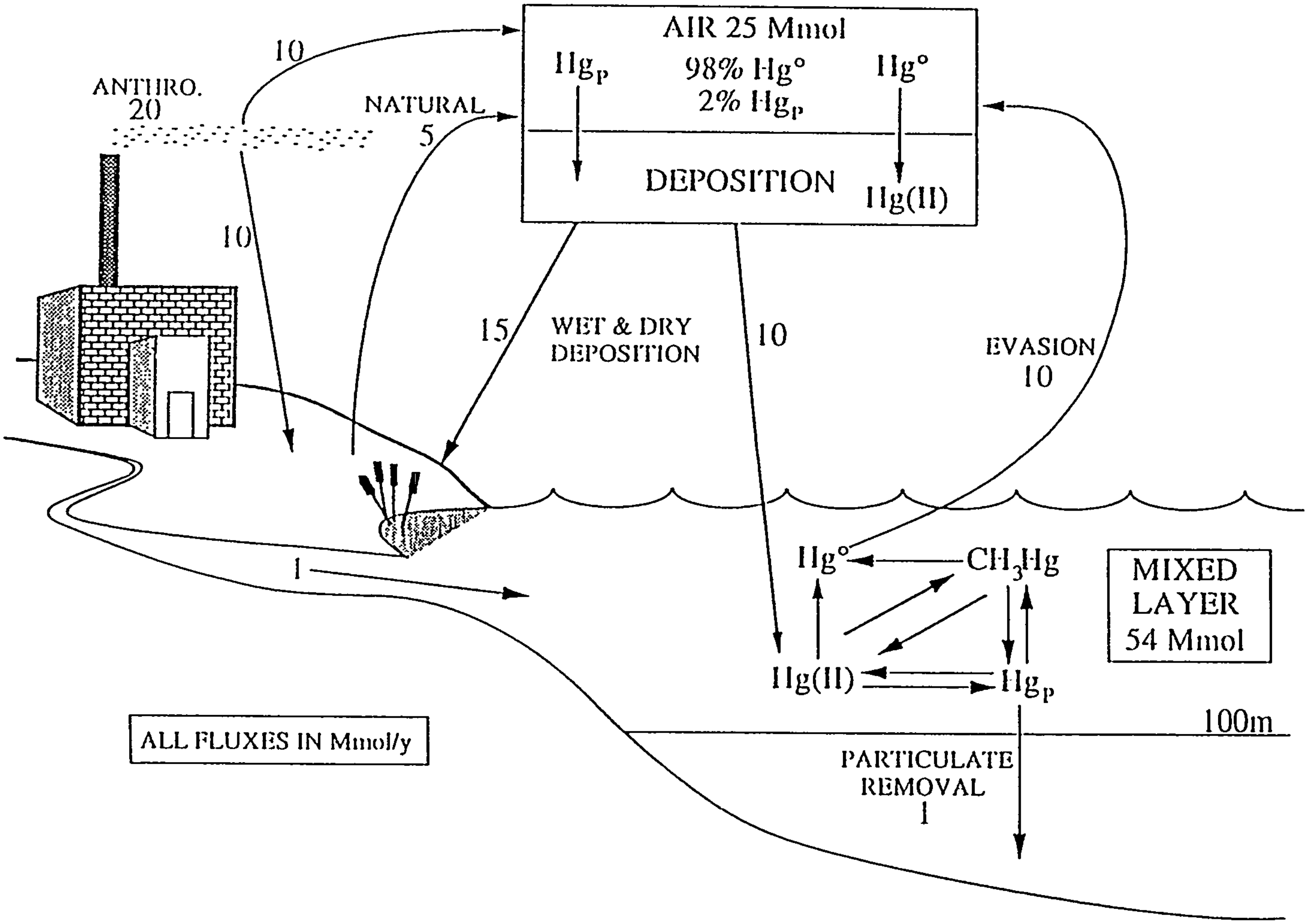

Figure 34. Current global Hg cycle (adapted form Mason et al., 1994).

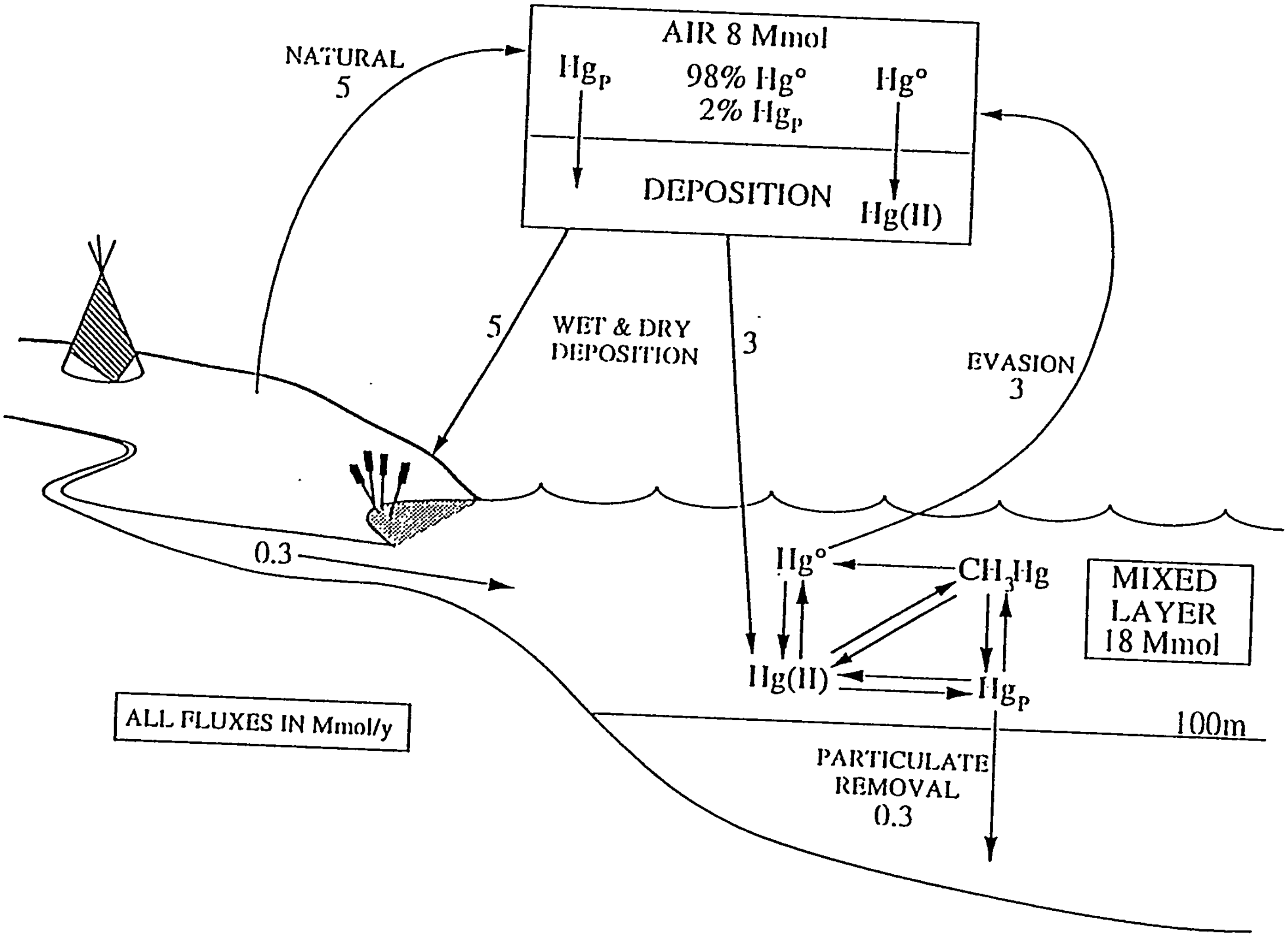

Figure 35. Preindustrial Hg cycle. Preindustrial fluxes are based on the current deposition and emission patterns as outlined in Figure 34 and estimates for preindustrial terrestrial emissions (Adapted from Mason et al., 1994).

WORKSHOP DISCUSSION

A question arose regarding the limiting factors of the analysis. The concern was based on information that multiple factors contributed to a three-fold increase of Hg as seen in soil-sensitive lakes along the Michigan/Canadian border.

Participants asked about the measurability of global Hg flows. A reply stated that the background of the chart in the text (see Figure 34) is based on existing information gathered from Eastern Europe. Another participant asked why the chart displayed 15 mmoles of Hg entering into the earth's surface, while only 10 mmoles enter into the ocean. One possibility suggested was that the earth's land surface was closer to the sources. It was also pointed out that ozone, SO_2, and particles are effective in removing Hg over land. Incorporating wet deposition into this cycle posed a small problem because precipitation data are limited, however, the numbers are based on average concentrations and are weighted.

In the discussion about trends in the Hg levels in the various compartments, the estimated increase is about 1 to 2%/year. This should be detectable over periods ranging from 20 to 30 years. However, this trend has not been observed over the last 30 years. Although, this could possibly be due to the clean-up of Hg point sources, chlor-alkaki plants, in the 1970s, it is more likely that experimental design and analytical approaches employed have been inadequate to determine accurately secular changes in the environmental Hg distribution.

7. EXPOSURE OF U.S. CONSUMERS TO METHYLMERCURY FROM FISH

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INTRODUCTION

Public health officials have been concerned about methylmercury in fish ever since it was first tied to poisoning episodes in Japan that occurred in Minimata Bay (1953-1960) and Nigata (1965). High levels of mercury in seafood from these areas were tied to severe local industrial pollution. Analysis of fish from Minimata Bay in the 1950's showed a median level of total mercury of 11 mg/kg (ppm) wet weight. Fish samples from the Agano River in Nigata had a median total mercury level of less than 10 ppm (World Health Organization, 1976).

BACKGROUND INFORMATION ON LEVELS OF MERCURY IN FISH

Federal testing of fish

The concern for mercury in 1970 focused on the need for better characterization of the levels of methylmercury in fishery products as well as the patterns of fish consumption. In the early 1970's, the NMFS conducted testing for total mercury levels in over 200 seafood species of commercial and recreational interest. The published report from this survey (Hall et. al., 1978) provides considerable insight into the ranges of mercury levels that are likely to be encountered in different fishery products. Most finfish had mean mercury levels below 0.3 ppm (31% had less than 0.1 ppm). Shellfish samples (oysters, clams, scallops, shrimp, and crabs) averaged only 0.05 ppm. Only 31 species had mean mercury levels in excess of the 0.5 ppm limit proposed at that time. Of the 31 species, 10 were sharks and 4 were billfishes. The highest levels of mercury were found in large top predator species of fish. Based on the percent of the U.S. catch represented by these 31 species, it was concluded that less than 2% of the U.S. catch intended for consumption was likely to have levels in excess of the proposed 0.5 ppm limit. The following table summarizes some of the findings from this study.

Table 12. Mercury Levels in Selected Fishery Products from NMFS Survey

Fish Species	Range of Means (ppm) (wet weight basis)
Anchovy	<0.1
Striped bass	0.5-0.6
Bluefish	0.3-0.4
Channel catfish	0.1-0.2
Cod, Atlantic	0.1-0.2
Cod, Pacific	0.1-0.2
Eel, American	0.2-0.3
Flounder, various species	<0.1-0.2
Grouper, black	0.7-0.8
Grouper, red	0.3-0.4
Haddock	<0.1
Halibut	0.2-0.3
Herring, Atlantic	<0.1
Mackerel, Atlantic	<0.1
Mullet, silver or striped	<0.1
Perch, sand	0.6-0.7
Perch, shiner or silver	<0.1
Perch, white	0.1-0.2
Pollock	0.1-0.2
Salmon, various species	<0.1
Shad, American	<0.1
Snapper, red	0.2-0.3
Sole, Dover	0.1-0.2
Trout, cutthroat	0.2-0.3
Trout, rainbow	<0.1
Tuna, various species	0.1-0.3
Yellowtail	0.1-0.2

* Fish from a single survey site formed a sample. Mercury content was averaged for each sample. Each species was sampled at many sites. This table reports the range of the mean mercury levels that encompassed all samples.

Recent information from NMFS indicates that the mercury levels reported in the 1978 report have not significantly changed (National Marine Fisheries Service, 1990). The following table provides the results of FDA's analysis of domestic fishery products for fiscal year 1979 (U.S. Food and Drug Administration, 1982).

Table 13. Mean Mercury Levels in FDA Fiscal Year 1979 Survey
(ppm-wet weight basis)

Species	Mean	Maximum level
Bass, fresh water	0.19	0.62
Bass, salt water	0.07	0.25
Bluefish	0.19	0.81
Carp	0.11	0.37
Catfish	0.10	0.74
Cod	0.15	0.83
Halibut	0.27	0.51
Perch, fresh water	0.13	0.30
Perch, salt water	0.17	0.44
Pike, walleye	0.26	0.75
Pollack	0.05	0.14
Swordfish	0.83	1.82
Trout, fresh water	0.13	1.01
Trout, sea	0.09	0.24
White fish	0.06	0.24

FDA continues to monitor seafood for methylmercury. The results of recent surveys parallel the results of FDA's and NMFS's earlier findings. A recently completed survey of 245 samples of canned tuna, the most frequently consumed seafood item, showed mean methylmercury levels of 0.17 ppm (Yess, 1993). An FDA study in 1973 of 253 samples of canned tuna showed a mean total mercury level of 0.24 ppm. The author has estimated that the mean methylmercury content of the 1973 samples is about 0.21 ppm. The small difference between these two studies may reflect increased use in canned tuna of tuna species with slightly lower average methylmercury levels.

FDA has focused considerable attention in the past couple of years on analyzing shark for methylmercury. Although shark was not commercially important at the time of the earlier studies, the 10-fold increase in domestic harvesting in the last decade had made this fish readily available to consumers. Methylmercury levels as high as 4.2 ppm have been found in some lots of shark with levels averaging about 1.3-1.5 ppm for a variety of sharks.

Local testing of fish

Recently a number of states have been finding elevated levels of methylmercury in fish collected from local waters. The State of New Jersey just issued a report (The Academy of Natural Sciences of Philadelphia, 1994) that indicated that 15 of the 55 sampling sites had fish concentrations higher than 1 ppm. The highest levels were found in the 3-9 ppm range. The State of Florida (Private communication, T. Lange, 1994) has found some species of sports fish in some areas with levels as high as 7 ppm and median levels as high as 2.5 ppm. The State of Minnesota (Private communication, P. Shubat, 1994) has found levels as high as 4.5 ppm at sites remote from specific sources of mercury contamination. For species such as pike, levels routinely approach 1 ppm. The Clean Water Action Group in their August, 1993 report "Gone Fishing" (Walsh and Ketelsen, 1993) reported levels of mercury in fish from various New England waters that occasionally exceeded 1.0 ppm, and in one case, averaged 5.77 ppm for fish from a particular body of water.

ESTIMATES OF FISH CONSUMPTION

Background

In order to address methylmercury exposure among population sub-groups reflecting a variety of sociodemographic characteristics, detailed information is needed to address long term patterns of how often and in what amounts people of different population sub-groups eat particular fish species. Many approaches can be taken for characterizing fish consumption. The simplest approach, per capita consumption, depends on estimates of the total amounts fish available for consumption and the size of the fish eating population. This information can be used to characterize national average consumption of all fish species as well as individual species, but it can not be used to characterize consumption patterns of eaters of specific seafood items or seafood in general or, for that matter, particular sub-populations of interest. Currently, the per capita consumption of seafood is 14.8 pounds per year (about 18.5 g/p/d) (Seafood Business, 1993) and the top ten species and pounds per capita are shown in the next table.

Table 14. Top 10 Seafood Species: Annual Pounds Per Capita for 1992

Species	Pounds per capita (ave daily intake)	
Tuna	3.50	(4.4 g/p/d)
Shrimp	2.50	(3.1 g/p/d)
Alaska Pollock	1.23	(1.5 g/p/d)
Salmon	1.16	(1.4 g/p/d)
Cod	1.08	(1.3 g/p/d)
Catfish	0.91	(1.1 g/p/d)
Clams	0.62	(0.8 g/p/d)
Flatfish	0.51	(0.6 g/p/d)
Crabs	0.33	(0.4 g/p/d)
Scallops	0.27	(0.3 g/p/d)

To address the consumption patterns of seafood in general or specific seafood items, some form of food consumption survey is needed. Ideally, such survey information should specifically address the target population of interest. Food consumption surveys are generally either recall surveys or food diaries. Each can be quite expensive, especially when information is needed to characterize national patterns of consumption. In the case of recall surveys, individuals are asked to recall information about the amounts, types, and frequency of food consumption for given periods of time. The quality of the information obtained from such surveys can be significantly influenced by the length of the time over which individuals are asked to recall and describe their previous eating habits.

Consumption surveys using food diaries provide records of food consumption over given periods of time. They may simply involve recording how often a particular food is eaten, or may be more detailed and require the recording of the weight of each serving of food. This latter approach circumvents errors associated with the estimation of serving sizes, but it is labor intensive and expensive. Further, it can suffer from underreporting if the survey periods are lengthy.

The NPD Survey

In 1973-74 the Tuna Research Foundation commissioned the National Purchase Diary Panel Inc. (NPD) to conduct a survey for the purpose of providing a representative and projectable sample of seafood consumption patterns among the continental U.S. population. To date, this survey (Tuna Research Foundation, 1975) represents the largest and most comprehensive study that specifically focuses on seafood consumption (marine and freshwater species). The objective of the survey was to provide data on seafood consumption by species, by individuals within families, by young children (10 year or less), and by pregnant women. The survey involved 25,165 individuals. The panel recorded their seafood consumption by family member in a diary for a 1-month period. The total amount of seafood consumed by each family was recorded for each meal. Data for one twelfth of the sample population were recorded each month for a year. Estimates of individual intakes were derived using USDA data on average serving sizes and information on the total amount of seafood available at each meal. The following table summarizes some of the important results from this study.

Table 15. 1973-1974 National Purchase Diary

- 93 % of individuals surveyed consume seafood during 1-month survey period
- 18 g/p/d is average consumption of all seafood
- 20 g/p/d is average consumption of seafood for individuals in Great Lakes states
- < 1.5% of individuals consume > 85 g/p/d
- 187 g/p/d is highest consumption in survey population
- Consumption by pregnant women was not evaluated because the number who were pregnant was limited
- Tuna consumption
    - 61.5% of all individuals consume tuna
    - 5.6 g/p/d is average tuna consumption
    - < 5% of tuna eaters ate > 14 g/p/d
- Shrimp consumption
    - 22% of all individuals consume shrimp
    - 7.5 g/p/d is average shrimp consumption
    - < 5% of shrimp eaters consume > 19 g/p/d
- Additional species specific data are reported in study
- The top ten consumed fish species in decreasing importance

    Tuna
    Shrimp
    Flounders
    Perch, marine
    Salmon
    Clams
    Cod
    Pollock
    Haddock
    Herring

Other Consumption Studies

In general, national food consumption surveys are used to address exposure issues that are national in scope. In cases such as sports fish, where safety issues may be local, it is recommended that local consumption patterns be considered instead.

Two nationwide food consumption surveys frequently used by FDA are broad dietary surveys that collect information on seafood products as well. One is the Nationwide Food Consumption Survey (NFCS) conducted by USDA during 1977-78 (Pao et. al., 1982) and again in 1987-88 (United States Department of Agriculture 1988). The other is a set of surveys conducted by the Market Research Corporation of America (MRCA) in 1977-78 (Market Research Corporation of America, 1988) and 1982-1987 (Market Research Corporation of America, 1988). The surveys differ in size and methodologies and these differences are likely to yield differences in estimates of fish consumption.

The 1977-78 USDA survey consists of 30,770 individuals and the 1987-88 USDA survey consists of 10,342 individuals. The surveys involve 3-day periods with data for the first day collected by personal interview and the data for days 2 and 3 surveys obtained by a self administered diary. Fish consumption in the survey include fish consumed from all sources. The amounts of food consumed were recorded.

MRCA collects data describing what kind and how often foods are consumed at home and away from home over a 14-day survey period. The 1977-78 survey includes 11,500 individuals and the 1982-87 survey contains records for 27,721 individuals. These surveys are self-administered diaries that only record the frequency that various foods are consumed. In order to convert the frequency of eating occasions for 14-days to estimates of average daily food intake, MRCA uses mean serving size information calculated from the 1977-78 USDA survey. The MRCA 1982-87 survey found that about 77% of the survey population ate "seafood" at least once during the 14-day survey interval. The following table summarizes estimates of seafood consumption for different age groups.

Table 16. MRCA Estimates of 14-Day Average Fish/Seafood Consumption

Age Category	Mean Consumption (g/p/d)	90th %ile (g/p/d)
2+ years (all ages)	32	64
2-5 years	16	32
18-44 years	35	72

In contrast to MRCA's results, USDA found for the shorter 3-day survey interval that only 24.5% of the surveyed population ate fish and shellfish. As a consequence of the shorter survey period, estimates of average daily seafood consumption appear to be somewhat higher than when consumption amounts are averaged over the longer survey interval employed by MRCA.

Table 17. USDA Estimates of 3-Day Average Fish/Shellfish Consumption

Age Category	Mean Consumption (g/p/d)	90th %ile (g/p/d)
All ages	48	94
19-34 years (male)	62	128
19-34 years (female)	44	85

Special Population Subgroups

Subsistence fishers form a group of consumers likely to eat fish more frequently than the general population. This group would be quite small and would be limited to areas of the U.S. where fish are easily caught. The amounts of fish consumed by subsistence fishers is the subject of considerable speculation. When FDA was faced in 1990 with addressing dioxin risk to subsistence fishers downstream from pulp and paper mills, they assumed, due to a lack of fish consumption data for such a sub-group, that subsistence fishers consume fish at the same level that individuals in the general population consume red meat (U.S. Food and Drug Administration, 1990). FDA used MRCA red meat consumption figures to predict long-term consumption of fish (mean consumption was estimated to be 65 g/p/d and 90th %ile consumption was 116 g/p/d).

Eventhough these estimates of fish consumption for subsistence fishers may seem reasonable, it seems clear that they may not adequately describe fish consumption under all circumstances among persons who depend on sport caught fish as a primary source of food. For example, Alaskan natives living in isolated fishing areas where other food sources are limited may be expected to fulfill their elevated caloric needs by consuming much greater levels of seafood. Surveys of Alaskan fishermen living on Kodiak Island under the most isolated circumstances have been reported to consume an average of 369 g/p/d. Persons living in less isolated areas consumed an average of only 124 g/p/d (Stratton and Chisum, 1984). "Subsistence" fishers living in the lower 48 states under much less calorically demanding circumstances might be expected to consume less seafood than these groups of Alaskan natives.

Sports fishers form another group of consumers where there is considerable variation in the estimates of fish consumed. As noted above, localized consumption information is recommended for addressing sports fish issues. A survey of fresh water sportsfish caught in different areas of the Great Lakes (Humphrey, 1983) reported that the most frequently consumed quantity of fish was in the 26-27 pounds per year range (roughly 30 g/person/day). This figure is somewhat higher than the average consumption 20 g/p/d that was reported above in the NPD survey for persons in the Great Lakes. The highest recorded consumption in one year was 180 pounds (or about 224 g/p/d). EPA's Exposure Factors Handbook (U.S. Environmental Protection Agency 1989) summarizes the results of other surveys of sports fishers (see attachment).

The last group, probably the most important population sub-group, is that of pregnant women. As noted above, the number of pregnant women in the NPD were too few to characterize their fish consumption patterns. A reasonable assumption may be to assume that their consumption pattern parallels that of women who might get pregnant, i.e., women in the 18-44 year age range. The MRCA survey figures suggest that mean and 90th% ile consumption levels for pregnant women might be about 35 g/p/d and 72 g/p/d, respectively.

CONSUMER EXPOSURE TO METHYLMERCURY FROM FISH

FDA's Total Diet Study

As a starting place for discussing consumer exposure to methylmercury, I believe that the results from FDA's Total Diet Study provides some useful insights. This is an annual program that involves the purchase of selected foods in grocery stores across the US and the analysis of these foods as composite groups for essential minerals, toxic elements, radionuclides, industrial chemicals, and pesticides (Pennington, 1983). The intent of this program is to provide a means to monitor on a yearly basis the average nutrient and contaminant content of the US food supply and to observe any trends in the consumption of those substances over time. The diets for these studies are based on data derived from the 1977-78 USDA Nationwide Food Consumption Survey (NFCS) and the Second National Health and Nutrition Examination Survey (NHANES II) carried out by the National Center for Health Statistics (NCHS) in 1976-80.

Four seafood products (canned tuna, shrimp, fish sticks, and cod/haddock fillets) are included in the 234 foods covered in this study. All of the food composites in the Total Diet Study are analyzed for total mercury (this particular study does not distinguish inorganic mercury from methylmercury.) The concentrations of mercury in these composites (see attachment) have remained relatively unchanged over the past decade. Based on the concentrations of mercury in each of the food composites and the relative contribution of these food items to the hypothetical Total Diets, FDA has derived estimates of average total mercury exposure from the diet. These estimates have remained relatively unchanged over the past decade, roughly 0.03-0.04 ug/kg b.w./day for adults 14 and older. For an adult weighing 70 kg, this is equivalent to an average total mercury intake of about 2 ug/person/day. Of particular interest, FDA has found that 86% of the total mercury in the 1986-1991 diet composites is derived from the four seafood composites (Private communication, E. Gunderson, 1994). The attached table summarizes the estimated average daily total mercury intake adjusted for weight for each of the 8 population sub-groups.

NMFS Analysis of NPD Survey and Consumer Exposure

NMFS used the results of the NPD survey and information they had developed on mercury levels in the fishery resource to examine potential exposure to mercury. In 1978 their "**Report on the Chance of U.S. Seafood Consumers Exceeding the Current Acceptable Daily Intake for Mercury and Recommended Regulatory Controls**" was submitted to FDA. This document summarizes their analysis of individual consumption patterns, discusses the weight adjusted mercury exposures, and compares the weight adjusted exposures to the acceptable daily intake for each group of consumers (30 µg/p/d for 70 kg person). Only about 0.1% of the 25,000 panelists would have a 5% chance of exceeding their individual acceptable daily intake of mercury, i.e., they had a 5% chance of having mercury intakes with less than a 10-fold safety factor. Interestingly, about half of those with a 5% chance of exceeding their individual acceptable daily intake were eaters of fresh water fish. On the basis of this analysis, they suggested that freshwater fish may be a principal contributor to mercury intake.

FDA Analysis of Consumer Exposure to Mercury

Tollefson (Tollefson, 1989; U.S. Food and Drug Administration, 1992) commented on mercury exposure using fish consumption data from the NPD Survey and mercury residue data from the 1978 NMFS survey. The following table summarizes some of the species-specific estimates from these articles.

Table 18. Estimates of Average Daily Mercury Exposure*

Mercury Intake at Different Levels of Fish Consumption

Species	Mean Consumption	95th %ile Consumption
Tuna	1.8 µg/p/d	4.5 µg/p/d
Halibut	1.3 µg/p/d	2.9 µg/p/d
Swordfish	9.8 µg/p/d	17.3 µg/p/d

* Estimates of mercury exposure derived using fish consumption figures from NPD Survey and mercury residue data from 1978 NMFS Survey.

FDA has recently evaluated consumer exposure to mercury using fish consumption figures from the more recent MRCA and USDA surveys. Estimates for consumers of tuna were developed using mercury residue data from FDA's recent survey of canned tuna and tuna consumption information from the 3-day USDA 1987-88 NFC (U.S. Food and Drug Administration, 1992). The following table summarizes estimates of tuna consumption (and mercury intake) for persons of two different age groups.

Table 19. Estimates of Average Daily Intake of Tuna[1] **(and Mercury)**[2]

Age/Sex	Mean Consumption	90th %ile Consumption
13-17 yr M/F	27 g/p/d (**4.6 μg/p/d**)	56 g/p/d (**9.5 μg/p/d**)
18-44 yr M/F	35 g/p/d (**6.0 μg/p/d**)	65 g/p/d (**11 μg/p/d**)

1. Tuna intake figures from 3-day USDA 1987-88 NFCS.
2. Average mercury level of 0.17 ppm used for estimates.

Three different approaches have been taken for evaluating possible exposure from all fish (U.S. Food and Drug Administration, 1992, 1994). One approach combines the MRCA estimates of 14-day average fish/seafood consumption mentioned above with an assumed average mercury residue figure of 0.3 ppm (most finfish species in the NMFS Survey had mercury levels less than 0.3 ppm). The second approach is a more sophisticated data treatment (Monte Carlo modeling) that combined information on the distribution of fish consumption amounts from the MRCA 1982-87 Survey with information on the distribution and occurrence of mercury residues in fishery products. A third approach provides an estimate of the per capita exposure to mercury from the top 10 commercial species (this estimate was derived by summing the individual per capita exposures for each of the top 10 species). The results of these three analyses are presented in the following table.

Table 20. Estimates of Average Daily Intake of All Fish **(and Mercury)**

Age Group	Mean Consumption	90th %ile Consumption
All ages	32 g/p/d (**10 μg/p/d**[a])	64 g/p/d (**19 μg/p/d**[a])
2-5 years	16 g/p/d (**5 μg/p/d**[a])	32 g/p/g (**10 μg/p/d**[a])
18-44 years	35 g/p/d (**11 μg/p/d**[a])	72 g/p/d (**22 μg/p/d**[a])
All ages	(**4.4 μg/p/d**[b])	(**10 μg/p/d**[b])

Per Capita top 10 species 14.9 g/p/d (1.6 μg/p/d[c])

a. Estimates derived assuming average mercury concentration of 0.3 ppm.
b. Estimates derived using Monte Carlo modeling approach.
c. Per capita intake for top 10 species = 80% of per capita all species (mercury intake calculated by adding per capita mercury intake for each species).

CONCLUSION

The foregoing estimates primarily address general population fish consumption and mercury exposure. They have been developed using nationally representative food consumption data bases. The estimates do not address exposures that may occur with subsistence or sports fishers. Estimates for these sub-groups would need to specifically address the consumption pattern of species that are of concern as well as the levels of mercury that are found in these species.

As can be seen from these estimates, many different conclusions can be reached about fish consumption and mercury exposure. The types and methods of surveys, their duration, specificity to seafood, size of survey population and its sociodemographic characteristics, as well as seasonal variation are all factors that can influence estimates of fish consumption and mercury exposure. The age of available surveys can also be a factor, particularly when the surveys do not address fishery products, such as shark, which have high mercury levels and whose availability have shown dramatic increases since previous surveys were conducted.

The difficulty of developing credible estimates of fish consumption and mercury exposure for sports fishers is illustrated in a recent paper by Richardson and Currie (1993). These authors estimated fish consumption rates for Ontario Amerindians using hair analysis (the best indicator of the level of mercury exposure), the results of mercury analysis of commonly consumed fish for the area, and pharmacokinetic parameters that are used to describe the relationship between ingested mercury and hair mercury levels. In one population sub-group, the authors concluded that average fish consumption of adults was about 33 g/p/d. An earlier survey of fish consumption for this same group, however, had estimated their consumption at about 195 g/p/d. The authors suggested that discrepancies in these estimates probably resulted from the design of the earlier fish consumption survey. The authors of the earlier survey had based their estimates solely on respondents recall of food use for the previous year, an approach that is likely to introduce considerable error in estimated fish intake. Such errors would certainly lead to erroneous conclusions about mercury exposure among sports fishers.

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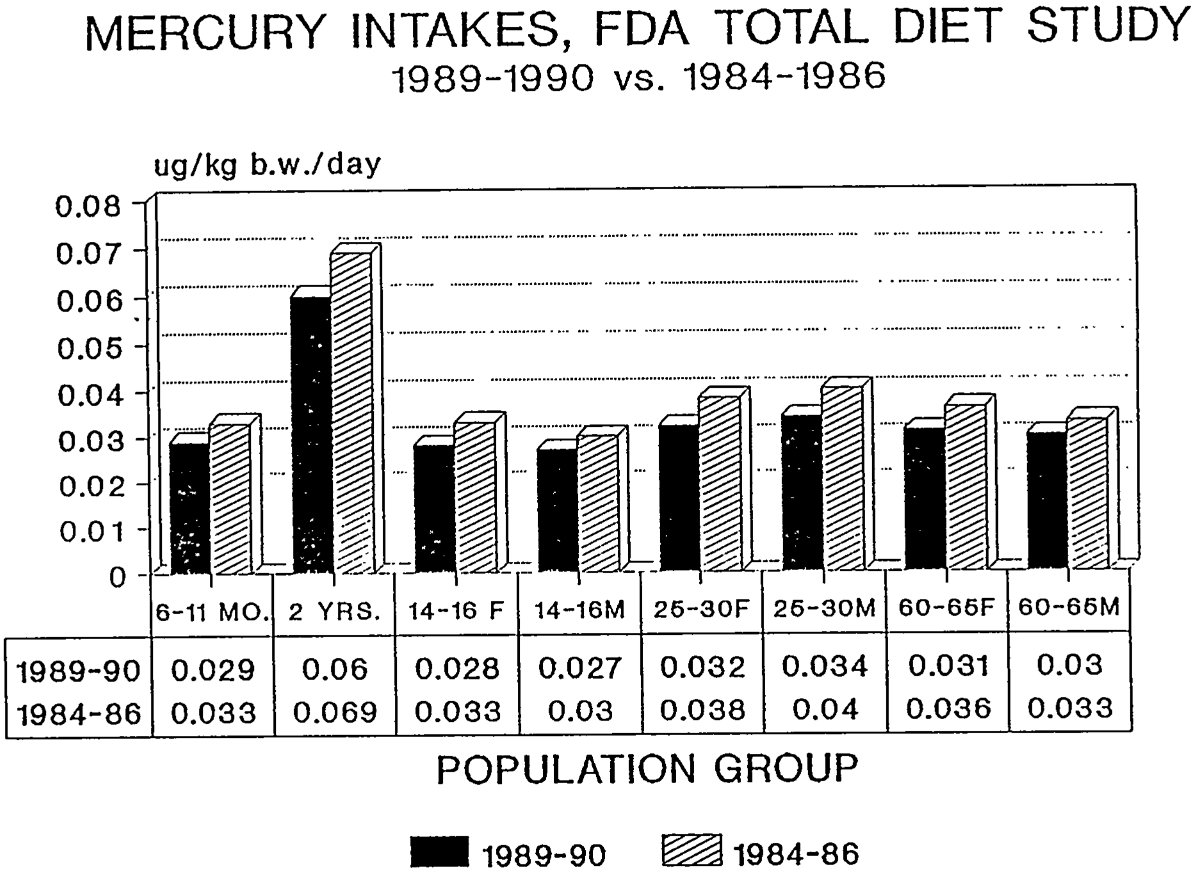

	6-11 MO.	2 YRS.	14-16 F	14-16M	25-30F	25-30M	60-65F	60-65M
1989-90	0.029	0.06	0.028	0.027	0.032	0.034	0.031	0.03
1984-86	0.033	0.069	0.033	0.03	0.038	0.04	0.036	0.033

Figure 36. Mercury intakes, FDA total diet study.

WORKSHOP DISCUSSION

The first issue to be discussed was survey reliability. One participant noted that three day surveys are much more reliable than longer term recall. Surveys, however, eliminate all people who don't eat fish during the survey period, which may be appreciable for such short-term studies.

Comparison of the National Marine Fisheries Service survey of 1970 and the recent FDA survey shows that MeHg levels in fish are remarkably similar. Survey data that are becoming available indicate that 32-34 g/day is the mean consumption rate for the fish-eating population; tuna represents about 30% of the fish consumption. A typical size of a tuna serving is smaller than for other fish dishes.

A participant asked why fish consumption was so high in the 2-5 year-old age group. The reply was that the data are biased because they are only based on fish eaters; nonfish eaters were eliminated. This led into a discussion concerning consumption. Values of reported consumption levels included 15 g/ day for sport fishermen in Michigan; 6.5 g/day is generally used by EPA for establishing water quality criteria. This information comes from the National Purchase Diary Fish Consumption Survey which included only fish eaters, who represent about 93% of the population. Food stamp surveys had indicated a consumption of about 60 g/ day. The appropriate estimates of per capita fish consumption depend on the use to which the data will be put.

One participant, impressed with the difficulty of the task of gathering consumption data, suggested eliminating the uncertainties by using biomarkers only. It was echoed that analysis of red blood cells and hair for Hg would provide useful data. Problems, however, may arise from the unreliability of using pharmacokinetic models and from relying on blood Hg measurements to estimate background exposure. Blood and urine samples obtained in the next HANES, which is scheduled for 1997, will be tested for Hg.

NMFS is sponsoring a study by the National Fisheries Institute to develop models for consumption surveys to address national issues and selected populations. This model hopes to capture consumption patterns for recreational and commercial catches. The models will be available this summer and will respond to many questions that were raised. An important issue is the consumption derived from sport fishing. It was stated that the 25% estimate found in the literature may grossly overestimate the true consumption.

A study that found PCBs in hatchery-reared fish and farm-raised salmon suggests that it might be worth some attention with regard to Hg. This comment was followed by a short discussion supporting this topic. Of the total fish market, 14% is now farm-raised; 3% of that is shrimp. Also, wild catfish and trout are 100% domestic; 90% of wild shrimp and salmon are imported.

8. HEALTH EFFECTS OF METHYLMERCURY

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INTRODUCTION

Methylmercury has attracted attention as a potential environmental threat to human health since the 1950's when the first of a series of outbreaks of poisoning occured. An acetaldehyde manufacturing factory in Minamata, Japan, used inorganic mercury salts as catalysts. Some of the mercury was chemically converted to methylmercury compounds, released in waste water into a large ocean bay (Minamata Bay, Japan) with devastating consequences to fishermen, their families and fish consumers in that area. This outbreak illustrated a unique property of methylmercury - that it could be released into ocean water and return in such high concentrations in fish tissues as to cause widespread human fatalities. We now know that the bioaccumulation factor from water to edible fish tissue exceeds ten million for certain species of fresh and ocean water fish.

Its potential for ecological damage was illustrated by reports of devastated bird populations in the 1960's (Johnels et al., 1969). Methylmercury compounds had been used as fungicides on seed grain both in Europe and North America. As fungicides they were economical and highly effective in suppressing such cereal infections as "blunt" disease and in this way greatly increased crop yields. However, treated seeds were consumed by birds and small mammals who in turn were part of the food chain for predatory birds.

The agricultural use of methylmercury fungicides has also taken its toll on developing countries due to the misuse of methyl and ethylmercury fungicides (Clarkson & Marsh, 1982). Farmers and their families, instead of using the fungicide treated grain for planting, used it for home made bread. In the winter of 1971-72 in rural Iraq, over 6000 cases of severe poisoning and over 600 deaths were recorded in hospitals throughout the country (Bakir et al., 1973). Morbidity and mortality outside the hospital may have been much higher (Greenwood, 1985).

To date all these outbreaks were characterized by the use or accidental release of "man made" methylmercury compounds. In one of the most surprising environmental findings of this century, it was discovered that fish caught in waters where no methylmercury had been released, nevertheless had high methylmercury levels in their tissues. Subsequently, Jensen and Jernelov (1969) in Sweden and Wood et al., (1969) in the USA demonstrated that certain classes of microorganisms were capable of methylating inorganic mercury to mono- and dimethylmercury compounds. Methylmercury released from microorganisms associated with sediments in bodies of fresh and ocean water bioaccumulated up the aquatic food chain. This finding explained the presence of methylmercury in wide ranging ocean fish and in fresh water fish caught in areas where only inorganic mercury had been released or where geologic sources of inorganic mercury were present.

MERCURY AND ITS COMPOUNDS: TOXIC HAZARDS TO HUMAN HEALTH

Mercury exists in a number of chemical and physical forms (Table 21).

Table 21. The Major Physical and Chemical Forms of Mercury

	INORGANIC	
Hg^0 Metallic	$Hg\text{-}Hg^{++}$ Mercurous	Hg^{++} Mercuric
	ORGANIC	
$C_6H_5Hg^+$ Phenyl Mercuric		CH_3Hg^+ Methyl Mercuric

Note 1. Oxidation States
2. Organic versus Inorganic

The inhalation of mercury vapor has been responsible for most of the cases of occupational poisoning. Chronic occupational poisonings have been known for centuries. The signs and symptoms are well summarized by the behavior of the Mad Hatter in "Alice in Wonderland". These include intentional tremors, emotional lability (erethism) and kidney dysfunction.

Mercury vapor poisoning is unknown in terms of environmental exposures. Clor-alkali plants were a common site of occupation exposures. They were also a point source of environmental contamination of sediments in rivers, lakes and even ocean bays. This contamination has never led to atmospheric levels, even in the local areas of discharge, that offered a significant risk of human poisonings.

Mercurous mercury is the first oxidation state, involving two atoms of mercury from which a single electron is lost from each atom. Its most common compound is mercurous chloride, Hg_2Cl_2. This was once used in children's teething powders and caused the childhood disease of acrodynia.

Mercuric mercury, the second oxidation state, Hg^{++}, is the most common form of mercury and forms many compounds. The mercuric salts, such as mercuric chloride are highly toxic and have been the cause of numerous fatalities. Death is due, usually, to kidney failure. Effects on the peripheral nervous system have been reported after chronic inhalation of mercuric oxide.

The oxidized forms of mercury may be formed in waters contaminated by discharge from chlor-alkali plants. No cases of human poisoning have been associated with drinking contaminated water.

The potential hazard to human health comes from the methylation of mercuric mercury, and subsequent bioaccumulation into edible tissues of fish. The remainder of this review, therefore will be devoted to the human toxicology of methylmercury including disposition and health risks.

Disposition of Methylmercury

Early studies on animals indicated that methylmercury compounds added to the diet were virtually completely absorbed (Clarkson, 1971). Similar findings were reported from an experimental test in human volunteers in a study in Finland (Miettinen et al., 1973). Our observations on blood levels in subjects ingesting known amounts of methylmercury in fish were consistent with a high efficiency of absorption, more than 90% of the ingested amount (Kershaw et al., 1980).

It distributes to all regions of the body. The study by Kershaw et. al., showed that distribution to the blood compartment was complete in about 30 hours and accounted for 7% of the ingested dose. Earlier work in Sweden using radio labeled methylmercury had indicated that distribution to the brain took longer, about 3 days (Aberg et al., 1969).

Elimination of methylmercury from the body follows first-order kinetics. As pointed out by Berglund and Berlin (1960), this implies that methylmercury distributes within the tissue compartments at a rapid rate compared to the rate of excretion. Thus we should expect tissue concentration ratios to be steady and not subject to fluctuations due to excretion. Evans et al., (1977) demonstrated that brain to blood ratios were constant for any given animal species. Primates had the highest brain to blood ratios. Their findings confirmed those of Berlinet et al. (1975) who reported concentration ratios in the range of 5 to 1 in primates. Information on humans is sparse but is consistent with a ratio in this range (Aberg et al., 1969).

The finding that blood levels are predicative of levels in the target organ, the brain, makes blood a valuable indicator media. However, it turns out that scalp hair is an excellent indicator of blood levels and can also recapitulate blood levels for months or even years prior to the collection of the hair sample. An illustration of the close parallel between blood and hair levels is given in figure 37 taken from a clinical study on infant mother pairs exposed to methylmercury in the Iraq outbreak (Amin-Zaki et al., 1976). The mother was admitted to hospital during pregnancy and blood samples were collected and analyzed for mercury. Subsequently, a hair sample was collected, divided into centimeter segments measured from the scalp end and each segment analyzed for mercury. Hair grows at approximately one centimeter per month. Thus it was possible to plot the mercury value in the segment according to the month the hair segment had been formed. This close parallel between hair and blood has been reported in many other studies (for review, see Suzuki 1988) and indicated that methylmercury in the hair follicle is proportional to the simultaneous blood concentration. Once incorporated into the newly formed hair, its concentration remains constant. The scalp hair sample is the indicator medium of choice as it can reveal both past and present blood concentrations and can be collected non-invasively, and easily stored and transported. It has been widely used in studies of exposed populations in Iraq (Marsh et al., 1987), Peru (Turner et al., 1980) American Samoa, (Marsh et al., 1974) and in Canada (Phelps et al. 1980). These and other studies have shown that the hair to blood concentration ratio, on the average, is about 250 to 1 (WHO, 1976).

Numerous studies have shown that the decline in blood (or hair) levels after cessation of exposure follows first order kinetics and can be described, therefore, by a single biological half time. Our observations on six subjects ingesting a single low dose (Kershaw et al., 1980) and on Iraqi mothers exposed to daily intake for many months (Cox et al., 1989) yielded almost identical average half times of about 50 days. These values are in agreement with those reported by Miettinen et al. (1973) in young adult males taking a single oral dose of radio labeled methyl mercury.

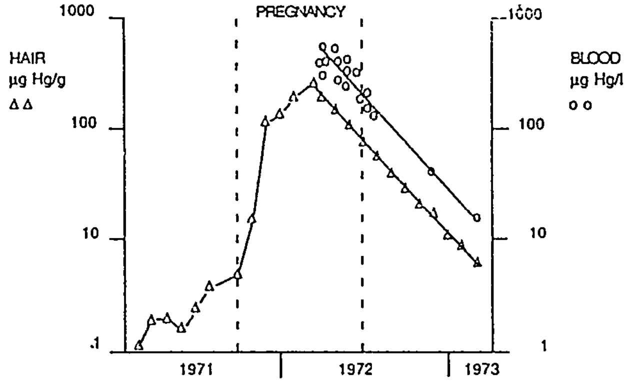

Figure 37. The concentrations of mercury in 1 - cm segments of a sample of hair and in blood samples taken from an Iraqi mother to recapitulate exposure to methylmercury during pregnancy. The hair sample was collected in early 1973, cut close to the scalp and divided into centimeter segments for mercury analysis. The mercury concentration on each segment was plotted according to its date of formation assuming a growth rate of 1 centimeter per month (adapted from figure 6 of Amin-Zaki et al., 1976).

We now have information on all the parameters that relate long term daily exposure to hair levels. Thus it may be shown that the blood level, b (µg Hg/liter), is given by the equation

$$b = d\,f\,\ln 2/t_{1/2} \qquad (1)$$

where d (µg Hg) is the daily ingested dose, f the fraction that is deposited in one liter of blood and $t_{1/2}$ (days) is the biological half time in blood. Equation (1) holds after a steady state body burden has been attained (for further discussion, see WHO, 1976). This will take a period of time equivalent to approximately five half times. It turns out that the steady state blood level when expressed in units of µg Hg per liter is approximately numerically equal to the daily intake in µg Hg (WHO, 1976).

Population studies in which daily intake has been measured and directly compared to blood levels indicate that the observed blood level is somewhat lower than that predicted by equation (1). The reasons for this discrepancy are not known but it may be that thse populations were not in true steady state. Also the estimation of daily intake in cross sectional studies of populations is notoriously difficult.

Blood levels may be converted to hair levels using the average value for the concentration ratio. Our studies in Iraq (Amin-Zaki et al., (1976), and in Canada (Phelps et al., (1980) are consistent with other reports (WHO, 1976) that, on the average, the hair concentration is about 250 times the corresponding blood level. However, considerable individual differences exist. Ultimately, the key relationship is between hair levels and those in the brain. At this time, we do not know if the individual differences seen in hair to blood ratios also are reflected in hair to brain ratios.

Toxic Effects and Dose-Response Relationships

The outbreaks of severe poisoning in Japan, Iraq and elsewhere revealed important characteristics of methylmercury action in human adults. Overt signs and symptoms usually take weeks or months to manifest themselves. In the 1971-72 outbreak in Iraq, for example, some victims ingested what would eventually prove to be a lethal dose without experiencing any untoward symptoms during the intake period (weeks or months). The length of this "latent" period has been shown to be inversely related to the blood concentration in primate experiments (Evans et al., 1977).

Except at the very highest doses, all the signs and symptoms are due to selective damage to the nervous system. The brain is the primary target, and even within this organ, selective or "focal" damage is the dominant characteristic. Thus, in severe cases of human poisoning as well as in animal experiments, certain anatomical areas of the brain appear to be specially susceptible to damage. These include the visual cortex and the granule layer of the cerebellum (Hunter and Russell, 1954). Severe damage manifests itself as a loss of neuronal cells in these areas.

Dose response relationships were reported in adults in our studies of the Iraq outbreak (Figure 38). We chose to use a threshold model as it gave an excellent "fit" to the data and also illustrated that the more severe effects appear at higher "threshold" levels of methylmercury. The dose response relationship for each effect is characterized by a horizontal segment and an inclined segment. The horizontal segment indicates a "background" frequency of the sign of symptom that is found in this population and is not related to methylmercury exposure. The inclined segment indicates an increase in frequency over and above the background level as the methylmercury levels increase. The intersection of the two lines is a "practical" threshold above which effects due to methylmercury become detectable. It may be seen that the threshold for paresthesia is the lowest, a finding consistent throughout most clinical and epidemiological studies of adult poisoning. The fact that the earliest effect of methylmercury is a non specific symptom of paresthesia makes diagnosis of incipient methylmercury poisoning very difficult.

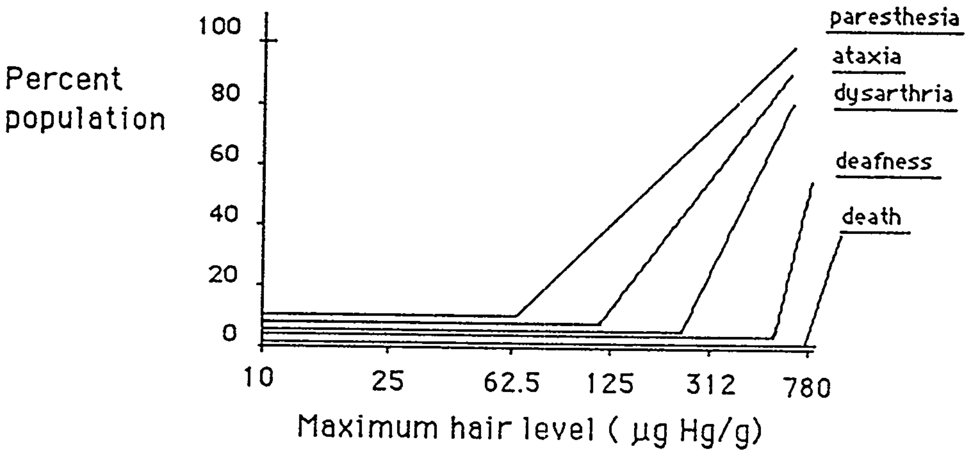

Figure 38. A dose response relationship for the effects of methylmercury on adults. The percentage of the population having a specified symptom or sign is plotted against the maximum hair concentration. The hair concentration was calculated from the body burden assuming 1% of the body burden is in one liter of whole blood and that the hair is 250 times the corresponding concentration in blood (adapted from 5 in Bakir et al. 1973). An alternative method was used by Bakir et al. to estimate body burdens of methylmercury. This alternative method would yield corresponding hair values about double those given in figure 38.

More recent studies have revealed that prenatal exposure is this stage of the life cycle most susceptible to methylmercury poisoning. The first indication that prental exposure was the most hazardous form of exposure came from reports of the Minamata outbreak (Harada, 1966). Females exposed to methylmercury during pregnancy gave birth to infants suffering from severe brain damage. The mothers were asymptotic or experienced only mild effects such as transient paresthesia. Animal experiments soon confirmed the unique sensitivity of the fetus. (Spyker et al., 1972). We also noted severe cases of mental retardation early in the Iraq outbreak (Amin -

Zaki et al., 1974). However, later follow up studies revealed a milder form of prenatal damage characterized by psychomotor retardation (Marsh et al., 1980).

In a study of prenatally exposed Canadian Indians, McKeown-Eyssen et al., (1983) were first to report that males were more affected than females. An examination of the cases in Iraq confirmed that more severe effects were seen in male infants (Marsh et al., 1987).

Kjellstrom et al. (1986) applied sophisticated psychological and scholastic tests on 61 children, ages 6-7 years, that had been prenatally exposed to methylmercury due to fish consumption by the mothers. According to the authors' summary, "...methylmercury exposure contributres only a small part of the variation in test results."

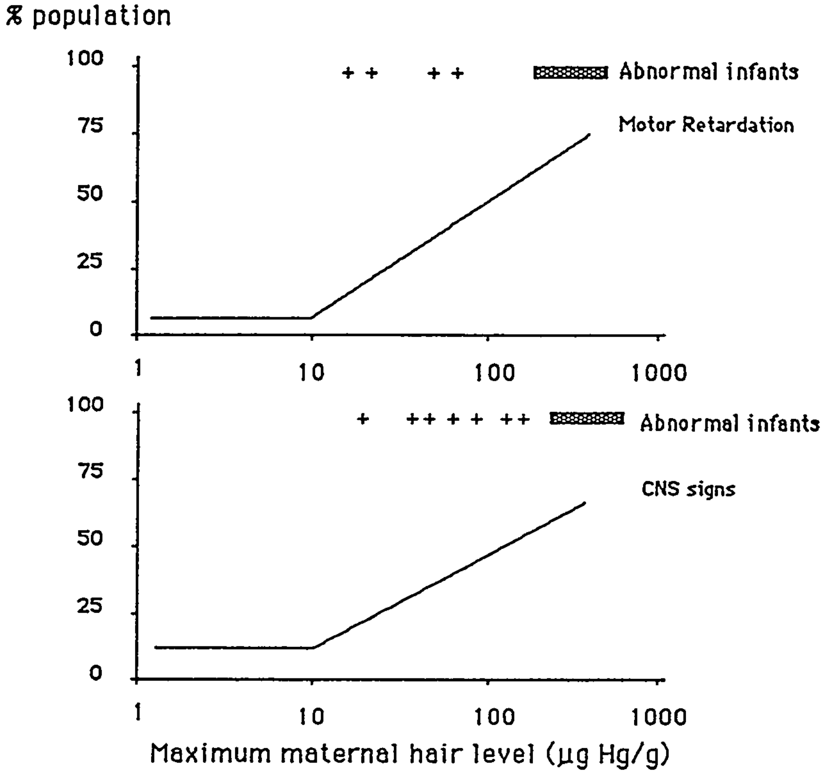

Figure 39. Dose response relationships for prenatal exposure to methylmercury. The percentage of infants exhibiting delayed motor development or abnormal reflexes (CNS signs) are plotted against the maximum maternal hair concentration during pregnancy (adapted from Cox et al., 1989).

The nature of prenatal damage appears to differ fundamentally from that of adult damage to the central nervous system. Unlike focal damage in adults, damage to the developing brain is diffuse and widespread. In severe cases, ectopic neurons are seen suggesting that methylmercury has interfered with neuronal migration, (Choi et al., 1978). Microcephaly suggests that cell division has been suppressed.

Quantitative information on the greater susceptibility of the fetus became available in our follow up studies of the Iraq outbreak (Marsh et al. 1980; Marsh et al., 1987; Cox et al., 1989). Two of these relationships are depicted in figure 38. We used the same threshold model as in the adult study to allow a direct comparison of adult and prenatal exposures. Whereas the practical threshold in the adult dose response was in the range of 50 to 100 µg Hg/g hair, the prenatal threshold was about 10 µg Hg/g hair (Table 22).

McKeown-Eyssen et al. (1983) found abnormality of muscle tone or reflexes was positively associated with the prenatal index of methylmercury exposure. Kjellstrom et al. (1989) in their summary statements noted that "...an average hair mercury level during pregnancy of 13-15 mg/kg (equivalent to 25 mg/kg peak mercury level) may be associated with a decreased test performance."

Table 22* The Practical Threshold Levels (PTL) by "Hockey-Stick" Model and Estimated Upper Limits (PTL-Max) as Determined by the Model as Applied to Motor Retardation and CNS Signs

Response	Estimated Background[a]	PTL[b]	PTL-max[c] (ppm Hg in hair)
Motor retardation	0	7.3	14
	4	9.0	190
CNS signs	9	10.0	287

*adapted from Cox et al. (1989)

a Determined by the hockey-stick analysis.

b Determined as the point of intersection of the two lines in the hockey-stick analysis

c Determined from the 95% upper confidence limits for estimated threshold.

Nevertheless, the extrapolation of these findings to other populations must be made with caution. First, there is a large degree of statistical uncertainty in the estimates of the practical thresholds for prenatal exposure (table 22). This statistical uncertainty is at least in part related to the fact that few abnormal points occur near the practical threshold value, as well as to the limited sample size and the high level of many of the exposures. Second, the practical threshold value is highly sensitive to assumptions concerning the background frequency of abnormal values. For examples, the upper 95% limit of the PTL is 4 ppm if the background frequency of motor retardation is 0% but rises to 190 ppm if the background is 5%. Third, abnormal motor retardation was defined as not walking at the age of 18 months. This may not be an appropriate definition for other populations. Fourth, the vehicle of exposure to methylmercury was homemade bread whereas the vehicle in the USA is fish tissue. Fifth, infants with mild abnormalities were found at all levels of methylmercury in hair but abnormalities clearly attributable to methylmercury were all above levels to 100 µg Hg/g.

Two large studies are now underway on the outcome of prenatal exposure to methylmercury in populations where exposure is the methylmercury in ocean fish and sea mammals. These should provide more accurate information on the dose-response relationships at the lower range of mercury levels in hair.

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WORKSHOP DISCUSSION

The issue of confounding factors was introduced after the presentation. Selenium and nutrients found in fish may confound the use of the Iraqi data with regard to a fish-eating vs. a nonfish-eating population. One participant suggested that the selenium/Hg relationship is not clear due to administering the wrong kind of selenium in animal studies. It was added that dimethylmercury selenide is very lipid-soluble and that the compound easily crosses the blood-brain barrier.

Prenatal exposures are different because they can impact on brain development rather than damaging existing cells. With regard to the Iraqi children's data, questions were raised about whether the lowest exposure levels are representative of the background for that area.

A brief discussion ensued regarding the measurement of outcomes and the specific measurement protocols being used in the Faroe and Seychelles Islands. Concern was expressed that different protocols may be in use in these studies. If this is correct, interstudy comparisons could be difficult.

A discussion regarding thresholds and acute vs. chronic exposure ensued. Participants pointed out that although some of the data had shown very high exposure levels, there was little observed effect. One participant observed that there are no thresholds; they can't be measured; nor are they needed for explanatory purposes. However, a response indicated that they are useful for safety assessment. It was then pointed out that differences between statistical models and biological realities exist. For statistical purposes, any model that best describes the data is useful, as long as it doesn't overextend the data. Within the context of biology, compensation mechanisms exist. Therefore, effects from a high exposure over a short period of time may differ from a lower exposure over a longer period of time.

9. RESEARCH NEEDS

After all of the invited papers were presented and discussed, a questionnaire (Table 23) was distributed to all workshop participants. The aim of this questionnaire was to solicit an initial list of research needs. The last session of the workshop was devoted to reviewing this list and modifying it; P. Moskowitz was the facilitator for this session.

Table 24 presents an overview of the final list of research needs. Each research need was discussed in terms of the focal area and potential organizations that should attempt to fill these gaps.

The participants identified gaps in each of the major focal areas. There were several gaps and issues that dominated the discussions. For example, the participants expressed strong reservations about the gaps in the existing fish consumption surveys and the need for better data. The following specific recommendations were made regarding the problems with the existing surveys and the designs for new surveys:

- Because of individual variations in diet, a three-day survey may not be sufficient to adequately characterize fish consumption patterns.

- All surveys should collect blood and/or hair measurements for calibration purposes.

- All surveys should quantitatively assess measurement/survey error so that measurement variance can be subtracted from total variance to obtain estimates of the true heterogeneity in consumption rates.

- All surveys should report the full percentile distributions.

The need for additional dose-response information was also discussed at length. In these discussions, the following points were raised.

- Confounding exposures (e.g., PCBs in fish) and factors (e.g., maternal alcohol and tobacco consumption) exist in all epidemiological studies. These confounders make it difficult to identify the true risk presented by MeHg exposures.

- The fetus may represent the most sensitive population. The period of maximum sensitivity during pregnancy and the magnitudes of risks to the fetus are poorly known. The same may hold true for elderly populations.

- The benefits of eating fish must be weighed against the risks presented by contaminants they contain. This is an unexplored issue that should be evaluated when risk management decisions are being made.

- Measurement outcomes and protocols for subtle neurological disorders associated with low-level MeHg exposures need to be examined in greater detail.

- Animal studies may help describe mechanisms of action and sensitivity of the fetus to maternal exposures.

- More research is needed on biomarkers and their relationship to the pharmacokinetic cycling of MeHg exposure and uptake in humans.

This list of research needs can serve as a focal point for future interagency cooperation.

Table 23. Questionnaire On Research Needs

NAME:

AREA: RISK ASSESS./EMISSIONS/AIR TRANS./AQUATIC PROCESSES /EXPOSURE ASSESSMENT/DOSE-RESPONSE (CIRCLE AREA)

GAP:

RESPONSE/DOE

RESPONSE/FDA

RESPONSE/EPA

RESPONSE/INTERAGENCY

AREA: RISK ASSESS./EMISSIONS/AIR TRANS./AQUATIC PROCESSES /EXPOSURE ASSESSMENT/DOSE-RESPONSE (CIRCLE AREA)

GAP:

RESPONSE/DOE

RESPONSE/FDA

RESPONSE/EPA

RESPONSE/INTERAGENCY

Table 24. List of Research Needs

AREA	RESPONDENT	GAP
Emissions	DOE/EPA	• Inventory of natural and anthropogenic sources of emissions, including chemical speciation
Air Transport	DOE/EPA	• Regional air quality impacts from multiple sources
Biogeochemical	ALL	• Historical trends in Hg in the environment
	DOE/EPA	• Role of biogeochemical parameters in MeHg production and cycling • Air -water exchange of Hg
Exposure Assessment	ALL	• Surveys that are: ⇒ Better designed for risk assessment ⇒ Targeted to sensitive populations ⇒ Targeted to potentially high exposures ⇒ Paired with biomarkers
Dose/Response	EPA/FDA	• Characterization of maternal/developmental effects
	FDA/EPA	• Mechanistic studies • Clarification of outcomes and measurement protocols

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