

# Proceedings and Summary Report

## Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments





# **Proceedings and Summary Report**

## **Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments**

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West Palm Beach, Florida

National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268

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Office of Water Quality  
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## **NOTICE**

This document was compiled from presentations and open discussion at a U.S. Environmental Protection Agency (USEPA) Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments held in West Palm Beach, Florida. The agenda and speaker/poster abstracts are presented in the appendices. Information presented herein does not necessarily represent the views of USEPA, nor is it specifically tied to reference materials. In many cases, the information presented is the opinion of the speaker, generated by his or her background and operations experience.

## **FOREWORD**

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods, and their cost-effectiveness, for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director  
National Risk Management Research Laboratory

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## TABLE OF CONTENTS

Section		Page Number
NOTICE		ii
FOREWORD		iii
TABLE OF CONTENTS		v
ACRONYMS		ix
ACKNOWLEDGMENTS		xi
<b>SECTION 1</b>	<b>INTRODUCTION</b>	1
<b>SECTION 2</b>	<b>SCOPE AND OBJECTIVE OF THE WORKSHOP</b>	3
<b>SECTION 3</b>	<b>SUMMARY OF THE PLENARY SESSION</b>	5
3.1	Plenary Session	5
3.1.1	USEPA's Mercury Research Strategy — <i>Douglas W. Grosse, USEPA, National Risk Management Research Laboratory (NRMRL)</i>	5
3.1.2	USGS/USEPA Mercury Roundtable: Enhancing Interagency Collaborations — <i>Sarah Gerould, USGS</i>	6
3.1.3	State of Florida/Mercury Science Program — <i>Tom Atkeson, Florida Department of Environmental Protection (DEP)</i>	7
3.1.4	USEPA STAR Program — <i>Bill Stelz, USEPA, National Center For Environmental Research (NCER)</i>	8
3.1.5	Electric Power Research Institute — <i>Leonard Levin, EPRI</i>	8
3.1.6	National Wildlife Federation (NWF) Great Lakes Natural Resource Center — <i>Mike Murray, NWF</i>	10
3.2	Keynote Speakers	11
3.2.1	Atmospheric Deposition Overview — <i>Gerald Keeler, University of Michigan</i>	11
3.2.2	Historic Perspectives on Mercury — <i>Don Porcella, Environmental Science &amp; Management</i>	14
<b>SECTION 4</b>	<b>SUMMARY OF THE TECHNICAL SESSIONS</b>	17
4.1	Session A: Mercury and Methylmercury Transport in the Environment	17
4.1.1	Determination of the Sediment-Water Exchange of Mercury and Methylmercury: Approaches, Limitations, Observations — <i>G. Gill, Texas A&amp;M University</i>	17
4.1.2	Mercury and Methylmercury Accumulation in Lake Sediment: What Can We Infer from Dated Cores? — <i>D. Engstrom, Science Museum of Minnesota</i>	17
4.1.3	An Overview of Mercury Cycling in the Boreal Ecosystem — <i>V. St. Louis, University of Alberta</i>	18
4.1.4	Is the Arctic a Missing Sink for Mercury? New Measurements of Depletion Events, Deposition and Speciation in Air and Snow at Point Barrow, Alaska — <i>Steven E. Lindberg, Oak Ridge National Laboratory</i>	19
4.1.5	Putting into Perspective Mercury Emissions from Geologic Sources — <i>M. Sexauer Gustin, University of Nevada-Reno</i>	19
4.1.6	Mercury Cycling in the Boreal Forest: Insights from Models, Experiments, and Isotopes — <i>B. Branfireun, University of Toronto at Mississauga</i>	20
4.2	Session B: Bioaccumulation of Mercury in Aquatic Food Webs	21

Section		Page Number
4.2.1	Evolution of a Contaminant Problem: Mercury in Freshwater Fish — <i>J. Wiener, University of Wisconsin-La Crosse</i>	21
4.2.2	Projecting the Population-Level Effects of Mercury on the Common Loon in the Northeast — <i>D. Evers, BioDiversity Research Institute</i>	22
4.2.3	USGS National Pilot Study of Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish — <i>W. Brumbaugh, National Pilot Study of Mercury</i>	22
4.2.4	Interactions of Trophic Position and Habitat with Mercury Bioaccumulation in Florida Everglades Largemouth Bass ( <i>Micropterus salmoides</i> ) — <i>T. Lange, Florida Fish and Wildlife Conservation Commission</i>	23
4.2.5	Bioaccumulation of Mercury in the Everglades: Patterns in the Foodweb — <i>J. Trexler, Florida International University</i>	24
4.2.6	Effects of Rainbow Smelt Invasion on Mercury Concentrations of Predatory Fish of Northwestern Ontario and Manitoba, Canada — <i>R. Bodaly, Department of Fisheries and Oceans, Freshwater Institute, Canada</i>	24
4.3	Session C: STAR Program Review	25
4.3.1	Formation/Transport of Methylmercury in Ecosystems and Watersheds	25
4.3.1.1	Watershed Influences on the Transport, Fate, and Bioavailability of Mercury in Lake Superior — <i>J. Hurley, University of Wisconsin</i>	25
4.3.1.2	Factors Controlling Methylmercury Production in Sediments and Fate in Aquatic Systems — <i>R. Mason, University of Maryland</i>	26
4.3.1.3	Response of Methylmercury Production and Accumulation to Changes in Mercury Loading: A Whole-Ecosystem Mercury Loading Study — <i>C. Gilmour, The Academy of Natural Sciences, Estuarine Research Center</i>	26
4.3.1.4	Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition? — <i>J. Jeremiason, Minnesota Pollution Control Agency</i>	27
4.3.2	Biogeochemical Controls on Mercury Methylation/Demethylation Rates	29
4.3.2.1	Photochemistry of Mercury in Saginaw Bay Watershed, Michigan: Annual USEPA STAR Project Meeting — <i>J. Nriagu, University of Michigan</i>	29
4.3.2.2	Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern United States — <i>C. Driscoll, Syracuse University</i>	29
4.3.3	Physical and Chemical Processes Affecting Mercury Cycling	30
4.3.3.1	Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury from Contaminated Mine Sites — <i>G. Brown, Stanford University</i>	30
4.3.3.2	Microbiological and Physiochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones — <i>W. Fitzgerald, University of Connecticut</i>	31



Section		Page Number
4.3.3.3	Redox Transformation of Mercury — <i>F. Morel, Princeton University</i>	32
4.3.3.4	Assessing the Role of Plants in the Biogeochemical Cycle of Mercury — <i>M. Gustin, University of Nevada</i>	32
4.3.3.5	Mercury and Methylmercury Burdens in Sediments, Water, and Biota of VT and NH Lakes, and Trends in Paleolimnology-Inferred Mercury Deposition to VT and NH — <i>N. Kamman, VT Department of Environmental Conservation</i>	33
4.3.3.6	Mercury in Fish and Sediments of Clear Lake, California: Defining the Problem and Developing Cleanup Options through the USEPA Superfund Program — <i>E. Mange</i>	33
4.4	Session D: Managing Mercury Contamination in Aquatic/Terrestrial Systems	35
4.4.1	An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed: A CALFED Study — <i>C. Foe, Central Valley Regional Water Quality Control Board</i>	35
4.4.2	An Evaluation of USEPA's Bioaccumulation Factor for Mercury: A Regulated Industry Perspective — <i>R. Reash, American Electric Power</i>	36
4.4.3	Methylmercury in Terrestrial Ecosystems: Summary of Swedish Research — <i>J. Munthe, IVL Swedish Environmental Research Institute</i>	36
4.4.4	Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades Phase II — <i>D. Krabbenhoft, U.S. Geological Survey</i>	36
4.4.5	Modeling Mercury Fate in Seven Georgia Watersheds — <i>R. Ambrose, Jr., USEPA</i>	37
4.4.6	Fitting into the North American Mercury Emissions Reduction Priority — <i>L. Trip, Environment Canada</i>	38
4.5	Session E: Methylmercury Production in the Environment	39
4.5.1	Overview of Microbial Methylmercury Production and Degradation: What Do We Know? What Don't We Know? — <i>C. Gilmour, The Academy of Natural Sciences</i>	39
4.5.2	Environmental Controls on Methylmercury Production and Degradation in Florida Everglades Sediment — <i>M. Marvin-DiPasquale, U.S. Geological Survey</i>	39
4.5.3	Group VI Anions and Mercury Transformation within the S-cycle in the Carson River System, Nevada — <i>J.C. Bonzongo, University of Florida</i>	40
4.5.4	A Bacterial Biosensor for Aquatic Hg(II) Speciation and Bioavailability — <i>P. Barrocas, Florida State University</i>	40
4.5.5	Facilitated Uptake of Mercury at Trace Concentrations by <i>Escherichia coli</i> and <i>Vibrio anguillarum</i> — <i>G. Golding, University of Manitoba</i>	41
4.5.6	Mercury Transport and Transformation in the Wider Idrija Region and the Gulf of Trieste — <i>M. Horvat, Institute Jozef Stefan</i>	42

Section		Page Number
4.5.7	The Everglades Mercury Cycling Model: Development and Application to Two Marsh Sites in the Florida Everglades — <i>R. Harris, Tetra Tech, Inc.</i>	42
4.6	Combined Session	43
4.6.1	Landscape Patterns of Mercury Contamination Across the Everglades Ecosystem — <i>J. Stober, USEPA Region 4 and K. Thornton, FTN Associates Ltd.</i>	43
4.6.2	Use of Path Analysis to Integrate the Effects of Multiple Stressors on Mercury Contamination in the Everglades Ecosystem — <i>K. Thornton, FTN Associates Ltd. and J. Stober, USEPA Region 4</i>	44
4.6.3	METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and Methylmercury Concentrations of Fish — <i>J. Rudd, Department of Fisheries and Oceans Canada and R. Harris, Tetra Tech Inc.</i>	44
SECTION 5	SUMMARY OF THE PANEL DISCUSSIONS	47
5.1	Mercury And Methylmercury Transport in The Environment — <i>D. Krabbenhoft</i>	47
5.1.1	What We Know	47
5.1.2	What We Don't Know	48
5.1.3	Open Discussion	49
5.2	Methylmercury Production in The Environment — <i>C. Gilmour</i>	50
5.2.1	What We Know	50
5.2.2	What We Don't Know	50
5.2.3	Open Discussion	50
5.3	STAR Program Review — <i>J. Hurley</i>	52
5.3.1	What We Know	52
5.3.2	What We Don't Know	52
5.3.3	Open Discussion	53
5.4	Management of Mercury Contamination in Aquatic/Terrestrial Systems — <i>Luke Trip</i>	53
5.4.1	What We Know	53
5.4.2	What We Think We Know	53
5.4.3	What We Don't Know	54
5.4.4	Open Discussion	54
5.5	Bioaccumulation of Mercury in Aquatic Food Webs — <i>Jim Wiener</i>	55
5.5.1	What We Know	55
5.5.2	What We Don't Know	56
5.5.3	Open Discussion	57
FIELD TRIP TO THE EVERGLADES		57
APPENDIX A	WORKSHOP AGENDA	A-1
APPENDIX B	SPEAKER ABSTRACTS	B-1
APPENDIX C	POSTER ABSTRACTS	C-1

## ACRONYMS

ACME	Aquatic Cycling of Mercury in the Everglades
AMD	Acid Mine Drainage
ATSDR	Agency for Toxic Substances and Disease Registry
AVS	Acid-volatile sulfide
BAF	Bioaccumulation Factor
CEC	Commission for Environmental Cooperation
CEM	Continuous Emissions Monitoring
CRS	Carson River System
CV-AFS	Cold-Vapor Atomic Fluorescence Spectrometry
CWA	Clean Water Act
DGM	Dissolved Gaseous Mercury
DEP	Department of Environmental Protection
D-MCM	Dynamic Mercury Cycling Model
DOC	Dissolved Organic Carbon
E-MCM	Everglades Mercury Cycling Model
Eh	Redox potential
EMAP	Environmental Monitoring and Assessment Program
ELA	Experimental Lakes Area
ENRP	Everglades Nutrient Removal Project
USEPA	United States Environmental Protection Agency
EPG	Electric Power Generation
EPRI	Electric Power Research Institute
FDA	Food and Drug Administration
GEM	Gaseous Elemental Mercury
GIS	Geographic Information System
ICP	Inductively Coupled Plasma
LFG	Landfill Gas
LIF	Laser Induced Fluorescence
LIS	Long Island Sound
MARB	Mobile-Alabama River Basin
MAWLTS	Mercury in Adirondack Wetlands Lakes and Terrestrial Systems
MCL	Maximum Contaminant Level
MDE	Mercury Depletion Events
MDN	Mercury Deposition Network
MeHg	Methylmercury (monomethylmercury)
METAALICUS	Mercury Experiment To Assess Atmospheric Loading In Canada and the United States
NADP	National Atmospheric Deposition Program

NARAP	North American Regional Action Plan
NAWQA	National Water Quality Assessment
NCER	National Center For Environmental Research
NRMRL	National Risk Management Research Laboratory
NWF	National Wildlife Federation
OC	Organic Carbon
ORD	Office of Research and Development (USEPA)
ORNL	Oak Ridge National Laboratory
PBT	Persistent, bioaccumulative and toxic [chemicals]
POC	Particulate Organic Carbon
RARE	Regional Applied Research Effort
RELMAP	Regional Lagrangian Model of Air Pollution
RGM	Reactive Gaseous Mercury
SBMM	Sulphur Bank Mercury Mine
SFWMD	South Florida Water Management District
SoFAMMS	South Florida Atmospheric Mercury Monitoring Study
SRB	Sulfate-Reducing Bacteria
STA	Stormwater Treatment Area
STAR	Science to Achieve Results [Program]
SUVA	Specific Ultra-Violet Absorbance
THg	Total Mercury
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TP	Total Particulates
TRV	Toxicity Reference Value
USGS	United States Geological Survey
WASP5	Water Quality Analysis Simulation Program
WCA	Water Conservation Area (Everglades)
WCS	Watershed Characterization System
WTF	Waste Treatment Facility
XAFS	X-Ray Absorption Fine Structure
XRD	X-Ray Diffraction

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<b>Leonard Levin</b>	Electric Power Research Institute
<b>Michael Murray</b>	National Wildlife Federation
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## **SECTION 1**

### **INTRODUCTION**

The Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments was held on May 8 – 10, 2001 in West Palm Beach, Florida. The workshop was conducted by the United States Environmental Protection Agency (USEPA) Office of Research and Development (ORD) and cosponsored by the United States Geological Survey (USGS) Toxics Program, the USEPA Science to Achieve Results (STAR) Program, the South Florida Mercury Science Program, and the USGS/USEPA Mercury Roundtable. Representatives from industry, academia, environmental organizations, consulting firms, and government attended.

The purpose of the workshop was to bring researchers, decision makers, government representatives, and others together to discuss the state of the science regarding the fate and transport of mercury in aquatic and terrestrial systems, mercury transformation processes (biotic and abiotic), and methods for managing ecological and human exposures to methylmercury (MeHg).

Five technical sessions were presented during the 2 1/2-day workshop. These sessions addressed the following topics:

- Mercury and Methylmercury Transport in the Environment
- Methylmercury Production in the Environment
- USEPA STAR Mercury Research Program Review
- Bioaccumulation of Mercury in Food Webs
- Managing Mercury Contamination in Terrestrial and Aquatic Systems

The presentations were followed by a panel discussion at the end of the workshop. After each technical session was summarized, participants were given an opportunity to comment on some of the critical issues or concerns associated with the material presented for each technical session.

Two very successful and well-attended poster sessions also took place during the workshop. The poster sessions covered a number topics/areas that could not be included in the workshop due to time constraints. These sessions expanded both the breadth and scope of the workshop and were a key element of the workshop's success.

This document contains a more detailed description of the scope and objectives of the workshop, followed by bulleted summaries of the plenary session, the technical presentations, and the panel discussion. The final agenda, speaker abstracts, and poster abstracts are presented in Appendices A, B, and C, respectively.

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## **SECTION 2**

### **SCOPE AND OBJECTIVE OF THE WORKSHOP**

The USEPA held this workshop to bring together researchers, decision makers, government representatives, and others interested in the fate and transport of mercury in aquatic and terrestrial environments. It designed this workshop to achieve the following three goals:

- Describe the current state of knowledge, and gaps and areas of consensus, regarding the fate and transport of mercury in aquatic and terrestrial systems.
- Present ongoing efforts to develop a better understanding of aquatic and terrestrial mercury transformation processes (biotic and abiotic), with implications for ecological and human exposures.
- Explore possible resources, actions, and tools for managing ecological and human exposures to methylmercury via aquatic and terrestrial systems, including decreasing mercury emission rates and implementing means of reducing methylation rates.

To facilitate these goals, presentations were made by representatives of government, academia, consulting firms, and environmental organizations during the following five technical sessions:

- Mercury and Methylmercury Transport in the Environment
  - Watersheds
  - Sediments and sediment-water interface
  - Terrestrial systems
  - Air-water interface
- Methylmercury Production in the Environment
  - Methylation and demethylation processes
  - Geochemical controls
  - Methods for measurement
  - Internal and external sources in aquatic systems
  - Abiotic transformations in soils and surface water
- USEPA STAR Mercury Research Program Review (presentations by invited current investigators)
- Bioaccumulation of Mercury in Aquatic Food Webs
  - Control of bioavailability for uptake
  - Organism barriers for uptake
  - Differences at the species level
  - Impacts of food web structure and water chemistry



- Managing Mercury Contamination in Terrestrial and Aquatic Systems
  - Ecosystem responses to changes in mercury loading
  - Management factors affecting toxicity to ecosystems
  - Modeling
  - Responses of fish levels to changes in external loadings

## SECTION 3

### SUMMARY OF THE PLENARY SESSION

#### 3.1 Plenary Session

##### 3.1.1 USEPA's Mercury Research Strategy — *Douglas W. Grosse, USEPA, National Risk Management Research Laboratory (NRMRL)*

- USEPA released the *Mercury Research Strategy* in December 2000 to guide ORD's Mercury Research Program. The focus of the research strategy is on domestic impacts of mercury.
- The *Mercury Research Strategy*
  - outlines and summarizes the health and ecological risks posed by mercury.
  - indicates that mercury needs to be considered on local, regional, and global scales.
  - identifies key scientific questions of greatest importance to the Agency.
  - describes a research program to be implemented to answer those questions.
- The goal of the *Mercury Research Strategy* is to “provide information and data that reduce scientific uncertainties that limit USEPA's ability to assess and manage mercury and methylmercury risks.”
- ORD's Mercury Research Program is designed to provide methods, models, and data that address the following research areas: 1) transport, transformation, and fate; 2) risk management for combustion sources; 3) risk management for noncombustion sources; 4) ecological effects and exposure; 5) human health effects and exposure; and 6) risk communication.
- ORD research priorities to address the transport, transformation, and fate of mercury include
  - improved understanding of transport, transformation, and fate of mercury in the atmosphere.
  - enhanced monitoring of atmospheric mercury deposition for model application by developing better monitoring tools.
  - improved understanding of transport, transformation, and fate of mercury in aquatic and terrestrial environments.
  - enhanced monitoring of mercury and methylmercury in aquatic and terrestrial media for improved risk management.
- ORD risk management research priorities for noncombustion sources include
  - characterization of the mercury life cycle in human activities.
  - improved understanding of mercury releases from sources and sinks.

- development of approaches for minimizing mercury releases with pollution prevention, collection programs, and materials substitution.
- ORD research efforts addressing mercury effects and assessment will gradually increase in emphasis over the next 5 years. Research priorities in ecological effects and exposure include
  - improved understanding of methylmercury toxicity effects on avian and mammalian wildlife.
  - refined ecological assessments for avian and mammalian wildlife risks.
  - improved understanding of ecological impacts of methylmercury on avian and mammalian wildlife.
  - identification of interactions among methylmercury and other chemical and nonchemical stressors on all ecological receptors.
- When preparing the *Mercury Research Strategy*, ORD noted that the success of the Agency's risk assessment and risk management efforts relies on 1) improving mercury emissions inventories and collecting source emissions data; 2) monitoring mercury in various media; and 3) understanding the international implications of mercury (e.g., as it relates to the global pool).

### **3.1.2 USGS/USEPA Mercury Roundtable: Enhancing Interagency Collaborations — *Sarah Gerould, USGS***

- The Mercury Roundtable provides scientific input for future mercury program directions and initiatives. The Roundtable was developed to enhance interactions, technical support, and collaborations between the USGS and USEPA in the area of mercury.
- Roundtables have been held on the following topics from June 2000 to May 2001: 1) sources—mining and coal combustion; 2) cycling—transport, transformation, and fate; 3) effects—human health and wildlife; and 4) monitoring. Roundtables are planned on the following topics between August 2001 and April 2002: 1) historic trends—via sediment and ice cores and museum specimens; 2) modeling—aquatic and atmospheric; 3) arctic—deposition, risk to northern peoples, the “Arctic Sunrise” effect; and natural emissions—volcanos, oceans, geothermal sources.
- The USGS is actively researching a variety of mercury sources including coal combustion, mining, atmospheric deposition [to support the Mercury Deposition Network (MDN)], fire, and sediment.
- The USGS has also been working on a materials flow analysis of mercury that tracks contributions from the different sources (e.g., stockpile releases, mine production, secondary production, and net imports) and consumption associated with different types of uses (e.g., dental, instruments, batteries, switches, lighting, laboratory, paint, chlor-alkali). Results indicate that both domestic industrial mercury production and use declined in response to

legislation in 1984 banning its use in batteries and paint.

- The USGS has performed a number of mercury cycling studies that include the following sites: Carson River; Bear-Yuba and Trinity River; Everglades; Coast Range of Southwest Alaska; Minnesota reservoirs; Animas River; Sacramento River; Sierra Nevada mountains; Michigan; Wisconsin; Northwest Ontario, Canada; and Mississippi River.
- The USGS is also performing a number of studies on the biotic effects of mercury. One study is currently examining the demethylation process in fish-eating birds. This study is investigating why higher concentrations of total mercury are associated with lower concentrations of methylmercury in fish-eating birds. This study has implications on the burden of mercury passed on to eggs. The USGS is also involved in a study that injects mercury into bird eggs in order to assess the comparative toxicity of mercury on developing bird embryos.
- USGS has been involved in a number of monitoring programs that included mercury, including the National Water Quality Assessment (NAWQA) Program, which looked at mercury concentrations in fish tissue, and the MDN. The USGS is also involved in a number of studies that are assessing historical mercury concentrations using core sediment samples. These studies have associated rises in mercury with major land clearance activities in the 19th century.

### **3.1.3 State of Florida/Mercury Science Program—*Tom Atkeson, Florida Department of Environmental Protection (DEP)***

- The Florida DEP initiated mercury monitoring in 1983. These efforts ultimately led to the realization in the late 1980s that Florida had a mercury contamination problem. Until then, mercury contamination problems had not been identified in the southern latitudes. Research efforts in Florida added a new geographic dimension to the recognition of the mercury problem.
- After the initial recognition of the mercury problem, Florida soon developed approaches to address the problem. These efforts led to the founding of the South Florida Mercury Science Program. This program has evolved into a successful collaboration between state, Federal, and private agencies to fund and carry out mercury research in Florida.

### **3.1.4 USEPA STAR Program — *Bill Stelz, USEPA, National Center For Environmental Research (NCER)***

- ORD is the research arm of the Agency. Extramural research in ORD is mainly done through the STAR Program.
- ORD provides the leadership in science and conducts most of USEPA's research and development; NCER is ORD's extramural research arm.
- In cooperation with other USEPA offices and using the ORD Strategic Plan, national environmental research needs, relevance to Agency mission, and research being done in ORD's intramural program, ORD selects topics for the STAR Program.
- The STAR Program was established in 1995 as part of the overall reorganization of ORD. Its mission is to "include this country's universities and nonprofit centers in USEPA's research program and to ensure the best possible quality of science in areas of highest risk and greatest importance to the Agency."
- The STAR Program awards approximately \$100 million dollars annually and manages about 1,000 active research grants and fellowships.
- The STAR Program makes yearly research announcements, some of which are repeated year after year, while others have been changed to reflect changes in the USEPA planning process, to meet Agency needs, or to complement in-house research efforts.
- Mercury Speciation and Atmospheric Chemistry was included in the general research announcements made in 2001. The application period opened on April 20, 2001 and closed on August 15, 2001.
- STAR Program progress and results are communicated to the public online via NCER's web site (<http://es.epa.gov/ncer/>) and through research summaries, annual science progress review workshops, scientific conferences, and email announcements.

### **3.1.5 Electric Power Research Institute — *Leonard Levin, EPRI***

- Improvements in mercury methods and data assessment have enabled mercury researchers to perform field studies that can be compared over time and space. Efforts have advanced to the point that integrative studies may soon be feasible using contemporaneous data sets that relate mercury trends in different cycling systems to source and effects research.

- The development of a large set of good quality data is critical to developing integrative studies. This data needs to be of appropriate duration in order to establish trends in mercury concentrations with a reasonable degree of certainty.
- Drops in mercury deposition have been paired to drops in sulfate deposition in various lake studies. Because sulfur and sulfur-reducing bacteria play a significant role in the methylation of mercury in aquatic systems, future research is needed to separate changes in sulfate concentrations from changes in mercury concentrations.
- It is clear that the long-range transport of mercury outside the local and regional scale may be significant. In 2000 EPRI estimated that ~2,300 megagrams of mercury is being emitted per year from global anthropogenic sources. Approximately 40% of this total is emitted from the Asian mainland and nearby islands. Since half of the mercury emitted globally is believed to be ionic mercury, with the remainder emitted primarily as elemental mercury and a small part as particulate phase mercury, roughly half of the mercury emitted globally will deposit near the source area; the remainder will go into the global background.
- Benign tracers need be developed to assess where mercury deposits relative to the source and mercury's effect on the local, regional, and global environments. Ideally, these tracers will be introduced to the sources and traced through the entire complex cycling of mercury.
- Recent experiments have used stable isotopes of mercury to trace the flow of mercury from source to receptor and to observe how these isotopes move through the ecosystems over time, with the hope of eventually allowing researchers to differentiate anthropogenic mercury from background or natural sources of mercury.
- EPRI is involved in estimating how rapidly mercury from background sources (e.g., mine waste disposal from closed operations; re-emission of mercury from all sources; and native mercury from crustal deposits, volcanos, and hot springs) moves into the free atmosphere and the general circulation.
- EPRI is involved in wildfire field experiments in the northwestern United States. Initial data indicate that fairly small wildfires introduce a relatively large amount of mercury to the atmosphere.
- Research that addresses 1) how mercury moves between different compartments as it cycles through the systems and 2) which sources and reservoirs contribute to mercury's eventual deposition to receiving waters and sensitive receptors (via fish consumption) is critical to determining potential mercury management steps and whether those steps will be efficacious within a reasonable time period.

### **3.1.6 National Wildlife Federation (NWF) Great Lakes Natural Resource Center — *Mike Murray, NWF***

- NWF is a national conservation and education advocacy organization which was formed in 1936 as a federation of state conservation groups. The Great Lakes Natural Resource Center is one of 10 NWF field offices. This office focuses on toxics research issues, including mercury.
- NWF's Clean the Rain campaign is an educational campaign to raise awareness of air deposition issues and the health and ecological effects of mercury. NWF also runs a regional and national effort to promote the virtual elimination of mercury releases from anthropogenic sources consistent with goals in the Clean Water Act and Great Lakes Water Quality Agreement.
- NWF has worked on a number of Federal mercury air issues, including
  - regulatory determination for air toxics released from power plants.
  - land disposal restriction regulations (for mercury-bearing hazardous wastes) and other Federal actions involving mercury.
  - the Great Waters Program/Air-Water Interface Action Plan, which discusses water quality impacts from air pollutants, and the Air-Water Interface Action Plan, an implementation plan developed by USEPA to address the goals defined in the Great Waters Program.
  - the Mercury Action Plan, which addresses both voluntary and regulatory actions to reduce mercury releases and exposures.
- NWF has also provided input on the following Federal and state mercury water issues:
  - Total Maximum Daily Load (TMDL) regulation revisions within the Clean Water Act (CWA)
  - TMDL stakeholder work in Ohio and Minnesota
  - review of individual TMDLs
  - water quality (human health) criteria development for mercury
  - effluent guidelines for mercury and other persistent, bioaccumulative and toxic chemicals (PBTs)
- NWF has provided comment/input on a number of human health/fish consumption advisories, including revisions to the USEPA RfD and the Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk level for mercury.
- NWF also provides sector-specific support to hospitals, dental offices, and other sectors on pollution prevention, mercury disposal, and reducing mercury use and releases.

- NWF is involved internationally with the Canada-US Binational Toxics Strategy, which was signed in 1997 to implement the recommendations in the Great Lakes Water Quality Agreement. NWF has also recently become involved with the Department of Defense Logistics Agency's mercury stockpile and trade issues. NWF also plans to play a role in the United Nations Environment Program's efforts to conduct a global mercury assessment in 2003.

## **3.2 Keynote Speakers**

### **3.2.1 Atmospheric Deposition Overview — *Gerald Keeler, University of Michigan***

Over the past decade, researchers have realized that the atmosphere plays an important role in the biogeochemical cycling of mercury.

#### **Mercury Cycle in the Biosphere**

- Mercury is emitted into the atmosphere in various forms (e.g., elemental, particulate, and mercuric chloride). Elemental mercury is the dominant form of mercury in the atmosphere. Elemental mercury is fairly insoluble and has a lifetime of 6 months to more than 1 year. Particulate mercury is emitted from stacks and other sources associated with particulate-phase matter.
- Once emitted to the atmosphere, mercury can be directly deposited to sensitive ecosystems or remain suspended in the atmosphere, where it is subject to a very complex chemistry. The current understanding of the biogeochemical cycles of mercury is oversimplified and does not fully address the heterogeneous atmospheric chemistry in clouds.
- Atmospheric emissions data indicate that fossil fuel combustion is the leading source of mercury emission to the atmosphere. Although mercury emissions from fossil fuel combustion have dropped dramatically in North America, fossil fuel combustion remains the leading source of mercury to the atmosphere worldwide. Waste combustion and other sources also have a significant impact. According to results from the South Florida Atmospheric Mercury Monitoring Study (SoFAMMS), emissions from municipal and medical waste incinerators were largely mercuric chloride.
- Despite recent efforts to control mercury emissions, scientists continue to see elevated levels of mercury in runoff from urban areas and elevated background levels of both gas and particle-phase mercury in urban areas, possibly due to motor vehicles.

#### **Mercury Speciation**

- The speciation of mercury is important because it controls the fate of the mercury that is



emitted into the atmosphere, as demonstrated by a recent study of wet deposition of mercury to Lake Superior. In the study, modeled mercury deposition was two orders of magnitude higher when emissions from point sources were assumed to be mercuric chloride rather than elemental mercury. Regional Lagrangian Model of Air Pollution (RELMAP) simulation results also indicate that areas with the highest wet deposition of total mercury were associated with areas that have the highest emissions of Hg(II).

- Speciation also determines how much mercury enters the global pool. Researchers have used RELMAP data to estimate that approximately 98% of the elemental mercury emitted from combustion sources is transported outside the United States.

### **Atmospheric Chemistry**

- Although Hg(II) can be emitted from sources, it can also be produced in the atmosphere via cloud water chemistry reactions. Although reactions between mercury and chlorine and mercury and ozone have been investigated, more work is needed in order to better understand the complex chemical reactions that occur in cloud water. More information is also needed about the relationship between mercury and particles, both inside and outside the cloud. Ultimately, atmospheric chemistry will determine the wet deposition of the mercury species and control its dry deposition.
- Urban studies indicate that vapor phase mercury tends to attach itself or absorb to particles from other sources. Since these particles can be quite large (e.g., >10 microns) this can result in high deposition of particulate mercury near urban sources.
- Elemental mercury and Hg(II) data from rural locations outside larger cities suggest that a natural process is occurring whereby the elemental mercury is converted to Hg(II). Variations in reactive gaseous mercury (RGM) concentrations also indicate that transport can have a significant impact on Hg(II) concentrations in the atmosphere.
- Additional research is needed to determine whether the marine boundary is a source of mercury to land surfaces and to better understand the chemistry and recirculation issues associated with the marine boundary layer.
- Based on recent studies in Barrow, Alaska, a huge loss of elemental mercury is caused by the chemistry related to the Arctic Sunrise phenomenon.

### **Importance of Dry Deposition**

- Dry deposition occurs when mercury contacts the surface in the absence of precipitation.
- Dry deposition is currently believed to be the source of elevated mercury concentrations in

both thru fall and litter fall. (Note: Litter fall is the dominant source of mercury to the forest floor.)

- Vapor-phase mercury compounds tend to deposit very quickly, in part through interactions with large bodies of water. An examination of data from the Lake Michigan mass balance study indicates that dry deposition of reactive mercury is approximately two thirds of the wet deposition amount. Also, reactive and particulate mercury leads to elevated levels in mercury runoff.

### **Source-Receptor Relationships**

- The sources of mercury deposited to various ecosystems are moving targets. Thus, efforts to determine the relative importance of natural vs. anthropogenic sources or long-range vs. local sources are often relatively unimportant.
- Deposition and source impacts were studied using a wide array of event/precipitation sampling sites in the Everglades from 1995 to 1996. Researchers determined that precipitation chemistry varies dramatically from sample to sample on an event basis. This variation was a function of meteorology.
- The Community Multi-Scale Air Quality model, which accounts for oxidant, acid rain, and particle chemistry, has been recently applied to the South Florida domain to assess how well it simulates atmospheric chemistry and deposition and to help users better understand what measurements need to be made. In general, the model showed that spatial patterns of mercury deposition are based on local meteorology and mercury emissions. Thus wet and dry deposition simulations varied substantially from day to day. The model also showed that elevated mercury deposition depends upon precipitation.

### **Mercury Atmospheric Deposition Science Questions Left to Be Answered**

The following mercury science questions need to be answered:

- How important are atmospheric inputs in terms of the cycling of mercury to different ecosystems?
- Given the same aquatic ecosystems, do we know enough yet about the physical and chemical nature of the mercury deposition to be able to predict its fate?
- Is wet deposition equivalent to dry deposition? Is the form of mercury in wet deposition the same, and will it be processed in the ecosystem the same way the dry deposition is processed?

- Do we know enough about mercury deposition to simulate deposition to the experimental ecosystems?
- Atmospheric mercury science questions related to emission sources, emission characteristics, chemistry, wet deposition, and dry deposition need to be addressed.
- Is RGM deposition to the ocean as significant a global sink as what our present understanding leads us to believe?

### **3.2.2 Historic Perspectives on Mercury — *Don Porcella, Environmental Science & Management***

- An historic perspective on mercury can be used to identify factors that control its accumulation in biota via transformations, transfer, and cycling among compartments that are biological and physical.
- An historic perspective can also help identify and clarify 1) mercury's natural cycle and possible impacts from mankind's substantial use of mercury during the last 500 years, 2) the relative significance of changes in mercury emissions in terms of mercury loading to ecosystems, and 3) the relationship between mercury loading and monomethylmercury (MeHg) in fish.
- Although mercury comes from several significant natural and anthropogenic sources, anthropogenic sources have increased human exposure to mercury, raising concerns that the health of humans and ecosystems has been compromised.
- The development of a variety of tools has led to better understanding of mercury in the environment by providing scientists, engineers, and policy makers an historic perspective of how it cycles and accumulates in biota.
- Concerns about mercury exposures have led some countries to control mercury emissions and discharges, resulting in documented reductions in mercury exposures and bioaccumulation in certain locations.
- In the majority of cases, mercury loading to the environment in the United States is dominated by atmospheric deposition. Its subsequent transformation to and accumulation in fish as methylmercury constitutes almost the entire exposure to humans. Questions have been raised whether additional reductions of mercury emissions in the United States will result in reduced exposures to methylmercury, given background mercury circulation from global sources. Cost-effective strategies that result in measurable benefits in human and ecosystem health need to be developed.

- Mass balance data presented in 1994 by Mason et al. indicate that current global mercury has increased by a factor of 5 over pre-industrial times, suggesting that reductions in anthropogenic emissions might be fairly effective in reducing loading.
- In 1995, Hudson et al. published a global model suggesting that a more careful inclusion of historic mercury uses could lead to a more accurate assessment of mercury exposure. Loss of mercury during precious metal extraction since the 1500s; industrial/commercial consumption of mercury since the 1850s; and an estimate of mercury's incidental release in combustion of fossil fuels, ore-roasting, and waste combustion were factored into the analysis.
- Comparison with lake cores provided some support for Hudson et al.'s analysis, which concluded that background (natural plus previous anthropogenic) could have accounted for about 60% of today's global circulation of mercury. Hudson et al. contended that increased oxidation of atmospheric mercury accounts for the observed increases in deposition.
- Based on the research to date, the following conclusions can be made about mercury: 1) biotic mercury likely responds slowly to mercury deposition reductions, 2) global efforts will most affect marine fish, 3) global efforts will also reduce re-emissions and freshwater ecosystem mercury, and 4) there are signals from natural and anthropogenic events.
- It is clear, however, that additional research is needed. The following questions were identified as priorities for future research: 1) Why do ice cores and lake sediment cores show different resolution on inputs? 2) What role does the ocean play in the mercury cycle? and 3) What are the linkages between local, regional, and global cycles of mercury?

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## SECTION 4

### SUMMARY OF THE TECHNICAL SESSIONS

#### 4.1 Session A: Mercury and Methylmercury Transport in the Environment

The pathway of mercury through aquatic and terrestrial ecosystems is very complex. Currently, this is an area of active research, and one in which we are only now starting to unravel the vexing questions that result from the rapid transformations, phase distributions, and transport vectors that mercury incurs in the environment. The papers presented in this session were brought together to show a cross section of research types, up-to-date findings, and leading investigators in this area of mercury research.

##### 4.1.1 Determination of the Sediment-Water Exchange of Mercury and Methylmercury: Approaches, Limitations, Observations — *G. Gill, Texas A&M University*

- Sediment-water exchange fluxes for mercury and monomethylmercury are generally determined using two approaches: 1) an indirect determination based on modeling of interstitial porewater concentration gradients, and 2) a direct approach using benthic flux chambers.
- These fluxes need to be interpreted relative to the limitations associated with the sampling approach and environmental setting. For example, flux chamber results give short-term (a few hours to a few days), instantaneous determinations which may or may not be in steady-state relative to the sampling interval. Porewater gradient modeling usually portrays a longer-term trend and can give biased results depending on resolution capability and biogeochemical processes acting in surficial sediments (e.g., chemical species involved, the precision of the near-surface concentration gradient, and spatial heterogeneity issues).
- Good agreement between flux chamber and modeling approaches for the determination of mercury fluxes is not always obtained. If there is significant infaunal activity, flux chamber results can be appreciably higher than simple diffusion calculations.

##### 4.1.2 Mercury and Methylmercury Accumulation in Lake Sediment: What Can We Infer from Dated Cores? — *D. Engstrom, Science Museum of Minnesota*

- Lake-sediment records from North America, Europe, the polar regions, and the Southern Hemisphere provide the most compelling evidence thus far that remote regions of the Earth receive significant inputs of anthropogenic mercury by long-range atmospheric transport.

- Lake-sediment records 1) integrate short-term variations in mercury deposition, 2) provide information on past deposition rates and recent trends, and 3) provide a relative measure of impact that can be compared across large geographic areas.
- Catchment soils export a portion of atmospheric mercury to downstream lakes. The size of the contributing watershed, the presence of wetlands and other upstream retention basins, the percentage of watershed area under urban or agricultural land-use, and local hydrology and vegetation also influence catchment mercury inputs. Mercury losses through gaseous evasion and hydrologic outflows must also be considered when determining atmospheric mercury fluxes from lake-sediment records.
- Mercury concentrations and accumulation rates in lake sediments are subject to errors of interpretation, including dilution by the sediment matrix, dating uncertainty, and changes in sediment focusing. The propagation of these errors into mercury flux calculations can produce spurious results. Changes in mercury accumulation may also reflect shifts in the pattern of sediment deposition within a basin, as opposed to changes in mercury input to the lake itself.
- Although sediment records have shown recent increases in the methylated portion of total mercury (THg), which may represent historical changes in methylmercury production that are independent of the flux of total mercury, these data also indicate that only a small portion of the methylmercury present at the sediment surface is preserved deeper in the core. Factors affecting mercury methylation/demethylation within the sediment column will have to be resolved before sedimentary records can provide reliable reconstructions of aquatic methylmercury exposure.

#### **4.1.3 An Overview of Mercury Cycling in the Boreal Ecosystem — *V. St. Louis, University of Alberta***

- The forest canopy is an important contributor to fluxes of methylmercury and total mercury to the forest floor of boreal uplands and wetlands at the Experimental Lakes Area (ELA) in Northwestern Ontario.
- Fluxes of methylmercury and total mercury in throughfall plus litterfall below the forest canopy were 2 and 3 times greater than annual fluxes by direct wet deposition. Almost all of the high flux of methylmercury and total mercury under the forest canopy occurred as litterfall.
- Average annual accumulation of methylmercury and total mercury in the surficial litter/fungal layer of soils in a 20-year-old fire-regenerated forest varied between 0.6–1.6 mg MeHg ha<sup>-1</sup> and 130–590 mg THg ha<sup>-1</sup> among sites differing in drainage and soil moisture.

- Four terrestrial boreal forest catchments containing different types of wetlands were studied to determine their strength as sources or sinks of methylmercury and total mercury. All catchments were sinks for total mercury. Upland catchments retained/demethylated methylmercury and wetland areas of catchments were always net sources of methylmercury, although the source strength varied by wetland types.

#### **4.1.4 Is the Arctic a Missing Sink for Mercury? New Measurements of Depletion Events, Deposition, and Speciation in Air and Snow at Point Barrow, Alaska — *S. E. Lindberg, Oak Ridge National Laboratory***

- Reactive gaseous mercury (RGM), total gaseous mercury [Hg(0)], and Hg accumulation in snowpack were measured at Point Barrow, Alaska in an effort to determine the geographic extent and reaction mechanism of the mercury depletion events (MDE) previously reported in the high Arctic at Alert, Canada.
- During the fall and early winter, Hg(0) and RGM exhibited only minor variation, with Hg(0) remaining within ~10% of global background and RGM remaining near the detection limit (<2 pg/m<sup>3</sup>).
- Within days of Arctic sunrise in January, Hg(0) exhibited major variations from the mean, rapidly dropping as low as 0.05 ng/m<sup>3</sup> and then cycling back to typical levels, sometimes exceeding global background. These events continued throughout the Arctic spring, then ended abruptly following snowmelt, in early June.
- RGM levels increased dramatically after Arctic sunrise (to levels as high as 900 pg/m<sup>3</sup>) in synchrony with the “depletion” of Hg(0). Both phenomena exhibit a strong diel cycle, in parallel with UV-B.
- Based on these results, MDEs involve rapid in-air oxidation of Hg(0) to a species of RGM by photochemically driven reactions, probably involving the same reactive bromine and chlorine compounds involved in ozone destruction. Sharp increases in mercury in the surface snowpack after sunrise are coincident with periods of peak RGM and suggest surface accumulation of the RGM by dry deposition.

#### **4.1.5 Putting into Perspective Mercury Emissions from Geologic Sources — *M. Sexauer Gustin, University of Nevada-Reno***

- Mercury emissions from naturally enriched terrestrial landscapes constitute a significant long-term source of mercury to the atmosphere. Areas of natural mercury enrichment are concentrated in three global belts associated with active plate boundaries. Mercury enrichment is associated with mercury, base and precious metal mineralization, areas of high crustal heat flow (geothermal areas), and areas of recent volcanic activity.



- Emission estimates were established for representative areas and then used, along with an understanding of emission/re-emission from background sources, to estimate mercury emissions from large areas.
- Geologic parameters, such as substrate mercury concentration, general geologic setting and type of rock hydrothermal alteration, and environmental parameters, such as temperature, light and precipitation, were used to determine area fluxes.
- In general, large areas with substrates containing slightly elevated mercury concentrations (0.08 to 5 µg/g above background) contribute more mercury to the atmosphere than smaller areas of high enrichment. For example, 90% of the mercury emissions from the 230-km<sup>2</sup> area encompassing the New Idria Mining District of California were from undisturbed areas, whereas 10% were from mine waste and mining-disturbed areas. Mercury emissions from geologic sources in the state of Nevada, which lies within a global belt of mercury enrichment, were estimated at 14,000 kg/yr versus 41,500 kg/yr from U.S. coal-fired utilities in 1999.

#### **4.1.6 Mercury Cycling in the Boreal Forest: Insights from Models, Experiments, and Isotopes — *B. Branfireun, University of Toronto at Mississauga***

- During nearly 9 years of field investigations at the Experimental Lakes Area in Northwestern Ontario, Canada, porewater sampling studies revealed that peatlands were methylmercury “hot-spots” in the catchment. Field measurements and a catchment-scale model indicated that peatlands were large sources of methylmercury.
- Recent studies involving the *in situ* addition of sulfate to peat and peat porewater resulted in an increase in porewater methylmercury concentrations in both dose-and-response and chronic sulfate loading experiments.
- A whole-catchment study of hydrology and mercury processes indicated that hydrological flowpaths, sulfate delivery, carbon quality, and temperature appear to influence the production of methylmercury at a range of scales. In addition, the mass flux of methylmercury within and from the catchment is highly dependent on the mass flux of water and the placement of landscape units in the catchment hydrologic cascade.
- Recent plot-scale experiments undertaken as part of the Mercury Experiment To Assess Atmospheric Loading In Canada and the United States (METAALICUS) Project have effectively utilized stable isotope mercury tracers to demonstrate the importance of antecedent moisture, soil quantity and composition, and vegetation cover in mercury fate and transport.

## **4.2 Session B: Bioaccumulation of Mercury in Aquatic Food Webs**

Although a great deal of emphasis is currently placed on biogeochemical factors that affect mercury transport and speciation (especially methylation) in the environment, our fundamental understanding of factors controlling bioaccumulation through food webs is still not clear. For example, cursory examinations of bioaccumulation factors (BAFs) of mercury among ecosystems where data are available to facilitate these calculations show wide variations among BAFs in otherwise similar settings. Disparate results such as these bring into question just how well we can understand bioaccumulation, or maybe more importantly, how well we can predict it. The papers in this session brought together a diversity of studies describing the factors that are known to affect bioaccumulation of mercury and the extent of mercury bioaccumulation in living systems.

### **4.2.1 Evolution of a Contaminant Problem: Mercury in Freshwater Fish — *J. Wiener, University of Wisconsin-La Crosse***

- The bioaccumulation of methylmercury in fish is influenced by an array of biotic, ecological, and environmental factors and processes.
- Much of the modern spatial variation in fish mercury levels is attributed to differences in the biogeochemical processes and transformations that control the abundance of methylmercury, particularly the rate of microbial conversion of inorganic Hg(II) to methylmercury by sulfate-reducing bacteria in aquatic sediments or adjoining wetlands.
- Long-range atmospheric transport and deposition are widely believed to be important contributors to the present mercury problem, particularly in semi-remote and remote areas.
- Several environmental variables can affect the net microbial production of methylmercury in the landscape. These include physicochemical characteristics of surface waters, flooding and inundation of vegetated areas, and density of wetlands in the watershed. Moreover, some human activities, such as the construction of new reservoirs, can greatly increase mercury levels in fish by creating environmental conditions that increase the microbial methylation of inorganic Hg(II).
- Concern about mercury contamination of fish has been motivated largely by potential adverse effects on humans and wildlife, given that consumption of fish is the primary route of methylmercury exposure. Widespread mercury and methylmercury contamination are also adversely affecting the quality of our fishery resources and fish populations.

#### **4.2.2 Projecting the Population-Level Effects of Mercury on the Common Loon in the Northeast — *D. Evers, BioDiversity Research Institute***

- The common loon (*Gavia immer*) is a top-level predator in aquatic systems and is at risk from mercury contamination, particularly in the Northeast.
- Matrix population models were used to estimate population-level effects of mercury on loons in four states in the Northeast exhibiting different levels of risk to methylmercury. Four categories of risk to methylmercury were established based on methylmercury levels observed in loons and associated effects observed at the individual and population levels in the field (e.g., behavior and reproductive success). Deterministic matrix population models were parameterized using survival estimates from a 12-year band-resight data set and productivity estimates from a 25-year data set of nesting loon observations in NH.
- The mean fertility was 0.26 fledglings per individual at low to moderate risk. There were 53% fewer fledged young per individual at high to extra high risk.
- Productivity was weighted by risk for each state. The portion of the breeding population at high to extra high risk was 10% in NY, 15% in VT, 17% in NH, and 28% in ME.
- A stochastic model was also constructed in which productivity was randomly selected in each time step from the 25 estimates in the NH data set. Model results indicated a negative population growth rate for some states. There was a decreasing trend in population growth rate as the percentage of the loon population at high to extra-high risk increased. The stochastic model showed that the population growth rate varied over a range of about 0.05 from year to year, and this range decreased as the percentage of the loon population at high to extra-high risk increased.
- These results suggest that an increase in mercury risk that causes a change in reproductive success may have a negative population-level effect on loons.

#### **4.2.3 USGS National Pilot Study of Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish — *W. Brumbaugh, National Pilot Study of Mercury***

- Water, sediment, and fish samples were collected in 1999 from 106 stations in 21 U.S. watershed basins during a national pilot study to examine relations of mercury and methylmercury in aquatic ecosystems.
- The mercury bioaccumulation rate in fish from 20 of these basins was evaluated in relation to species, selected watershed characteristics, and total Hg and methylmercury in surficial sediment and water.

- Mercury bioaccumulation in fish was correlated strongly (positively) with methylmercury concentrations in water but only moderately with methylmercury in sediment or total mercury in water. There was no correlation with the concentration of total mercury in sediment. Four parameters [methylmercury in water, pH of the water, % wetlands in the basin, and the acid-volatile sulfide (AVS) content of the sediment] accounted for 45% of the variability of length-normalized mercury concentration in fish, but the majority was described by methylmercury in water.
- On the whole, mixed agriculture/forest watersheds exhibited the highest concentration of methylmercury in water and the highest bioaccumulation in fish; urban watersheds exhibited a relatively low bioaccumulation rate despite a moderately high concentration of methylmercury in water and sediment.
- Based on sampling data, the following five basins had the greatest mercury contamination: Nevada Basin and Range, South Florida Basin, Sacramento River Basin (California), Santee River Basin and Coastal Drainages (South Carolina), and the Long Island and New Jersey Coastal Drainages.

#### **4.2.4 Interactions of Trophic Position and Habitat with Mercury Bioaccumulation in Florida Everglades Largemouth Bass (*Micropterus salmoides*) — T. Lange, Florida Fish and Wildlife Conservation Commission**

- Intensive food web studies were conducted at five sites in the Northern Florida Everglades to relate trophic position and habitat associations with mercury bioaccumulation in the aquatic food web. As the top piscine predator, the largemouth bass was the most intensively studied component of the food web.
- The largest size classes of bass fed almost exclusively on large-bodied fish (mainly adult Lepomids and cichlids). Concurrent with size-related shifts in diet, trophic position and mercury concentrations increased due to the importance of diet to bioaccumulation of mercury.
- Bioaccumulation in largemouth bass is greatly influenced by the degree of piscivory, however, omnivory influenced both mercury concentrations and trophic classification in specific habitats (e.g., marsh habitats remote from canal fish populations).
- A strong relationship between species trophic classification and mercury was observed at each site; however, variations in prey species populations and availability of mercury for bioaccumulation among sites resulted in a disconnect between trophic classification and mercury bioaccumulation.

#### **4.2.5 Bioaccumulation of Mercury in the Everglades: Patterns in the Foodweb — *J. Trexler, Florida International University***

- In September 1997, September 1999, and March 2000, diet and total mercury concentrations were examined in eastern mosquitofish (*Gambusia holbrooki*) obtained from over 100 locations across the Everglades landscape, to search for possible correlations between trophic position and mercury level in this omnivorous fish. A separate collection of mosquitofish was made simultaneously and analyzed for total mercury.
- There was no correlation between trophic score or niche breadth and mercury in these samples.
- In a separate study of Everglades fish species, a significant correlation was observed between mercury level and trophic score,  $r = 0.73$ ; however, the difference in mercury level between adjacent trophic groups (e.g., mosquitofish varied from 1.3 to 2.7) was not significant.
- Mercury uptake was also tested by placing neonate mosquitofish in cages at short- and long-hydroperiod sites located at three different regions of the Everglades. In general, greater uptake of mercury was observed in short-hydroperiod marshes than in long-hydroperiod marshes.
- This underlying environmental signal of unknown origin eliminated the hydroperiod effect seen at the other study sites, suggesting that complex spatial patterns of mercury availability may interact with other mercury bioaccumulation processes, obscuring the general patterns resulting from trophic relationships.

#### **4.2.6 Effects of Rainbow Smelt Invasion on Mercury Concentrations of Predatory Fish of Northwestern Ontario and Manitoba, Canada — *R. Bodaly, Department of Fisheries and Oceans, Freshwater Institute, Canada***

- Rainbow smelt, which feed at a higher trophic position than most native forage species, expanded their range in northwestern Ontario and Manitoba during the 1980s and 1990s.
- Predator populations (i.e., lake trout walleye and northern pike) were tested to determine if lakes invaded by smelt experienced an upward trophic shift and increases in mercury concentrations.
- Mercury in predatory fish in the region was found to be generally stable or declining over the last ~20 years. Mercury in predatory fish decreased by greater amounts in reference lakes compared to lakes invaded by smelt.

- Trophic position, as measured by  $d^{15}N$ , was higher in walleye in reference lakes compared to smelt lakes, but again, these differences were not statistically significant.
- It was concluded that the effect of smelt invasion on mercury levels in piscivorous fishes is slight.

### **4.3 Session C: STAR Program Review**

In 1999, the USEPA STAR Program initiated nine investigations of environmental factors that control mercury methylation, ranging from small-scale microbial effects, to large-scale mercury source identification. These studies, and their respective lead investigators, are taking very different approaches toward understanding this very complex environmental process, and collectively will hopefully provide a new and improved scientific basis on which future studies can build. Each of the nine STAR-funded projects provided a project update to this workshop.

#### **4.3.1 Formation/Transport of Methylmercury in Ecosystems and Watersheds**

##### **4.3.1.1 Watershed Influences on the Transport, Fate, and Bioavailability of Mercury in Lake Superior — *J. Hurley, University of Wisconsin***

- Field, laboratory, and modeling studies were performed to evaluate important watershed processes that control mercury fate and transport in the Lake Superior basin.
- Field research efforts during Year 1 focused on investigating differences between processes influencing offshore and near shore bioaccumulation of mercury in Lake Superior, and investigating watershed processes that enhance production and transport of methylmercury to tributaries.
- Results indicated that mercury species concentrations were low ( $0.49 \pm 0.22$  ng L<sup>-1</sup> THg with 1.5% MeHg, 3.5% Hg(0), 10% reactive Hg(II), and 85% unreactive organic Hg(II) complexes).
- Initial comparisons of phytoplankton revealed about a two- to three-fold enrichment of methylmercury in riverine mixing zones versus offshore regions of the lake. Rivers that drain specific, contrasting homogeneous sub-watersheds and monitoring wells in the East Creek watershed in the Tahquamenon River were sampled to assess watershed and subsurface influences on methylmercury production and transport.
- Preliminary results indicate that groundwater and stream porewater are significant sources of methylmercury, with wetland-dominated sites exhibiting the highest methylmercury concentrations, at times exceeding 12 ng/L.

#### **4.3.1.2 Factors Controlling Methylmercury Production in Sediments and Fate in Aquatic Systems — *R. Mason, University of Maryland***

- The bioavailability of mercury to sulfate-reducing bacteria was hypothesized to be controlled by the concentration of neutral mercury-sulfide complexes in solution as these compounds readily pass across the cell membrane by passive diffusion.
- A model has been used to predict decreases in the fraction of the dissolved mercury that is present as neutral mercury complexes with increasing sulfide concentration in both the field and the laboratory.
- Initial results from experiments looking at net methylmercury in laboratory cultures and natural sediments indicated that methylation rates decreased as sulfide concentrations increased. These experiments, which relied on optical measurements of bacterial culture densities (indicative of methylmercury in the system), were also performed using solid phase ores as the mercury source. Overall, this series of culture experiments indicated that concentrations of neutral mercury sulfide complexes decreased as sulfide concentrations increased, resulting in a decrease in the mercury bioavailability to bacteria.
- Iron oxide experiments investigating mercury and methylmercury binding to organic matter and solid phases, and their impacts on bioavailability and partitioning between solid phase and porewater and sediments, suggest that 1) methylmercury may behave differently (relative to binding with iron oxide) from inorganic mercury in the presence of dissolved organic carbon (DOC), and 2) inorganic mercury may be binding to iron oxides as a neutral complex rather than as a charged complex.
- Sequential extraction experiments were also performed on sediments from the Experimental Lakes Area (ELA) in northwestern Ontario to show partitioning of the mercury to the organic fraction, pyritic fraction, and reactive iron fraction.
- These studies are providing the information necessary to develop a predictive understanding of the factors controlling the formation, degradation, fate, and transport of methylmercury in watersheds.

#### **4.3.1.3 Response of Methylmercury Production and Accumulation to Changes in Mercury Loading: A Whole-Ecosystem Mercury Loading Study — *C. Gilmour, The Academy of Natural Sciences, Estuarine Research Center***

- Mercury methylation is being studied as part of a multidisciplinary, whole-ecosystem, stable isotope mercury-addition experiment (the METAALICUS project) at the ELA in northwestern Ontario. The primary objective of this work is to quantify the response of methylmercury production and accumulation to a change in ecosystem mercury loading.

- Three pilot isotope-addition studies were conducted at the ELA in 2000: a 1000-m<sup>2</sup> upland plot, a comparable wetland plot, and four 10-m diameter lake enclosures. Mercury stable isotope data were used to follow methylmercury production and accumulation from the new stable isotope mercury spike separately from the existing mercury pools.
- Relative methylmercury production in the first hours after new mercury was introduced was compared to 1) methylmercury production through the first summer after introduction and 2) methylmercury production from stored mercury pools. The mobility and phase speciation of new versus old mercury in these pilot systems was also used to assess how the changing geochemistry of mercury after addition affected bioavailability for methylation.
- The following was observed during the lake enclosure studies at the ELA: 1) methylmercury was being formed slowly over time from the newly added <sup>200</sup>Hg; 2) <sup>200</sup>Hg was measured in the same sediment cores used to measure methylation rates; 3) plots that received only one dose of mercury had more mercury than plots that received the same cumulative dose of mercury over the course of the summer; 4) the newly added <sup>200</sup>Hg appeared to be more bioavailable than the “old” mercury (e.g., 20% of <sup>200</sup>Hg was found as methylmercury in the sediment, compared to 3.5% of the ambient Hg).
- The wetlands experiments at the ELA showed that newly added mercury was more bioavailable than “old” mercury, except for experiments where the ambient mercury was absorbed to peat.
- The uplands experiment at the ELA showed large variations in methylation based on soil conditions (e.g., dry soils, riparian soils, saturated soils, etc.). As expected, saturated soils produced the most methylmercury.
- To provide a comparison with a very different ecosystem type (i.e., a subtropical wetland), mercury loading studies were also performed using 1-m diameter *in situ* enclosures at four sites across the Florida Everglades under the ACME project. This study showed that methylmercury production is driven by the sulfur gradient across the Everglades.

#### **4.3.1.4 Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition? — J. Jeremiason, Minnesota Pollution Control Agency**

- Although there is strong evidence that mercury deposition is now about 3 to 4 times greater than natural rates in Minnesota, a comparison of modern fish to museum specimens of fish caught in Minnesota in the 1930s suggests that fish mercury levels have increased by a factor of 10 in low-alkalinity systems.



- It has been hypothesized that increased sulfate deposition has increased the activity of bacteria that methylate mercury in sulfate-poor ecosystems of northern Minnesota, causing mercury concentrations in fish to exceed levels expected based on atmospheric deposition.
- A three-tiered study at the Marcell Experimental Forest in north-central Minnesota involving microscale experiments, lake/wetland studies, and modeling other lakes is being performed to test this hypothesis. The microscale studies are focusing on testing for enhanced methylation or inhibited demethylation in wetland mesocosms and lake sediment cores. Field studies will quantify the external and internal methylmercury sources to the lake (and, ultimately, to its fish), focusing on transport from different types of wetlands. A full-scale addition of sulfate to a wetland will also be conducted in the final year of this study. Modeling will involve quantifying methylmercury loads to lakes from wetlands based on hydrology and wetland classifications.
- Total mercury and methylmercury transport studies from several of the wetlands are being performed. These studies have focused on establishing mass budgets for methylmercury and total mercury and have included sediment core collections, dissolved Hg(0) measurements, deployment of porewater equilibrators, and collection of food chain components. Initial porewater equilibrator data were variable and a gradient for methylmercury was not observed.
- Sulfate reduction rates were measured across a spatial gradient in the lake and at depth in several sediment cores. Sulfate reduction was observed to 15 cm in lake sediment cores. Sulfate was also added to several cores at varying concentrations. Methylmercury generation will be related to sulfate reduction rates and to sulfate load. Future studies on peat blocks from two wetlands and on lake sediments will involve additions of nitrogen and organic matter.
- Wetlands at the Marcell site were characterized by aerial photography, based on the Cowardin classification system used by the National Wetland Inventory, and incorporated into a Geographic Information System (GIS) database. Wetland characterization, lake watershed hydrology, and measured mercury export from similar wetlands at the Marcell site will be used during the modeling phase of the study to estimate fish mercury levels and the wetland loading of mercury to these lakes. A very wide range of methylmercury concentrations have been observed in the northern pike analyzed thus far.

#### **4.3.2 Biogeochemical Controls on Mercury Methylation/Demethylation Rates**

##### **4.3.2.1 Photochemistry of Mercury in Saginaw Bay Watershed, Michigan: Annual USEPA STAR Project Meeting — *J. Nriagu, University of Michigan***

- Field measurements, *in situ* incubation tests [to study photochemical production of dissolved gaseous mercury (DGM) in near shore waters of the bay], and simulations in lab microcosms under different light conditions have been performed to study the role of photochemistry in the cycling of mercury in various components of the Saginaw Bay watershed.
- Ambient airborne mercury levels, mercury soil emission fluxes, the diurnal cycle of DGM, and mercury levels in soil samples and water samples from the streams and rivers draining into the Saginaw Bay were measured.
- A thermal desorption technique developed during the project was used to determine the forms of mercury in soil and solid material.
- Results from the first year of field studies emphasized the role of photo-induced reactions as critical components in the cycling of mercury in the bay watershed.

##### **4.3.2.2 Chemical and Biological Control of Mercury Cycling in Upland, Wetland, and Lake Ecosystems in the Northeastern United States — *C. Driscoll, Syracuse University***

- Total mercury and methylmercury in wet deposition, throughfall, litter, soil, soil waters, ground waters, surface waters, and sediments were measured in the Sunday Pond watershed in the Adirondack region of the State of New York.
- Wet deposition of total mercury to the site was estimated at 10.8  $\mu\text{g}/\text{m}^2$  yr, with 0.6% of this occurring as methylmercury. Mass balance results indicate that 77% of mercury deposited through wet deposition is retained in the watershed.
- Sunday Pond was also a sink for inputs of total mercury, although the watershed and lake were sources of methylmercury to downstream surface waters.
- The wetlands appear to be important to the supply of methylmercury to surface waters.
- The mercury biogeochemistry data have been used to calibrate the Mercury in Adirondack Wetlands Lakes and Terrestrial Systems (MAWLTS) model to the Sunday Pond lake/watershed system.

### 4.3.3 Physical and Chemical Processes Affecting Mercury Cycling

#### 4.3.3.1 Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury from Contaminated Mine Sites — *G. Brown, Stanford University*

- The major objectives of this project were to 1) determine the chemical speciation and relative abundance of different forms of mercury in mine wastes, 2) investigate the role of colloidal transport as a mechanism for dispersal of mercury from waste sites, 3) identify the mode of mercury sorption in downstream sediments and fine-grained precipitates in the presence of common complexing ligands, and 4) determine the effects of aqueous complexing ligands on the desorption and sorption inhibition of mercury.
- Synchrotron-based X-Ray Absorption Fine Structure (XAFS) spectroscopy—a nondestructive element-specific structural method that requires no special sample preparation—was used to probe the chemical speciation of mercury in mine wastes from abandoned mercury mine sites in California and Nevada.
- Results indicate that the main mercury-bearing phases in calcines are cinnabar and metacinnabar. Several relatively soluble mercury-bearing phases that were not previously detectable by X-Ray Diffraction (XRD) were identified, including montroydite (HgO), schuetteite (HgSO<sub>4</sub>), and several Hg-Cl phases. Speciation in mine waste samples depends on the geologic history of the mine and the processes that occurred following mining.
- XAFS has been used to determine the chemical forms of mercury associated with colloidal material generated in laboratory column experiments on mine wastes. These experiments indicate that the colloidal transport of mercury is a potentially important dispersal mechanism. Colloids identified by continuous emissions monitoring (CEM) include cinnabar, metacinnabar, and montroydite, gheritite, alumina silicate gel, etc. In general, however, mercury is not adsorbed onto these particles and is instead in the form of pure mercury phases.
- XAFS has also been used to examine the sorption of Hg(II) on model mineral surfaces to determine the effects of the inorganic ligands sulfate and chloride on Hg(II) sorption. Adsorption experiments show that Hg(II) is strongly adsorbed onto ferric hydroxides and less strongly onto aluminum hydroxides. Complexing ligands (e.g., chloride and sulfate) have also been determined to affect the adsorption process. In general, chloride disfavors the formation of surface complexes, whereas sulfate slightly favors complexation on surfaces. Adsorption also does not initially appear to be that important in the California Coast range, although it should not be ruled out.
- The substrate mercury concentration speciation appears to be the dominant factor controlling the emissions measured by M. Gustin. The isotopic ratios (<sup>201</sup>Hg and <sup>202</sup>Hg) are being

developed for different mercury metal samples from around the world. These ratios may eventually show significant material-specific variations that can be used to track the origin of deposited mercury.

#### **4.3.3.2 Microbiological and Physiochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones — *W. Fitzgerald, University of Connecticut***

- A field and laboratory study was performed to investigate physicochemical/microbiological reactions and processes controlling mercury cycling, speciation, and bioavailability in the waters and sediments of Long Island Sound (LIS) and its watershed/coastal water interface (i.e., Connecticut River and East River).
- The following hypotheses were tested:
  1. The Hg(0) distribution in LIS is spatially/temporally variable and is related to the distribution of labile inorganic and organically associated mercury species and to the *in situ* supply of reducing agents (e.g., bacterial activity and solar radiation).
  2. Estuarine reactions (i.e., mixing of river-borne mercury species with seawater high in Cl<sup>-</sup> and major cations) and direct Waste Treatment Facility (WTF) discharges (sewage) increase the labile mercury fraction available for reduction, enhancing localized production of Hg(0).
  3. Hg(0) is the predominant mercury cycling product of bacterial activity in the oxic zone, while net *in situ* synthesis of monomethylmercury is most significant in redox transition zones (i.e., shallow sedimentary regimes and water basins that experience seasonal hypoxia).
- Study results show that organic matter-mercury interactions are major factors controlling the behavior and fate of mercury in aquatic systems.
- Organic content, microbial activity (based on oxygen respiration), and methylation potential are higher in the west portion of Long Island Sound than in the east. Active-volatile sulfide is much higher in the west than the east; therefore, the dominant sulfide complex in the west is a charged species whereas the dominant sulfide complex in the east is uncharged. Also, mercury is in a better form in the east, even though the methylation potential is down. Follow up studies will be performed.

#### **4.3.3.3 Redox Transformation of Mercury — *F. Morel, Princeton University***

- Oxidation-reduction reactions were quantified to provide information on the environmental factors that control their rate. The study focused on the oxidation of Hg(0), a reaction that has been all but ignored.
- The results demonstrated that the oxidation of Hg(0) is induced by UV-A light under appropriate conditions (e.g., the presence of chloride and a primary photo-oxidizing agent such as quinones).
- Oxygen appears to be the ultimate electron acceptor, and the net oxidation rate is not related to biological activity.
- The rate of oxidation of Hg(0) is often comparable to, and sometimes faster than, the predicted rate of gas exchange, resulting in lower rates of volatilization than normally calculated.

#### **4.3.3.4 Assessing the Role of Plants in the Biogeochemical Cycle of Mercury — *M. Gustin, University of Nevada***

- The role of plants in the biogeochemical cycling of mercury was investigated using two EcoCELLs (5 x 7-m mesocosms) containing soil, gravel, and mercury-amended substrate (12 µg/g) designed as open-flow mass balance systems.
- Parameters monitored continuously within each EcoCELL included 1) CO<sub>2</sub>, H<sub>2</sub>O, and mercury vapor flux; 2) incident light; 3) air temperature; 4) soil temperature at six locations in each soil container; and 5) relative humidity. Soil moisture, CO<sub>2</sub>, and mercury in soil gas were also monitored.
- Approximately 33 aspen were planted in each soil container allowing for development of a full tree canopy. Leaf rinses and leaf tissue, petioles, branches, stems, and root material were analyzed.
- Each EcoCELL also contained six aspen potted in soil with low mercury concentrations ( $0.031 \pm 0.001$  µg/g), from which foliar material was sampled and analyzed to estimate foliar uptake of airborne mercury.
- As plants leafed out within the EcoCELLs, daily CO<sub>2</sub> and mercury vapor flux declined and H<sub>2</sub>O vapor flux increased. Experiments are ongoing to determine if the decline in mercury flux with leaf out may be attributed to the vegetation or to changing physical parameters of the soils.

- Mercury emission from plants within the EcoCELLs was not apparent at the elevated air concentrations within the EcoCELLs (10-100 ng/m<sup>3</sup>). Foliar mercury concentrations increased as a function of time.
- Ancillary experiments are being done with ecopods, which allow for assessment of foliar uptake of mercury under a variety of air exposure concentrations, and with a single-plant gas exchange chamber to investigate mercury emission from plants to help understand the processes being observed at the ecosystem scale.

#### **4.3.3.5 Mercury and Methylmercury Burdens in Sediments, Water, and Biota of VT and NH Lakes, and Trends in Paleolimnology-Inferred Mercury Deposition to VT and NH — *N. Kamman, VT Department of Environmental Conservation***

- A comparative study of mercury burdens and exposure risks in VT and NH lakes was performed using the regional Environmental Monitoring and Assessment Program (EMAP) approach.
- The study had four distinct components: 1) measuring mercury, methylmercury, and related parameters in the waters and sediments of 90 lakes; 2) measuring mercury in the macrozooplankton and yellow perch of 45 lakes; 3) measuring mercury and biomarkers in loons and other piscivores in up to 45 lakes; and 4) comparing recent mercury deposition to 13 relatively undisturbed lakes with earlier data using paleolimnological techniques.
- A synchronous increase in flux rates to all lakes was evident, beginning around the year 1850. In all but two lakes, mercury fluxes began to decline around 1980.
- Direct atmospheric mercury contribution to lakes was estimated at 10.1, 29.8, and 19.8 ug m<sup>-2</sup> yr<sup>-1</sup>, for pre-1850, the 1980s, and 1998, respectively.
- Watershed mercury retention has declined steadily since the 1970s, suggesting that watersheds in the study region may be mercury-saturated, and possibly ‘leaking’ mercury to down-gradient lakes.

#### **4.3.3.6 Mercury in Fish and Sediments of Clear Lake, California: Defining the Problem and Developing Cleanup Options through the USEPA Superfund Program — *E. Mange***

- Clear Lake is a large recreational lake located in northern California, approximately 100 miles north of San Francisco in the northern part of the California volcanic field. It is the largest freshwater lake in northern California (approximately 20 miles long and 10 miles wide) and is used for bass fishing.

- Elevated levels of mercury were first found in fish in the mid 1970s. This mercury is associated with historical mining activities from the abandoned Sulfur Bank Mercury Mine. The site was listed as a Superfund site in 1990. Due to the complex hydrogeology of the site, it has taken 10 years to complete the remedial investigation for the mine.
- Although originally deep mined, the site was strip mined in the 1930s, resulting in a 100-ft deep, 22-acre pit (the Herman Impoundment) containing approximately 600 million gallons of pH 3 water (with little mercury). Although concentrations at the shoreline of the mine are very high, since the lake is shallow and eutrophic, mercury has been transported throughout the lake.
- Approximately 2.5 million cubic yards of waste rock, tailings, and overburden are located on this site. Erosion controls have been implemented at the mine to reduce inorganic mercury erosion into the lake from approximately 132 kg/yr to less than 2 kg/yr. Approximately 1 kg of total mercury is leaching into the groundwater from this site per year and approximately 100 gallons of water per minute is flowing through this system. Air samples from mine tailings and natural rock show high mercury concentrations. It is estimated that as much as 14 kg/year of mercury is being emitted from these sources.
- USEPA has determined that approximately 35% to 40% of the water flowing through the mine system is coming from hydrothermal systems. The rest is from surface infiltration, surface water entering the pit. Thus, both anthropogenic and natural Hg is entering the lake.
- A Feasibility Study will be started shortly to define potential options for reducing mercury flux into the lake (e.g., regrading, revegetating, etc.). Remediation efforts will be complicated by the fact that a mercury ore body is located around the lake and that mercury is actively being deposited by geothermal gases coming up through the lake.
- The University of California at Davis has attempted to define a footprint of the acid drainage that is entering Clear Lake. This inflow is visible as a white flocculant precipitate that forms when the low-pH water from the mine meets the high pH water of the lake. This flocculant has been hypothesized to act as a substrate for sulfur-reducing bacteria to methylate the inorganic mercury coming from the site.
- A second operable unit will examine what has happened to the mercury deposited within the lake since the mine first started operation (up to as much as 2000 kg/year) and how this mercury has been cycling through the environment. In addition to determining the pathway from deposition as an inorganic compound to methylmercury in fish tissue, researchers need to know how the mercury is being transported, where the methylation sites are located, how mercury is entering the food chain, and other potential sources of mercury before they can evaluate remedies for this site.

#### **4.4 Session D: Managing Mercury Contamination in Aquatic/Terrestrial Systems**

Although in recent years focused attention has been placed on understanding how mercury emissions, nonatmospheric mercury sources, and environmental biogeochemistry influence the expressed toxicity of mercury in specific ecosystems, relatively little emphasis has been placed on risk assessment and risk management. This session attempted to bring together a series of presentations that described various management schemes that may be used to evaluate and quantify risks, and determine the efficacy of various reduction scenarios for improving environmental mercury levels.

##### **4.4.1 An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed: A CALFED Study — *C. Foe, Central Valley Regional Water Quality Control Board***

- In September 1999, CALFED funded an investigation into the mercury impacts in the San Francisco Bay-Delta watershed, specifically the Cache Creek watershed area and the Bay-Delta areas downstream. Both watersheds have been the recipient of mercury-laden runoff from mercury mining and gold mining activities.
- The mass loading studies have found that 1) the Sacramento River is the main source of water and mercury to the Delta; 2) there appears to be a net loss from the water column of particulate and filter-passing monomethylmercury (MeHg) in the Delta during spring and summer, because the input mercury concentrations to the Delta are higher than the export concentrations; 3) the pattern of higher methylmercury concentrations in the rivers and adjoining Bay-Delta waterways, and lower methylmercury levels in the Central Delta, and at the export pumps, is consistent with the biotic mercury data from this and other studies.
- The bioaccumulation studies in this project and others have shown that Asiatic clams, silversides, white catfish, and largemouth bass in and near river mouths have higher mercury body burdens. There does not seem to be a difference in bioavailability between mercury from Cache Creek (a cinnabar source) and mercury from Sierra Nevada Range runoff (an elemental mercury source). Methylmercury concentrations and methylmercury-to-total mercury ratios in sediments are lower in the Delta and San Francisco Bay than ratios described in the literature for the East Coast or Southern Florida.
- Ecological and human health effects studies have found that 1) most of the largemouth bass, white catfish, and striped bass in the Delta were above the mercury screening value of 0.3 ppm, indicating a potential human health concern; and 2) mercury concentrations measured in avian species were elevated enough in the Bay-Delta system to put up to one-third of the species sampled at risk.



#### **4.4.2 An Evaluation of USEPA's Bioaccumulation Factor for Mercury: A Regulated Industry Perspective — *R. Reash, American Electric Power***

- Bioaccumulation factors (BAFs) are used as a measure of the bioaccumulative potential for mercury and other pollutants of concern.
- Although a BAF is simple to determine and provides a means to conveniently compare mercury bioaccumulation potential between water bodies, an empirical relationship between fish-tissue and water-column mercury is not demonstrated in the scientific literature.
- Even using a site-specific BAF value, a back-calculated water quality criterion for total mercury or methylmercury assumes, implicitly, that a decrease in water-column mercury will result in a proportional decrease in fish-tissue mercury. The accuracy of this assumption has significant regulatory implications.

#### **4.4.3 Methylmercury in Terrestrial Ecosystems: Summary of Swedish Research — *J. Munthe, IVL Swedish Environmental Research Institute***

- Cycling of mercury and methylmercury in forest ecosystems has been investigated at the Gårdsjön research station north of Göteborg.
- Investigations included catchment-scale input-output and mass balance estimations, deposition processes, soil methylation processes (using stable isotopes), and the effects of reducing atmospheric input on mercury and methylmercury levels in catchment run-off.
- Mercury and methylmercury in run-off has been monitored since the start in 1991. Average concentrations are 2.58 and 0.10 ng L<sup>-1</sup> for total mercury and methylmercury, respectively.
- During the first 1 to 3 years, a slight decrease in mercury and methylmercury output was observed, but after that, no significant changes have been observed in comparison to the reference catchment.

#### **4.4.4 Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades Phase II — *D. Krabbenhoft, U.S. Geological Survey***

- One of the principal objectives of the Aquatic Cycling of Mercury in the Everglades (ACME) Project was to provide process-level information on mercury cycling in the Everglades, which could be used to advise management decisions about the elevated levels of methylmercury in the food web.

- Mercury cycling was found to be highly dynamic in this ecosystem, with rapid rates of methylation, demethylation, reduction, and evasion.
- Because rainfall is the dominant source of mercury to this ecosystem, a consistent downward flux of inorganic mercury from surface waters into sediment interstitial waters was observed.
- Microbial methylation and demethylation were most pronounced in surficial sediments, and an upward gradient of methylmercury from porewaters to surface waters was generally observed. An ecosystem-scale sulfur gradient and DOC concentrations also affected methylmercury production. Gradients in net methylmercury production, rather than gradients in bioaccumulation, appear to control mercury uptake into the food web.
- The ACME project is currently seeking information that directly addresses management concerns for the Everglades. The project focuses on evaluating the effects of the four key biogeochemical parameters (sulfur, mercury loading, DOC, and wetting and drying cycles) that were revealed to have the greatest effect on bioaccumulation. The sequence of events following rewetting (methylmercury production and bioaccumulation, sulfate mobilization, DOC, pH, total mercury behavior, etc.,) supports the working model that mercury methylation in the Everglades is tightly linked to the sulfur cycle.
- Experimental manipulations of intact sediment cores showed sulfide inhibition of mercury methylation beginning between 10–100  $\mu\text{M}$  sulfide, which was consistent with patterns of methylmercury production *in situ* in this ecosystem. Together with research on mercury speciation uptake mechanisms, these studies provide high confidence in the sulfide inhibition level in the Everglades.
- Mesocosm mercury dose-response experiments conducted in 2000 examined the concentration of methylmercury in long-term phosphate-addition mesocosms and helped quantify the separate impacts of nutrient, mercury, and sulfur loading within different freshwater marsh habitats in the Everglades.
- Ultimately, these research efforts will guide ecosystem managers who must decide whether reducing local mercury emission, intercepting sulfur in runoff, regulating water levels, or a combination of all these actions will be the best approach for minimizing methylmercury exposure to wildlife and humans in South Florida.

#### **4.4.5 Modeling Mercury Fate in Seven Georgia Watersheds — R. Ambrose, Jr., USEPA**

- Field and modeling studies were conducted to assess TMDLs for mercury in six south-Georgia rivers and the Savannah River.
- Mercury is introduced to these rivers primarily by atmospheric deposition.

- The GIS-based Watershed Characterization System (WCS) and a mercury delivery spreadsheet were developed and applied with the Water Quality Analysis Simulation Program (WASP5) to calculate mercury buildup in watershed soils, loading and delivery through the watershed tributary system, and mercury fate in the mainstem rivers.
- These models were checked against site-specific survey data gathered during very dry conditions in June and July, 2000.
- Calculated mercury concentrations in soils, sediment, and water compared reasonably well with the observed data in most of the watersheds. Sensitivity analyses point to the processes and parameters controlling mercury fate in these river systems, including atmospheric deposition, impervious watershed area, soil reduction rate constant, tributary reduction rate constant, and tributary methylation status.
- Future development should focus on mercury transport and transformation reactions in the tributary systems.

#### **4.4.6 Fitting into the North American Mercury Emissions Reduction Priority — *L. Trip, Environment Canada***

- Canada, the United States, and Mexico are attempting to address their mercury emissions concerns on a continental scale.
- Institutional arrangements of the North American Free Trade Agreement of 1992 led to the development of the North American Agreement on Environmental Cooperation and the consequent North American Regional Action Plan (NARAP) on Mercury, Phases I and II, under the Sound Management of Chemicals Initiative.
- Canadian mercury management measures have been developed to comply with the intent of the Mercury NARAP and to simultaneously discharge domestic, bilateral, and international obligations to manage mercury emissions.

## **4.5 Session E: Methylmercury Production in the Environment**

Of all the processes that affect mercury speciation, bioaccumulation, and toxicity, probably none is more important than methylation. As such, this aspect of the mercury cycle has received a great deal of attention and funding over the past 10 years or so. Mercury methylation is a very complex process that, from what we currently understand, is primarily mediated by combined geochemical and microbial factors. Because of this, studies in this area of research need to be multidisciplinary in their approach. This session brought together a variety of systematic studies that demonstrated not only the complex nature of this problem, but also the significant headway scientists have made in recent years.

### **4.5.1 Overview of Microbial Methylmercury Production and Degradation: What Do We Know? What Don't We Know? — C. Gilmour, *The Academy of Natural Sciences***

- Mercury methylation is perhaps the key process in mercury bioaccumulation.
- A conceptual model for net methylmercury production contains two major components: 1) the bioavailability of mercury to methylating bacteria, and 2) the metabolic activity of those bacteria.
- Important issues include 1) the neutral species bioavailability model, 2) the types of bacteria that produce methylmercury and the conditions under which they produce methylmercury, 3) progress in understanding how the community structure of sulfate-reducing bacteria affects methylation, 4) the biochemistry of methylation within cells, 5) the confounding roles of sulfur in methylation, 6) the importance of hydrology to methylation, and 7) relationships derived from ecosystem studies of mercury biogeochemistry.
- Advances in oxidative demethylation and the distribution of the *mer* operon in the environment have led to a better understanding of demethylation.
- Promising new research techniques include use of mercury stable isotopes to study bioavailability and developments in the use of microbial mercury “bioreporters” and “bioaccumulators.”

### **4.5.2 Environmental Controls on Methylmercury Production and Degradation in Florida Everglades Sediment — M. Marvin-DiPasquale, *U.S. Geological Survey***

- The net production of methylmercury by sediment bacteria is the most critical step in the chain of events leading to mercury contamination of Everglades wildlife.
- Radiotracer experiments using  $^{203}\text{Hg}(\text{II})$  and  $[^{14}\text{C}]\text{MeHg}$  amendments examined the relative impact of key environmental parameters on both mercury methylation and methylmercury degradation in sediment (0 to 4 cm) at five sites along the existing north-south nutrient gradient.

- Temperature, sulfur chemistry, organic matter, and redox conditions were varied. Mercury methylation generally increased from nutrient-enriched to pristine sites, while methylmercury degradation rates varied comparatively little among sites in unamended anaerobic samples.
- These experiments confirm earlier findings that sulfur biogeochemistry plays a critical role in regulating net methylmercury production in the Everglades. Further, net methylmercury production appears to be primarily a function of gross mercury methylation, as gross rates of microbial methylmercury degradation were largely constant over a wide range of geochemical manipulations.

#### **4.5.3 Group VI Anions and Mercury Transformation within the S cycle in the Carson River System, Nevada — *J.C. Bonzongo, University of Florida***

- The Carson River System (CRS) in western Nevada is contaminated with mercury from historic mining activities. Total mercury concentrations have been reported for sediments and surface water in excess of 1000 mg/kg and 7000 ng/L, respectively. Methylmercury was present at levels less than 1% of total concentrations.
- Field and lab studies were performed to explain the lower-than-expected methylmercury levels observed. The role that sulfate and chemically similar and naturally occurring Group VI oxyanions ( $\text{SeO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ , and  $\text{WO}_4^{2-}$ ) played in controlling mercury methylation rates in the CRS was investigated.
- Results suggest the following: 1) Group VI anions are evapoconcentrated in the CRS due to the aridity of the climate, reaching anomalously high levels with potential impact on mercury methylation; 2) rates of methylmercury production in sediments tend to increase with increasing flow regimes, as Group VI anions get diluted; 3) laboratory experiments confirmed the inhibition potential of tested Group VI anions, and both noncompetitive (S versus Se and Te) and competitive inhibition (S versus W) were observed.

#### **4.5.4 A Bacterial Biosensor for Aquatic Hg(II) Speciation and Bioavailability — *P. Barrocas, Florida State University***

- The movement of Hg(II) into an ecosystem and its bioaccumulation as methylmercury in higher trophic levels are strongly influenced by the uptake of bioavailable forms of Hg(II) by bacteria.
- A biosensor bacterium that emits 550 nm photons of light when exposed to bioavailable forms of Hg(II) was initially calibrated against Hg(II) solutions of known (i.e., modeled) speciation. Hg(II) speciation and bioavailability with a variety of inorganic and organic ligands were then examined by manipulating the Hg(II):ligand ratios and by using various

ligand combinations. An anaerobic chamber was also used to study Hg(II) complexation by hydrogen sulfide.

- Hg(II) bioavailability in natural water samples collected from nearby lakes, rivers, and the Everglades will be tested in the future.

#### **4.5.5 Facilitated Uptake of Mercury at Trace Concentrations by *Escherichia coli* and *Vibrio anguillarum* — G. Golding, University of Manitoba**

- The bioavailability of inorganic mercury (Hg(II)) to bacteria under aerobic and anaerobic conditions was studied using well-defined chemical solutions and at trace Hg(II) levels to assess whether facilitated transport was occurring. A *mer lux* bioreporter bacterium that is only capable of producing luciferase enzyme and light in response to Hg(II) entering the cytoplasm of the cell was used to measure Hg(II) crossing the cell membrane.
- Under anaerobic conditions, light production did not occur after exposure to Hg(II) in a minimal medium unless mercury concentrations greater than 100 ng L<sup>-1</sup> were added, even though the bioreporter was capable of responding to mercury concentrations < 1 ng L<sup>-1</sup> under aerobic conditions in the same minimal medium. The lack of a light response under anaerobic conditions was due to a lack of Hg(II) transport and not to differences in cellular energetics. Bioreporter responses were elicited to trace mercury concentrations under anaerobic conditions following the addition of a variety of low-molecular weight organic compounds.
- For the compound studied in greatest detail, the amino acid histidine, anaerobic uptake was proportional to the formation of Hg(HHis)(His)<sup>+</sup>, a charged species. Histidine additions did not affect the rate of Hg(II) uptake. These results demonstrated the existence of facilitated transport processes in aerobic studies.
- The aerobic facilitated mechanism of Hg(II) transport appeared to be repressed under anaerobic conditions. The addition of low-molecular weight organics may present an alternative pathway for Hg(II) uptake by the nonspecific transport of complexes of mercury with low-molecular weight organic acids.
- Thus, models of Hg(II) uptake based only on passive diffusion of neutral species may be too simple to accurately describe Hg(II) uptake for all microorganisms. Also, different uptake models may be needed for aerobic and anaerobic environments.

#### **4.5.6 Mercury Transport and Transformation in the Wider Idrija Region and the Gulf of Trieste — *M. Horvat, Institute Jozef Stefan***

- The Idrija mercury mine in Slovenia is the second largest mercury mine in the world. Approximately 17% of the approximately five million metric tons of mercury ore mined from this site were dissipated into the environment.
- The tailings and contaminated soils in the Idrija region are continuously eroding and entering the river, the flood plains, and the Gulf of Trieste, as demonstrated by consistently high mercury concentrations in river sediments and water over the last 10 years.
- Recent studies in the Idrijca-Soča-Gulf of Trieste region focus on quantifying mercury fluxes and understanding mercury fate, its accumulation in the flood plain, and its entry into the marine environment.
- In order to develop realistic strategies for minimizing the effects of the Idrija mining on human health and the environment, a more integrated research approach is needed.

#### **4.5.7 The Everglades Mercury Cycling Model: Development and Application to Two Marsh Sites in the Florida Everglades — *R. Harris, Tetra Tech, Inc.***

- The Everglades Mercury Cycling Model (E-MCM) was applied to two sites varying widely in primary productivity: 1) the Everglades Nutrient Removal Project (ENRP), a highly-eutrophic, constructed marsh situated at the northernmost (upstream) end of the remnant Everglades; and 2) Water Conservation Area (WCA) 3A-15, an oligotrophic marsh with low phosphorus concentrations and comparatively low sulfate concentrations that are similar to historical conditions. Mercury levels observed in largemouth bass during the study period were high at WCA 3A-15 and low at ENRP.
- Field data and modeling both indicate mercury cycling is very rapid in Everglades marshes. The dominant predicted source of methylmercury at WCA 3A-15 was *in situ* production ( $7.6 \text{ mg m}^{-2} \text{ yr}^{-1}$ , 87% of total methylmercury load). At ENRP, the best model fit to observations occurred with minimal on-site methylation, and was consistent with field estimates of low methylation rates.
- These results support the hypothesis that local site factors are driving the variability and the “hot spots” observed for methylmercury across the Everglades. Atmospheric mercury deposition rates also appear to affect fish mercury concentrations.
- Model simulations were run to predict the response of fish mercury concentrations to reductions in mercury loading to WCA 3A-15. The model suggested that mercury in 3-year-old largemouth bass (the index fish for health advisory purposes) is nearly proportional to the atmospheric load of mercury. Fish mercury concentrations were predicted to change by 50%

of the ultimate response within approximately 10 years and 90% within 20 to 30 years.

- Gaps regarding mercury cycling in aquatic systems impose uncertainty on the predictive capability of the model. Research is ongoing to address these gaps.

#### **4.6 Combined Session**

##### **4.6.1 Landscape Patterns of Mercury Contamination Across the Everglades Ecosystem — *J. Stober, USEPA Region 4 and K. Thornton, FTN Associates Ltd.***

- USEPA Region 4 initiated a project in 1992 to assess the effects of mercury contamination on the South Florida Everglades ecosystem. A final technical report was completed in 2001.
- During the first phase of this project (1994 – 1996), soil, water, and biota were sampled at about 500 sites throughout the 9600-km<sup>2</sup> marsh to assess the effects of hydropattern, phosphorus loading, habitat alteration, and mercury contamination on the marsh ecosystem.
- The Phase I report (USEPA 1998) noted significant interactions among water depth, total organic carbon (TOC), total phosphorus (TP), SO<sub>4</sub> concentrations, food web dynamics, and fish mercury concentrations. These interactions exhibited different spatial patterns in the three areas: north of Alligator Alley, between Alligator Alley and Tamiami Trail, and south of Tamiami Trail in Everglades National Park. Three conceptual models, one for each of the subareas, were needed to describe the pathways and interactions among factors affecting fish mercury concentrations in this ecosystem gradient.
- During Phase II (1999), the study was expanded to include the collection and analysis of porewater, floc, macrophyte tissue, and plant community samples. Wet- and dry-season samples were collected at about 240 marsh sites. Six system-wide synoptic surveys provided a spatial data base from which a full range of water depths could be compared with other key interacting variables.
- Selected variables (e.g., TOC, TP, SO<sub>4</sub>, S<sup>2-</sup>, THg, MeHg, tissue Hg, and BAF) illustrated changes among wet and dry cycles, seven geographic subareas, and system-wide gradients, which supported the interactive conceptual models being developed to address the spatial changes in the system.
- Important declines were observed in total phosphorus and mercury contamination in 1999.



#### **4.6.2 Use of Path Analysis to Integrate the Effects of Multiple Stressors on Mercury Contamination in the Everglades Ecosystem — *K. Thornton, FTN Associates Ltd. and J. Stober, USEPA Region 4***

- USEPA Region 4 initiated a project in 1992 to assess the effects of mercury contamination on the South Florida Everglades ecosystem (see Section 4.6.1).
- Path analysis or structural equation models were developed based on the three conceptual models developed in Phase I of this project. Structural equation models are particularly applicable for survey-based data and have been used extensively in the socioeconomic sciences with statistical survey information. These structural equation models were used to determine the strength of associations among the variables included in the conceptual models.
- In general, there were significant differences in mercury pathways among the three areas. North of Alligator Alley, bottom-up (chemical) processes controlled mercury bioavailability and bioaccumulation. South of Tamiami Trail, in Everglades National Park, top-down (biological) processes controlled mercury bioaccumulation in fish. Between the Alley and the Trail, these processes interact in a dynamic transition zone.
- The bioaccumulation of mercury through the food chain appears to be analogous with models of eutrophication processes.
- Management implications were presented.

#### **4.6.3 METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and Methylmercury Concentrations of Fish — *J. Rudd, Department of Fisheries and Oceans Canada and R. Harris, Tetra Tech Inc.***

- METAALICUS is a whole-ecosystem experiment for assessing impacts to fish mercury concentrations when there is a change in atmospheric mercury deposition. Three stable, nonradioactive isotopes of inorganic mercury [Hg(II)] will be added to a headwater lake and an ELA watershed to track mercury flow separately from the background mercury.
- METAALICUS is being carried out in two phases over a five-year period. Phase 1 pilot studies performed in 1999–2000 determined whether stable isotope additions to whole ecosystems are feasible, and to give the team a preview of how newly deposited stable isotopes of Hg(II) will move through the terrestrial and aquatic ecosystems and be methylated and bioaccumulated by fish and food-chain organisms.
- In addition to the practical information obtained, the pilot studies are yielding fundamental new information about the cycling of mercury in terrestrial and aquatic ecosystems.

- After  $^{202}\text{Hg}(\text{II})$  was added to an upland catchment at the ELA, isotopic and ambient mercury movement was tracked to the atmosphere, through soils (including methylation), and from the catchment as outflow.
- Initially, the newly deposited mercury was more reactive than the very large mercury pool that had accumulated in the soils over many decades. For example, evasion rates and methylation rates of isotopic mercury were initially higher than those for the ambient mercury pool. However, in the longer term, over the first growing season, only about 8% of the  $^{202}\text{Hg}(\text{II})$  was lost to the atmosphere, and only 0.3% of the  $^{202}\text{Hg}(\text{II})$  was exported from the upland catchment.
- The isotopic mercury also eventually equilibrated with the mercury in the entire soil column and became indistinguishable from the large ambient mercury pool. Thus, most of the mercury exported during the first growing season was “old” mercury (>99%), which had been accumulating in the soils for many years.
- This result suggests that export of mercury from upland watersheds to lakes will respond slowly to expected decreases in the rate of atmospheric deposition of mercury. If mercury exported from upland watersheds is an important mercury source for in-lake methylation, fish mercury concentrations will respond slowly to expected decreased atmospheric deposition.
- In 2000,  $^{200}\text{Hg}(\text{II})$  was added to the same catchments to assess whether mercury movement throughout the upland ecosystem on a multiyear time frame could begin to be examined. Several isotopic additions were also made at the microcatchment scale to assess the mechanisms governing the transport of newly deposited mercury at the subcatchment scale.
- In 2000,  $^{200}\text{Hg}(\text{II})$  was added to four 10-m diameter lake enclosures. The enclosures received varying doses of  $^{200}\text{HgCl}_2$  at the beginning of the experiment and at discrete time intervals to simulate whole-lake addition.
- Preliminary results demonstrated loss of  $^{200}\text{Hg}(\text{II})$  to the atmosphere, and rapid movement of  $^{200}\text{Hg}(\text{II})$  to the periphyton on the sediment surface and walls of the enclosure, but minimal movement into sediments.
- Production of  $^{200}\text{Hg}[\text{MeHg}]$ , uptake of  $^{200}\text{Hg}[\text{MeHg}]$  by small fish, and uptake of inorganic  $^{200}\text{Hg}$  and  $^{200}\text{Hg}[\text{MeHg}]$  by zooplankton were also detected.

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## SECTION 5

### SUMMARY OF THE PANEL DISCUSSIONS

Brief presentations were given on each of the workshop sessions. In addition to a brief summary of each session, each panel speaker was asked to briefly discuss what is known and not known about various research efforts, and future research needs.

#### **5.1 Mercury And Methylmercury Transport in The Environment – *David Krabbenhoft***

This session focused on aquatic and terrestrial transport of mercury and methylmercury in the environment.

##### **5.1.1 What We Know**

- Sediment-water exchange research is needed so that aqueous mercury and methylmercury levels can be better understood. Current tests are difficult to execute in the field and results vary depending on the field approach used.
- Mercury fluxes developed using static porewater calculations are probably underestimated.
- Sediment cores provide useful data regarding changes in mercury concentration, deposition, etc., over time. These data can be used to assess mercury delivery to aquatic ecosystems; terrestrial versus atmospheric impacts; local, regional, and global impacts; and the historical impacts of man.
- Methylmercury production and delivery mechanisms vary by wetland type.
- Mercury, and sometimes methylmercury, fluxes from thru-fall and litter-fall can be significant. When mercury deposition exceeds deposition estimates, it is important to resolve where the “extra” mercury originated.
- Very large fluxes of mercury are occurring in the Arctic. These fluxes have global implications and possibly significant local effects. Interactions with halogen cycling need to be considered when addressing this issue.
- Estimates of “natural or geologic” sources of mercury have been underestimated.
- Fluxes from mercury-enriched soils and geologic materials are large and strongly diel.
- The impact of sulfate loading on methylmercury production in wetland systems may equal or exceed that of mercury loading.

- In boreal ecosystems, stream runoff to wetlands is more effective in delivering methylmercury to downstream aquatic ecosystems than groundwater.
- In aquatic ecosystems, the colloidal transport of mercury and methylmercury is an important, if not a dominant, vector in the movement of mercury and methylmercury.
- Diffusion coefficients for mercury and methylmercury vary widely, depending on speciation, and are difficult to select when performing flux calculations.

### **5.1.2 What We Don't Know**

- The best approach for estimating sediment-water exchange, although chambers appear to give realistic values.
- A simpler method for selecting diffusion coefficients for mercury when performing flux calculations.
- Whether future core data will corroborate lower methylmercury production rates observed in recent methylmercury studies.
- The impact that wetland type can have on methylmercury production and downstream delivery.
- The origin of the “added mercury and methylmercury” associated with thrufall/litterfall. This question has global implications.
- The reactants that drive mercury capture in the Arctic, and where this mercury currently resides.
- Implications for a larger geologic source estimate for the global mercury cycle.
- Whether the mechanisms that produce methylmercury in groundwater are the same as the mechanisms observed in surficial methylmercury production (e.g., sulfate reduction).
- Whether the chemical makeup of the colloids that transport mercury are similar or ecosystem specific.

### 5.1.3 Open Discussion

- Mercury needs to be examined from a more holistic, long-term perspective. Too much emphasis has been placed on freshwater ecosystems, and more attention needs to be placed on air/landscape transport mechanisms and ocean fluxes.
- Current ocean research is very limited, particularly when considering possible exposures due to fish consumption. More research is needed to better understand the ocean cycling of mercury, particularly with regards to flow from tributaries to coastal areas. Possible response times to reductions in global emissions would interest policy makers.
- Methylation can occur in a variety of locations (e.g., in the water column, in sediments, in the rain, in wetlands, etc.) It is important to determine if the location of methylation affects whether methylmercury will enter fish.
- In one study presented during the workshop (see M. Marvin), methylation decreased after sulfate was added. However, in general, sulfate addition appears to have a significant positive effect on methylation. Additional research is needed to address this discrepancy.
- The biotic transport of methylmercury needs to be considered more often. However, the generalization that methylmercury resides in biological organisms has to be tempered by the bioenergetics of the system. If a system does not support a dense standing crop population, then most of the methylmercury is not being stored biologically, and methylmercury transport will not be dominated by biological organisms. Conversely, in systems with a large standing crop and a great deal of turnover of biological material, biological organisms can dominate methylmercury transport. Researchers need to understand the following phenomena before discussing the importance of biological storage relative to other transport pathways: 1) the carbon budget; 2) the bioenergetics of carbon transfer and energy transfer efficiencies; and 3) standing crops of various organisms and their affinity for methylmercury.
- Not much is known about mercury in groundwater, particularly from anthropogenic influences. More research is needed in this area.
- When using a sediment core profile, it is important to assess methylmercury to first establish that the methylmercury is not mobile in the sediment.
- Researchers need to report pH and Eh (redox potential) when sulfate is added during their studies.

## **5.2 Methylmercury Production in The Environment – *Cynthia Gilmour***

This presentation included a brief summary of major points from the session followed by a recommendation for more research in the microbial ecology of methylation.

### **5.2.1 What We Know**

- Locations of methylmercury formation and ecosystem types sensitive to methylation are both well known. Understanding of the bioavailability of mercury for methylation is growing quickly.
- Sulfide models may be used to predict methylmercury production in high sulfide systems in the near future.
- The relationship between sulfide and sulfate is very complex. Sulfate can stimulate the activity of the microorganisms that produce methylmercury, while sulfide inhibits methylation by producing a mercury complex that cannot be taken up by cells. The balance between these two processes controls how sulfur affects mercury methylation.
- Sulfur-reducing bacteria are important methylators. Although sulfate stimulates methylation in most low-sulfate ecosystems, it is a poor predictor of methylation across freshwater ecosystems.

### **5.2.2 What We Don't Know**

- Although methylation appears to be more sensitive to temperature and chemistry than demethylation, little is known about demethylation relative to methylation. As a result, methylation is often considered a more important indicator of methylmercury concentrations than demethylation. More information is needed about demethylation.
- More information is needed about which species methylate mercury and how these species are distributed in order to be able to model mercury methylation in freshwater ecosystems.
- The relative importance of mercury complexation versus the activity of methylating bacteria is poorly understood. To improve models for methylation, more information is needed about the organisms that methylate mercury and how they are distributed.

### **5.2.3 Open Discussion**

- Research efforts have focused on methylation in ecosystems. Not enough is known about the biochemistry of methylation and the bacteria that methylate mercury. Research is needed to

- determine the biochemical pathway of the methylation reaction, particularly the identity of a currently unknown enzyme that is active in methylation but has never been isolated.
- The focus on freshwater ecosystem research is derived from the agencies funding the research [i.e., USEPA, USGS, and the Food and Drug Administration (FDA)]. These agencies are concerned with the effects of mercury primarily on human health and, to a lesser extent, on ecosystems. However, the oceans are tremendously important globally and from a human health perspective.
- In marine studies performed in a high-sulfide marsh, sulfides did not have a significant negative impact on methylation rates (e.g., methylmercury production), even at elevated concentrations. The interplay between the chemistry and microbial activity needs to be better understood.
- Methylation rates are highly subject to community structure. Pure cultures have been used in sediments to show, with real world systems, that methylation rates can differ by as much as 100 times based on phylogenetic group (e.g., from  $10^{-5}$  to  $10^{-7}$  moles of methylmercury per mole of sulfate reduced). The distribution of the phylogenetic groups is driven by a system's internal source of carbon (e.g., bioavailability). It may be possible to manipulate conditions (e.g., via the carbon cycle) to inhibit sulfate-reducing bacteria activity by encouraging competing bacteria to limit methylmercury production.
- Researchers can normalize methylation rates with respect to sulfate reduction rates to normalize the data relative to the base activity of the sediment in marine systems. In some cases, differences in methylation rates may be caused by the inhibition of microbial populations rather than the inhibition of the methylation process.
- The static porewater flux approach does not consider the dynamic production of methylmercury, which is very active in the top layer. Actual methylmercury production needs to be considered in addition to the diffusive transport.
- Coastal and urban airsheds have a higher concentration of halides and experience a significant amount of photochemical activity. More information is needed regarding mercury inputs to airsheds, including the chemical composition of the output and downwind impacts.
- More information is needed on the atmospheric production of methylmercury. Atmospheric deposition can contribute up to half the methylmercury deposition to some areas (e.g., Lake Superior). Also, the only known direct sources of methylated gas phase emissions in the Midwest and Florida are associated with municipal sludge-amended soils and landfill gas.
- It is important to determine whether methylmercury is photodegraded as soon as it enters an ecosystem (e.g., Lake Superior) or whether it is quickly taken up by organisms.



### **5.3 STAR Program Review – *James Hurley***

This presentation contained general observations about the STAR Program and its mercury research efforts.

#### **5.3.1 What We Know**

- Bioavailability plays a key role in mercury uptake and incorporation in the food web. The mechanisms that regulate the bioavailability and bioaccumulation of mercury are being researched (e.g., the bioavailability of inorganic mercury for methylation and the bioavailability of methylmercury up the food chain).
- Chemical speciation of Hg(II) and methylmercury dictates bioavailability, particularly with respect to 1) neutral species ( $\text{HgSO}_4$ ) diffusion versus facilitated transport, and 2) redox effects on sorption/complexation.
- Stable mercury isotopes may help unravel pathway analysis and resolve source allocation issues.
- Natural fractionation of mercury sources may provide insight for addressing pathway and source allocation questions.
- Methods to model and measure mercury fluxes (sediment-to-water, air-to-water, air-to-soil) remain a research challenge.
- Different approaches to flux estimates give widely different results, particularly with respect to air-water and air-soil flux calculations versus measured fluxes.
- Redox status affects mercury fluxes, especially at the sediment-water interface. Because flux processes can be rapid (e.g., occur in minutes), field approaches need to be developed to examine how chemical status affects mercury flux.

#### **5.3.2 What We Don't Know**

- The precise dominant ligands (e.g., the mercury-sulfur relationship) and their formation constants need to be identified. Direct approaches are being used to examine reactivity, size fractionation, etc., to determine the dominant ligands.
- The bioavailability of “new” versus “old” mercury in ecosystems is being investigated. This is important from both policy and research perspectives.
- Although redox processes are better understood, certain factors (reducing and oxidizing agents) still need to be defined/assessed.

### 5.3.3 Open Discussion

- Important research that could not be performed because funding was unavailable includes
  - direct ways to measure the ligands responsible for complexation and bioavailability.
  - increased monitoring of deposition near sources.
  - direct effects of local deposition out of the stack to a lake or through a lake.
  - atmospheric research that examines how methylmercury is formed and why it is seen in rain.
- A molecular probe is needed for measuring mercury-methylating bacteria and mercury formation in the oceans.

## 5.4 Management of Mercury Contamination in Aquatic/Terrestrial Systems – *Luke Trip*

In addition to summarizing the policy issues associated with mercury relative to what we know and what we do not know, Mr. Trip also included some observations about these issues.

### 5.4.1 What We Know

- In many locations, mercury concentrations in fish are at levels of concern for both human health and wildlife, as demonstrated by expanding fish advisories. More information is needed on the validity of using fish advisories to assess and respond to human health risk.
- Regional deposition gradients are observed in some areas (e.g., Sweden) showing the importance of local versus longer range emissions.
- Contaminated sites (e.g., mining districts and other locations) can impact biotic mercury levels for decades after activity ceases. Increases in the use of hydroelectric power need to be assessed relative to mercury methylation impacts associated with flooding.
- Bioaccumulation factors are imperfect parameters for describing mercury uptake by biota.
- Concerted international action will be needed to address the mercury problem worldwide, particularly since increasing mercury emissions from other continents may be depositing mercury, via long-range transport, in North America.

### 5.4.2 What We Think We Know

- Data on mercury emissions to the atmosphere in industrial countries over the past two to three decades are ambiguous, but some inventories suggest declining emissions over this period. Mercury deposition may have also decreased during this period although the supporting data (e.g., from sediment cores) are more ambiguous.

- Measured data and modeling indicate a relatively close relationship between atmospheric mercury loadings and fish tissue levels in the Everglades, and decreased loadings are predicted to result in decreased tissue levels with time. Continued monitoring is needed to confirm observations and predictions.
- Relatively simple watershed and aquatic pollutant-fate models could be used to estimate a system's response to decreased mercury loadings via a TMDL approach.

#### **5.4.3 What We Don't Know**

- Emissions from developing countries have not been accurately quantified. Developing and newly developed countries (e.g., Mexico) need help to develop emission inventories.
- More information is needed on the interplay of multiple factors affecting biotic mercury levels and implications for policy decisions.
- More information is needed on the importance of direct deposition, thru-fall, and litter-fall on mercury loadings to terrestrial systems, and the implications for responses to policy decisions.

#### **5.4.4 Open Discussion**

- Changing economic drivers associated with the need for more energy (e.g., in California) and more water (in Florida) may have a significant impact on mercury inputs to the environment. The environmental community needs to be aware of the impacts that economically driven decisions can have on mercury inputs to the environment.
- USEPA is developing a long-term, multi-media monitoring strategy for persistent, bioaccumulative, and toxic chemicals (PBTs), such as mercury and polychlorinated biphenyls. Input is needed regarding what approaches should be used to monitor the emission, transport, fate, and deposition of these chemicals.
- A highly empirical approach involving a large quantity of data is needed to effectively use simple watershed/water quality models for TMDLs.
- A number of TMDLs for mercury will be required throughout the United States to address the large number of water bodies that are considered impaired due to mercury. A more streamlined approach is needed that does not require an excessive amount of costly, site-specific, empirical data. The scientific-policy community needs to develop recommendations that state agencies with limited budgets (e.g., less than \$50,000) can use to develop TMDLs. A number of practical constraints also need to be addressed before a full-scale mercury cycling model can be implemented to address TMDLs for an impaired water body.

- Some inventories have shown a two-fold decrease in emissions over the last two decades in Europe and the United States. However, more information is needed regarding how the system is responding to these reductions, particularly with respect to expected decreases in deposition, which have not yet been observed.
- More information is needed to address the ambiguity associated with using sediment cores to assess deposition within the last 15 years.
- A number of information gaps need to be addressed to improve emission inventories, particularly with regard to uncertainties in developing countries. Emissions inventories should attempt to quantify contributions using data measurements rather than estimates.
- Current deposition monitoring data are not of sufficient duration to track longer-term responses to reductions in mercury emissions. In some cases, more recent efforts (e.g., through MDN) may have missed a possible major decline in deposition. Responses can vary depending on location and data- collection methods. For example, sediment core data indicate very substantial drops in deposition in some urban areas (e.g., in the upper Midwest).

## **5.5 Bioaccumulation of Mercury in Aquatic Food Webs – *James Wiener***

This presentation summarized some of the issues associated with the bioaccumulation of mercury in aquatic foods webs relative to what the scientific community currently knows and doesn't know.

### **5.5.1 What We Know**

- High concentrations of mercury, sufficient to prompt fish-consumption advisories, are present in fish from surface waters not affected by direct discharges of mercury.
- Spatial variation in fish-mercury concentrations is attributed to differences among surface waters and their watersheds, particularly their tendency to convert inorganic mercury to methylmercury and their tendency to deliver the mercury to an aquatic environment where it can enter the food web.

- In a national pilot study (mostly NAWQA streams; Brumbaugh et al.), mercury concentrations in fish were correlated with concentrations of methylmercury in water, with lesser influences by pH and wetland density.
- The net rate of microbial conversion of inorganic Hg(II) to methylmercury in aquatic sediments or adjoining wetlands (i.e., M/D) appears to be a key process influencing mercury levels in fish.
- Fish obtain methylmercury almost entirely through dietary uptake, which is influenced by size, diet, and food-web structure.
- The bioaccumulation of mercury in largemouth bass within study sites in the Everglades is strongly correlated with trophic position. Efforts involving stable isotope analysis of fish and their diets are making a significant contribution to our understanding of this area.
- Mercury concentrations in piscivorous gamefish in Ontario (lake trout, walleye, northern pike) have not increased, as predicted, in response to invasions by rainbow smelt.

### **5.5.2 What We Don't Know**

- Concentrations of mercury in gamefish appear to be declining in some semi-remote or remote lakes (e.g., Ontario and Minnesota) and increasing in others (Minnesota). Factors causing these temporal changes have not been established. It would be useful to know what, if any, lake characteristics are associated with increases or decreases of fish mercury concentrations over time.
- The ecological effects of methylmercury exposure remain largely unknown and understudied. Laboratory and field studies are needed.
- Recent evidence suggests that the reproductive success and survival of fish are reduced by dietary exposure to methylmercury encountered in waters with contaminated food webs. The maternal transfer of mercury to fish eggs is currently being studied. Additional research is needed.
- Criteria for identifying ecosystems or landscapes that are sensitive to mercury bioaccumulation are needed. These criteria can be used to identify areas that may pose mercury risks.
- Whether landscapes can be managed to decrease the production of methylmercury and reduce contamination of our aquatic and fishery resources.

### **5.5.3 Open Discussion**

- Research should not focus on fish bioaccumulation. There are a lot of other lower and higher trophic organisms that can provide valuable information (e.g., loons) on other wildlife effects, including top predators. Groundwork is needed for future studies that examine food sources for other organisms.
- A number of good ecological risk assessments have been performed on top predators (e.g., great egrets, alligators, and racoons) that contain exposure measurements, but do not include well-developed toxicological endpoints. More population studies are needed to improve these endpoints. These studies should involve organismal and population biologists.
- Researchers should try to archive their sediment samples for future research efforts.

### **FIELD TRIP TO THE EVERGLADES**

The South Florida Water Management District (SFWMD) and the State of Florida are undertaking a water quality management program in the Everglades to reduce phosphorus pollution by runoff from urban areas and farmlands. This involves construction of over 40,000 acres of Stormwater Treatment Areas (STAs). In the early 1990s, the District constructed a 3820-acre pilot-scale treatment wetland, the Everglades Nutrient Removal Project (ENRP), to test this concept. The ENRP, now subsumed by one of the larger STAs, was the site of much intensive mercury research and monitoring and was carefully mass balanced for mercury species during the “proof of concept” phase of STA operation. The field trip visited the ENRP and gave participants a view of the Everglades and of this massive environmental restoration program. Field trip guides discussed the extensive mercury monitoring, modeling, and research conducted at the ENRP and other sites. Additional information can be found on the SFWMD web site (<http://www.sfwmd.gov>).

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## APPENDIX A

### WORKSHOP AGENDA

# Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments

**Tuesday, May 8, 2001**  
*(Combined session) - Regency ABCD*

7:00 AM	Registration Starts
<b>Plenary Session</b>	
8:00 - 8:10 AM	Opening Remarks - <i>Scott Minamyer, USEPA</i>
8:10 - 8:30 AM	USEPA - <i>Doug Grosse, USEPA</i>
8:30 - 8:50 AM	USGS/EPA Round Table - <i>Sarah Gerould, USGS</i>
8:50 - 9:10 AM	State of Florida/Mercury Science Program - <i>Tom Atkeson, Mercury Program, FDEP</i>
9:10 - 9:30 AM	EPA STAR Program - <i>Bill Stelz, USEPA</i>
9:30 - 9:45 AM	Electric Power Research Institute - <i>Leonard Levin, EPRI</i>
9:45 - 10:00 AM	National Wildlife Federation - <i>Mike Murray, National Wildlife Federation</i>
10:00 – 10:30 AM	Break
10:30 - 11:15 AM	Keynote Number 1: Atmospheric Deposition Overview - <i>Gerald Keeler, University of Michigan</i>
11:15 - 12:00 PM	Keynote Number 2: An Old Dog Looks Backward: Historic Perspectives on Mercury - <i>Don Porcella, Environmental Science and Management</i>
12:00 – 1:25 PM	Lunch



**Tuesday, May 8, 2001**

	<i>(Concurrent Sessions)</i>	
	Session A: Mercury and Methylmercury Transport in the Environment <i>(Chair: Dave Krabbenhoft, USGS)</i>	Session B: Bioaccumulation of Mercury in Aquatic Food Webs <i>(Chairs: Paul Randall and Scott Minamyer, USEPA)</i>
Room	Gallery	Regency ABC
1:25 - 1:30 PM	Session Introduction	Session Introduction
1:30 - 2:00 PM	Determination of the Sediment-Water Exchange of Mercury and Methylmercury: Approaches, Limitations and Observations – <i>G. Gill, Texas A&amp;M University</i>	Evolution of a Contaminant Problem: Mercury in Freshwater Fish - <i>J. Wiener, University of Wisconsin-La Crosse</i>
2:00 - 2:30 PM	Mercury and Methylmercury Accumulation in Lake Sediments: Can We Infer from Dated Cores? – <i>D. Engstrom, Science Museum of Minnesota</i>	Projecting the Population-Level Effects of Mercury on the Common Loon in the Northeast - <i>D. Evers, BioDiversity Research Institute</i>
2:30 - 3:00 PM	An Overview of Mercury Cycling in the Boreal Ecosystem – <i>V. St. Louis, University of Alberta</i>	USGS National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients: Bioaccumulation in Fishes - <i>W. Brumbaugh, Columbia Environmental Research Center</i>
3:00 – 3:30 PM	Break	
3:30 - 4:00 PM	Is the Arctic a Missing Sink for Mercury?: New Measurements of Depletion Events, Deposition and Speciation in Air and Snow at Point Barrow Alaska – <i>S. Lindberg, ORNL</i>	Interactions of Trophic Position and Habitat with Mercury Bioaccumulation in Florida Everglades Largemouth Bass ( <i>Micropterus salmoides</i> ) - <i>T. Lange, Florida Fish and Wildlife Conservation Commission</i>
4:00 - 4:30 PM	Putting into Perspective Mercury Emissions from Geologic Sources – <i>M. Gustin, University of Nevada-Reno</i>	Bioaccumulation of Mercury in the Everglades: Patterns in the Foodweb - <i>J. Trexler, Florida International University</i>
4:30 - 5:00 PM	Mercury Cycling in the Boreal Forest: Insights from Models, Experiments and Isotopes - <i>B. Branfireun, University of Toronto</i>	Effects of Rainbow Smelt Invasion on Mercury Concentrations of Predatory Fishes of Northwestern Ontario and Manitoba, Canada - <i>D. Bodaly, Department of Fisheries and Oceans Canada, Freshwater Institute</i>
5:30 – 7:00 PM	Poster and Mixer Session - Regency DE	

### Wednesday, May 9, 2001

	<i>(Concurrent Sessions)</i>	
	Session C: STAR Program Review <i>(Chair: Bill Stelz, USEPA)</i>	Session D: Managing Mercury Contamination in Aquatic/Terrestrial Systems <i>(Chairs: Leonard Levin, EPRI and Mike Murray, National Wildlife Federation)</i>
Rooms	Gallery	Regency ABC
8:25 - 8:30 AM	Session Introduction	Session Introduction
8:30 - 9:00 AM	Watershed Influences on the Transport, Fate and Bioavailability of Mercury in Lake Superior - <i>J. Hurley, University of Wisconsin</i>	An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed: A CALFED Study - <i>C. Foe, Central Valley Regional Water Quality Control Board</i>
9:00 - 9:30 AM	Factors Controlling Methylmercury Production in Sediments and Fate in Aquatic Systems - <i>R. Mason, University of Maryland</i>	An Evaluation of EPA's Bioaccumulation Factor (BAF) for Mercury: A Regulated Industry Perspective - <i>R. Reash, American Electric Power</i>
9:30 - 10:00 AM	Response of Methylmercury Production and Accumulation to Changes in Hg Loading: A Whole-Ecosystem Mercury Loading Study - <i>C. Gilmour, The Academy of Natural Sciences</i>	Methylmercury in Terrestrial Ecosystems - Summary of Swedish Research - <i>John Munthe, IVL Swedish Environmental Research Institute</i>
10:00 – 10:30 AM	Break	
10:30 – 11:00 AM	Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition? - <i>J. Jeremiason, Minnesota Pollution Control Agency</i>	Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades (ACME) Phase II - <i>D. Krabbenhoft, U.S. Geological Survey</i>
11:00 – 11:30 AM	Photochemistry of Mercury in Saginaw Bay Watershed, Michigan: Annual EPA STAR Project Meeting - <i>J. Nriagu, University of Michigan</i>	Modeling Mercury Fate in Seven Georgia Watersheds - <i>R. Ambrose, Jr., U.S. EPA</i>
11:30 – 12:00 PM	Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern U.S. - <i>C. Driscoll, Syracuse University</i>	Fitting into the North American Mercury Emissions Reduction Priority - <i>L. Trip, Environment Canada</i>
12:00 – 1:25 PM	Lunch	

11:30 – 12:00 PM	<i>(Concurrent Sessions)</i>	
	Session C: STAR Program Continued <i>(Chair: Bill Stelz, USEPA)</i>	Session E: Methylmercury Production in the Environment <i>(Chair: Tom Atkeson, Florida Dept. of Environmental Protection)</i>
Rooms	Gallery	Regency ABC
1:25 - 1:30 PM	Session Introduction	Session Introduction
1:30 – 2:00 PM	Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury from Contaminated Mine Sites - <i>G. Brown, Stanford University</i>	Overview of Microbial Methylmercury Production and Degradation: What do we know? What don't we know? - <i>C. Gilmour, The Academy of Natural Sciences</i>
2:00 – 2:30 PM	Microbiological and Physiochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones - <i>W. Fitzgerald, University of Connecticut</i>	Environmental Controls on Methylmercury Production and Degradation in Florida Everglades Sediment - <i>M. Marvin-DiPasquale, U.S. Geological Survey</i>
2:30 – 3:00 PM	Redox Transformation of Mercury - <i>F. Morel, Princeton University</i>	Group VI Anions and Mercury Transformation within the S-cycle in the Carson River System, Nevada - <i>J.C. Bonzongo, University of Florida</i>
3:00 – 3:30 PM	Break	
3:30 – 4:00 PM	Assessing the Role of Plants in the Biogeochemical Cycle of Mercury – <i>M. Gustin, University of Nevada</i>	A Bacterial Biosensor for Aquatic Hg(II) Speciation and Bioavailability - <i>P. Barrocas, Florida State University</i>
4:00 – 4:30 PM	Mercury and Methylmercury Burdens in Sediments, Water, and Biota of VT and NH Lakes, and Trends in Paleolimnology-Inferred Mercury Deposition to VT and NH – <i>N. Kamman, VT Department of Environmental Conservation</i>	Facilitated Uptake of Mercury at Trace Concentrations by <i>Eschericia coli</i> and <i>Vibrio anguillarum</i> - <i>G. Golding, University of Manitoba</i>
4:30 – 5:00 PM	Mercury in Fishes and Sediments of Clear Lake, California: Defining the Problem and Developing Cleanup Options through the USEPA Superfund Program - <i>Ellen Manges, USEPA</i>	Mercury Transport and Transformation in the Wider Idrija Region and the Gulf of Trieste - <i>Milena Horvat, Institute Jozef Stefan</i>
5:00 - 5:30 PM	N/A	The Everglades Mercury Cycling Model (E-MCM): Development and Application to Two Marsh Sites in the Florida Everglades - <i>R. Harris, Tetra Tech, Inc.</i>
5:30 – 7:00 PM	Poster and Mixer Session	

**Thursday, May 10, 2001**

	<i>(Combined Session) - Regency ABCD</i>
8:00 – 8:30 AM	Landscape Patterns of Mercury Contamination Across the Everglades Ecosystem - <i>J. Stober, USEPA Region 4</i>
8:30 - 9:00 AM	Use of Path Analysis to Integrate the Effects of Multiple Stressors on Mercury Contamination in the Everglades Ecosystem - <i>K. Thornton, FTN Associates Ltd.</i>
9:00 – 10:00 AM	METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and Methylmercury Concentrations of Fish - <i>J. Rudd, Department of Fisheries and Oceans Canada</i> and <i>R. Harris, Tetra Tech Inc.</i>
10:00 – 10:30 AM	Break
10:30 – 11:45 AM	Panel Discussion (Facilitator: Dave Krabbenhoft, USGS)
11:45 – 12:00 PM	Summary and Adjourn
1:00 – 5:30 PM	Everglades Field Trip - Meet in lobby

## **Poster Presentations**

**May 8 - 9, 2001**

**5:30 - 7:00 PM**

**Regency DE**

**C. Alpers, U.S. Geological Survey** - Mercury and Methylmercury in Water, Sediment, and Biota in an Area Impacted by Historic Gold Mining: The Bear River and South Yuba River Watersheds, California

**C. Babiarz, University of Wisconsin** - Partitioning of Mercury to the Colloidal Phase in Fresh Waters

**R. Back, Lake Superior State University** - Mercury Content and Speciation of the Plankton and Benthos of Lake Superior

**J. Barringer, U.S. Geological Survey** - Distribution of Mercury in Shallow Ground Water of the New Jersey Coastal Plain and a Possible Mechanism of Transport

**N. Belzile, Laurentian University** - The Positive Effect of Selenium on Mercury Assimilation by Freshwater Fish

**J. Benoit, Princeton University** - Chemical and Biological Controls on Methylmercury Production in Aquatic Sediments

**A. Chalmers, U.S. Geological Survey** - Mercury Distribution Along an Urban Gradient in New England Streams

**S. Duvall, Waterstone Environmental Hydrology and Engineering, Inc.** - A Screening Level Probabilistic Risk Assessment of Mercury in Florida Everglades Food Webs

**G. Edwards, University of Guelph** - Measurements of Mercury Fluxes from Natural Sources

**A. Green, Ohio State University** - Mercury Concentrations in Water and Fish from the Mobile-Alabama River Basin: A Preliminary Assessment

**S. Harting, Michigan Technological University** - Mercury in Keweenaw Waterway and Lake Superior Sediments: Sources, Dispersal, and Behavior

**A. Heyes, University of Maryland** - The Effect of Sediment Disturbance on Methylmercury Production in Estuarine Sediment

**A. Hynes, University of Miami** - Rapid, Ultra-Sensitive Detection of Gas Phase Elemental Mercury Under Realistic Atmospheric Conditions Using Sequential Two-Photon Laser Induced Fluorescence - A Viable Sensor for Eddy-Correlation Measurements

**R. Jacquet, Solvay SA** - Ionic Mercury Adsorption to Soils --The Influence of Physico-Chemical Parameters Relevant to Industrial Site Situations

**D. Jewett, USEPA ORD NRMRL** - Hydrogeological and Geochemical Factors Influencing Mercury Fate and Transport at the Sulphur Bank Mercury Mine, Lake County, California

**C. Kelly, Freshwater Institute** - Is "Reactive" Mercury (Stannous Chloride Reducible) a Good Indicator of Bioavailable Mercury in Water?

**C. Kendall, USGS** - Effects of Temporal and Spatial Variability in Food Webs on Bioaccumulation of Hg in the Everglades: The Combined Use of Stable Isotopes, Gut Contents, and Hg/MeHg Data

**C. Kendall, USGS** - Spatial and Temporal Changes in Foodweb Structure and Biogeochemical Reactions in the Everglades

**C. Kim, Stanford University** - Determining Mercury Speciation in Natural Environmental Systems Using X-ray Absorption Fine Structure (XAFS) Spectroscopy

**T. Lange, Florida Fish and Wildlife Conservation Commission** - Trends of Mercury Bioaccumulation in Largemouth Bass (*Micropterus Salmoides*) from the Florida Everglades

**E. Lapshin, University of Southampton** - Mercury in Industrial Landscapes of Former USSR: A Case of Kazakhstan

**E. Lapshin, University of Southampton** - Microbiological Processes in Regions of Mercury Contamination: Special Circumstances and Studies in Kazakhstan

**E. Lapshin, University of Southampton** - The Influence of pH and Redox Conditions to the Methylation of Mercury in Freshwater Sediments

**S. Lindberg, Oak Ridge National Laboratory** - Atmospheric Mercury Emissions from Municipal Solid Waste Landfills

**S. Lindberg, Oak Ridge National Laboratory** - Evaluation on Environmental Factors Affecting Gaseous Hg Emission from Subtropical Vegetation in the Florida Everglades

**M. Lindeman, Blasland, Bouck & Lee, Inc.** - The Fate and Cycling of Mercury in the Sunday Lake Watershed, Adirondack Mountains, New York: A Preliminary Mass Balance

**P. Lorey, Syracuse University** - Historical Trends of Sediment Mercury Deposition in Adirondack Lakes

**B. Lourie, York University** - Standard Setting for Electric Power Generation: A Review of Risk and Uncertainty

**E. McLaughlin, University of Maryland Center for Environmental Science** - Mercury Concentrations in Water Bodies and Fish of Western Maryland

**K. Rolfhus, University of Wisconsin-Madison** - The "Reservoir Effect": Synthesis and Biological Uptake of Methylmercury in Seasonally Inundated Systems

**J. Rytuba, U.S. Geological Survey** - Release and Transport of Mercury in Watersheds Impacted by Mercury Containing Mineral Deposits

**P. Schuster, U.S. Geological Survey** - The Influence of Organic Carbon on the Mobility of Mercury in Contrasting Ecosystems

**K. Scott, University of Manitoba** - Methylmercury and Bioavailable Hg(II) in Arctic Snow During Polar Sunrise

**J. Shanley, U.S. Geological Survey** - Episodic Transport of Mercury in Streamwater

**C. Sharpe, Syracuse University** - Mercury Dynamics and a Hypolimnetic Model of Onondaga Lake, NY

**S. Shaw** - Physical and Chemical Properties of Hg-Bearing Colloids Released from New Idria and Sulfur Bank Mercury Mine Tailings

**C. Sweet, Illinois State Water Survey** - Wet Deposition of Mercury in Florida, 1995-2000

**Y. Tatsy, Vernadsky Institute of Geochemistry and Analytical Chemistry** - Crust Degassing Mercury Flux: The Role in Evaporation from Soil

**A. VanArsdale, USEPA New England** - Mercury Flux from Tidal Sediments Located in an Isolated Bay in the Great Bay Estuary of New Hampshire

**K. Warner, The University of Alabama** - Effect of Different Electron Accepting Conditions on Net Microbial Mercury Methylation Potential in Mineral-Rich Sediments

**APPENDIX B**  
**SPEAKER ABSTRACTS**

**Session A:**

**Mercury and Methylmercury Transport in the Environment**



## **Determination of the Sediment-Water Exchange of Mercury and Methylmercury: Approaches, Limitations and Observations**

**Gary A. Gill**

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Sediment-water exchange fluxes are generally determined using two approaches: an indirect determination based on modeling of interstitial pore water concentration gradients and a direct approach using benthic flux chambers. Our laboratory has used both approaches for mercury and methylmercury flux determinations in a variety of aquatic systems including freshwater lakes, the Everglades, and estuarine systems. Interpretation of these fluxes needs to be viewed in terms of the limitations associated with the sampling approach and environmental setting. For example, flux chamber results give short term (few hours to a few days) instantaneous determinations which may, or may not, be in steady-state relative to the sampling interval. Pore water gradient modeling usually portrays a longer term trend and can give biased results depending on resolution capability and biogeochemical processes acting in surficial sediments. Obtaining a reliable estimate of the diffusion of aqueous mercury species out of near surface sediments depends critically on knowledge of the chemical species involved, the ability to resolve the near surface concentration gradient with sufficient precision, and spatial heterogeneity issues. Sampling of interstitial pore water gradients has been successfully accomplished using whole core squeezing, sectioning and centrifugation, and in situ dialysis (peepers). While often more operationally complex, whole core squeezing has advantages of larger sample sizes. In situ dialysis has limitations associated with long equilibration periods and residual oxygen introduction into anoxic or sub-oxic sample from gas trapped in the peeper construction materials (e.g., Teflon). Benthic flux chambers operate by capturing a sample of bottom water in contact with sediments and allowing an incubation of this water at natural conditions. Limitations associated with chamber deployments often result from short duration sampling intervals relative to diel changes in surficial biogeochemical processes (e.g., light/dark cycles) and sediment heterogeneity. The relative importance of such process can vary widely between ecosystems. Good agreement between flux chamber and modeling approaches for the determination of mercury fluxes is not always obtained. If there is significant infaunal activity, flux chamber results can be appreciably higher than simple diffusion calculations.

## **Mercury and Methylmercury Accumulation in Lake Sediments — What Can We Infer from Dated Cores?**

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Lake-sediment records provide the most compelling evidence thus far that remote regions of the earth receive significant inputs of anthropogenic mercury by long-range atmospheric transport. Historic increases in deposition have been documented in a growing number of sediment records from North America and Europe, and more recently from polar regions and the southern hemisphere. From mid-latitude sites there is a convergence of data indicating that Hg deposition has increased by a factor of 3-4 since pre-industrial times, while from more remote parts of the globe the increase appears closer to a factor of 2. These findings have greatly improved our understanding of the global biogeochemistry of Hg by constraining source strengths for natural and anthropogenic processes.

The power of lake-sediment records lies in several areas: (1) they integrate short-term variations in mercury deposition, (2) they provide information on past deposition rates and recent trends, and (3) they provide a relative measure of impact that can be compared across large geographic areas. However, lakes are not simply passive recorders of atmospheric deposition, but impart their own signature on the Hg profiles that accumulate in their sediments.

Catchment soils export a portion of atmospheric Hg to downstream lakes, and these inputs increase significantly with the percentage of watershed area under urban or agricultural land-use. The size of the contributing watershed, the presence of wetlands and other upstream retention basins, and local hydrology and vegetation also influence catchment Hg inputs. Because Hg loading is enhanced by soil erosion and possibly runoff from impervious surfaces, it is difficult to disentangle land-use effects from elevated atmospheric Hg deposition in sediment records from urban areas. Hg losses through gaseous evasion and hydrologic outflows must also be considered when determining atmospheric Hg fluxes from lake-sediment records. Although it is thought that evasion may represent a substantial portion of the Hg budget in high-alkalinity lakes, such fluxes are typically modeled from infrequent measurements of Hg<sup>0</sup> saturation and are not well-constrained, especially on an annualized basis.

In the sediments themselves, Hg concentrations and accumulation rates are subject to additional errors of interpretation including dilution by the sediment matrix, dating uncertainty, and changes in sediment focusing. Sedimentation rates by most dating methods contain a high level of uncertainty, especially for older (preindustrial) strata, and the propagation of these errors into Hg flux calculations can produce spurious results. Changes in Hg accumulation may also reflect shifts in the pattern of sediment deposition within a basin, as opposed to changes in Hg input to the lake itself. The possibility that sediment focusing underlies an increase (or decrease) in sedimentation at a core-site is not easily recognized from single-core studies.

Although empirical and experimental evidence indicates that inorganic Hg(II) is diagenetically stable and does not readily diffuse in most lake sediments, the same may not be said for methylmercury (MeHg). A growing number of sediment records show recent increases in the methylated portion of total mercury (THg) which may represent historical changes in methylmercury production that are independent of the

flux of total mercury. However, these data also indicate that only a small portion of the MeHg present at the sediment surface is preserved deeper in the core. Factors affecting Hg methylation/demethylation within the sediment column will have to be resolved before sedimentary records can provide reliable reconstructions of aquatic MeHg exposure.

## **An Overview of Mercury Cycling in the Boreal Ecosystem**

**Vincent L. St. Louis<sup>1</sup>, John W.M. Rudd<sup>2</sup>, Carol A. Kelly<sup>2</sup>, Britt D. Hall<sup>1</sup>, Kristofer R. Rolfhus<sup>3</sup>,  
Karen J. Scott<sup>4</sup>, R. Drew Bodaly<sup>2</sup>, Ken Beaty<sup>2</sup>, and Steve E. Lindberg<sup>5</sup>**

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We will present an overview of methylmercury (MeHg) and total mercury (THg) cycling in the Boreal ecosystem at the Experimental Lakes Area (ELA) in northwestern Ontario. The forest canopy was an important contributor to fluxes of MeHg and THg to the forest floor of Boreal uplands and wetlands. The estimated fluxes of MeHg and THg in throughfall plus litterfall below the forest canopy were 2 and 3 times greater than annual fluxes by direct wet deposition of MeHg ( $0.9 \text{ mg MeHg ha}^{-1}$ ) and THg ( $71 \text{ mg THg ha}^{-1}$ ). Almost all of the high flux of MeHg and THg under the forest canopy occurred as litterfall. We found that average annual accumulation of MeHg and THg in the surficial litter/fungal layer of soils in a 20 year-old fire regenerated forest varied between  $0.6\text{-}1.6 \text{ mg MeHg ha}^{-1}$  and  $130\text{-}590 \text{ mg THg ha}^{-1}$  amongst sites differing in drainage and soil moisture. Four terrestrial Boreal forest catchments containing different types of wetlands were studied to determine their strength as sources or sinks of MeHg and THg. All catchments were sinks for THg, and percentage wetland area in the catchment did not appear to have consistent affects on the magnitude of this retention. Whereas purely upland catchments retained/demethylated MeHg, wetland areas of catchments were always net sources of MeHg, and there were large and consistent differences in the source strength among wetland types for MeHg. For example, the riverine wetland studied annually yielded  $\sim 3 \text{ mg MeHg ha}^{-1}$ , whereas a basin wetland yielded  $20 \text{ mg MeHg ha}^{-1}$  in one year. When the riverine wetland was flooded to simulate reservoir creation, it went from annually yielding  $\sim 3 \text{ mg MeHg ha}^{-1}$  to yielding  $70 \text{ mg MeHg ha}^{-1}$  due to Hg methylation associated with the decomposition of flooded organic matter. Annual yields of MeHg slowly decreased during the six years postflood to approximately  $15 \text{ mg MeHg ha}^{-1}$ . This increase in methylation in the reservoir immediately resulted in elevated MeHg concentrations in food web organisms.

**Is the Arctic a Missing Sink for Mercury? New Measurements of Depletion Events, Deposition, and Speciation in Air and Snow at Point Barrow, Alaska**

**S. E. Lindberg<sup>1</sup>, S. Brooks<sup>2</sup>, J. Lin<sup>3</sup>, K. Scott<sup>4</sup>, T. Meyers<sup>2</sup>, M. Landis<sup>5</sup>, and R. Stevens<sup>6</sup>**

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In the past decade many new sources of diffuse mercury emissions have been measured. These sources significantly increase the estimates of global Hg emissions, and suggest there may be missing Hg sinks in global models. Mercury levels in Arctic wildlife are elevated above normal levels, but there are few known Arctic Hg sources, and long range transport of Hg<sup>0</sup> must be considered. The discovery of mercury depletion events (MDE, similar to ozone depletion) at Alert, NWT suggests a mechanism for Hg accumulation from the global pool. One hypothesis is that Hg<sup>0</sup> is transformed into a reactive gaseous mercury (RGM) species which deposits locally. This species has never been measured in the Arctic, and MDE's must be confirmed at other Arctic sites.

We have measured total gaseous mercury concentrations (Hg<sup>0</sup>) at Point Barrow, Alaska since September 1998 in an effort to determine the geographic extent and reaction mechanism of the so-called mercury depletion events (MDE) previously reported in the high Arctic at Alert, Canada. Hg<sup>0</sup> has been sampled now for nearly 2 years at Barrow. In September 1999, we began making the first automated measurements of reactive gaseous mercury (RGM) attempted in the Arctic, along with measurements of Hg accumulation in snowpack to determine the fate of the "depleted" Hg<sup>0</sup>. During the fall and early winter, Hg<sup>0</sup> and RGM exhibit only minor variation, Hg<sup>0</sup> remaining within ~10% of global background, near 1.6-1.8 ng/m<sup>3</sup>. The MDE periods are quite different, however; within days of Arctic sunrise in January, Hg<sup>0</sup> exhibits major variations from the mean, rapidly dropping as low as 0.05 ng/m<sup>3</sup> and then cycling back to typical levels, sometimes exceeding global background. These events continue throughout Arctic spring, then end abruptly following snowmelt, in early June. Prior to Arctic sunrise, RGM remains near detection (<2 pg/m<sup>3</sup>), but after sunrise increases dramatically (to levels as high as 900 pg/m<sup>3</sup>) in synchrony with the "depletion" of Hg<sup>0</sup>. Both phenomena exhibit a strong diel cycle, in parallel with UV-B. We conclude that MDE's involve rapid in-air oxidation of Hg<sup>0</sup> to a species of RGM by photochemically-driven reactions, probably involving the same reactive bromine and chlorine compounds involved in ozone destruction. Sharp increases in Hg in the surface snowpack after sunrise coincident with periods of peak RGM suggest surface accumulation of the RGM by dry deposition.

Research sponsored by NOAA and the USEPA OIP under contract with ORNL. ORNL is managed by UT-Battelle for the U.S. Department of Energy.

## **Putting into Perspective Mercury Emissions from Geologic Sources**

**Mae Sexauer Gustin<sup>1</sup>, Mark Coolbaugh<sup>2</sup>, Mark Engle<sup>2</sup>, Brian Fitzgerald<sup>1</sup>,  
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Mercury emission from naturally enriched terrestrial landscapes constitutes a significant long term source of mercury to the atmosphere. Areas of natural Hg enrichment are concentrated in, but not limited to, three global belts associated with active plate boundaries. Mercury enrichment is associated with mercury, base and precious metal mineralization, areas of high crustal heat flow (geothermal areas), and areas of recent volcanic activity. This paper reports on the development of methods for scaling up mercury emissions from broad terrestrial areas and presents flux estimates for representative areas in the western U. S. Parameters used in scaling were developed based on the use of empirical data to assess those factors most important in controlling emissions. Geologic parameters, such as substrate mercury concentration, general geologic setting and type of rock hydrothermal alteration, and environmental parameters, such as temperature, light and precipitation, are used for determining area fluxes. Once emission estimates have been established for representative areas, this information is used along with an understanding of emission/re-emission from background sources to estimate mercury emissions from large areas. In general large areas with mercury concentrations in substrate slightly elevated (0.08 to 5  $\mu\text{g/g}$ ) above background concentrations contribute more mercury to the atmosphere than smaller areas of high enrichment. For example, 90% of the mercury emissions from the 230-km<sup>2</sup> area encompassing the New Idria Mining District of California were from undisturbed areas, whereas 10% were from mine waste and mining disturbed areas. A similar distribution of emissions was found for the Ivanhoe Mining District, NV. Mercury emissions from geologic sources in the state of Nevada, which lies within a global belt of mercury enrichment, are on the order of 14,000 kg/year. To put this into perspective, the estimated emissions from U.S. coal fired utilities in 1999 was 41,500 kg/yr.

## **Mercury Cycling in the Boreal Forest: Insights from Models, Experiments and Isotopes**

**Dr. Brian A. Branfireun**

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Nearly nine years of field investigations at the Experimental Lakes Area in Northwestern Ontario, Canada have contributed to the understanding of the mercury cycle in this susceptible environment. Pore water sampling revealed that peatlands were methylmercury (MeHg) “hot-spots” in the catchment, with the distribution of high MeHg zones being strongly linked to areas of groundwater upwelling. Field measurements and a catchment-scale model indicated that peatlands were large sources of MeHg, confirming the findings of previous mass balance studies. To further investigate the role of peatlands in boreal catchment Hg cycling, sulfate addition experiments were undertaken to examine the controls on MeHg production. It was found that the in situ addition of sulfate to peat and peat pore water resulted in an increase in pore water MeHg concentrations in both dose-and-response, and chronic sulfate loading experiments.

A whole-catchment study of hydrology and Hg processes indicated that hydrological flowpaths, the delivery of sulfate, carbon quality and temperature appear to influence the production of MeHg at a range of scales. In addition, the mass flux of MeHg within, and from the catchment is highly dependent upon the mass flux of water and the placement of landscape units in the catchment hydrologic cascade. Recent plot-scale experiments undertaken as part of the METAALICUS project has effectively utilized stable isotope Hg tracers to demonstrate the importance of antecedent moisture, soil quantity and composition, and vegetation cover in Hg fate and transport.

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**Session B:**

**Bioaccumulation of Mercury in Aquatic Food Webs**

## **Evolution of a Contaminant Problem: Mercury in Freshwater Fish**

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Scientific interest in the mercury contamination of aquatic food webs was heightened in the 1950s and 1960s, when it was discovered that human poisonings in Minamata, Japan, were caused by consumption of fish contaminated by a local industrial source of methylmercury. This tragedy prompted widespread reductions in direct releases of mercury into surface waters, and mercury levels in fish in industrially affected waters typically declined in the years and decades thereafter. High concentrations of mercury have since been found in fish from surface waters not affected by direct discharges of mercury; these include humic and low-alkalinity lakes, dark-water coastal streams, newly flooded reservoirs, and surface waters influenced by wetlands, which are sites of active methylmercury production. Methylmercury contamination now accounts for 78% of the fish-consumption advisories in the United States. Forty-one states had advisories attributed to mercury as of 1999, and the number of statewide fish-consumption advisories issued for lakes, rivers, and coastal waters has increased substantially in the last decade. Many waters with contemporary fish-consumption advisories can be characterized as lightly contaminated systems, and seemingly small inventories or inputs of mercury can cause significant contamination of fish.

The bioaccumulation of methylmercury in fish is influenced by an array of biotic, ecological, and environmental factors and processes. Fish obtain methylmercury almost entirely through dietary uptake, which is influenced by size, diet, and food-web structure. Much of the modern spatial variation in fish-mercury levels is attributed to differences among lakes and their watersheds in biogeochemical processes and transformations that control the abundance of methylmercury, the highly toxic form that readily crosses biological membranes, accumulates in exposed organisms, and can biomagnify to high concentrations in aquatic food webs. In particular, the rate of microbial conversion of inorganic Hg(II) to methylmercury by sulfate-reducing bacteria in aquatic sediments or adjoining wetlands is a key process influencing methylmercury contamination of aquatic food webs. Long-range atmospheric transport and deposition are widely believed to be important contributors to the present mercury problem, particularly in semi-remote and remote areas, and the sensitivity of lakes and streams to atmospheric deposition of mercury can vary greatly. In the Upper Midwest, for example, concentrations of mercury in fish of a given species and trophic level can vary 10-fold or more among lakes within a small geographic area (presumably receiving equal rates of deposition), and lakes with the most contaminated fish tend to have low-alkalinity or highly colored waters. Several environmental variables can affect the net microbial production of methylmercury on the landscape. These include physicochemical characteristic of surface waters, flooding and inundation of vegetated areas, and density of wetlands in the watershed. Moreover, some human activities, such as the construction of new reservoirs, can greatly increase mercury levels in fish by creating environmental conditions that increase the microbial methylation of inorganic Hg(II).

Concern about mercury contamination of fish has been motivated largely by potential adverse effects on humans and wildlife, given that consumption of fish is the primary route of methylmercury exposure. Widespread mercury contamination is also adversely affecting the quality of our fishery resources, which have substantial economic, nutritional, and cultural value. Moreover, some fish populations may be adversely affected by methylmercury, given recent findings showing diminished reproductive success, survival, and fitness of fish exposed experimentally to methylmercury during early development.

## **Projecting the Population-Level Effects of Mercury on the Common Loon in the Northeast**

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The Common Loon (*Gavia immer*) is a top-level predator in aquatic systems and is at risk to mercury contamination. This risk is of particular concern in the Northeast, the region of North America in which loons have the highest mean body concentration of methylmercury (MeHg). We used matrix population models to project the population-level effects of mercury on loons in four states in the Northeast (New York, Vermont, New Hampshire, and Maine) exhibiting different levels of risk to MeHg. Four categories of risk to MeHg (low, moderate, high, and extra high) were established based on MeHg levels observed in loons and associated effects observed at the individual and population levels in the field (e.g., behavior and reproductive success). We parameterized deterministic matrix population models using survival estimates from a 12-year band-resight data set and productivity estimates from a 25-year data set of nesting loon observations in NH. The juvenile loon survival rate was 0.55 (minimum) and 0.63 (maximum) (ages 1-3), and the adult loon survival rate was 0.95 (ages 4-30). The mean age at first reproduction was 7. The mean fertility was 0.26 fledglings per individual at low to moderate risk; there were 53% fewer fledged young per individual at high to extra high risk. Productivity was weighted by risk for each state. The portion of the breeding population at high to extra high risk was 10% in NY, 15% in VT, 17% in NH, and 28% in ME.

We also constructed a stochastic model in which productivity was randomly selected in each time step from the 25 estimates in the NH data set. Model results indicated a negative population growth rate for some states. There was a decreasing trend in population growth rate as the percentage of the loon population at high to extra high risk increased. The stochastic model showed that the population growth rate varied over a range of about 0.05 from year to year, and this range decreased as the percentage of the loon population at high to extra high risk increased. These results suggest that an increase in risk to mercury that effects a change in reproductive success may have a negative population-level effect on loons.

**USGS National Pilot Study of Mercury Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish**

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A national pilot study to examine relations of mercury (Hg) and methylmercury (MeHg) in aquatic ecosystems was conducted by sampling water, sediment, and fish in the summer and fall of 1998 at 106 stations from 21 U.S. watershed basins. The Hg bioaccumulation rate in fish from 20 of these basins was evaluated in relation to species, total and MeHg in surficial sediment and water, and selected watershed characteristics. Mercury bioaccumulation in fish was strongly (positively) correlated with the MeHg concentration in water but only moderately with the MeHg in sediment or the total Hg in water. There was no correlation with the concentration of total mercury in sediment. Of the other measured parameters, pH, DOC, sulfate, sediment LOI, and the percentage of wetlands of each basin were also significantly correlated with Hg bioaccumulation in fish. The best model for predicting Hg bioaccumulation included MeHg in water, pH of the water, % wetlands in the basin, and the AVS content of the sediment. These four parameters accounted for 45% of the variability of length-normalized mercury concentration in fish, but the majority was described by MeHg in water. For largemouth bass, the MeHg bioaccumulation factor (MeHg in fish divided by MeHg in water) tended to decrease with increasing concentration of MeHg in water.

On the whole, watersheds categorized as predominantly mixed agriculture/forest exhibited the highest concentration of MeHg in water and the highest bioaccumulation in fish. Urban watersheds as a group exhibited a relatively low bioaccumulation rate despite a moderately high concentration of MeHg in the water and sediment. Based on rankings by various Hg criteria, sampling sites from the following five basins had the greatest Hg contamination: Nevada Basin and Range, South Florida Basin, Sacramento River Basin (California), Santee River Basin and Coastal Drainages (South Carolina), and the Long Island and New Jersey Coastal Drainages.

## **Interactions of Trophic Position and Habitat with Mercury Bioaccumulation in Florida Everglades Largemouth Bass**

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In a collaborative effort between the Florida Fish and Wildlife Conservation Commission and the United States Geologic Survey, intensive food web studies were conducted at five sites in the Northern Florida Everglades to relate trophic position and habitat associations with mercury bioaccumulation in the aquatic food web. As the top piscine predator, largemouth bass were the most intensively studied component of the food web with food habits assayed in 2,871 individual fish ranging in size from 150 to 550 mm. Largemouth bass in the Everglades generally fit the mold of a piscivorous predator with fish occurring in 74.4% of stomachs and contributing 91.2% of the total weight of all food consumed. Other prey items contributing significant biomass to largemouth bass diet were crayfish (*Procambarus* sp.) and grass shrimp (*Palaemonetes paludosus*). Small-bodied prey fish (predominantly mosquitofish, *Gambusia holbrooki*; least killifish, *Heterandria formosa*; bluefin killifish, *Lucania goodei*), juvenile Lepomids, juvenile cichlids and grass shrimp dominated diet of small size classes of largemouth bass. The importance of these prey items decreased dramatically in mid-sized largemouth bass as crayfish became an important transitional prey item. The largest size classes of bass fed almost exclusively on large-bodied fish (mainly adult Lepomids and cichlids). Concurrent with size related shifts in diet, trophic position and mercury concentrations increased due to the importance of diet to bioaccumulation of mercury. Bioaccumulation in largemouth bass is greatly influenced by the degree of piscivory. However, omnivory can exert a great deal of influence on both mercury concentrations and trophic classification in specific habitats. We observed a more varied and omnivorous diet in largemouth bass from marsh habitats in the water conservation areas, particularly in the marsh of Water Conservation Area 3A, which is the site most remote from canal fish populations. We observed a strong relationship between species trophic classification and mercury at each site; however, trophic classification did not accurately describe mercury concentrations in largemouth bass among sites. Variations in prey species populations and availability of mercury for bioaccumulation among sites resulted in a disconnect between trophic classification and mercury bioaccumulation.

## **Bioaccumulation of Mercury in the Everglades: Patterns in the Foodweb**

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We examined patterns of diet and total mercury in eastern mosquitofish (*Gambusia holbrooki*) across the Everglades landscape to search for possible correlations between trophic position and mercury level in this omnivorous fish. Mosquitofish have proven to be a useful indicator species for mercury study because of their ubiquity across the Everglades ecosystem. Mosquitofish were collected in September 1997, September 1999, and March 2000 from over 100 locations using the REMAP stratified random design and analyzed for gut contents. A separate collection of mosquitofish was made simultaneously and analyzed for total mercury. We used Adam's formula to calculate a weighed estimate of trophic position and Levin's measure of niche breadth for each sample of fish. There was no correlation between trophic score or niche breadth and mercury in these samples. In a separate study, we observed a significant correlation between mercury level and trophic score ( $r = 0.73$ ) when comparing a large sample of Everglades fish species (trophic score 1-5, Hg level 64-784 ng/g). However, the difference in mercury level between adjacent trophic groups was not significant. Trophic score for mosquitofish varied from 1.3 to 2.7, suggesting that we probably did not have the statistical power to observe changes in mercury level within this species. While the diet of mosquitofish is quite varied and changes spatially and temporally in their dependence on surface, benthic, and water-column prey, as well as herbivory, most of these prey have similar mercury levels and this diet variation has little impact on mosquitofish relative to mercury level.

We conducted a mercury uptake experiment by placing neonate mosquitofish in cages at short and long-hydroperiod sites located at 3 different regions of the Everglades. These experiments indicated greater uptake of mercury in short-hydroperiod marshes than in long-hydroperiod marshes, except where the long-hydroperiod cages were placed in a mercury "hot spot" indicated by analysis of mercury in periphyton samples. This underlying environmental signal of unknown origin eliminated the hydroperiod effect seen at the other study sites. This suggests that complex spatial patterns of mercury availability may interact with other mercury bioaccumulation processes, obscuring general patterns resulting from trophic relationships.

**Effects of Rainbow Smelt Invasion on Mercury Concentrations of Predatory Fishes of Northwestern Ontario and Manitoba, Canada**

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Rainbow smelt rapidly expanded their range in northwestern Ontario and Manitoba during the 1980s and 1990s. Rainbow smelt tend to feed at a higher trophic position than most native forage species and we hypothesized that predator populations in lakes invaded by smelt should experience an upward trophic shift and increases in Hg concentrations. We tested this hypothesis by sampling lake trout, walleye and northern pike from smelt-invaded and reference lakes. We selected lakes that had been sampled for Hg in fish prior to smelt invasion. We found that Hg in predatory fish in the region was generally stable or declining over the last approximately 20 years. Hg in predatory fish decreased by greater amounts in reference lakes as compared to lakes invaded by smelt. These differences were greatest for walleye, however they were not statistically significant. Trophic position, as measured by  $d^{15}N$ , was higher in walleye in reference lakes as compared to smelt lakes, but again, these differences were not statistically significant. We conclude that the effect of smelt invasion on Hg in piscivorous fishes is slight.

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**Session C:**  
**STAR Program Review**

## **Watershed Influences on Transport, Fate, and Bioavailability of Mercury in Lake Superior**

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The goal of our study is to assess the importance of watersheds in controlling sources, transport, fate, and bioavailability of mercury (Hg) in Lake Superior, a lake with Hg consumption advisories for some piscivorous fish. Our combined approach of field, laboratory and modeling studies is strongly linked to better evaluate important watershed processes that control Hg fate and transport in the Lake Superior basin. Techniques developed and adapted by our group during previous projects (i.e., “clean” ultrafiltration, resin techniques, biota processing) are being supplemented by additional techniques (i.e., stable isotope Hg analysis by ICP-MS; phytoplankton and zooplankton uptake experiments). Modeling efforts combine efforts of ongoing GIS-based watershed yield modeling with the Dynamic Mercury Cycling Model (D-MCM) model development at Tetra Tech, Inc.

Our field research efforts during Year 1 focused on investigating differences between processes influencing offshore and near shore bioaccumulation of Hg in Lake Superior, and investigating watershed processes that enhance production and transport of methyl Hg to tributaries. Results from two cruises on Lake Superior aboard the R/V Lake Guardian indicated that Hg species concentrations were quite low, similar to Lake Michigan and oceanic waters ( $0.49 \pm 0.22 \text{ ng L}^{-1} \text{ THg}$ ). During August 2000, methyl Hg (MeHg) averaged  $6.4 \pm 3.8 \text{ pg L}^{-1}$ , dissolved gaseous Hg was  $20 \pm 10 \text{ pg L}^{-1}$ , and reactive Hg averaged  $45 \pm 33 \text{ pg L}^{-1}$ . For the August 2000 cruise, aqueous samples averaged 1.5% MeHg, 3.5% Hgo, 10% reactive Hg(II), and 85% unreactive organic Hg(II) complexes. Initial comparisons of phytoplankton revealed about a two to threefold enrichment of MeHg in riverine mixing zones versus offshore regions of the lake. The role of watershed influences on MeHg transport is being examined by sampling rivers draining specific, contrasting homogeneous sub-watersheds. We are also investigating the role of subsurface processes on MeHg production and transport using an extensive set of monitoring wells in the East Creek watershed in the Tahquamenon River. Our preliminary results indicate that groundwater and stream porewater are significant sources of MeHg, with wetland-dominated sites exhibiting the highest MeHg concentrations, at times exceeding 12 ng/L.

## **Factors Controlling Methylmercury Production in Sediments and Fate in Aquatic Systems**

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The presentation will discuss progress toward realizing the principal objective of this study - to understand the role of sulfide and other parameters in mercury (Hg) methylation and methylmercury (MeHg) fate and transport. We have hypothesized that the bioavailability of Hg to sulfate-reducing bacteria, the main Hg methylators, is controlled by the concentration of neutral Hg-sulfide complexes in solution as these compounds readily pass across the cell membrane by passive diffusion. Our model, which predicts a decrease in the fraction of the dissolved Hg that is as neutral complexes with increasing sulfide concentration, adequately predicts observations both in the field and the laboratory. Our current studies are further pursuing this notion and experiments looking at net MeHg production in laboratory cultures and natural sediments will be presented. In addition, our initial results from the study of the abiotic decomposition of MeHg in saline waters will be discussed. The talk will also cover our current studies which are probing the factors influencing the speciation of Hg and MeHg in sediments and porewaters, and their importance in controlling the efflux of MeHg from sediments. The results of our studies of Hg and MeHg binding to organic matter, as well as those on the association of Hg and MeHg with solid phases will be presented. These studies have employed both model phases such as iron oxide as well as sequential extraction studies of natural sediment to investigate Hg partitioning. In addition, the results of sediment flux studies will be discussed to illustrate the importance of sediment redox status in controlling the diffusive flux of MeHg from sediments to the water column. Overall, these studies are providing the information necessary for development of a predictive understanding of the factors controlling the formation, degradation, fate and transport of MeHg in watersheds.

**Response of Methylmercury Production and Accumulation to Changes in Hg Loading:  
A Whole-Ecosystem Mercury Loading Study**

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This STAR grant supports the Hg methylation component of a multi-disciplinary, whole-ecosystem stable isotope Hg-addition experiment (the METAALICUS project) that is being carried out at the Experimental Lakes Area (ELA) in northwestern Ontario. The primary objective of this work is to quantify the response of MeHg production and accumulation to a change in ecosystem Hg loading. Other specific objectives are to determine the bioavailability of Hg delivered to different parts of the watershed for methylation; to determine the contribution of newly deposited Hg to MeHg production relative to existing Hg pools in sediments and soils, and how the bioavailability of new Hg changes over time; to develop stable isotope techniques for 1) tracing Hg cycling in watersheds; 2) making simultaneous Hg methylation and demethylation rate measurements; and 3) examining the bioavailable pool of Hg(II). To provide comparison in a very different ecosystem type we are also conducting Hg loading studies, using 1 m diameter in situ enclosures, in a subtropical wetland, the Florida Everglades. The Everglades work is an extension of a recently completed study of the biogeochemical cycling Hg across that ecosystem (the ACME project).

During 2000, we conducted 3 pilot isotope addition studies at ELA: a 1000 m<sup>2</sup> upland plot, a comparable wetland plot and four, 10 m diameter lake enclosures. We also conducted Hg loading experiments in replicate 1 m diameter enclosures at 4 sites across the Everglades. Use of Hg stable isotopes has allowed us to follow MeHg production and accumulation from the new stable isotope Hg spike separately from the existing Hg pools. For comparison, short-term methylation rates were also assessed using a different isotope. Using ICP-MS, we are able to track the methylation of Hg stable isotopes added at levels of about 5% of the existing pool in sediments and upland and wetland soils. Cores were removed from the test plots for these assays, injected with 199Hg and incubated for up to four hours. Peat and vegetation, soaked in a Hg isotope, was placed in a wetland to allow study of Hg isotope behavior on intermediate (month long) time scales. We will compare the relative amount of MeHg production from new Hg from the first hours after its introduction, to production through the first summer after introduction, and with MeHg production from stored Hg pools of Hg. In some cases, we also followed the mobility and phase speciation of new vs. old Hg in these pilot systems. We are using that information to begin to assess how the changing geochemistry of Hg after addition affects bioavailability for methylation.

## **Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition?**

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Given the strong evidence that Hg deposition is now about 3 to 4 times greater than natural rates in Minnesota, a first estimate would be that fish are 3 to 4 times more contaminated than natural levels. Surprisingly, a comparison of modern fish to museum specimens of fish caught in Minnesota in the 1930s suggests that fish Hg levels have increased by a factor of 10 in low-alkalinity systems. Recent Hg sediment core profiles from 16 lakes in Minnesota demonstrate that, beginning about 1940, the Hg present as methylmercury (MeHg) began to comprise a larger percentage of Hg accumulation. The sediment data support the idea that enhanced MeHg loads to many lakes have resulted in Hg concentrations in fish above what would be expected based on total Hg deposition alone. We hypothesize that Hg concentrations in fish in sensitive ecosystems have increased relative to atmospheric deposition due to enhanced methylation in lake sediments or associated wetlands. Our major hypothesis is that in the sulfate-poor ecosystems of northern Minnesota, increased sulfate deposition has increased the activity of bacteria that methylate mercury.

To address the above hypothesis, we developed a three-tiered study involving microscale experiments, lake/wetland studies, and modeling other lakes. The microscale studies focus on testing for enhanced methylation or inhibited demethylation in wetland mesocosms and lake sediment cores. Field studies will allow us to quantify the external and internal MeHg sources to the lake (and, ultimately, to its fish), focusing on transport from different types of wetlands. A full-scale addition of sulfate to a wetland will also be conducted in the final year of this study. Modeling will involve quantifying MeHg loads to lakes from wetlands based on hydrology and wetland classifications.

Our selected study site in the Marcell Experimental Forest in north-central Minnesota has several different wetland types that have been hydrologically monitored since the early 1970s. Total Hg has also been measured at many of the wetland outflows and in overland and subsurface runoff collectors at the site in recent years. The site also contains several lakes. We are monitoring total Hg and MeHg transport from several of the wetlands and have begun field studies on Spring Lake, a small humic-rich lake surrounded by bogs. These studies have focused on establishing mass budgets for MeHg and total Hg and have included sediment core collections, dissolved Hg measurements, deployment of porewater equilibrators, and collection of food chain components.

Lab studies have been conducted on intact sediment cores and blocks of peat from two wetlands. In the sediment core studies, sulfate reduction rates were measured across a spatial gradient in the lake and at depth in several cores. Sulfate was also added to several cores at varying concentrations. We will relate MeHg generation to sulfate reduction rates and to sulfate load. Future studies on the peat blocks and lake sediments will involve additions of nitrogen and organic matter.

For the modeling phase of the study, wetlands at the Marcell site were characterized by aerial photography based on the Cowardin classification system used by the National Wetland Inventory and incorporated into a GIS database. Wetlands in 12 other Minnesota lakes also were characterized. Coupling the wetland characterizations, lake watershed hydrology, and measured Hg export from similar wetlands at the Marcell site, will allow us to estimate the wetland loading of Hg to these lakes, and in turn these results will be related to fish Hg levels.

**Photochemistry of Mercury in Saginaw Bay Watershed, Michigan: Annual USEPA STAR Project Meeting**

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This project is designed to study the role of photochemistry in the cycling of mercury in various components of the Saginaw Bay watershed including wetlands, soils (agricultural and forested), streams, and along a transect from near shore to offshore zones of the bay. Planned studies include field measurements, in situ incubation tests, and simulations in lab microcosms under different light conditions. The first year of the project was devoted to establishing background levels of Hg in various components of the bay ecosystem. We have measured ambient airborne Hg levels and Hg soil emission fluxes at 26 sites (covering forest soils, agricultural soils, wetlands, city park soils, beach sands, and industrial/municipal waste dumps), Hg levels in soil samples from 12 of these stations, as well as in water samples from the streams and rivers draining into the Saginaw Bay. We have monitored the diurnal cycle of dissolved gaseous mercury (DGM) and performed in situ incubation experiments to study photochemical production of DGM in near shore waters of the bay. Results from field studies during the first year were interesting, often unpredictable and emphasized the role of photo-induced reactions as a critical process in the cycling of Hg in the bay watershed. We have developed a thermal desorption technique for determining the forms of mercury in soil and solid material and the results obtained using various samples from the bay will also be presented.

**Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern US**

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A detailed study was conducted on the biogeochemistry of mercury (Hg) at Sunday Pond watershed in the Adirondack region of New York State, USA. Sunday Pond watershed is largely forested, with an abundance of wetlands. This study involved the measurement of total Hg and methyl Hg in wet deposition, through-fall, litter, soil, soil waters, ground waters, surface waters and sediments. We estimated wet deposition of total Hg to the site to be 10.8 mg/m<sup>2</sup> yr, with 0.6% of this occurring as methyl Hg. Concentrations and fluxes of total Hg were greatly elevated in forest floor leachate, with soil solution concentrations decreasing in the mineral soil. Concentrations of methyl Hg were very low in upland soil solutions, near the analytical detection limit. Soil concentrations of total Hg were elevated in the forest floor (13 to 188 ng/g). Soil Hg concentrations were low in the E horizon (3.7 to 25.2 ng/g), higher in the zone of organic deposition or Bh horizon (1.3 to 3.4 ng/g) and low in the lower mineral soil or Bs horizon (1.7 to 3.1 ng/g). We observed elevated concentrations of methyl Hg in ground waters draining wetlands in the watershed. Lake inlet concentrations of total Hg ranged from 1.9 to 3.3 ng/L, with a mean of 3.0 ng/L. Methyl Hg concentrations were somewhat lower ranging from less than 10 to over 50 % of total Hg. Lake concentrations of total Hg ranged from 2.0 to 4.6 ng/L, with methyl Hg ranging from 0.2 to 2.53 ng/L. Drainage water concentrations of total Hg appeared to be related to concentrations of dissolved organic carbon. A mass balance showed that 77 % of wet Hg deposition is retained in the watershed. Sunday Pond was also a sink for inputs of total Hg. However, the watershed and lake were sources of methyl Hg to downstream surface waters. It appears that wetlands were important for the supply of methyl Hg to surface waters. The current lake/watershed mass balance was compared to historical patterns of Hg deposition in lake sediments. The Hg biogeochemistry data have been used to calibrate the Mercury in Adirondack Wetlands Lakes and Terrestrial Systems (MAWLTS) model to the Sunday Pond lake/watershed system.



**Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury from Contaminated Mine Sites**

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The major objectives of this project are to (1) determine the chemical speciation and relative abundance of different forms of Hg in mine wastes, (2) investigate the role of colloidal transport as a mechanism for dispersal of Hg from waste sites, (3) identify the mode of Hg sorption in downstream sediments and fine-grained precipitates in the presence of common complexing ligands, (4) determine the effects of aqueous complexing ligands on the desorption and sorption inhibition of Hg, (5) measure and correlate the emission of Hg into the atmosphere with Hg speciation, climate, and geologic factors, and (6) examine Hg isotope fractionation as a potential means of identifying Hg from specific localities and correlate the information on chemical and isotopic speciation of Hg along the various pathways by which Hg may travel. This presentation will focus on objectives (1) through (4), and a separate presentation by Gustin will focus on objective (5).

Using synchrotron-based X-ray Absorption Fine Structure (XAFS) spectroscopy – a nondestructive element-specific structural method that requires no special sample preparation – we have probed the chemical speciation of Hg in mine wastes from a variety of abandoned Hg mine sites in California and Nevada. This work has revealed that the main Hg-bearing phases in calcines are cinnabar and metacinnabar. Also identified were several relatively soluble Hg-bearing phases that were not previously detectable by XRD, including montroydite (HgO), schuetteite (HgSO<sub>4</sub>), and several Hg-Cl phases. XAFS has also been used to examine the sorption of Hg(II) on model mineral surfaces to determine the effects of the inorganic ligands sulfate and chloride on Hg(II) sorption, and to determine the chemical form(s) of Hg associated with colloidal material generated in laboratory column experiments on mine wastes. Selected examples of these studies will be presented.

**Microbiological and Physicochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones**

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Our USEPA-STAR research is focused on several major features of the aquatic biogeochemistry of Hg, particularly elemental mercury [Hg(0)], which plays a governing role in affecting the production and bioavailability of Hg species (e.g., inorganic Hg complexes; monomethylmercury), and interactions between terrestrial watersheds and near shore marine waters. We have undertaken a comprehensive field and laboratory study to investigate physicochemical/microbiological reactions and processes controlling Hg cycling, speciation and bioavailability in the waters and sediments of Long Island Sound (LIS) and its watershed/coastal water interface (i.e., Connecticut River and East River). We are testing the following hypotheses: (1) The Hg(0) distribution in LIS is spatially/temporally variable, related to the distribution of labile Hg (labile inorganic and organically associated Hg species), and the in situ supply of reducing agents (bacterial activity and solar radiation); (2) Estuarine reactions (i.e., mixing of river borne Hg species with seawater high in Cl<sup>-</sup> and major cations) and direct Waste Treatment Facility (WTF) discharges (sewage) increase the labile Hg fraction available for reduction, enhancing localized production of Hg(0); (3) Hg(0) is the predominant Hg cycling product of bacterial activity in the oxic zone, while net in situ synthesis of monomethylmercury is most significant in redox transition zones (i.e., shallow sedimentary regimes and water basins that experience seasonal hypoxia); and (4) Organic matter-Hg interactions are a major control on the behavior and fate of Hg in aquatic systems. We will present results and future plans relating to our studies of mercury cycling and exchange in the coastal/estuarine waters of LIS and its river-seawater mixing zones.

## **Redox Transformation of Mercury**

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The volatilization of elemental mercury is a major route of mercury elimination from water. The redox transformations of mercury – the reduction of ionic mercury Hg(II) to elemental mercury, Hg(0), and the reverse oxidation reaction – are thus important in determining the total burden of mercury in water bodies.

The main objective of this project is to quantify these oxidation-reduction reactions and to elucidate the environmental factors that control their rate. The initial focus of the work has been on the oxidation of Hg(0), a reaction that has been all but ignored until now. A systematic series of laboratory and field experiments has demonstrated that this reaction is indeed induced by light under appropriate conditions. These conditions include the presence of chloride and a primary photo-oxidizing agent such as quinones. Light in the very near UV (UV-A) is most important in promoting the reaction. Neither long-lived redox intermediates, nor superoxide are involved, but oxygen appears to be the ultimate electron acceptor. Removing suspended particles results into a surprising acceleration of the net oxidation rate, which is not related biological activity. According to field data, the rate of oxidation of the Hg(0) is often comparable and sometimes faster than the predicted rate of gas exchange. It must thus result in lower rates of volatilization than normally calculated. A new apparatus for continuous measurements of elemental mercury in water has been developed and tested. It will allow precise studies of the Hg(0) dynamics in natural waters. Progress has also been made on ancillary projects dealing with the availability of mercury to methylating bacteria.

## **Assessing the Role of Plants in the Biogeochemical Cycle of Mercury**

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We are investigating the role of plants in the biogeochemical cycling of mercury using two EcoCELLs (5 x 7 m mesocosms) designed as open-flow mass balance systems, located in the Great Basin Environmental Research Laboratory at Desert Research Institute, Reno, NV. Within each EcoCELL are three soil containers (2.8 x 1.3 x 1.8 m (l x w x d)) filled with ~ 5 tonnes of gravel overlain by ~4.5 tonnes of mercury amended substrate (12 µg/g). The EcoCELLs allow for precise manipulation of environmental conditions and measurement of system level responses with high resolution. Parameters monitored continuously within each EcoCELL include CO<sub>2</sub>, H<sub>2</sub>O and mercury vapor flux, incident light, air temperature, soil temperature at six locations in each soil container, and relative humidity. Soil moisture, CO<sub>2</sub> and mercury in soil gas are also monitored. Mercury flux from soils within the EcoCELLs was monitored prior to planting by measuring whole cell flux and flux from the immediate soil surface using field flux chambers. Approximately 33 aspen were planted in each soil container allowing for development of a full tree canopy. Leaves were categorized into young, intermediate and old based on their position on the plant and sampled at 0, 0.5, 1, 2, 3 and 4 months. Leaves were rinsed with deionized water, and leaf rinses were analyzed to determine soluble aerosol and gas dry deposition rates. Leaf tissue, petioles, branches, stems and root material were analyzed for total mercury using a Milestone<sup>TM</sup> mercury analyzer. Also in each EcoCELL were six aspen potted in soil with low Hg concentrations (0.031 ± 0.001 µg/g) from which foliar material was sampled and analyzed to estimate foliar uptake of airborne mercury. As plants leafed out within the EcoCELLs, daily CO<sub>2</sub> and mercury vapor flux declined and H<sub>2</sub>O vapor flux increased. Experiments are ongoing to determine if the decline in mercury flux with leaf out may be attributed to the vegetation or changing physical parameters of the soils. Mercury emission from plants within the EcoCELLs was measured using polycarbonate chambers but was not apparent at the elevated air concentrations within the EcoCELLs (10-100 ng/m<sup>3</sup>) and foliar mercury concentrations increased as a function of time. Ancillary experiments are being done with ecopods, which allow for assessment of foliar uptake of mercury under a variety of air exposure concentrations, and with a single plant gas exchange chamber to investigate mercury emission from plants to help understand the processes being observed at the ecosystem scale.

**Mercury and Methylmercury Burdens in Sediments, Water, and Biota of VT and NH Lakes, and Trends in Paleolimnology-Inferred Mercury Deposition to VT and NH**

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From 1998 to present, we have been conducting a comparative study of mercury (Hg) burdens and exposure risks in VT and NH lakes following the regional EMAP approach. Our study has four distinct components: 1) measuring Hg, methylHg, and related parameters in the waters and sediments of 90 lakes; 2) measuring Hg in the macro zooplankton and yellow perch of 45 lakes; 3) measuring Hg and biomarkers in loons and other piscivores in up to 45 lakes; and 4) comparing recent Hg deposition to 13 relatively undisturbed lakes using paleolimnological techniques.

Total and methyl Hg in the water ranged from 0.22 to 34.5, and 0.04 to 3.14 ng/l, respectively. Hypolimnetic concentrations were higher than epilimnetic values, and percentage of methyl Hg was enhanced in the presence of sulfides. Total and methylHg in the sediment ranged from 72 to 624, and 0.41 to 21 ng/g (d.w.) respectively. Total Hg in bulk zooplankton ranged from 119 to 799 ng/g (d.w.). Hg in prey-sized whole yellow perch composites varied from 40 to 324 ng/g, while Hg in filets of human consumption-sized individual perch ranged from 41 to 700 ng/g (d.w.). The relationship of age to Hg in consumption-sized perch varied with lake buffering capacity. Common loons (*Gavia immer*) had a strong likelihood of developing Hg toxicity in 12% of VT lakes, and 29% of NH lakes.

Total Hg flux rates in undisturbed lakes have increased significantly in modern times. A synchronous increase in flux rates to all lakes was evident, beginning around the year 1850. In all but two lakes, Hg fluxes began to decline around 1980. Direct atmospheric Hg contribution to lakes was estimated at 10.1, 29.8, and 19.8  $\mu\text{g m}^{-2} \text{yr}^{-1}$ , for pre-1850, the 1980's, and 1998, respectively. The latest values are within the range of measured atmospheric wet-Hg deposition reported from Underhill, VT, but are lower than estimated wet+dry deposition. Watershed Hg retention has declined steadily since the 1970's, suggesting that watersheds in the study region may be Hg-saturated, and possibly 'leaking' Hg to down-gradient lakes.

**Source, Transport, Transformation and Fate of Mine-Derived Mercury from Acid Mine Drainage in Sediments of Clear Lake, California**

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Historical mining activities and subsequent sediment erosion of wasterock piles and acid mine drainage from the abandoned Sulphur Bank Mercury Mine on the shoreline of Clear Lake, California (a USEPA Superfund site since 1990) has deposited an estimated 100 metric tons of mercury (Hg) into the Clear Lake aquatic ecosystem. Sediment cores to ca. 3 m depth indicate only a slight increase in total Hg concentrations in lake sediments with the onset of underground shaft mining in 1872, but demonstrate an exponential increase in Hg when open pit mining and bulldozing of tailings and wasterock into near shore areas began on a large scale in the 1920s. A 30 m deep 8.1 ha excavation (the Herman Pit) holds pH 3 water containing 2000 ppm sulfate which leaches through a wasterock berm into Clear Lake. Remediation of the shoreline wasterock piles in 1992 by USEPA may have reduced Hg loading from sediment erosion. However, acidic fluids originating from the Herman Pit and contaminated groundwater acidified by the oxidation of iron sulfide minerals still strip Hg from the wasterock piles, via surface/subsurface flow through lake sediments into Clear Lake, producing a white flocculent precipitate (floc) in near shore regions adjacent to the mine. A plume of acid waters emanating from the mine and waste rock piles has been mapped in these near shore regions through a transect of interstitial porewaters extracted from sediment cores. Core tube microcosm experiments also demonstrate that sediments containing mine-derived floc exhibit Hg methylation rates 5-20 times higher than nonfloc sediments. Therefore, sediments containing floc likely contribute significantly to the bioaccumulation of methyl Hg in Clear Lake biota. Remediation of the Sulphur Bank Mercury Mine must account for the ongoing influx of Hg from acid mine drainage from the Sulphur Bank Mine. Integrated Clear Lake sediment accumulations of total Hg continue to be on the order of 1 to 2 metric tons per year, 500-1,000-fold higher than current USEPA estimates of annual soluble Hg flow from the mine site to the lake.

**Session D:**

**Managing Mercury Contamination in Aquatic/Terrestrial Systems**

**An Assessment of the Ecological and Human Health Impacts of Mercury in the Bay-Delta  
Watershed: A CALFED Study**

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CALFED is a partnership between the federal government and the state of California, established to address California's complex water supply and water quality issues. In September 1999, CALFED funded a team of 18 researchers at 12 institutions to investigate the impacts of mercury (Hg) in the San Francisco Bay-Delta watershed vicinity. The study is partitioned into two components, the Cache Creek watershed area, and the Bay-Delta areas downstream. The Bay-Delta watershed has through time been the recipient of more than a century of potentially Hg-laden runoff from Cache Creek and the Sierra Nevada Range. The Cache Creek watershed area historically contained more Hg mines than any other area in the Coast Range, and the Sierra Nevada Range has an extensive number of gold mines that used elemental Hg in their processing of gold ore. The Bay-Delta portion of the study has three main objectives: 1) Determination of mass loading from the various tributary inputs; 2) Investigation of potential ecological and human health effects; and 3) Assessment of bioaccumulation in organisms found in the downstream watershed. The Cache Creek portion of the study has four main objectives: 1) Assessment of bioaccumulation in organisms found in the watershed; 2) Determination of Hg species found in the watershed; 3) Assessment of upstream mass loading into the Cache Creek watershed; and 4) Evaluation of the potential for mine remediation, and post-remediation assessment of water quality and habitat improvements. The project is slated to complete field sampling efforts near the end of 2001 and is currently near the middle of the field program for most project participants.

The following is a summary of preliminary conclusions for the Bay-Delta portion of the study. The mass loading studies have found: 1) The Sacramento River is the main source of water and mercury to the Delta; 2) There appears to be a net loss from the water column of particulate and filter-passing monomethylmercury (MeHg) in the Delta during spring and summer, since the input Hg concentrations to the Delta are higher than the export concentrations; 3) The pattern of higher MeHg concentrations in the rivers and adjoining Bay-Delta waterways, and lower MeHg levels in the Central Delta, and at the export pumps, is consistent with the biotic mercury data from this study and others. A mass loading box model also indicates there is a net loss of MeHg in the Delta, however, this model has several components that have a large variation, and no definitive



conclusions can be made until more data is collected. A large effort is currently underway to obtain more data on Hg inputs, exports and sediment-water exchange fluxes. The bioaccumulation studies in this project and others have shown that Asiatic clams, silversides, white catfish and largemouth bass have higher Hg body-burdens in and near river mouths. There does not seem to be a difference in bioavailability between Hg from Cache Creek (a cinnabar source) and Sierra Nevada Rivers (an elemental Hg source). MeHg concentrations and MeHg:Total Hg ratios in sediments are lower in the Delta and San Francisco Bay than ratios described from the East Coast or Southern Florida. Ecological and human health effects studies have shown that: 1) Most of the largemouth bass, white catfish, and striped bass in the Delta were above the Hg screening value of 0.3 ppm, indicating a potential human health concern; and 2) Hg concentrations measured in avian species are elevated enough in the Bay-Delta system to put up to one-third of the species sampled at risk.

## **An Evaluation of USEPA's Bioaccumulation Factor (BAF) for Mercury: A Regulated Industry Perspective**

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USEPA's final Water Quality Guidance for the Great Lakes System (1995) incorporated the bioaccumulation factor (BAF) as a measure of the bioaccumulative potential for mercury (Hg) and other pollutants of concern. Subsequently, USEPA has imbedded the BAF into a variety of regulatory and technical guidance initiatives: derivation of human health criteria calculation methodologies and numeric criteria, thresholds for new chemical screening, and development of water quality criteria for TMDL implementation. One of the underlying assumptions of the BAF is that both fish tissue and water-column Hg are at steady state. This assumption (and others) will be evaluated in light of current understanding of Hg cycling and bioaccumulation dynamics.

A review of recent publications from the peer-reviewed literature was conducted, using studies that report (at minimum) fish tissue and water-column Hg concentrations. Almost all of the studies reviewed showed no relationship between fish tissue Hg and water-column Hg. Significant correlations between fish Hg and sediment Hg (or MeHg) levels were reported in some studies. A similar review was conducted for published studies that report Hg in benthic food-chain organisms and Hg levels in water and sediment. In most of these studies, significant correlations were reported for benthic organism Hg and sediment MeHg levels.

The utility of site-specific BAFs will be discussed from a regulatory perspective. Fish tissue and low level water-column Hg data from the main stem Ohio River will be used to illustrate potential implementation problems. Although a BAF is simple to determine and provides a means to conveniently compare Hg bioaccumulation potential between water bodies, an empirical relationship between fish tissue and water-column Hg is not demonstrated in the scientific literature. Even using a site-specific BAF value, a back-calculated water quality criterion for total Hg or MeHg assumes, implicitly, that a decrease in water-column Hg will result in a proportional decrease in fish tissue Hg. The accuracy of this assumption has significant regulatory implications.

## **Methylmercury in Terrestrial Ecosystems – Summary of Swedish Research**

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Cycling of mercury and methylmercury in forest ecosystems has been investigated at the Gårdsjön research station north of Göteborg. Investigations include catchment scale input-output and mass balance estimations, deposition processes, soil methylation processes and investigations of the effects of reducing atmospheric input on mercury and methylmercury levels in catchment run-off.

The Covered Catchment Experiment (or Roof project) was initiated as a study of soil acidification recovery. It consists of a plastic roof covering a 6300 m<sup>2</sup> forested sub-catchment at 1 to 3 m above the ground. Wet deposition is removed by the roof and the forest soil is irrigated with water of pre-industrial composition. Mercury and methylmercury in run-off has been monitored since the start in 1991. Average concentrations are 2.58 and 0.10 ng L<sup>-1</sup> for total Hg and MeHg, respectively.

During the first 1 to 3 years, a slight decrease in Hg and MeHg output was observed but after that no significant changes have been observed in comparison to the reference catchment. These results, along with deposition data, soil methylation studies using stable isotopes and the catchment contribution to MeHg loadings in lakes will be presented and discussed.

**Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades (ACME) Phase II**

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From 1995 to 1998, the Aquatic Cycling of Mercury in the Everglades (ACME) project studied the biogeochemistry of mercury (Hg) in detail across most of the remnant Everglades. One of our principal objectives was to provide process-level information on Hg cycling in the Everglades, which could be used to advise management decisions about the elevated levels of methylmercury (MeHg) in the food web. Mercury cycling was found to be highly dynamic in this ecosystem, with rapid rates of methylation, demethylation, reduction and evasion. Because rainfall is the dominant source of Hg to this ecosystem, a consistent downward flux of inorganic Hg from surface waters into sediment interstitial waters was observed. Microbial methylation and demethylation are most pronounced in surficial sediments, and an upward gradient of MeHg from pore waters to surface waters is generally observed. However, MeHg concentrations in surface water and sediments were only weakly related to total Hg concentrations across the ecosystem, suggesting multiple controlling factors of MeHg production. An ecosystem-scale sulfur gradient originating from sources north of the Everglades has an important controlling influence on net MeHg production. Dissolved organic carbon (DOC) interacts strongly with aqueous Hg and provides an effective transport vector for Hg and likely affects MeHg production as well. Mercury concentrations in *Gambusia*, a ubiquitous small fish in the Everglades, are very well correlated with MeHg in surface flocs, supporting the idea that gradients in net MeHg production, rather than gradients in bioaccumulation, control Hg uptake into the food web. Although our studies have provided a basis for understanding the complexities of Hg cycling in the Everglades, there is an immediate need for better information that relates Hg loading to MeHg production and bioaccumulation, particularly as it relates to proposed whole ecosystem changes that will result from the Everglade Restoration effort.

As a follow-up to our Phase I research, the ACME project is now pursuing a series of new approaches that are designed to provide information that directly addresses management concerns for the Everglades. Our project design focuses on evaluating the effects of the four key biogeochemical parameters (sulfur, Hg loading, DOC, and wetting and drying cycles) that were revealed to have the greatest effect on MeHg production and bioaccumulation. Experimental approaches included medium-term and long-term studies in situ mesocosms,

sort-term manipulations of sediment cores, and extensive field measurements following an intense drying and burning period in 1999. In weeks following rewetting, MeHg production and bioaccumulation was very significantly enhanced relative to historical averages at the sites examined. The sequence of events following rewetting confirmed our working model that Hg methylation in the Everglades is tightly linked to the S cycle. Sulfate was mobilized from peat upon rewetting, although Hg was not mobilized, and DOC, pH and total Hg in sediments were not affected. Sulfate, and later sulfide, accumulated in pore waters, both to 5-10X higher concentrations than 5-year historical averages for these sites. Sulfide affects Hg bioavailability to methylating bacteria by affecting dissolved Hg speciation, while sulfate affects the overall activity of methylating organisms. Experimental manipulations of intact sediment cores showed sulfide inhibition of Hg methylation beginning between 10-100  $\mu$ M sulfide, consistent with patterns of MeHg production in situ in this ecosystem. Together with research on Hg speciation uptake mechanisms, these studies provide high confidence in the sulfide inhibition level in the Everglades. Sulfate stimulated methylation in cores taken from low sulfate sites. However, the relationship between sulfate and MeHg in the southern Everglades, where surface water sulfate is generally below 100  $\mu$ M, is unclear. This relationship is being studied during 2001 in mesocosms at four sites within the Everglades. Mesocosm Hg dose-response experiments, conducted in 2000, will also be presented. In addition, we are examining the concentration of MeHg in long-term phosphate-addition mesocosms. The studies will help quantify the separate impacts of nutrient, Hg and S loading within different freshwater marsh habitats in the Everglades. Ultimately, we hope our research results will guide ecosystem managers who must decide whether reducing local Hg emission, intercepting sulfur in runoff, or regulating water levels (or a combination of all these factors) will be the best approach for minimizing MeHg exposure to wildlife and humans in south Florida.

## **Modeling Mercury Fate in Seven Georgia Watersheds**

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Field and modeling studies were conducted in support of total maximum daily loads (TMDLs) for mercury in six south Georgia rivers and the Savannah River. Mercury is introduced to these rivers primarily by atmospheric deposition, with minor point source loadings. To produce mercury TMDLs in these rivers, the GIS-based Watershed Characterization System (WCS) and a mercury delivery spreadsheet were developed and applied with the water pollutant fate model WASP5. Together, these models calculate mercury buildup in watershed soils, loading and delivery through the watershed tributary system, and mercury fate in the mainstem rivers. Site specific mercury data are required for model parameterization. These models were applied to the seven rivers and their watersheds, and checked against survey data gathered during very dry conditions in June and July, 2000. Despite environmental variability and scientific uncertainties, calculated mercury concentrations in soils, sediment, and water compared reasonably well with the observed data in most watersheds. The accuracy of these model predictions within and among these watersheds is described. Sensitivity analyses point to those processes and parameters controlling mercury fate in these river systems, including atmospheric deposition, impervious watershed area, soil reduction rate constant, tributary reduction rate constant, and tributary methylation status. Future development should focus on mercury transport and transformation reactions in the tributary systems.

## **Fitting into the North American Mercury Emissions Reduction Priority**

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This paper will describe how the three North American countries of Canada, the USA and Mexico intend to address their mercury emissions concerns on a continental scale. The paper will discuss how the institutional arrangements of the North American Free Trade Agreement of 1992 led to the development of the North American Agreement on Environmental Cooperation and the consequent North American Regional Action Plan (NARAP) on Mercury, Phases I and II, under the Sound Management of Chemicals initiative. The emphasis of the discussion will focus on the development of Canadian mercury management measures intended to comply with the intent of the Mercury NARAP and to simultaneously deliver on domestic, bilateral and international obligations to manage mercury emissions. Presented as contextual background will be a brief overview on recent NARAP developments relating to emission source inventories, research/monitoring efforts to look at deposition patterns and trends in Canada, new initiatives/regulations at the federal levels, and an update on the status of CEC North American Regional Action Plan on Mercury.

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**Session E:**

**Methylmercury Production in the Environment**

## **Overview of Microbial MeHg Production and Degradation: What Do We Know? What Don't We Know?**

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Mercury methylation is perhaps the key process in Hg bioaccumulation. Mercury deposited to aquatic ecosystems can be converted to methylmercury through the action of natural bacteria, mainly in wetland soils and aquatic sediments. Methylmercury production varies widely among and within ecosystems, complicating models that attempt to relate Hg deposition to Hg in fish. To gauge the importance of methylation in making regulatory decisions, consider that the range of MeHg concentrations in aquatic sediments is much larger than the range of Hg deposition rates across the US. A number of studies have shown that MeHg concentrations and/or production rates are the best predictors of Hg in fish among and within ecosystems that receive roughly equivalent Hg deposition rates.

I will present a conceptual model for net MeHg production. The talk will be a discussion of which parts of that model I feel are well understood and which are not. In my model, Hg methylation has two major components: 1) the bioavailability of Hg to methylating bacteria and 2) the metabolic activity of those bacteria. I will summarize the status of research in each area, including the neutral species bioavailability model, the types of bacteria that produce MeHg and the conditions under which they produce MeHg, progress in understanding how the community structure of sulfate-reducing bacteria affects methylation, the biochemistry of methylation within cells, the confounding roles of sulfur in methylation, the importance of hydrology to methylation, and relationships derived from ecosystem studies of Hg biogeochemistry. I will also discuss advances in understanding demethylation including oxidative demethylation and the distribution of the mer operon in the environment. Models for Hg bioaccumulation are beginning to incorporate routines for Hg bioavailability and microbial activity. As an example, I will discuss how these concepts are being incorporated in to the Mercury Cycling Model. I will also mention some promising new techniques, including the use of Hg stable isotopes to study bioavailability and developments in the use of microbial Hg “Bioreporters” and “Bioaccumulators.”

## **Environmental Controls on Methylmercury Production and Degradation in Florida Everglades Sediment**

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The net production of toxic methylmercury (MeHg) by sediment bacteria is arguably the most critical step in the chain of events leading to mercury (Hg) contamination of Everglades wildlife. Experiments were conducted examining the relative impact of key environmental parameters on both Hg-methylation and MeHg degradation in sediment (0-4 cm) at five sites along the existing north-south nutrient gradient. Manipulated variables included temperature, sulfur chemistry, organic matter, and redox conditions. MeHg production and degradation potential rates were measured using radiotracer  $\{^{203}\text{Hg}(\text{II}) \text{ and } [^{14}\text{C}]\text{MeHg} \text{ amendment}\}$  techniques. Hg-methylation generally increased going from nutrient enriched to pristine sites, while MeHg degradation rates varied comparatively little among sites, in unamended anaerobic samples. The increase in Hg-methylation with temperature was greatest at the most southern and pristine site. While increasing temperature also stimulated MeHg degradation, among-site differences were minor. Manipulations in sulfur chemistry and redox conditions exerted a much stronger influence on Hg-methylation than did variations in organic matter quantity or quality. Increased levels of both pore-water sulfide and solid-phase FeS typically inhibited Hg-methylation. Increases in sulfate also generally inhibited methylation, by stimulating the activity of sulfate reducing bacteria and subsequently increasing the concentration of reduced sulfur end-products. Results from these experiments confirm earlier findings that sulfur biogeochemistry plays a critical role in regulating net MeHg production in the Everglades. Further, net MeHg production appears to be primarily a function of gross Hg-methylation, as gross rates of microbial MeHg degradation were largely constant over a wide range of geochemical manipulations.

## **Group VI Oxyanions and Mercury Transformation Within the S-cycle in the Carson River, Nevada**

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The Carson River System (CRS) in western Nevada is extensively contaminated with mercury (Hg) from historic mining activity, and total mercury concentrations above 1000mg/kg and 7000ng/L have been reported for sediments and surface water, respectively. While relatively high concentrations of methyl-Hg have been also measured in the system (e.g., up to 7ng/L in the aqueous phase), the latter is always present at levels less than 1% of total concentrations. The low percentage of methyl-Hg in the CRS presents a unique scenario in that more methyl-Hg might be expected in an area of such high Hg contamination. Several factors could explain the observed depressed methyl-Hg levels. Based on the reported ability of SRB to produce Methyl-Hg in most aquatic sediments, we conducted field and laboratory studies to investigate the role of sulfate chemically similar and naturally occurring group VI oxyanions ( $\text{SeO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ , and  $\text{WO}_4^{2-}$ ) in controlling Hg methylation rates in the CRS. Our results suggest the following: (1) Group VI anions are evapoconcentrated in the CRS due to the aridity of the climate, reaching anomalously high levels with potential impact on Hg methylation; (2) Rates of methyl Hg production in sediments tend to increase with increasing flow regimes, as Group VI anions get diluted; (3) Laboratory experiments confirmed the inhibition potential of tested group VI anions, and both noncompetitive (S versus Se and Te) and competitive inhibition (S versus W) were observed.

## **A Bacterial Biosensor for Aquatic Mercury(II) Speciation and Bioavailability**

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The chemical forms of Hg(II) that can be classified as “bioavailable” are determined by the nature of the transport mechanism used by a particular organism for a particular chemical species. For mercury, research suggests that phytoplankton and bacteria take in neutral inorganic complexes such as  $\text{HgCl}_2^0$  and  $\text{HgS}^0$  in addition to neutral Hg(II) complexes with low molecular weight organic ligands. The rate of production of MeHg by sulfate reducing bacteria appears to be controlled to a large extent by the concentrations of these neutral Hg(II) complexes and their rates of passive diffusion into cells. As a result, the movement of Hg(II) into an ecosystem, and its bioaccumulation as MeHg in higher trophic levels, is strongly influenced by the very first step in the sequence; the uptake of bioavailable forms of Hg(II) by bacteria. We are working with a sensitive and stable Hg(II) “biosensor,” reported by Marko Virta, who coupled the mer operon with firefly luciferase enzyme expression in a common E-coli bacterium. These bacteria then emit 550 nm photons of light when exposed to bioavailable forms of Hg(II). Our initial experiments have centered on the calibration of the biosensor bacteria vs. Hg(II) solutions of known (i.e. modeled) speciation. We are studying Hg(II) speciation and bioavailability with a variety of inorganic and organic ligands by manipulating the Hg(II):ligand ratios, and by using various ligand combinations. We use an anaerobic chamber to study Hg(II) complexation by hydrogen sulfide. Once the method has been calibrated, we plan to test Hg(II) bioavailability in natural water samples collected from nearby lakes and rivers, as well as from the Everglades.

## **Facilitated Uptake of Mercury at Trace Concentrations by *Escherichia coli* and *Vibrio anguillarum***

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The behavior of mercury uptake in two bacterial species was inconsistent with the passive diffusion of neutrally charged species, but rather had the characteristics of facilitated transport processes. Studies on the bioavailability of inorganic mercury (Hg(II)) to bacteria under aerobic and anaerobic conditions were carried out in well-defined chemical solutions and at trace Hg(II) levels. Measurement of Hg(II) crossing the cell membrane was done using a bioreporter bacterium. The bioreporter construct is a fusion of the Tn21 mer operon to a promoterless luxCDABE operon from *Vibrio fischeri* and was transformed into the facultative anaerobe *Vibrio anguillarum*, a natural aquatic species, and *E. coli*. The advantage of this method is that the mer-lux bioreporter is only capable of producing luciferase enzyme, and light, in response to Hg(II) that has entered the cytoplasm of the cell. Anaerobic assays were done by exposing the bacteria to mercury under anaerobic conditions and measuring light production after adding O<sub>2</sub>.

Light production did not occur after anaerobic exposure to Hg(II) in minimal medium unless mercury concentrations greater than 100 ng L<sup>-1</sup> were added, even though the bioreporter was capable of responding to mercury concentrations < 1 ng L<sup>-1</sup> under aerobic conditions in the same minimal medium. The lack of a light response under anaerobic conditions was due to a lack of Hg(II) transport and not to differences in cellular energetics. Unexpectedly, we were capable of eliciting a bioreporter response to trace mercury concentrations under anaerobic conditions following the addition of a variety of low molecular weight organic compounds. Aerobically, the addition of these compounds was not required, nor did they affect the uptake rate of the mercury. For the compound studied in greatest detail, the amino acid histidine, anaerobic uptake was proportional to the formation of Hg(HHis)(His)<sup>+</sup>, a charged species. Again, this behavior was different from aerobic conditions, where histidine additions did not affect the rate of Hg(II) uptake. These results were not compatible with the model of passive diffusion of neutral mercury species, but rather demonstrated the existence of facilitated transport processes. The aerobic facilitated mechanism of Hg(II) transport appeared to be repressed under anaerobic conditions and the addition of low molecular weight organics may present an alternative pathway for Hg(II) uptake by the nonspecific transport of mercury-low molecular weight organic acid complexes. Thus, models of Hg(II) uptake based only on passive diffusion of neutral species may be too simple to accurately describe Hg(II) uptake for all microorganisms. Further, the finding that differences exist in mercury uptake aerobically and anaerobically suggests that there may be a need for different uptake models for aerobic and anaerobic environments.

## **Mercury Transport and Transformation in the Wider Idrija Region and the Gulf of Trieste**

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The Idrija mercury mine in Slovenia is the site of the second largest Hg mine in the world, which was in operation continually for 500 years until about 20 years ago. Over five million metric tonnes of Hg ore was mined, and much of the residues were spread around the town and its vicinity. It has been estimated that 73% of the Hg mined was recovered, and the remaining 17% dissipated into the environment (Miklavèič, 1996).

Mercury in the terrestrial environment of the region is effectively transferred from soil (and air) to vegetation, herbivores and carnivores further up the food web. Interestingly, a higher accumulation of MeHg was observed in those environments polluted with high concentrations of inorganic mercury compared to less contaminated and control areas (Gnamuš et al., 2000).

The tailings and contaminated soils in the Idrija region are continuously eroded and serve as a continuous source for the river, the flood plains, and the Gulf of Trieste. This is confirmed by the fact that even after 10 years of closure of the Hg mine, Hg concentrations in river sediments and water are still very high and there are no signs of the expected decrease of Hg in the Gulf of Trieste (Horvat et al. 1999, Covelli et al. 1999, Širca et al. 1999). Recent studies in the Idrijca – Soča – the Gulf of Trieste region are mainly directed towards the quantification of Hg fluxes and better understanding of the fate of mercury, its accumulation in the flood plain, and its final input to the marine environment. An assessment of the extent of contamination in the Gulf of Trieste after the closure of the Hg mine was also made (Horvat et al. 1999, Hines et al. 2000) and mass balance calculated (Širca et al. 1999).

A number of studies were conducted in recent years, each addressing a separate environmental and health related Hg problem in the area. In order to develop realistic strategies for minimizing the effects of the Idrija mining on human health and the environment, a more integrated approach is needed. In support of this objective, the presentation will provide a short review of mercury research activities carried out in the region.

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## **The Everglades Mercury Cycling Model (E-MCM): Development and Application to Two Marsh Sites in the Florida Everglades**

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In conjunction with the Aquatic Cycling of Mercury in the Florida Everglades (ACME) project from 1995-98, the Everglades Mercury Cycling Model (E-MCM) was developed and applied to Everglades marsh areas. This presentation discusses the application of E-MCM to two sites varying widely in primary productivity. The Everglades Nutrient Removal (ENR) Project is a highly eutrophic, constructed marsh situated at the northernmost (upstream) end of the remnant Everglades. ENR was designed to reduce the downstream transport of nutrients originating upstream from agricultural activities. The second modeled site is in Water Conservation Area 3A (3A-15). Site 3A-15 is oligotrophic and more representative of historical or background conditions within the remnant marsh, with low phosphorus concentrations and comparatively low sulfate concentrations, although the latter is still elevated with respect to likely historical conditions. Mercury levels observed during the study period in largemouth bass were high at 3A-15 and low at ENR.

The E-MCM model was calibrated initially to conditions at 3A-15. The calibration data were derived from ACME field and laboratory studies. Field data and modeling both indicate Hg cycling is very rapid in Everglades marshes. The dominant predicted source for MeHg at 3A-15 was in-situ production (e.g. 7.6 mg m<sup>-2</sup> yr<sup>-1</sup>, 87% of total MeHg load). At ENR, the best model fit to observations occurred with minimal on-site methylation, consistent with low field estimates of methylation rates.

These results are consistent with the hypothesis that local site factors are driving the variability and “hot spots” observed for methylmercury across the Everglades. Although site conditions are important, atmospheric mercury deposition rates likely also affect fish mercury concentrations. As part of a pilot study sponsored by USEPA to develop an approach for establishing a Total Maximum Daily Load (TMDL) for surface waters with high concentrations of mercury in biota, model simulations were run to predict the response of fish mercury concentrations to reductions in mercury loading to 3A-15. The model suggests that mercury in 3-year old largemouth bass (the index fish for health advisory purposes) is nearly proportional to atmospheric load of mercury, with a slight sub-linear response related to long-term response to sediment mercury load. Fish Hg concentrations were predicted to change by 50% of the ultimate response within approximately 10 years and 90% within 20-30 years. This predicted response time is discussed in the context of some recent observations showing rapid declines in largemouth bass concentrations over a few years at some, but not all Everglades sites. There remain gaps in the state of knowledge of mercury cycling in aquatic systems that impose uncertainty on the predictive capability of the model. Ongoing research is addressing these gaps, however, and the predictive strength of the model continues to evolve.



## **Landscape Patterns of Mercury Contamination Across the Everglades Ecosystem**

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The US Environmental Protection Agency (USEPA) Region 4 initiated a project in 1992 to assess the effects of mercury contamination on the South Florida Everglades Ecosystem. This project was designed around the USEPA Ecological Risk Assessment Framework and implemented using a statistical survey design to conduct synoptic surveys during the wet and dry seasons from 1994-1996. During this first phase of the project soil, water and biota were sampled at about 500 sites throughout the 9600 km<sup>2</sup> marsh to assess the effects of hydropattern, phosphorus loading, habitat alteration and mercury contamination on the marsh ecosystem. The Phase I report (USEPA 1998) found there were significant interactions among water depth, TOC, TP, and SO<sub>4</sub> concentrations, food web dynamics and fish mercury concentrations. These interactions exhibited different spatial patterns in the area north of Alligator Alley, between Alligator Alley and Tamiami Trail and south of Tamiami Trail in Everglades National Park. Three conceptual models were developed, one for each of these three areas, as part of the Phase I report to describe the pathways and interactions among factors affecting fish mercury concentration.

In 1999, USEPA initiated Phase II of the Everglades Ecosystem Assessment Project which added parameters in pore water, floc, macrophyte tissue, and plant community sampling in addition to the constituents and media sampled in Phase I. Wet and dry season samples were collected at about 240 marsh sites in 1999. Six system wide synoptic surveys provide a spatial data base from which a full range of water depths can be compared with other key interacting variables. Selected variables (e.g., TOC, TP, SO<sub>4</sub>, S<sup>2-</sup>, THg, MeHg, tissue Hg and BAF) will be presented to illustrate changes among wet and dry cycles, seven geographic subareas and system wide gradients which support the interactive conceptual models being developed to address the spatial changes in the system. Important changes in TP and mercury contamination were observed in 1999.

## **Use of Path Analysis to Integrate the Effects of Multiple Stressors on Mercury Contamination in the Everglades Ecosystem**

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The US Environmental Protection Agency (USEPA) Region 4 initiated a project in 1992 to assess the effects of mercury contamination on the South Florida Everglades Ecosystem. This project was designed around the USEPA Ecological Risk Assessment Framework and implemented using a statistical survey design to conduct synoptic surveys during the wet and dry seasons from 1994-1996 (Phase I) and 1999 (Phase II). The study area extended from Lake Okeechobee on the north to Florida Bay in the south, from the urban area on the east to Big Cypress National Preserve on the west. During these two Project Phases, soil, water, and biota were sampled at about 750 sites throughout a 5500-km<sup>2</sup> marsh area to assess the effects of hydropattern, phosphorus loading, habitat alteration and mercury contamination on the marsh ecosystem. Significant interactions among water depth, TOC, TP, and SO<sub>4</sub> concentrations, food web dynamics and fish mercury concentrations were found, with different spatial patterns in the area north of Alligator Alley (I-75), between Alligator Alley and Tamiami Trail (US Hwy 41), and south of Tamiami Trail in Everglades National Park. Three conceptual models were developed, one for each of these three areas to describe the pathways and interactions among factors affecting fish mercury concentration.

Path analysis or structural equation models were developed based on the conceptual model. Structural equation models are particularly applicable for survey-based data and have been used extensively in the socioeconomic sciences with statistical survey information. These structural equation models were used to determine the strength of associations among the variables included in the conceptual models. In general, there were significant differences in mercury pathways among the three areas. North of Alligator Alley, chemical interactions were important in affecting mercury bioaccumulation, while south of Tamiami Trail, biological pathways were important in affecting fish mercury concentrations. The bioaccumulation of mercury through the food chain appears to be analogous with models of eutrophication processes. North of Alligator Alley, bottom-up (chemical) processes appear to control mercury bioavailability and accumulation. South of Tamiami Trail, in the Everglades National Park, top-down (biological) processes appear to control mercury bioaccumulation. In between the Alley and the Trail, these processes interact in a dynamic transition zone. These processes and their management implications will be discussed in this presentation.

## **METAALICUS: A Study to Determine the Relationship between Mercury Deposition and MeHg Concentrations of Fish**

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Mercury is the most common contaminant responsible for fish advisories in the United States and Canada. Controls on industrial emissions of mercury have been proposed that will cost billions of dollars per year if implemented, yet the effectiveness of these controls to reduce fish mercury concentrations is unknown, both in magnitude and timing. The relationship between atmospheric mercury deposition and mercury in fish cannot be understood by examining existing historical or regional data. METAALICUS (Mercury Experiment To Assess Atmospheric Loading In Canada and the United States) is a whole-ecosystem experiment that will directly answer full-scale for the first time what happens to fish mercury concentrations when there is a change in atmospheric mercury deposition. Stable, nonradioactive isotopes of inorganic mercury (Hg(II)) will be added to a headwater lake and its watershed in the Experimental Lakes Area (ELA), Ontario, Canada. The mercury additions will increase the annual loading of atmospheric Hg(II) by a factor of 3-4 times. The power of using isotopes lies in the ability to follow the newly deposited mercury separately from the background mercury. Three different mercury isotopes will be added: one to the upland, a second to wetland areas and a third to the lake surface to examine the relative contributions of these sources to methylation and to MeHg supply to fish. Detailed process studies will be carried out to follow the concentrations, transformations and movement of mercury through the watershed and lake.

METAALICUS is being carried out in two phases over a 5-year period. Phase 1 involved pilot studies and baseline work in 1999-2000. The pilot studies were done at the sub-whole-ecosystem level in small hydrologically defined upland catchments, in a wetland (bog) plot of about 600 m<sup>2</sup> and in 10-m<sup>2</sup> diameter lake enclosures. The enclosures were sealed to epilimnetic sediments and contain complete food chains, including

small fish. The purpose of these pilot studies is to prove that our approach of stable isotopes additions to whole ecosystems is feasible, and to give the team a preview of how newly deposited stable isotopes of Hg(II) will move through the terrestrial and aquatic whole-ecosystems, be methylated and bioaccumulated by fish and food-chain organisms.

In addition to the practical information obtained, the pilot studies are yielding fundamental new information about the cycling of mercury in terrestrial and aquatic ecosystems. For example, in 1999, we added  $12.5 \mu\text{g}/\text{m}^2$  of  $^{202}\text{Hg}(\text{II})$  to a wetland plot. This approximately doubled the annual deposition rate of mercury at the ELA. The isotopic mercury was much more mobile than expected, penetrating into the 10-20 cm below the peat surface. This penetration was likely related to the fact that the partitioning  $K_d$ 's of the newly added mercury in peat porewater were smaller than the ambient mercury. Transport of the  $^{202}\text{Hg}$  is being further investigated by coupling the  $^{202}\text{Hg}$  data to a physical flow model. We also detected methylation of the  $^{202}\text{Hg}(\text{II})$ . Within a few months mercury deposited as  $^{202}\text{Hg}(\text{II})$  was detected as  $[^{202}\text{Hg}]\text{MeHg}$  in invertebrates, and some the  $[^{202}\text{Hg}]\text{MeHg}$  appeared in caged fish held at the wetland/lake interface.

In 1999, we also added  $12.5 \mu\text{g}/\text{m}^2$  of  $^{202}\text{Hg}(\text{II})$  to a  $680\text{-m}^2$  upland catchment at the ELA. We followed evasion of isotopic and ambient mercury to the atmosphere, its movement through soils (including methylation) and its loss from at the outflow of the catchment. We found that initially the newly deposited mercury was more reactive than the very large mercury pool which accumulated in the soils over many decades. For example, evasion rates and methylation rates of isotopic mercury were higher than for the ambient pool. But on the longer term, over the first growing season, only about 8% of the  $^{202}\text{Hg}(\text{II})$  was lost to the atmosphere, and only 0.3% of the  $^{202}\text{Hg}(\text{II})$  was exported from the upland catchment. On the longer term, the isotopic mercury equilibrated with the mercury in the entire soil column, and became indistinguishable for the large ambient mercury pool. Thus most of the mercury exported during the first growing season was old mercury (>99%), which had been accumulating in the soils for many years. This result suggests that export of mercury from upland watersheds to lakes will respond slowly to expected decreases in rates of atmospheric deposition of mercury. If mercury exported from upland watersheds is an important mercury source for in-lake methylation, fish mercury concentrations will respond slowly to expected decreased rates of atmospheric deposition. In 2000, we added  $^{200}\text{Hg}(\text{II})$  to the same catchments so that we could begin to look at movement of mercury throughout the upland ecosystem on a multi-year time frame. We also did several isotopic additions at the micro-catchment scale. The purpose of these smaller studies was to better understand the mechanisms governing transport of newly deposited at the subcatchment scale.

In 2000, we added  $^{200}\text{Hg}(\text{II})$  to four 10-m diameter lake enclosures. Two of the enclosures received a single dose of  $^{200}\text{HgCl}_2$  at the beginning of the experiment. The purpose of this single pulse experiment was to determine pool labeling times. The other two enclosures were dosed at discrete time intervals to simulate of the whole-lake addition, which will be done on five occasions during the ice free season. At the time of writing, many samples are still under analysis. Preliminary results demonstrate loss of  $^{200}\text{Hg}(\text{II})$  to the atmosphere, and rapid movement of  $^{200}\text{Hg}(\text{II})$  to the periphyton on the sediment surface and walls of the enclosure, but minimal movement into sediments. We are also detecting production of  $[^{200}\text{Hg}]\text{MeHg}$  and uptake of inorganic  $^{200}\text{Hg}$  and  $[^{200}\text{Hg}]\text{MeHg}$  by zooplankton, and uptake of  $[^{200}\text{Hg}]\text{MeHg}$  by small fish contained in the lake enclosures.

This information will also be useful for modeling the results of whole-ecosystem addition, which begins in 2001.

**APPENDIX C**  
**POSTER ABSTRACTS**

**Mercury and Methylmercury in Water, Sediment, and Biota in an Area Impacted by Historical Gold Mining — The Bear River and South Yuba River Watersheds, California**

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The extensive use of mercury in the mining and recovery of gold during the late 19th and early 20th centuries has led to widespread mercury contamination of water, sediment, and biota in the foothills of the northern Sierra Nevada region of California. The Bear River and South Yuba River watersheds were chosen for a pilot study by the U.S. Geological Survey (USGS) and other cooperating Federal, State, and local agencies on the basis several factors: (1) previous bioaccumulation results, (2) the observation of elemental mercury at numerous mine sites and in river sediments, and (3) extensive historical mining on federal lands managed by the Bureau of Land Management and the U.S. Forest Service.

Of 53 water samples analyzed for Hg<sub>T</sub> (total recoverable mercury) in unfiltered splits, 17 samples (32 percent) had concentrations in excess of the U.S. Environmental Protection Agency (USEPA) aquatic-life criterion of 50 nanograms per liter (ng/L). Water flowing from two separate tunnels in one mining district had Hg<sub>T</sub> concentrations greater than 100,000 ng/L, far in excess of the USEPA drinking water standard of 2,000 ng/L. Concentrations of Hg<sub>T</sub> in filtered water samples generally were less by 1–2 orders of magnitude than those in unfiltered samples, indicating that most mercury is transported along with suspended particulate material. Concentration of Hg<sub>T</sub> in filtered (pore diameter of 0.45 micrometer) subsamples was greater than 50 ng/L at some mine sites, indicating truly dissolved mercury or mercury associated with colloidal particles that pass through the filters. Monthly sampling of the Bear River near its mouth revealed that MeHg (monomethylmercury) concentrations in unfiltered water samples were greater than 0.4 ng/L during two distinct seasons, July–August 1999 and then again in January 2000.

Game fish were collected from 5 reservoirs and 14 stream sites during 1999 to assess the distribution of mercury in the food chain and to examine the potential risk for humans and wildlife. Of 141 fish fillet samples analyzed for total mercury, 52 percent exceeded the new (December 2000) USEPA water-quality criterion of

0.3 parts per million (ppm), wet weight. Mercury concentrations exceeded the Food and Drug Administration (FDA) action level for commercial fish of 1.0 ppm in 14 percent of the samples of black bass (*Micropterus* spp.). Eighty-nine percent of the bass contained concentrations greater than 0.3 ppm total mercury. Based on these data, three counties have issued an interim public health notification recommending limited consumption of game fish from the Bear and Yuba watersheds; this is the first such advice from public agencies with regard to mercury levels in fish in the Sierra Nevada region.

Invertebrates were collected from 41 sites, composited by taxon, and analyzed for methylmercury. The median concentration of methylmercury in predaceous semi-aquatic and aquatic insects ranged from 0.045 ppm in stoneflies (order Plecoptera, family Perlidae), collected from 19 sites, to 0.103 ppm in giant water bugs (Hemiptera, Belostomatidae) from only four sites. Water striders (Hemiptera, Gerridae), the most common insect collected, were found at 76 percent of the sites. Concentrations of methylmercury in striders (median 0.084 ppm) closely matched relative mercury contamination levels in water, sediments, and other biota. The highest methylmercury concentration (1.61 ppm) was found in dragonflies (Odonata, Aeshnidae) collected at a highly contaminated site. Other invertebrates analyzed included dobsonflies (Megaloptera, Corydalidae), predaceous diving beetles (Coleoptera, Dytiscidae), and banana slugs (*Ariolimax columbianus*).

Total mercury was analyzed in carcasses of individual amphibians from 25 sites, including Pacific tree frogs (*Hyla regilla*) from 14 sites, foothill yellow-legged frogs (*Rana boylei*) from 11 sites, and bullfrogs (*Rana catesbeiana*) from 6 sites. The median mercury concentrations in the treefrogs (0.044 ppm) and the yellow-legged frogs (0.046 ppm) were similar, but the maximum for the treefrogs (0.231 ppm), collected from the Polar Star Mine tunnel outlet, was more than twice the maximum for the yellow-legged frogs (0.106 ppm). The median mercury concentration for bullfrogs was 0.100 ppm, with a range from 0.052 ppm to 0.183 ppm.

Ongoing research in the Bear and Yuba River watersheds is focused on (1) quantifying aqueous MeHg concentrations (and assessing possible MeHg artifacts) in the presence of high concentrations of  $Hg_T$  at the mine sites, (2) documenting the seasonal variations of methylmercury concentrations in water at mine sites and downstream areas, and (3) evaluating correlations between water composition, sediment chemistry, and mercury bioaccumulation in invertebrates, amphibians, and fish.

## Partitioning of Mercury to the Colloidal Phase in Fresh Waters

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The colloidal phase has been long recognized as a potential vector for the transport and biouptake of methylmercury (MeHg), but the tools to cleanly isolate colloidal material have been only recently adapted for trace-metal research. As a result, very few data about this important size fraction have been reported in the literature, and data on freshwater systems are particularly rare. Using tangential-flow ultrafiltration, total mercury ( $Hg_T$ ) and MeHg concentrations in the colloidal phase (0.4 $\mu$ m–10kDa) were determined for 15 fresh waters located in the upper Midwest (MI, MN, WI), Georgia, and the Florida Everglades.

Colloidal phase concentrations of  $Hg_T$  and MeHg comprised up to 72% of the unfiltered concentration, but on average, the particulate (>0.4 $\mu$ m), colloidal, and dissolved (<10 kDa) pools each contained roughly one third of the mercury mass. Expressed as a percentage of the filtered-passing fraction (<0.4 $\mu$ m), the pool of mercury in the colloidal phase decreased with increasing specific conductance. Although the mechanism for this decrease is unclear, results from experiments on waters with artificially elevated specific conductance suggest that  $Hg_T$  and MeHg partition to different subfractions of colloidal material.

On a mass basis, the colloidal phase  $Hg_T$  concentrations (28 to 338 ng g<sup>-1</sup>) were similar to that of nonimpacted soils, but colloidal phase MeHg concentrations (3 to 90 ng g<sup>-1</sup>) were relatively enriched. For  $Hg_T$ , the highest concentrations (>200 ng g<sup>-1</sup>) were generally observed during the spring melt when high flow rates resuspend sediments. For MeHg, the *lowest* concentrations (<10 ng g<sup>-1</sup>) were observed during the melt – likely due to decreased biotic methylation during the preceding winter. LogK<sub>D</sub> ranged from 4.3 to 6.6 for both  $Hg_T$  and MeHg.

Together, these results identify seasonal conditions that favor colloidal phase partitioning of MeHg in fresh waters, and by extension provide important insight on the transport and bioavailability of MeHg.



## **Mercury Content and Speciation of the Plankton and Benthos of Lake Superior**

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As part of a study to assess the importance of watersheds in controlling sources, transport, fate, and bioavailability of monomethylmercury (MeHg) in Lake Superior, biotic samples were collected and analyzed to determine mercury and methylmercury content, and to examine size, species, trophic and geographic trends. Our primary interest was to compare near shore and offshore sites, and to examine the changes which occur in tributary plume waters. Plankton was collected in two ways: vertical and horizontal tows of nonmetallic, 153 m mesh net (bulk zooplankton), and by passively filtering near-surface water through stacked Nitex sieves, generating size-fractionated particulate matter (<35 m, 35 to 63 m, 63 to 112 m, 112 to 243 m). Benthos was sampled using a Ponar grab to collect sediment, and a nonmetallic sieve to separate biota. Samples were processed to quantify dry weights, total Hg and MeHg.

Results for bulk zooplankton sampled offshore in April 2000 showed a range of MeHg from 35 to 50 ng gdw<sup>-1</sup> and total Hg from 115 to 120 ng gdw<sup>-1</sup>. Our estimates of MeHg concentrations in zooplankton from near shore areas (mouths of tributaries) range from 120 ng gdw<sup>-1</sup> river plumes to 30 ng gdw<sup>-1</sup> away from the riverine influence. Samples from the summer (August) are currently being analyzed, and will be discussed with an eye to seasonal patterns.

Results from sieved, near-surface water from the offshore site in April show dominance by the <35 m size fraction both in the mass of suspended particulate matter and the mass of MeHg (on a volume basis). On a dry weight basis, we see little difference between the size fractions in April (MeHg ranges from 2 to 10 ng gdw<sup>-1</sup>). During the summer cruise, we found similar concentrations in the < 35 m fraction, but higher concentrations in the 112 to 243 m size fraction (MeHg 14 to 16 ng gdw<sup>-1</sup>). Pigment analysis of the size-fractionated plankton indicates the presence of cyanobacteria in the <35 m fraction, and suggests the microbial loop may enhance MeHg concentrations in the lower size classes. Such analyses of near shore (mixing zone) seston show clear differences from our different tributary sites. These trends will be discussed as part of our study of watershed characteristics which influence bioaccumulation of MeHg in biota.

# **DISTRIBUTION OF MERCURY IN SHALLOW GROUND WATER OF THE NEW JERSEY COASTAL PLAIN AND A POSSIBLE MECHANISM OF TRANSPORT**

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More than 400 domestic wells that tap the major unconfined aquifer in 72 areas in New Jersey's Coastal Plain have yielded water containing total mercury at concentrations exceeding the maximum contaminant level (MCL) of 2  $\mu\text{g/L}$ . Concentrations of mercury in the aquifer typically are less than 0.01  $\mu\text{g/L}$ . Additional water-quality data collected at several of these contaminated areas indicate that concentrations of chloride and nitrate also are elevated.

In a regional study conducted by the U.S. Geological Survey in cooperation with the New Jersey Department of Environmental Protection, 126 domestic and observation wells in different land-use areas and 28 clustered observation wells in undeveloped and agricultural land were sampled. Mercury concentrations typically were less than 0.01  $\mu\text{g/L}$  in filtered (0.45- $\mu\text{m}$  pore size) samples, but tended to increase with concentrations of chloride (and other constituents), indicating that mercury may be transported as a chloride complex. Concentrations of mercury  $>0.1$   $\mu\text{g/L}$  did not correlate with concentrations of other constituents, however, indicating that mercury near and at the MCL may not be transported in the same chemical form as mercury at lower concentrations. Mercury concentrations  $>1$   $\mu\text{g/L}$  typically are associated with residential land use, but such high concentrations have not been found in water underlying undeveloped land. The distribution of these elevated mercury concentrations appears to be "spotty" at both the regional and neighborhood scales, as the presence of extensive plumes of mercury-contaminated ground water could not be demonstrated.

In a related study of 31 observation and domestic wells in one residential area, 14 domestic wells yielding mercury-contaminated water were resampled; mercury concentrations in filtered samples were much smaller ( $<0.1$  to 3.1  $\mu\text{g/L}$ ) than those in previously collected unfiltered samples (2.0 to 15  $\mu\text{g/L}$ ), indicating that much of the mercury present is adsorbed to particulate and colloidal material. Mercury concentrations were lower and mercury commonly was more evenly distributed in the soil profile of residential soils than in adjacent undisturbed forest soils in the area. The depletion of mercury in the residential soils likely indicates that mercury has been mobilized and transported from these soils to ground water. Detections of surfactants, ammonia, and sulfide, and high sodium and chloride concentrations (up to 59 and 89 mg/L, respectively) in water from many of the 31 wells likely indicate that septic-system effluent has affected water quality; this may provide a geochemical environment conducive to mercury mobilization.

On the basis of results from these studies, a four-part hypothesis is advanced regarding mercury transport in shallow ground water. (1) Mercury has been contributed to soils by atmospheric deposition and historical use of mercurial pesticides. (2) Mercury is mobilized from soils by disturbance during development activities. (3) Septic-system effluent provides sulfur-rich organic matter to bind mercury to organic colloids or particles and surfactants to promote colloid mobility. (4) Periodic surges in well pumping increase interstitial pore-water velocity, enhancing mobility and capture of colloids by wells. This preliminary model may be applicable throughout much of southern New Jersey, as other residential areas with mercury-contaminated ground water typically are unsewered housing developments. A research program to evaluate this hypothesis is under development.

## **The Positive Effect of Selenium on Mercury Assimilation by Freshwater Fish**

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The possible protective action of Se on Hg assimilation by living organisms has sometimes been mentioned in the literature. However, most of the studies to date have been conducted under abnormally high dosages of both elements which could have caused unrealistic physiological reactions in the studied biological species. Our study was designed to investigate a possible Se-Hg antagonistic effect in two freshwater fish species living in natural aquatic systems with different Se and Hg concentrations. The two selected fish were perch (*Perca flavescens*) which feeds mainly on zooplankton and benthic invertebrates and walleye (*Stizosedion vitreum*), a piscivore and dominant predator in the food chain of many lakes in North America. The concentrations of total Se and Hg were determined in muscles of fish coming from nine lakes which varied in distances (4–204 km) from the metal smelters of Sudbury, Canada. Average concentrations of both Se and Hg in tissue for a limited fork length range (100–150 mm for perch; 300–350 mm for walleye) were compared. Significant inverse relationships between Se and Hg in perch ( $r^2 = 0.79$ ,  $p < 0.05$ ) and walleye tissue ( $r^2 = 0.97$ ,  $p < 0.01$ ) were observed, which suggests a strong antagonistic effect of Se on Hg assimilation by those fish species. Concentration of Hg decreased exponentially with an increase of Se in fish muscle. Total dissolved Se concentrations of the lake waters declined with distance from smelters and were correlated to Se in perch ( $r^2 = 0.75$ ,  $p < 0.05$ ) and walleye ( $r^2 = 0.95$ ,  $p < 0.01$ ). Hg concentrations in the fish from lakes near the smelter were well below average values in fish in boreal shield lakes of this region.

## **Chemical and Biological Controls on Mercury Methylation in Aquatic Sediments**

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Methylmercury (MeHg) production in aquatic sediments is controlled by two important factors: 1) the bioavailability of inorganic Hg to Hg-methylating sulfate-reducing bacteria (SRB), and 2) the metabolic activity of these microorganisms. We have hypothesized that Hg uptake by SRB occurs via passive diffusion of the neutral complex HgS(aq) across cell membranes. Here we present results of octanol-water partitioning experiments and pure culture Hg-methylation assays that support this hypothesis. These studies show that while the mercury methylation rate is directly proportional to the concentration of the HgS(aq) in solution, the estimated diffusive uptake of this complex is several orders-of-magnitude greater than the methylation rate.

Although passive uptake may adequately describe the mechanism that limits Hg bioavailability to SRB, metabolic controls on MeHg production are less well understood. It has been demonstrated that the corrinoid protein involved in the Acetyl-CoA pathway is responsible for Hg methylation in one SRB strain. However, a number of other anaerobic bacteria, the methanogens and acetogens, also use this pathway, but they do not methylate Hg. We hypothesize that the acetyl CoA pathway is the route for MeHg production in all Hg-methylating SRB and the corrinoid protein in SRB has some unique properties that allow for methyl-group transfer to Hg(II). We have designed experiments aimed at investigating the universal role of this corrinoid protein in MeHg production among SRB species. Further, we are developing techniques to isolate this protein from SRB, so that we can investigate the characteristics that facilitate Hg methylation exclusively in this bacterial group.

## **Mercury Distribution Along an Urban Gradient in New England Streams**

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Conditions increasing mercury methylation are of particular concern because methylmercury (MeHg) is the most toxic mercury species, and it is most rapidly bioaccumulated and biomagnified in wildlife and man. The New England Coastal Basins study unit, as part of the U.S. Geological Survey's NAWQA program, has evaluated relations between concentrations of total mercury ( $Hg_T$ ) and MeHg in stream water and streambed sediment over a range of urban land use. Fifty-five stream sites from Rhode Island to Maine were sampled between 1998 and 2000. Sediment and water samples were collected during summer low flow to show patterns of total mercury and MeHg accumulation and partitioning relative to site and watershed conditions.  $Hg_T$  concentrations in water and bed sediment ranged from 1 to 13 nanograms per liter (ng/L) and 5 to 3100 nanograms per gram (ng/g) dry weight respectively. Concentrations of MeHg in water and sediment ranged from 0.04 to 1.8 ng/L and 1 to 38 ng/g dry weight respectively. Data suggest that urban areas may have higher  $Hg_T$  loads but lower methylation rates than rural areas. Methylation efficiency, as estimated by  $MeHg/Hg_T$ , was higher at sampling sites with low urbanization and high wetland density. Concentrations of MeHg in sediment and water were positively correlated with concentrations of organic carbon. Results suggest that urbanization of ecosystems decreases the production and accumulation rates of MeHg.

## **A Screening Level Probabilistic Risk Assessment of Mercury in Florida Everglades Food Webs**

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We performed a screening level probabilistic assessment of risks to three species of piscivorous wildlife at the top of Everglades aquatic food webs: the American alligator (*Alligator mississippiensis*), the great egret (*Egretta alba*), and the raccoon (*Procyon lotor varius*). Ranges of dietary exposure concentrations (and probability distribution functions) were derived for two general areas of the Everglades: Shark Slough and the south-central Everglades (highly contaminated with Hg), and the northern Everglades (a lower Hg contaminated area in and near Water Conservation Area 1). Ranges of toxicity reference values (TRVs) and probability distribution functions were derived from literature on the toxicity of dietary methyl Hg to birds and mammals. Probability distributions of risk estimates for each receptor were generated using Monte Carlo simulations and indicated that piscivorous wildlife feeding in the south-central region of the Everglades are at high risk from consumption of Hg contaminated prey. Alligators had 100% exceedences of chronic risk thresholds, and great egrets had 99% exceedences. In the northern Everglades, exceedences of chronic risk thresholds were substantially lower but were still present (6-34% exceedences). Our results support previous studies suggesting top predators of the Everglades may be at risk from Hg contamination and indicate that Hg risks are location dependent.

Abstract taken from Duvall, Stephanie E. and Mace G. Barron, Ph.D. 2000. *A screening level probabilistic risk assessment of mercury in Florida Everglades food webs*. Ecotoxicology and Environmental Safety 47(3): 298-305.

## **Measurements Mercury Fluxes from Natural Sources**

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Through an interdisciplinary collaboration we have quantified gaseous elemental mercury (GEM) emissions from naturally mercuriferous soils and bedrock in contrasting landscapes and geological settings in Canada and the USA. Natural sources quantified include: mineralized fault zones in central BC and southeastern Ontario; carbonaceous shale outcrops and quarries near Thunder Bay, Ontario; agricultural lands near Ottawa, Ontario; sand and gravel outcroppings near Rouyn-Noranda, Quebec and in the USA at a geothermal zone south of Reno, Nevada (Gustin et al, 1999).

Both Micrometeorological and Chamber methodologies have been developed specifically for quantifying these sources of GEM to the atmosphere. The methods developed accommodated the high spatial and temporal variability of these emissions as well as the wide dynamic range of the flux rate, (Edwards et al., 2001). In addition to the measurement of the GEM air-surface exchange rates at each site, measurements of controlling environmental variables were undertaken. A complete suite of associated meteorological measurements was obtained as well as substrate temperature, moisture, and mercury concentration (Rasmussen et al., 1998).

This presentation discusses the methods used, their limitations and the measurements obtained. The field measurements are presented highlighting the relationships developed for scaling up these data to better estimate natural emissions inventories.

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**Mercury Concentrations in Water and Fish from the Mobile-Alabama River Basin:  
A Preliminary Assessment**

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The purpose of this study was to examine the relationship between land use and mercury (Hg) levels in water and fish in the Mobile-Alabama River Basin (MARB), and to investigate links between Hg levels in water and fish. Water and fish (largemouth bass) from 52 locations were collected and analyzed for total-Hg (THg) concentrations. Water samples were collected using ultra-clean techniques and analyzed using Cold-Vapor Atomic Fluorescence Spectrometry (CV-AFS) following reduction with tin chloride. After collection, fish were frozen to  $-20^{\circ}\text{C}$ , and freeze-dried aliquots were analyzed using detection by CV-AFS following acid digestion.

Preliminary results from water samples show low THg concentrations ( $0.43\text{--}2.23\text{ ng L}^{-1}$ ), which fall among background levels typically found in natural waters. THg concentrations greater than  $1.0\text{ mg/g}$  (wet wt.) have been detected in fish from three locations thus far, two of which were in reaches associated with wetlands. A significant correlation ( $r^2=0.70$ ,  $p=0.005$ ) was found between mean concentrations of THg in water samples and in fish when considering nine out of twelve general locations within the MARB. The log bioaccumulation factor between the fish and the water ranges between 5.0 and 5.5 with the exception of the three extraneous sample locations. The reason for these three sites being “outliers” is unknown. The above mentioned correlation is surprising since previous research in freshwater aquatic systems has shown little to no correlation between Hg concentrations in the water and those in fish. These results will be discussed in light of previous studies in freshwater systems.



## **Mercury in Keweenaw Waterway and Lake Superior Sediments: Sources, Dispersal, and Behavior**

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The perception that the Lake Superior watershed is influenced largely by long-distance transport of contaminants can be misleading. Along the shoreline, a high-energy coastal zone focuses terrestrial inputs into marginal troughs. Therefore, sampling only the central, deepest sediments misses these important anthropogenic contributions. Many of the sources are from mining operations which exploited the rich mineral resources of the basin for over 150 years, leaving tailing piles and abandoned smelters scattered throughout much of the watershed.

Mercury and copper inventories are low in central Lake Superior, increase toward shorelines and are highly correlated with copper and silver inventories, suggesting fine particle transport from terrigenous sources. Higher inventories are found in coastal troughs near mining regions, tripling previous estimates for mercury storage in Lake Superior sediments. In the Keweenaw Peninsula region, high mercury, copper, and silver inventories can be traced back to shoreline stamp sand piles, the parent native metal ores, and to smelters. Mercury is found in both copper and silver ores, but concentrations are consistently higher in Keweenaw native silver than in native copper, differing by an order of magnitude. Mercury concentrations are very low ( $< 5 \text{ ng g}^{-1}$ ) in the basaltic parent rock. Mercury was not imported into the region for amalgamation extraction of the Keweenaw Peninsula copper ore lodes. The silver-enriched native copper deposits contain relatively high concentrations of mercury. Mercury commonly occurs in metal ore deposits as a trace constituent in the Lake Superior region (copper, silver, gold). Assays of specimens from Ontario document the widespread incidence of mercury in regional silver and gold deposits. Mercury also is commonly present in silver, gold, copper, and lead deposits worldwide. Mercury was also imported for amalgam extraction in many Ontario precious metal mining districts such as the Lake Nipigon, Manitouwadge, and Marathon-Michipicoten regions.

At present, shoreline sources dominate, accounting for an estimated 51-76% of mercury and from 87-98% of copper loadings to Lake Superior sediments. The greatest concern regarding the deposition of mercury-containing mine waste in and near watersheds is the conversion of the mineral-bound mercury to the more bioavailable methylated forms in wetland regions or in organic-rich sediments. A recent study by Jeong, et al. (1999) of Keweenaw Waterway mine waste reveals that native copper within the mine waste slowly leaches from the tailings and is reprecipitated as soluble forms such as malachite and azurite on the surface of the tailings particles. As mercury is associated with the native copper, it can be assumed that mercury is being leached from these particles as well. In addition, there is evidence of early diagenesis of mercury from many of the cores, particularly those taken in the region of the Keweenaw Peninsula, potentially increasing mercury concentrations and residence times in surficial sediments.

## **The Effect of Sediment Disturbance on Methylmercury Production in Estuarine Sediment**

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Disturbance can temporarily upset the established redox chemistry and nutrient balance of sediments. The primary methylators of Hg are sulfate reducing bacteria, therefore their activity and ability to methylate are limited by the supply of sulfate, carbon and Hg. In the Patuxent River, an estuary of the Chesapeake Bay, we simulated sediment disturbance, associated with activities such as boating and crabbing, in enclosures. Sediment was disturbed to a depth of 5 and 10 cm, on two occasions two days apart, after which Hg, MeHg concentrations in sediment, sulfate, sulfide, and Mn concentrations in porewater and methylation rates (using stable isotopes) were followed. Neither MeHg concentrations nor Hg methylation rates increased significantly above the controls over the month long study despite obvious changes in porewater chemistry. More importantly, MeHg production and concentrations were measured together in the same sediment cores. MeHg production and MeHg concentration were significantly correlated ( $R^2 = 0.80$ ), suggesting MeHg concentration is a good indicator of short term MeHg production.

**Rapid, Ultra-sensitive Detection of Gas Phase Elemental Mercury Under Realistic Atmospheric Conditions Using Sequential Two-Photon Laser Induced Fluorescence — A Viable Sensor for Eddy-Correlation Measurements**

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An examination of the cycling of mercury in aquatic and terrestrial ecosystems necessarily requires an understanding of the rates and mechanisms of emission and deposition of elemental mercury. Soils and lakes can act as sources of mercury and can show diurnal variations in such emissions. Plants appear to act as sinks. To date all such measurements have used chamber or gradient methods. The reason that the most direct micro-meteorological approach, the eddy-correlation technique, has not been applied is the lack of a suitable chemical sensor with the requisite time response. The most commonly used techniques require preconcentration on gold traps and, while the sensitivity of such techniques is more than adequate for concentration measurements at ambient levels, the response time of several minutes precludes their use in eddy-correlation techniques. In this work we describe a novel laser based technique with an extremely high detection sensitivity and very fast time response. As part of a program to study the gas phase atmospheric chemistry of mercury we have examined the sensitivity of sequential two photon laser induced fluorescence (LIF) detection techniques. These involve an initial laser excitation of the  $6^3P_1-6^1S_0$  transition at 253.7 nm, the excitation used in techniques such as CVAFS (Cold Vapor Atomic Vapor Fluorescence Spectrophotometry) employed by the Tekran 2537A. In the sequential two photon LIF approach this is followed by excitation with a second laser to either the  $7^1S_0$  or  $7^3S_1$  levels followed by observation of blue or red shifted fluorescence. We have examined all the variants of these approaches. The excitation scheme, involving sequential excitation of two atomic transitions, followed by detection of the emission from a third is extremely specific and precludes detection of anything other than atomic mercury. We use a Nd-Yag pumped optical parametric oscillator and frequency doubled dye laser as our excitation sources. The most sensitive detection approach involves the initial 253.7 nm excitation followed by excitation of the  $7^1S_0-6^3P_1$  transition at 407.8 nm. Fluorescence is observed on the  $6^1P_1-6^1S_0$  transition at 184.9 nm using a solar blind photomultiplier tube. The advantage of this approach is that, since the observed LIF signal is blue shifted relative to the pumping lasers, it is possible to eliminate scattered light. Because of the difficulties associated with calibration at trace levels of  $\sim 1 \text{ ng/m}^3$  we chose to sample simultaneously with a Tekran Model 2537A. Hence all concentration data are based on levels reported after 2.5 minute sampling times by the Tekran and the accuracy is defined by the accuracy of the internal calibration source in the Tekran. Using our 10 Hz laser system we have achieved a detection sensitivity of  $0.1 \text{ ng/m}^3$  for a sampling rate of 1 Hz, i.e. averaging 10 laser shots. We have examined the linearity, generating flows containing levels between 1 and  $10000 \text{ ng/m}^3$  using a permeation tube and dynamic dilution, but relying on the Tekran concentrations at low levels and the concentration calculated from dilution at high levels, and find that the detection is linear over the five orders of magnitude that we were able to vary the concentration.

We thank Tom Atkeson for the loan of the Tekran 2537A. This work was supported by the Florida Department of Environmental Protection.

## **Ionic Mercury Adsorption to Soils — The Influence of Physico-Chemical Parameters Relevant to Industrial Site Situations**

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Risk assessment of mercury contaminated sites will be greatly influenced by its speciation which will define its mobility and toxicity. It is therefore fundamental to understand the fate of mercury when it is released in a soil. Furthermore, it must be recognised that at industrial sites, conditions prevail that are different to those in natural soils. Indeed, at industrial sites, soil often consist of a more or less thick layer of made up ground and the physico-chemical conditions can be strongly influenced by the above ground activities. Local conditions due to industrial operation may have led to specific local artificial conditions that can have an impact on mercury mobility.

A statistical design was used to evaluate the influence of parameters relevant to mercury-cathode chlor-alkali plants, i.e. pH, salinity, presence of oxidant on the adsorption of ionic mercury. The type of soil has also been studied.

The response modelled is the  $pK_a = -\log K_a = -\log C_s/C_l$ , where  $C_s$  = mercury concentration on the solid phase (mg/kg) and  $C_l$  = total mercury concentration in the liquid phase.

The parameters with the greater impact on adsorption of ionic mercury are the nature of the soil, the chloride concentration and the pH.

Ionic mercury adsorption is favoured by soil with higher organic content (peat >> loam 16 g-C/kg > sand 2 g-C/kg > clay 1.5 g-C/kg), and by alkaline pH, this effect being more pronounced on soil with low organic content maybe due to the precipitation of mercuric carbonate and/or oxide.

Ionic mercury desorption is favoured by high chloride concentration and the presence of active chlorine. Up to 10ppm of soluble humic acid had little impact on adsorption.

## **Hydrogeological and Geochemical Factors Influencing Mercury Fate and Transport at the Sulphur Bank Mercury Mine, Lake County, California**

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Clear Lake, located approximately 150 km north of San Francisco in Lake County, is one of the largest freshwater lakes in the California. Elevated mercury levels were first identified in fish from Clear Lake in the late 1970s and early 1980s. Although naturally occurring mercury deposits are common in this region, the Sulphur Bank Mercury Mine (SBMM), located adjacent to Clear Lake, also is a potential source for a modern-day mercury flux to the local aquatic ecosystem. The Sulphur Bank hot springs mineral deposit was discovered in 1857 and the hydrothermal system responsible for depositing the mercury ore is still active. Subsurface and surface mining operations produced an estimated  $4.7 \times 10^6$  kg of mercury from the SBMM. However, surface mining also created the Herman Pit (a 9.3 ha, 30 m deep, open pit) surrounded by over  $1.1 \times 10^6$  t of waste rock, tailings, and overburden. Mining ceased in 1957 and the open pit filled with water forming the Herman Impoundment. Herman Impoundment is a hydrologic sink for surface and ground waters in the immediate watershed. The impoundment also receives water upwelling from the underlying hydrothermal system. The water in the impoundment is acidic (pH~3) due to the oxidation of H<sub>2</sub>S gas and sulfide minerals. Herman Impoundment and Clear Lake are separated by a distance of about 250m, but the hydraulic head of the impoundment is approximately 3.8 m greater than that of the lake. Subsurface outflow is a major component of discharge from the impoundment with ground water migrating to Clear Lake through the mercury-laden waste rock and overburden.

The USEPA has been conducting a comprehensive site investigation to characterize the hydrogeologic and geochemical setting at the SBMM. Results from this investigation indicate that the majority of ground water discharge from the site to Clear Lake occurs through the waste rock/upper lake sediments unit (2,000 - 3,000 ft<sup>3</sup>/day, or 65% of the total discharge). The remaining subsurface discharge passes through the andesite (900-1,300 ft<sup>3</sup>/day) and lower lake sediments units (150-250 ft<sup>3</sup>/day). Surface and ground water quality samples have been collected and analyzed for a variety of constituents. Mercury concentrations (dissolved and solid phase) are greatest in the waste rock/upper lake sediments unit and the subsurface mercury flux from the impoundment to Clear Lake occurs almost entirely through this unit (99.8% of the total Hg flux). Water chemistry results suggest that water-rock interaction at a lower pH and an increased oxidation state within the waste rock and overburden is supplying more mercury to Clear Lake than the hydrothermal system beneath Herman Impoundment. These observations make it possible to entertain the concept of remediating this site in the presence of an active hydrothermal system, which itself is a natural mercury flux to the local ecosystem.

**Is “Reactive” Mercury (Stannous Chloride Reducible) a Good Indicator of Bioavailable Mercury in Water?**

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"Reactive" mercury is defined as the fraction of total mercury that is easily reducible by stannous chloride ( $\text{SnCl}_2$ ) under acidic conditions. It has been suggested as a measure of biologically active mercury, and so could be the fraction of mercury available for uptake and possibly methylation by bacteria. In this study, we tested the validity of this assumption by directly measuring the bioavailability of inorganic mercury ( $\text{Hg(II)}$ ) in water using a bioreporter bacterium and comparing these results to the chemically defined “reactive” mercury fraction. The bioreporter is a genetically engineered bacterial strain that emits light in amounts that are directly proportional to the bioavailable  $\text{Hg(II)}$  that enters their cells. Defined solutions of 3 ng  $\text{Hg(II)/L}$  as  $\text{Hg(NO}_3)_2$ , with various additions, as well as different types of whole water samples, were studied. Additions of  $\text{NaCl}$  to the  $\text{Hg(II)}$  solutions had a decreasing effect on bioavailable mercury, but no effect on “reactive”  $\text{Hg}$  concentration. Additions of dissolved organic carbon (DOC), using a concentrate ( $>10\text{K}$  and  $<100\text{K}$ ) from natural lake water, had an effect on both measurements, but a much greater effect on bioavailable  $\text{Hg(II)}$  than on “reactive”  $\text{Hg(II)}$ . Also, the DOC itself contained  $\text{Hg(II)}$  that was reduced by  $\text{SnCl}_2$  reduction but was not bioavailable to the bacteria. In 3 types of natural water samples, both reactive and bioavailable mercury measurements followed the order rain  $>$  groundwater  $>$  sewage, but the % reactive mercury was always greater than the % bioavailable. Thus, not all  $\text{Hg(II)}$  that was measured as “reactive” could be considered bioavailable to bacteria.

**Effects of Temporal and Spatial Variability in Food Webs on Bioaccumulation of Hg in the  
Everglades: The Combined Use of Stable Isotopes, Gut Contents, and Hg/MeHg Data**

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As part of a collaboration between the USGS and FFWCC, some 4000 plant, invertebrate, and fish samples were collected at about 15 sites in the Everglades and analyzed for  $d^{13}C$  and  $d^{15}N$ , with a subset analyzed for  $d^{34}S$ . The gut contents were evaluated and the total Hg and/or MeHg were determined for some 1500 of these samples, mostly fish. The isotopic and gut contents data provide complementary methods for determining average diets and relative trophic positions of biota in this ecosystem, which then can be used to estimate bioaccumulation factors. The gut contents data are most useful for identifying the major food sources to fish. In theory,  $d^{15}N$  values should provide more accurate assessments of long-term average trophic levels since the values reflect the material actually assimilated, not just ingested. For example, isotopic data suggest that most of the abundant periphyton commonly found in gambusia guts probably is not assimilated. However, interpretation of the isotopic data is complicated by the large (2-10‰) seasonal and spatial ranges in compositions caused by local biogeochemical processes that affect the compositions of primary producers. The  $d^{15}N$  values must be corrected for the effects of these processes before they can be used to identify relative trophic positions. In the Everglades,  $d^{13}C$  values are most useful for distinguishing between sites and seasons where the base of the foodweb leading to most fish species is primarily algal vs. detrital. Algal-dominated foodwebs appear to result in higher Hg concentrations in fish than macrophyte detritus-dominated foodwebs. Spatial changes in redox chemistry across the Everglades have caused very strong regional patterns in  $d^{13}C$ ,  $d^{15}N$ , and  $d^{34}S$  of local biota. Hence, under favorable conditions, stable isotopes can be used to determine whether fish migrate into some marshes in response to changes in water level or food availability. Such information can often explain anomalously low MeHg contents of fish from environments with high levels of MeHg.

## **Spatial and Temporal Changes in Food Web Structure and Biogeochemical Reactions in the Everglades**

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A clear understanding of the aquatic food web is essential for determining the entry points and subsequent biomagnification pathways of contaminants such as methyl-mercury in the Everglades. We are attempting to use the  $d^{15}N$ ,  $d^{13}C$ , and  $d^{34}S$  of biota in marshes and canals in the Everglades as (1) indicators of local environmental conditions that may impact water quality and biota, and (2) indicators of foodweb structure.

We find that  $d^{13}C$  values provide a powerful tool for distinguishing between sites where algae vs. macrophyte debris (and the bacteria living on it) are the dominant bases of the foodwebs. The  $d^{13}C$  values of organisms from relatively pristine marsh sites sampled by the USGS are consistent with algae being the dominant foodweb base most of the time (perhaps depending on water levels), whereas the  $d^{13}C$  and  $d^{15}N$  values of scavengers such as shrimp and crayfish are consistent with macrophyte debris being an important food source for the impacted sites most of the time. The  $d^{13}C$  values of samples collected by the REMAP program in September 1996 also show spatial differences in the importance of algae as a base of the foodweb. Macrophyte debris appears to be important to the mosquitofish foodweb at about half of these sites. Several chemical parameters measured at the sites by the REMAP program show significant differences between sites where the foodwebs are predominantly algal and ones with appreciable contributions from macrophyte debris. These data are consistent with sites where macrophyte debris is important to the local foodwebs generally having more anoxic conditions than sites where algae is the dominant base of the foodweb. The general agreement of the REMAP data with the conceptual model developed to explain temporal and spatial variability in foodwebs at ACME sites, provides moderate evidence that spatial differences in dominant foodweb base across the Everglades are related to environmental conditions such as nutrient conditions and hydroperiod.



## **Determining Hg Speciation in Natural Environmental Systems Using X-Ray Absorption Fine Structure (XAFS) Spectroscopy**

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The speciation of mercury is one of the primary factors that dictate its mobility, transport, and potential bioavailability in the environment. Determining the speciation of mercury in Hg-bearing waste materials is critical to understanding the release of mercury from such point sources and its distribution in surface aqueous systems. This study utilizes X-ray absorption fine structure (XAFS) spectroscopy to identify both the types and relative proportions of mercury species present in different natural systems where mercury contamination poses serious environmental concerns. These systems include abandoned mercury mine waste piles, sediments and colloidal particles released from mercury mine wastes [1], and gold mining regions where Hg has been introduced as part of the gold extraction process.

Mercury L<sub>III</sub>-edge XAFS spectra were collected on several samples from the contaminated regions listed above, with total mercury concentrations of samples analyzed ranging from 150-1060 ppm. The identities and relative proportions of mercury species present in the samples were then determined by linear combination fitting of the XAFS spectra with spectra from a model compound spectral database consisting of mercury minerals and model sorption complexes [2]. Linear fitting analysis of XAFS spectra indicates that insoluble mercuric sulfides, either as cinnabar (HgS, hex.) or metacinnabar (HgS, cub.) are the dominant mercury species in nearly all samples, ranging from 58-100% of the total mercury present. This is consistent with the identification of cinnabar as the primary ore mineral in mercury deposits. Several minor mercury species were also identified in the samples, including montroydite (HgO), schuetteite (Hg<sub>3</sub>O<sub>2</sub>SO<sub>4</sub>), corderoite (Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>), and a variety of Hg-Cl phases. Due to their increased solubilities compared to mercuric sulfides, these minor phases may represent the most significant contributors of Hg to the environment.

Mercury speciation in mine wastes correlates well with the initial geological conditions of mercury ore deposition, with the identification of Hg-Cl phases apparent only among samples collected from hot-spring mercury deposits, where chloride levels are elevated. Additional factors such as ore roasting, weathering reactions, Hg<sup>0</sup> transformation to microcrystalline mercuric sulfides [3], and particle size appear to impact both the speciation and total concentration of Hg present. Sorbed mercury phases were not detected on any samples analyzed, contradicting the common conception of mercury transport/sequestration as a dissolved aqueous species and introducing the possibility that mercury travels dominantly in the solid phase associated with small particles throughout surface aqueous systems. Using XAFS as a direct, *in-situ* technique for determining the speciation of Hg in natural systems may aid in the identification and prioritization of the most contaminated and potentially harmful sites, and guide remediation efforts towards these sites appropriately.

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## **Trends in Mercury Bioaccumulation in Largemouth Bass from the Florida Everglades**

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Significant bioaccumulation of mercury has occurred in the Everglades ecosystem. Top-level predators, such as largemouth bass, have accumulated mercury to levels resulting in vast areas of the Everglades being listed under state health advisories urging limited and in many cases no consumption by anglers. The significance of bioaccumulation to fish eating wading birds and the endangered Florida panther are not well understood. Spatial and temporal variations in the distribution of mercury have been evaluated through the collection and analyses of mercury in largemouth bass from 13 sites in the Everglades and peninsular Florida since 1989. Study sites, located in canals and marshes along a north-south transect through the Everglades, have been monitored annually to determine trends in bioaccumulation of mercury. In addition, two lakes and a river have been monitored in the peninsula of Florida. Interpretation of results are complicated by sexually dimorphic growth in largemouth bass. Standardization of mercury to an age 3 (*EHg3*) largemouth bass provided the most accurate method of standardization for distinguishing differences among sites and dates. Concentrations varied greatly among sites; however, a trend of increasing mercury concentrations was observed from the Everglades Nutrient Removal Project south into the water conservation areas where concentrations were maximal in the marsh of Water Conservation Area 3A. Mercury levels remained high south into Shark Slough in Everglades National Park. During the past three years decreases in standardized mercury concentrations have occurred throughout the Everglades with some of the more southern sites that lie within the mainstream drainage of the Everglades experiencing the most significant declines. Between 1996 and 1997 significant declines occurred at sites in the water conservation areas and Everglades National Park. In the L-67A Canal, in Water Conservation Area 3A, concentrations decreased from a eight year range of 0.96 to 1.95  $\mu\text{g/g}$  (1989-1996) to a three year range of 0.45 to 0.67  $\mu\text{g/g}$  (1997-1999). Similar declines occurred in other areas of the Everglades but no apparent trends were evident in peninsular Florida. The results of this ongoing study are providing a temporal and spatial database on the distribution of mercury in predatory fish from the Everglades and peninsular Florida for use in: investigating bioaccumulation and bioavailability of mercury to piscivorous wildlife; protecting human health; and providing a framework for evaluating the effects of future restoration efforts on mercury bioaccumulation in the Everglades.

**Mercury in Industrial Landscapes of Former USSR: A Case of Kazakhstan**  
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The joint venture "Khemprom" in Pavlodar City had some loss of mercury in the past into various areas of the industrial complex. For 18 years the grounds, waters and atmosphere of the industrial complex were contaminated with mercury during the production of chlorine and sodium hydroxide. Under one shop a deposition of 1130 tons of metal mercury was registered at a depth of 2 to 4 m on the perimeter of the shop with a floor space of 7500 m<sup>2</sup>. Also, major mercury emissions into the atmosphere took place. The soils of the industrial area and underground waters were contaminated at depths up to 20 m. The wastewater pool which has a volume of more than 80 million m<sup>3</sup> and a settling area of 25 km<sup>2</sup>, now contains 10-15 tons of mercury compounds in its bottom deposits. It has been established that the underground waters containing mercury have reached and are entering the Irtysh River, which is 5 km from the factory.

The joint venture Karbide in Temirtau has in the past dumped wastewater from acetaldehyde production into the Nura River for 47 years. Simultaneously, coal ash was also discharged into the river from a power-station just upstream. Over a period of 20 years more than 5 million tons of coal ash were discharged into the river. The Nura River has an average flow of only 6 m<sup>3</sup>/s. Currently, there are about 2 million tons of technogenic silts containing 75 tons of mercury compounds. Along the same 25 km stretch of the river there are an additional 40 tons of mercury compounds in the top layer of flood plain soils. The level of mercury pollution in the topsoil of this industrial complex exceeds the level in the Pavlodar case by many orders of magnitude.

**Microbiological Processes in Regions of Mercury Contamination:  
Special Circumstances and Studies in Kazakhstan**

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The regions of mercury contamination in Kazakhstan (cities Temirtau and Pavlodar) are characterised by an arid and sharply continental climate with long and cold winters. The conditions favourable for microbial growth in soils take place during the short spring. During this same period the peak of mercury flux into surface water and the atmosphere is observed. It has been established that the association of methanogenic bacteria do not undergo the competition from sulphate-reducing bacteria at low temperature, consequently, the processes of methylated mercury formation are dominant. The process of sulphate reduction, and correspondingly formation of mercury sulphide, is activated at high summer temperatures. It is observed, however, mainly in bottom aquatic sediments due to the lack of moisture in the soils. The case of Temirtau differs from Pavlodar by lower bioavailability of mercury because of its complexation with huge amounts of power station ash in sediments and flood plain soils of river Nura.

## **The Influence of pH and Redox Conditions to the Methylation of Mercury in Freshwater Sediments**

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The present laboratory study focuses on the effect of pH and aerobic/anaerobic conditions (along with changes in other conditions) on the methylation of mercury in freshwater sediments.

The model sediment mixture was incubated under agitation for a long period (usually, 3-4 weeks) in order to reach steady-state conditions. During this incubation under controlled pH and redox several biochemical parameters were monitored, i.e. composition of anions, total organic carbon, dissolved organic carbon and biochemical oxygen demand. A radiochemical technique using isotope  $^{203}\text{Hg}$  was used to determine the rates of methylation of mercury in incubated sediments.

It has been established that aerobic conditions stop methylation at all pH levels, whilst, anaerobic conditions stimulate methylation at neutral and basic pH. Acidic anaerobic conditions significantly reduce methylation and almost stop it at a pH of about 5.0. The concentration of dissolved mercury in sediment porewater as an indicator for the bioavailability of Hg was also studied at different pH levels. It was found that an increase of pH leads to significant growth of the dissolved mercury concentration at both aerobic and anaerobic conditions.

It should also be noted that the secondary parameters studied (mainly, anionic composition of porewater and dissolved organic carbon) showed trends, which could help to explain the indicated differences in methylation rates.

## **Atmospheric Mercury Emissions from Municipal Solid Waste Landfills**

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The volatility of mercury is well known, and the possibility that Hg may be emitted to the atmosphere from municipal landfills has been suggested, but rarely quantified. From 1997 to 1999, we conducted three studies of Hg emissions from four Florida landfills. Our original data documented that Hg losses occurred via two primary pathways; fugitive losses from the working face, and losses with landfill gas (LFG) emissions. Hg concentrations in LFG appear to decrease strongly with increasing landfill age, suggesting that once buried, Hg may be sequestered. This presentation describes our recent studies to reduce the uncertainties in Hg losses from waste management by (1) measuring Hg fluxes from additional landfills, (2) monitoring Hg emissions during the storage and processing of Hg-bearing wastes, and (3) speciating Hg emissions in LFG.

Mercury emissions from the landfill surface were quantified using an automated flux chamber approach that relies on in-field near-real-time mercury analyses using a Tekran Mercury Analyzer 2537A. Fluxes were measured at various landfill locations, as well as at a waste transfer station. Waste was collected and sorted to identify sources of mercury. Ambient Hg measurements were made approximately 30-50 m downwind from the landfill working face during routine placement and compaction of wastes.

Briefly, our new data indicate that the most significant quantities of Hg are lost to the air during waste handling and dumping, and that volatile methylated Hg compounds are being formed in landfills. We identified several sources of Hg in waste, including broken thermometers, fluorescent bulbs, and old batteries. Fugitive emissions from the working face were correlated with waste dumping and spreading activities. Perhaps of most interest was the identification of highly elevated levels of gaseous dimethylmercury in LFG, and methylmercury in LFG condensates. If LFG is not combusted, landfills could be important sources of atmospheric methylated Hg compounds.

Project is supported by the Florida Department of Environmental Protection and the Electric Power Research Institute; ORNL is operated by Lockheed Martin Energy Research for the US Department of Energy.

**Evaluation on Environmental Factors Affecting Gaseous Hg Emission from Subtropical Vegetation  
in the Florida Everglades**

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Intensive, seasonal field campaigns were implemented to evaluate atmospheric Hg fluxes over the Florida Everglades, where levels of Hg in fish exceed human health guidelines. We quantified Hg emissions intensively from the wetland vegetation, primarily cattail (*Typha domingensis*) and sawgrass ecosystems (*Cladium jamaicense*). We sampled Hg<sup>0</sup>, CO<sub>2</sub>, O<sub>3</sub>, and water vapor fluxes over emergent vegetation in the Everglades over 2 years. Plant stomatal conductance and leaf area indices as well as temperature for cattails and saw grass were also measured.

During Fall 1996 to Winter 1998, we completed the most extensive data set yet collected on Hg<sup>0</sup>, CO<sub>2</sub>, and water vapor fluxes over *Typha*. Mercury fluxes were dominated by emissions from the plant surfaces, and transpiration is now realized as an appropriate term for this phenomenon. The patterns of the emission of water vapor and Hg are clearly similar, with the latent energy flux explaining ~40% of the variance in Hg flux ( $r=0.62$ ,  $p<0.001$ ,  $n>200$ ). On the hand, weaker but still significant correlation exists for the sawgrass data as well ( $r=0.4$ ,  $p<0.01$ ,  $n=96$ ). These observations and the relationships also apparent for Hg<sup>0</sup> and CO<sub>2</sub> emissions form the basis for our flux modeling. Mercury fluxes appeared being influenced by solar radiation and temperature: for *Typha*, mean summer daytime emission =  $31\pm50$  ng m<sup>-2</sup> h<sup>-1</sup>, mean nighttime =  $0.2\pm15$  ng m<sup>-2</sup> h<sup>-1</sup>; for *Cladium*, mean daytime =  $17\pm29$  ng m<sup>-2</sup> h<sup>-1</sup>, mean nighttime approached zero. Comparing to the Hg flux data from open water surface, the “transpiration” of Hg<sup>0</sup> from aquatic macrophytes is the single largest flux of Hg in this ecosystem. Our study data are comparable to the data most recently reported for a Northern *Spartina* marshes.



Incubation studies on sediment and lacunal gas data both suggested that the source of Hg flux from vegetation was in the sediment. Presumably roots of vegetation interacts with mercury compounds in the sediments and reduce ionic mercury to elemental Hg which was then transpired and released into the atmosphere.

Research is sponsored by the South Florida Water Management District and the Electric Power Institute under contract with ORNL (managed by the Battelle Institute and the University of Tennessee for the US DOE).

**The Fate and Cycling of Mercury in the Sunday Lake Watershed, Adirondacks, New York: A Preliminary Mass Balance**

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The Sunday Lake watershed, located in the Adirondack region of New York, was studied in order to calculate a mercury mass balance for the lake and watershed systems. Analysis was conducted on surface water, soil, soil waters, and sediments to determine the fluxes of total mercury ( $\text{Hg}_T$ ), methylmercury ( $\text{CH}_3\text{Hg}^+$ ) and dissolved organic carbon (DOC). A program was established with the MDN to analyze precipitation samples for  $\text{Hg}_T$  and  $\text{CH}_3\text{Hg}^+$ . The wet deposition of  $\text{Hg}_T$  and  $\text{CH}_3\text{Hg}^+$  were estimated to be  $10.89 \text{ mg/m}^2\text{-yr}$  and  $0.06 \text{ mg/m}^2\text{-yr}$ , respectively. Fluxes of  $\text{Hg}_T$  in soil solution were highest in the Oa horizon (forest floor leachate), with concentrations decreasing in the Bh and Bs horizons (mineral soil). Soil water concentrations seem to be strongly correlated with DOC concentrations. The fluxes of  $\text{Hg}_T$  through the Oa, Bh, and Bs horizons were  $26.37 \text{ mg/m}^2\text{-yr}$ ,  $8.77 \text{ mg/m}^2\text{-yr}$ , and  $2.02 \text{ mg/m}^2\text{-yr}$ , respectively. The elevated flux of  $\text{Hg}_T$  draining the forest floor may be due to dry deposition or a net release of  $\text{Hg}_T$  from the forest floor. A preliminary mass balance shows that 79 percent of wet mercury deposition is retained in the watershed. According to the lake mass balance, 19 percent of  $\text{Hg}_T$  entering the lake is retained. Methylmercury is produced in Sunday Lake and in the watershed.

## **Historical Trends of Sediment Mercury Deposition in Adirondack Lakes**

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Sediment cores were collected from eight remote lakes in the Adirondack region of New York in the summer of 1998. The cores were sectioned, dated by  $^{210}\text{Pb}$ , and analyzed for the concentration of total mercury ( $\text{Hg}_T$ ) by cold vapor atomic fluorescence spectroscopy. Using sediment accumulation rates, the  $\text{Hg}_T$  fluxes were calculated to produce core Hg profiles on an historical timescale.

All Adirondack lakes showed an increase in  $\text{Hg}_T$  flux beginning in the period from 1850 to 1900, and had a maximum sediment Hg flux occurring in the period from 1973 to 1995. The ratio of maximum sediment Hg flux to values evident before Hg increases was 5.8. Seven of the eight lakes have shown decreasing fluxes from maximum values in recent years. The decreases ranged from 14% to 71%, with an average of 33%. The Hg flux ratio has decreased by 40% to 3.5 for the most recent sediments. The modern and preindustrial fluxes are positively correlated to the watershed area to lake surface area ratio. This indicates that the watershed surrounding a lake provides a significant contribution to the overall mercury flux to a lake. The change in slope of this relationship indicates that this contribution has increased in importance since preindustrial times.

These profiles were compared to sediment profiles from cores for the same eight lakes collected around 1982. There are many similarities between the two sets of cores even though the new cores were taken 15 years later and at different locations in the lake. The 1982 cores showed only three lakes with decreasing fluxes as opposed to seven for the 1998 cores, which provides additional evidence of recent declines in lake sediment mercury fluxes.

## **Standard Setting for Electric Power Generation: A Review of Risk and Uncertainty**

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This paper provides an overview of the scientific uncertainties associated with the establishment of control measures to address electric power generation (EPG) in Canada. In part, the paper looks at the research requirements and research undertakings as part of the Canada-Wide Standards process for the EPG sector. Standards will be set for the EPG sector in Canada between 1999 and 2002.

There are a number of uncertainties with respect to mercury in the environment other than those related to our understanding of the effects of mercury on human health. These uncertainties play a role in affecting the nature of the decisions made to control the use of mercury in Canada. The relative contributions of natural versus anthropogenic mercury, the transport and fate of mercury, ecosystem responses to mercury pollution and pollution controls, and the effectiveness of control technologies, are examples where scientific uncertainty influences policy decisions to control the use or release of mercury.

The format for the report follows this sequence and presents the discussion under five primary headings, Mercury in the Environment, Pathways of Exposure, Mercury Toxicity and Health Effects, Mercury Standards and Guidelines, Overcoming Uncertainty: A Research Agenda and Summary and Conclusions.

## Mercury Concentrations in Water Bodies and Fish of Western Maryland

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The purpose of this study was to examine the relationships between water quality and total mercury concentrations in recreational fish in three major water bodies (Deep Creek Lake, Lake Habeeb and Piney Creek reservoir) of western Maryland. This region has some of the highest atmospheric mercury deposition rates in the United States. We measured total mercury concentrations in the epilimnion, metalimnion and muscle tissue from 120 fish: 15 bluegill (*Lepomis macrochirus*) and 15 largemouth bass (*Micropterus salmoides*) from each of the three water bodies, and 15 yellow perch (*Perca flavescens*) from Deep Creek and Piney Creek reservoir. There were no yellow perch in Lake Habeeb. Average total mercury concentrations in the epilimnion and metalimnion were not significantly different in each water body. However, there were significant ( $p < 0.001$ ) differences in the average total mercury concentrations between water bodies. Average total mercury concentrations (standard deviations) were  $1.00 \pm 0.03$  ng/L for the Piney Creek reservoir,  $0.56 \pm 0.07$  ng/L for Deep Creek Lake and  $0.31 \pm 0.15$  ng/L for Lake Habeeb. These water quality differences were sometimes reflected in the total mercury concentration in fish tissue. Total mercury concentrations in bluegill ( $0.05 \pm 0.02$  ug/g) and largemouth bass ( $0.10 \pm 0.03$  ug/g) from Lake Habeeb were significantly lower than the total mercury concentrations in bluegill and largemouth bass from the Piney Creek reservoir (bluegill:  $0.13 \pm 0.04$  ug/g and largemouth bass:  $0.37 \pm 0.2$  ug/g) and Deep Creek Lake (bluegill:  $0.11 \pm 0.04$  ug/g and largemouth bass:  $0.30 \pm 0.1$  ug/g). Yellow perch from Piney Creek had significantly higher total mercury concentrations than yellow perch from Deep Creek Lake ( $0.2 \pm 0.1$  ug/g versus  $0.1 \pm 0.04$  ug/g). In contrast, total mercury concentration in largemouth bass from Piney Creek and Deep Creek Lake were not significantly different. We also observed very strong linear relationships between the size of largemouth bass and the total mercury concentration in largemouth bass from Piney Creek reservoir (total mercury (ug/g) =  $0.0976 + 0.000596 * \text{weight (g)}$ ;  $r^2 = 0.84$ ,  $n = 15$ ;  $P < 0.001$ ) and Deep Creek Lake (total mercury (ug/g) =  $0.182 + 0.000254 * \text{weight (g)}$ ;  $r^2 = 0.65$ ;  $n = 15$ ;  $p < 0.001$ ). The largest fish ( $> 800$  g and  $> 30$  cm) from these two systems had total mercury concentrations that exceeded the FDA consumption advisory of 0.5 ug/g. In contrast, total mercury concentrations in largemouth bass from Lake Habeeb were not highly correlated with the size and appeared to be almost independent of size (total mercury (ug/g) =  $0.0724 + (0.0000730 * \text{weight (g)})$ ;  $r^2 = 0.31$ ,  $n = 15$ ,  $p = 0.03$ ). The total mercury concentration in largemouth bass from Lake Habeeb did not exceed the consumption advisory.

**The “Reservoir Effect”: Synthesis and Biological Uptake of Methylmercury in  
Seasonally Inundated Systems**

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The biogeochemical cycling of mercury (Hg) in natural waters poses a threat to the health of humans and wildlife, due to the bioaccumulation and toxic effects of methyl Hg (MeHg). Prior investigations have shown that soil and wetland inundation is an important source of MeHg to overlying water, as well as to the aquatic food web. Our research group is presently participating in two studies that address this “reservoir effect” and its contribution to MeHg cycling in aquatic systems.

Recent work using experimental upland reservoirs (Experimental Lakes Area, Ontario, Canada) indicates that inorganic Hg is rapidly leached from flooded soils to overlying water, to the extent of 1-3% of the pre-flood soil burden within a few weeks. Methyl Hg, however, is rapidly synthesized by *in situ* microbial activity, and supplies up to 60 times more MeHg to overlying waters than physical leaching alone. These observations have important implications for Lake Superior, as its watershed contains large areas of seasonally flooded lowland soils, and much of its aquatic biota is found near-shore. Further, simple loading calculations based upon several years of tributary and atmospheric deposition data suggest that watersheds are the principal source of MeHg to the lake.

Our investigations of the Hg content of Lake Superior plankton indicate MeHg enhancement in near-shore zones during the spring melt/inundation stage, suggesting that flooding within the watershed is producing new MeHg as well as mobilizing the prior year’s supply. We present recent Hg speciation data for water, sediments, and plankton for three Lake Superior tributaries and their estuarine mixing zones (as part of our USEPA-STAR program funding), and discuss the potential for seasonal inundation processes within the watershed affecting the exposure of aquatic biota to MeHg in near-shore regions of the lake.

**Release and Transport of Mercury in Watersheds Impacted by  
Mercury Containing Mineral Deposits**

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Mineral deposits containing mercury are locally important sources of mercury and methylmercury to watersheds. Processes that control the release and transport of mercury species to watersheds from mercury enriched sites are dependent on: the ore deposit type; speciation of mercury in ores, contaminated soils; mine wastes, presence of acid mine drainage; and climate. Mercury sulfide is the primary ore mineral in mercury deposits and gold deposit that have produced byproduct mercury. Mercury bearing zinc sulfide is the dominant mercury phase in massive sulfide deposits. During ore processing more soluble mercury chloride, sulfate, and oxide phases form. Release of mercury-enriched sediment and colloids from mine sites to watersheds occurs primarily during high flow events and particulate transport dominates. At mine sites where acid mine drainage (AMD) impacts a watershed, the concentration of mercury and methylmercury in AMD is strongly dependent on the type of ore deposit. The concentration of both mercury species is highest where mine drainage flows through and leaches mercury from mine wastes. Both mercury species are initially transported as a dissolved species and colloids in AMD impacted streams. As acidity of these streams is buffered by country rocks, iron oxide phases, and clays remove essentially all mercury species and particulate transport is the dominant process. Total suspended solids or turbidity can be used as indicators of total mercury concentration. Mercury fluxes to watersheds impacted by mercury containing mineral deposits range from about 1 to over 1500 kg/year with the largest fluxes derived from silica-carbonate type mercury deposits. More limited data indicate that methylmercury fluxes may also be locally significant in some of these impacted watersheds.

## **The Influence of Organic Carbon on the Mobility of Mercury in Contrasting Ecosystems**

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There is evidence from northern Europe and northeastern North America that aqueous mercury (Hg) transport is linked to organic carbon (OC) transport. Recent data from several USGS research sites in the northeastern U.S. provide compelling support for the Hg-OC transport link. We report here evidence of Hg-OC transport from the Sleepers River Research Watershed in Vermont. This catchment is a moist temperate environment characterized by organic matter accumulation at the surface of podzolic soils. Within the research area, stream water samples pooled from 10 sub-watersheds of diverse size and land use during the Spring 2000 snowmelt displayed a highly significant statistical correlation between dissolved ( $Hg_D$ ) and particulate ( $Hg_P$ ) mercury and the respective dissolved organic carbon (DOC) and particulate organic carbon (POC) fractions. However, at Sleepers River, we also found a strong positive correlation of both DOC and Hg with stream discharge. This suggests that a Hg-OC correlation may exist because they are both being flushed from a common source: the soil organic horizon. Samples from an earlier snowmelt year at Nettle Brook, another forested Vermont watershed located 100 km to the west, were colinear with the Sleepers samples on the  $Hg_D$ -DOC plot and soil water samples showed both high Hg (~20 ng/L) and DOC (~20 mg/L) in the O-horizon and low Hg (~2 ng/L) and DOC (~2 mg/L) in the B-horizon.

The Florida Everglades is a subtropical marsh environment. Dissolved organic carbon concentrations are an order of magnitude higher than those in Vermont stream water while Hg concentrations are comparable in magnitude. However, contrary to the Vermont site, the relation between Hg and OC transport is absent. Specific ultra-violet absorbance (SUVA), an indicator of the character or quality of the DOC and a proxy measurement of the aromaticity or “reactiveness” with chemical species, generally decreased from north to south. Preliminary laboratory results from the Everglades samples indicate that certain fractions of the DOC are more reactive with Hg but lend no insight to the processes controlling Hg transport in this system. In the Everglades, redox conditions and especially the redox state of sulfur species in the sediment and water column are thought to play an important role in the bioavailability of Hg.

The amount and, perhaps more importantly in terms of Hg mobility, the character of DOC is driven by a combination of an aquatic system’s hydrology and biological characteristics. At Sleepers River, SUVA data varied during the Spring 2000 snowmelt suggesting the character of the DOC was changing. Our hypothesis



for Sleepers River, which is uncomplicated by the redox conditions such as those present in the Everglades, is that the character of the DOC may serve as the primary control on Hg movement in these northern temperate landscapes. To test this hypothesis, DOC will be fractionated chromatographically using XAD resins to partition the hydrophobic, transphillic, and hydrophillic acids, and the neutrals during the Spring 2001 snowmelt at Sleepers River to determine if Hg transport is associated with a particular DOC fraction.

## **Methylmercury and Bioavailable Hg(II) in Arctic Snow During Polar Sunrise**

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The Arctic atmosphere is a repository for many chemicals, including mercury (Hg), which originate elsewhere and travel poleward. The discovery of “mercury depletion events” (sunlight-induced oxidation of gaseous Hg associated with ozone depletion) in the Canadian Arctic by Schroeder and colleagues (Nature 1998, 394, p. 331) led to the conclusion that the Hg species produced by this mechanism have a shorter residence time in the atmosphere than their gaseous Hg precursor. Furthermore, Hg depletion events recently confirmed in Point Barrow, Alaska, were accompanied by significant levels of rapidly depositing reactive gaseous Hg (Lindberg *et al.*, 2001 in press). To further characterize the Hg species associated with Polar sunrise that are entering the Arctic ecosystem via the atmosphere, we analyzed Arctic snow collected at Point Barrow, Alaska (71°19' N) for methylmercury (MeHg), bioavailable inorganic Hg (bioHg(II)), and total Hg.

Total Hg in snow increased from 1 to 69 ng/L between January and June. BioHg(II) was determined using the *mer-lux* bioreporter *Vibrio anguillarum* pRB28. *mer-lux* bioreporters are genetically engineered bacteria that are able to distinguish biologically labile Hg(II) from inert Hg(II) species that cannot enter the bacterial cell. Prior to Polar sunrise, bioHg(II) was not detectable in Barrow snow. It then increased from 0.22 ng/L (~1% of total Hg) in March to 8.8 ng/L (nearly 13% of the total Hg) in May. Just prior to the intense snowmelt period in June, bioHg(II) decreased to 2.9 ng/L, but remarkably, this concentration represented over 50% of the total Hg in snow. We also measured a notable trend in MeHg, which increased from 0.01 ng/L before sunrise to 0.13 ng/L in March, and reached 0.59 ng/L in May; a concentration more common to Boreal wetland environments where MeHg is biotically produced by bacteria. Its production mechanism in the Arctic atmosphere is currently unknown; however, we suspect that the oxidation of dimethylmercury, rather than the methylation of Hg(II), may be involved. The Spring runoff period could represent a disturbingly important input of both MeHg and bioHg(II) to Arctic ecosystems at a biologically active time of the year.

## **Episodic Transport of Mercury in Streamwater**

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Mass balance calculations for mercury in nonurban temperate environments indicate that from 80 to 95% of atmospherically deposited mercury is retained in the terrestrial landscape. These calculations can be highly uncertain. Most studies acknowledge potentially large uncertainties in inputs of atmospheric mercury, principally due to difficulty in determining rates of dry deposition and revolatilization to the atmosphere. However, determinations of mercury outputs in streamflow may also be in error due to insufficient sampling during high-flow periods. Our research from several watersheds in Vermont consistently indicates a positive relation between total Hg concentrations and stream discharge. This correlation appears to be driven by increased DOC, POC, and suspended sediment at increased streamflow. At our study sites, which include small forested and agricultural watersheds as well as some larger rivers discharging to Lake Champlain, particulate Hg is the dominant form of Hg in stream export. Failure to sample during high-flow episodes may result in a significant underestimate of the Hg flux in streamflow. At one Vermont site, half of the annual Hg flux in streamwater was estimated to occur within a 24-hour period during peak snowmelt.

## **Mercury Dynamics and a Hypolimnetic Model of Onondaga Lake**

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In this study, the dynamics of mercury (Hg) were investigated in the hypolimnion of Onondaga Lake, NY. Concentrations and pool of total and methyl Hg (MeHg) and the fate of Hg inputs were investigated through summer lake stratification to the fall mixing period using measurements in the water column and sediment traps. Total mercury ( $Hg_T$ ) concentrations in the water column ranged from 1.4 ng/L to 17.5 ng/L, with MeHg ranging from 0 ng/L to 11.9 ng/L. Peak concentrations of MeHg were evident at 19 meters in early July, at 15 meters in early September, and below 15 meters through the month of October, during the anoxic period of the hypolimnion. Total Hg concentrations peaked at 19 meters in late July and late August and below 15 meters through October. Total Hg concentrations were uniformly elevated in the water column after the fall mixing period, with an average concentration of 13.4 ng/L. Methyl Hg concentrations ranged between 0% and 96% of the  $Hg_T$ . The percentage of  $Hg_T$  that occurred as MeHg displayed peaks matching decreases in  $Hg_T$  concentrations in the water column generally, rather than increases in MeHg. Settling particles collected using sediment traps at a depth of 10 meters were analyzed for  $Hg_T$  and MeHg concentrations and combined with water column concentrations below the thermocline to develop a hypolimnetic mass balance to address the ultimate fate of Hg in the lake.

## **Physical and Chemical Properties of Hg-Bearing Colloids Released from New Idria and Sulfur Bank Mercury Mine Tailings**

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Laboratory column experiments were performed to examine the importance of colloidal transport of Hg from mine tailings using tailings (calcines) from the New Idria (NI) and Sulfur Bank (SB) Hg mines in CA. Calcines were dry sieved (8 size fractions spanning 2.8mm to <0.045mm), and each fraction was characterized using cold vapor atomic fluorescence spectroscopy (CVAFS), XRD, BET, laser scattering, and TEM/EDAX. For the NI calcines, BET surface areas and Hg concentrations increase with decreasing particle size, ranging from 10 m<sup>2</sup>/g and 350 ppm Hg (2mm>d<sub>p</sub>>0.5mm) to 19 m<sup>2</sup>/g and 770 ppm Hg (d<sub>p</sub><0.045mm). For the SB calcines, BET surface areas are higher than for NI, and the maximum occurs for 0.5mm>d<sub>p</sub>>0.25mm (84 m<sup>2</sup>/g), and decreases with decreasing particle size (61 m<sup>2</sup>/g, d<sub>p</sub><0.045mm) and increasing particle size (66.5 m<sup>2</sup>/g, 2.7mm>d<sub>p</sub>>2mm). XRD indicates that NI calcines consist of quartz, alunite-jarosite, and hematite, with the fraction of quartz decreasing with decreasing particle size. TEM/EDAX analysis of the NI d<sub>p</sub><0.045mm size fraction also indicates an amorphous Si/Al-containing phase. XRD indicates that SB calcines consist of quartz, hematite, plagioclase feldspars, and montmorillonite.

Chromatographic columns filled with NI or SB calcines (2.0mm<d<sub>p</sub><0.5mm) were preconditioned by leaching with approximately 100 pore volumes of 0.1M NaCl. Colloid generation was then initiated by leaching with 5mM NaCl. A pH buffer (15mM malonic acid/25mM NaOH, pH=5.8) and biocide (1mM sodium azide) were present in all steps. The NI calcines released significant quantities of Hg-bearing colloids in the 50nm to 400nm size range. TEM/EDAX analyses indicate that colloids consist of crystalline alunite-jarosite, iron oxide, and a poorly ordered Si/Al-containing phase; thus the colloids are similar in composition to the bulk material. Total Hg concentration in the column effluent is less than 75 ug/L (ppb) during preconditioning, but greater than 2000 ug/L (ppb) when colloidal particles are present, indicating that Hg associated with colloids may be a significant transport mechanism for the NI tailings. The SB column effluent contained no observable colloids until the pH was increased to 8.0, resulting in the precipitation of a colloidal phase. This is presumably a poorly ordered Al-rich gel similar to that observed at the waste pile dam/lake interface at the USEPA Superfund site at Clear Lake, CA. Release of colloids from mine wastes significantly contributes to Hg loadings in watersheds impacted by Hg mining.

## **Wet Deposition of Mercury in Florida, 1995-2000**

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Mercury Deposition Network (MDN) operates sites in the United States and Canada to monitor total mercury in wet deposition. Weekly data from 43 locations, mostly located in the eastern U.S., are described for the years 1995-2000. Four of these sites are in Florida. Weekly precipitation samples are collected in a pre-cleaned, all-glass sampling train using a specially designed wet-only collector (Vermette et al., 1995). Site operators are trained in clean sample handling procedures. A dilute solution of HCl stabilizes mercury (Hg) in the collected precipitation during storage in the sampler and shipment to the laboratory. Upon receipt at the laboratory, samples are treated with BrCl to fully oxidize the Hg and are analyzed for total Hg by cold vapor atomic fluorescence (USEPA Method 1631). After quality assurance review, all data are posted on the NADP Web site (<http://nadp.sws.uiuc.edu>). The method detection level for a 100 mL sample aliquot is about 0.01 ng of Hg. Lab reagent blanks have about 0.03 ng of Hg and field blanks (sampling train and preservative solution exposed for one week in the field without rainfall) have about 0.06 ng of Hg. A typical 2.5 cm rain sample contains about 4 ng of Hg.

The median Hg concentration in over 6000 samples collected in North America between 1995 and 2000 is 9.7 ng/L. Average volume-weighted total Hg concentrations are lowest in New England and the Canadian Maritime provinces (6 ng/L) and highest in Florida (12 ng/L). Wet deposition of mercury from the atmosphere depends on both the Hg concentration in the rain and the total rainfall amount. The wet deposition flux of mercury in North America ranges from over 20 mg/m<sup>2</sup>-yr in south Florida to about 4 mg/m<sup>2</sup>-yr at remote sites in the western U.S. Mercury deposition is strongly seasonal in Florida. The average mercury concentration in summer rainfall is about double that found in the winter. The average wet deposition flux of mercury in Florida is more than 5 times higher in summer than in winter. The geographic distribution of mercury deposition is generally consistent with predictions from USEPA models based on U.S. and Canadian emissions inventory data. The high wet deposition of mercury in Florida seems to be mostly related to higher precipitation amounts in Florida compared to other regions. Between 1995 and 2000, no significant increasing or decreasing trends in mercury concentration, mercury deposition, or annual rainfall amount were found in the data for Florida or for eastern North America as a whole.

### **Reference**

Vermette, S., Lindberg, S., Bloom, N., 1995. Field tests for a regional mercury deposition network – sampling design and preliminary test results. *Atmospheric Environment* 29, 1247-1251.

## **Crust Degassing Mercury Flux: The Role in Evaporation from Soil**

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Mercury degassing of the earth's crust is one source of mercury flux in atmosphere. The estimation of such flux is undertaken during work on use of mercury as a precursor of earthquakes.

All measurements were carried out in the seismic active area of Tadgikistan. The equipment was installed in the thermostabilized vault completely buried in a soil. The mercury content in soil was 1.8-2 mg/kg. About 70 % of mercury was sorbed on a surface of soil particles.

Measurement of mercury vapor carried out by AF analyzer with preconcentration of mercury on bispiral gold collector. The detection limit - 20 pg Hg, RSD 0.1 ( $\bar{N}_{\text{Hg}}=50$  pg,  $n=21$ ). Two plastic boxes as samplers were placed upside down the floor of the vault on depth 1 and 2 m. The mercury vapor pumped and measured in closed system sampler-collector-analyzer-sampler (flow rate 0.5 l/min). All mercury after measurement came back in sampler. The measurements were carried out each hour in a round-the-clock mode. The total number of measurements was > 22000. Calibration was carried out daily by an injection (syringe) method with saturated mercury vapor. For all time of measurement the deviations at calibration did not exceed 20% (with absence the systematic deviations). The rate of mercury flow was measured by method of controlled indignation. 20 ng Hg was entered into one of the samplers and changes of the mercury content detected in another one. On a difference of concentration in samplers the various components of mercury flux were calculated. The total velocity of vertical upward flow (8 cm/h) consists of an ascending flow (2,64 cm/h) and diffusional flow (5,36 cm/h). The influence of the meteorological factors on results was estimated. The used system is less inertial than used by other researchers.

The long round-the-clock registration has given average logarithmic mercury flux 220 (411-120)  $\text{pg m}^{-2} \text{ h}^{-1}$  and has shown distinct periodic variations of Hg concentration in a soil gas. Computer Fourier-analysis detect a harmonic component in variations of mercury flow with periods 7.8; 11.8; 23.4 and 328 which coincide with periods of the crust tide oscillations, caused by gravitational forces among Earth-Moon-Sun.

The obtained data show that mercury vapor flow from crust in the atmosphere depends on size of crust deformation in point of measurement.

## **Mercury Flux from Tidal Sediments Located in an Isolated Bay in the Great Bay Estuary of New Hampshire**

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An investigation of mercury flux from undisturbed estuarine tidal sediments was conducted as part of an USEPA-ORD funded Regional Applied Research Effort (RARE) Study of mercury movement in the Great Bay Estuary (New Hampshire). Seasonal measurements of mercury flux from submerged and exposed sediments were made over several tidal cycles representing day and night conditions. Open water and above sediment measurements were made using a free floating teflon coated flux chamber located in a small bay next to the University of New Hampshire Jackson Marine Laboratory. Changes in the concentration of vapor phase mercury was measured with a TEKRAN model 2537A mercury vapor analyzer, located adjacent to the flux chamber. Results of measurements made during the winter 2000/2001 and spring 2001 will be discussed.



## **Effects of Different Electron Accepting Conditions on Net Microbial Mercury Methylation Potential in Mineral-Rich Sediments**

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Current investigations are exploring how biogeochemical conditions influence microbial mercury transformations in sediments of the Mobile-Alabama River Basin, U.S. Potential rates of microbial methylation of mercuric chloride (1 ppm spike) and demethylation of methylmercury (MeHg) (0.1 ppm spike) were investigated in anoxic mineral-rich wetland sediments under different electron accepting conditions. Rates of methylation were similar under methanogenic and sulfate-reducing conditions, while only minor production of MeHg was observed under iron-reducing conditions. In contrast, rates of demethylation of MeHg were similar under all three electron accepting conditions. Methylation to demethylation ratios, computed from total amounts of MeHg produced or lost in 9 days, were ca. 5 times lower under iron-reducing conditions, compared to sulfate-reducing and methanogenic conditions. These results suggest that net production of MeHg in riverine systems may be suppressed when underlying sediments contain an iron oxide-rich surficial layer. Further experiments are exploring controls on methylation under iron-reducing conditions and whether the transition to different electron accepting conditions results in changes in relative rates of MeHg production and consumption.



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