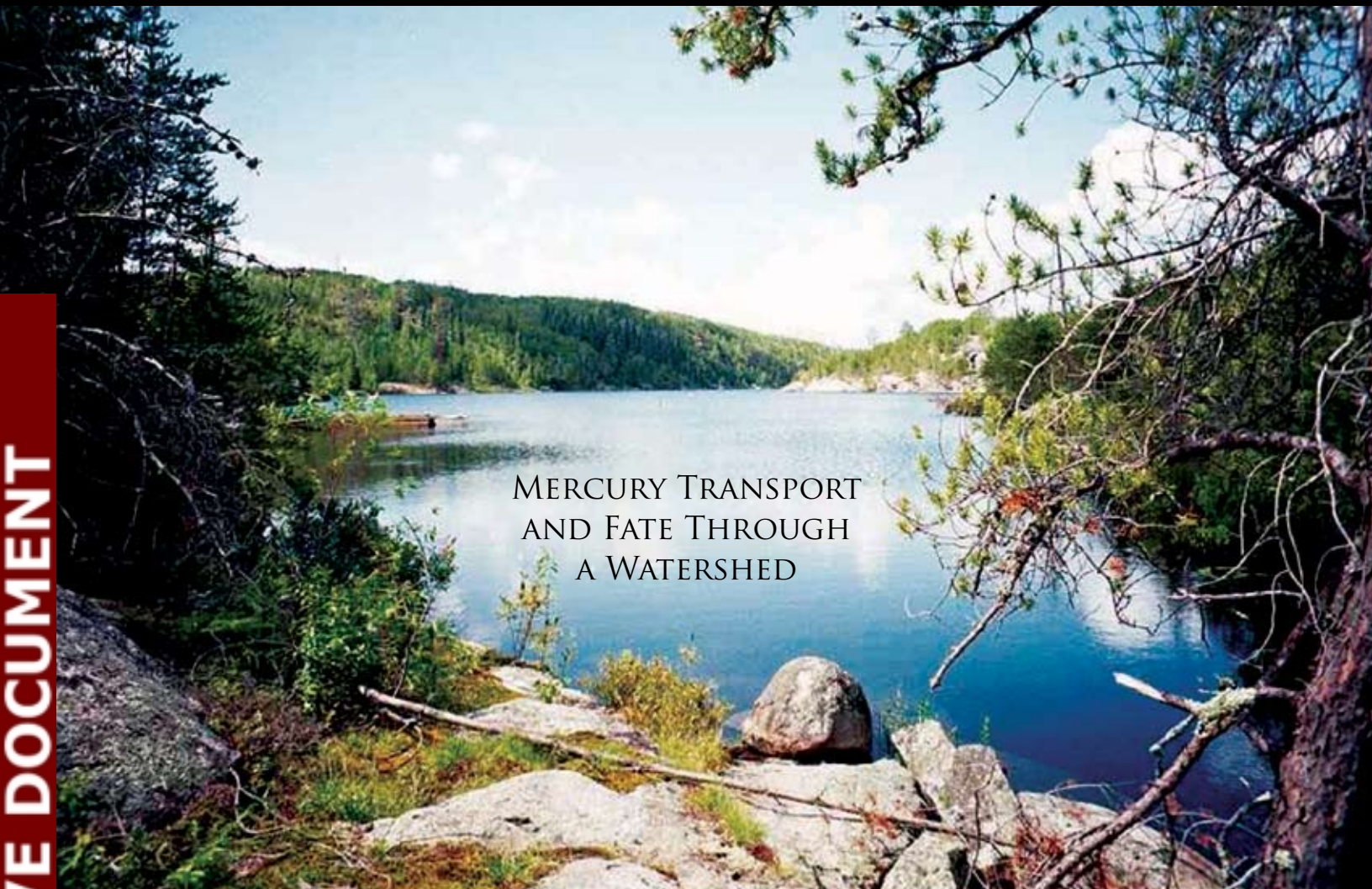


US EPA ARCHIVE DOCUMENT



MERCURY TRANSPORT
AND FATE THROUGH
A WATERSHED

JANUARY 2006

P R E P A R E D F O R

U.S. Environmental Protection Agency, Office of Research and Development
National Center for Environmental Research
Washington, DC

P R E P A R E D B Y

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DISCLAIMER

The research described in this document has been funded wholly by the United States Environmental Protection Agency (EPA) under the Science to Achieve Results (STAR) grants program. The information does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.

The information presented in this synthesis report is intended to provide the reader with insights about the progress and scientific achievements of STAR research grants. The report lists the grantees whose research is discussed and also indicates where more detailed peer-reviewed scientific data can be found. This report is not sufficiently detailed nor is it intended to be used directly for environmental assessments or decision making. Readers with these interests should instead consult the peer reviewed publications produced by the STAR grantees and conduct necessary data quality evaluations as required for their assessments.

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EXECUTIVE SUMMARY



Background

The U.S. Environmental Protection Agency's (EPA's) Science to Achieve Results (STAR) research grants program, managed by the National Center for Environmental Research, has funded significant research on the fate, transport, and transformation of mercury in aquatic and terrestrial environments. This report summarizes the research and findings generated through nine grants awarded under the 1999 Request for Applications (RFA) entitled "Mercury: Transport and Fate through a Watershed" and two other closely related STAR grants. The important scientific findings from these grants, data gaps, and additional research needs on this topic are described in this synthesis report.

The 1999 RFA funded fundamental research on the complex chemical and physical transformations and movement of mercury through the environment. The *overall goal* of the research solicited on mercury transport in a watershed was summarized in the original RFA as follows:

"...to develop a better understanding of terrestrial and aquatic fate and transformation processes (especially microbial) that mediate ecological and human exposures to mercury. The development of improved models of the fate of mercury in aquatic and terrestrial systems in order to estimate ecosystem response to decreased anthropogenic inputs of mercury is also needed."

The RFA specifically invited grant applications addressing the following *critical research questions*:

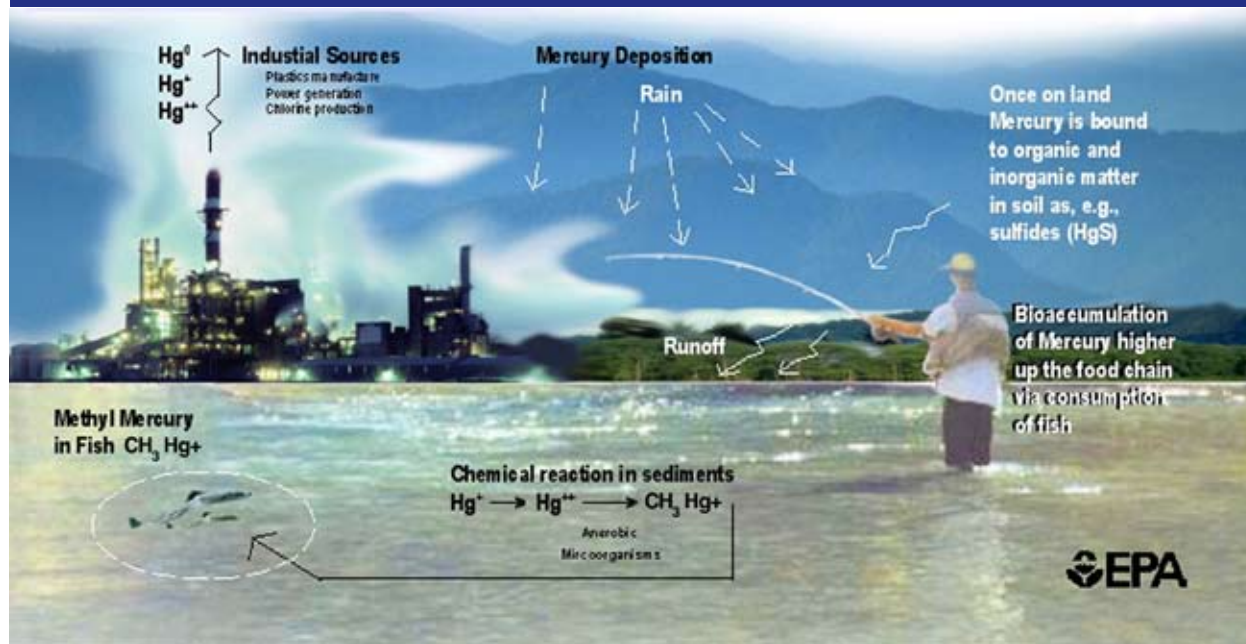
- (1) For a given amount of mercury transported into a watershed, what is the predicted concentration of methylmercury in fish? How do mercury and methylmercury spatially distribute across the terrestrial and aquatic components of a watershed? What controls bioavailability of mercury in the food chain?
- (2) What environmental and biochemical variables control transformation of mercury to methylmercury? What environmental variables control the reduction of divalent mercury to elemental mercury in soils, sediments, and surface waters?
- (3) How does mercury cycling vary within different geographic regions of the United States (e.g., south Florida, Great Lakes, northeast, or west)? How might the variability be accounted for (e.g., resource types (wetlands), temperature regimes, microbial communities)?

The eleven STAR grants discussed in this report examined how methylmercury transports into and within a watershed and concentrates in fish. Projects included studies of factors that control the partitioning and distribution of different mercury species in different environmental media in

aquatic and terrestrial ecosystems (Question 1), factors that influence bioavailability of mercury (Question 1), and studies of the factors controlling mercury transformations (Question 2). Most studies identified controlling factors that are likely to vary by geographic region, but a systematic examination of regional influences was not attempted (Question 3).

Note that the *critical research questions* are interrelated. For example, partitioning of mercury into different environmental media influences its availability to various transforming processes, and transforming processes can create mercury species that move through the environment via different pathways. Transformation processes also can create "sources" of given mercury species in the environment. Exhibit ES-1 illustrates these concepts. This synthesis report discusses the STAR grant project results along four research themes. These themes are intended to correspond with components needed to develop an integrated multimedia modeling framework for understanding mercury fate from source to fish concentrations. These four themes are: (1) controls of mercury transformations, (2) controls of mercury partitioning and transport (i.e., cycling) in the environment, (3) sources of mercury species in the environment, and (4) bioavailability and bioaccumulation of mercury in food chains. Key findings of the STAR grant projects are organized according to these four themes.

EXHIBIT ES-1: SOURCES AND PATHS OF MERCURY IN THE ENVIRONMENT



Study Results

(1) Biogeochemical controls of mercury transformations.

Net methylmercury (MeHg) production in aquatic systems is complex. Elemental mercury ($\text{Hg}(0)$) can be oxidized to $\text{Hg}(II)$, the form that is methylated by sulfate-reducing bacteria (SRB), and $\text{Hg}(II)$ is readily reduced to $\text{Hg}(0)$ in surface waters via abiotic and biotic pathways. $\text{Hg}(II)$ chemical complexes tend to become bound to sediment particles, whereas $\text{Hg}(0)$ is lost to the atmosphere via volatilization. In addition, there are rapid conversions between inorganic mercury ($\text{Hg}(II)$) and MeHg. While SRB in sediments methylate $\text{Hg}(II)$, MeHg is also demethylated via both abiotic (photochemical) and biotic pathways. STAR grant projects added to the understanding of these processes as highlighted below.

- STAR grant research has shown that, as mercury is deposited to surface waters from air, $\text{Hg}(II)$ becomes progressively bound in forms that are less easily meth-

ylated, even with rapid cycling between $\text{Hg}(II)$ and MeHg. Thus, newly deposited $\text{Hg}(II)$ is more available for methylation than older mercury in some environments. This may not be true in every environment, but was observed in both the Florida Everglades and the Experimental Lake Area in Canada.

- Mercury that is deposited directly to surface waters is readily methylated in the sediments. In contrast, it is unclear how long it takes mercury deposited to a watershed to be methylated (e.g., via transport to sites of methylation in surface water sediments).
- Studies demonstrated that the rate at which SRB methylate $\text{Hg}(II)$ depends on a variety of factors, including bacterial activity levels in general (e.g., seasonal), bacterial community structure (i.e., metabolic pathways of species present), and the bioavailability of $\text{Hg}(II)$, which depends on several factors (e.g., sulfides and dissolved organic carbon (DOC) concentrations) as discussed later.
- The addition of sulfate to freshwater environments can enhance rates of methylation, which is expected because sulfate and organic matter are the primary substrates used by SRB to produce energy. However, a build-up of sulfides as reaction products can reduce the availability of environmental $\text{Hg}(II)$ to the bacteria.
- Demethylation is less well studied than methylation, yet is important in determining net methylation rates. It occurs via both biotic and abiotic (photochemical) pathways. STAR grant research demonstrated photochemical demethylation requires UV radiation and is confined to the upper surface water layers.
- The availability of $\text{Hg}(II)$ for SRB also depends on the cycling between $\text{Hg}(0)$ and $\text{Hg}(II)$. Photochemical reduction of $\text{Hg}(II)$ appears to be an important reaction in surface waters, resulting in a diurnal cycle of $\text{Hg}(0)$ formation and release from surface water via volatilization. The rate of net reduction is related to several

factors including light intensity and DOC. Oxidation of Hg(0) to Hg(II) is enhanced by free radicals in surface waters, which tend to be formed via photolysis of DOC.

- Recently, understanding of the major processes that impact Hg methylation has improved so that it is now possible to model Hg methylation in a more comprehensive way than accomplished in previous models. Such approaches are now being developed and will soon be incorporated into models. However, the current understanding of biotic demethylation is not as complete, and models for this reaction remain relatively crude.

(2) Biogeochemical controls of mercury cycling in the environment.

Mercury cycling (i.e., phase partitioning and inter-media transport) is key to the distribution of mercury in the environment. Most of the STAR research in this area focused on processes controlling mercury transfer between surface water and sediment, surface water and soils and the atmosphere, and plants and the soil and atmosphere.

- STAR grant studies indicated that inorganic mercury (Hg(II)) in aquatic systems generally is bound with DOC. Complexes of reactive Hg(II) can coagulate and adsorb to suspended sediment particles which are deposited to the sediment bed. The influence of DOC on mercury partitioning in the sediment bed is complicated and is influenced by sulfide levels.
- Studies indicated that the bioavailability of Hg(II) to SRB depends on partitioning of Hg(II) between particulate and dissolved phases of the sediments. As expected, methylation rates vary inversely with the partition coefficient, K_D , of Hg(II) and positively with the concentration of Hg(II) in sediment pore water.

- A model of Hg(II) partitioning between sediment particles and pore water that accounts for adsorption and sulfide concentrations has been developed and validated for two ecosystems (Patuxent River, Florida Everglades). The model's predictions of neutral mercury-sulfide complexes, which are the bioavailable forms, correlated well with the methylmercury concentrations measured in field samples.
- STAR projects demonstrated that volatilization of Hg(0) from surface waters can be as important as sediment burial and methylation of Hg(II) in sediments as a mechanism of loss of inorganic mercury from different types of aquatic ecosystems (e.g., Long Island Sound, wetlands).

- Mercury in soils can emit to the air via volatilization of Hg(0) and light-enhanced emissions of mercury sulfide (and other) complexes, perhaps via photoreduction of Hg(II) to Hg(0) with subsequent Hg(0) volatilization.
- Studies demonstrated that plants take up Hg(0) directly from the atmosphere via their stomata, and plants can accumulate Hg in their leaves. The uptake of mercury from soils via plant roots appears to be a minor uptake pathway. At the end of the growing season, litterfall from deciduous plants to soils and to surface waters is a significant source of mercury input to those systems.

(3) Sources and distribution of mercury in terrestrial and aquatic systems.

Several STAR grant studies identified major sources and means of distribution of mercury in given study areas. Researchers identified and investigated important processes influencing movement of mercury throughout a watershed (e.g., production of methylmercury, predominant mercury fate and transport processes). In

addition, several researchers performed general mass balance studies to quantify sources and inputs within a given watershed.

- Mass balance models of different watersheds indicated that atmospheric deposition is the primary source of total mercury to most aquatic systems. As indicated by mercury loading from tributaries, in some watersheds, runoff and erosion also can be large sources of mercury to a water body. Mass balance models indicated that watersheds and lakes serve as sinks for total mercury, while wetlands and lakes serve as sources for methylmercury. These models also indicated that dry deposition (i.e., via litterfall) and throughfall (i.e., via precipitation passing through the plant canopy) can be more important than wet deposition. Total ecosystem mercury deposition is a combination of wet deposition, litterfall, and throughfall.
- Studies indicated that *in situ* methylation of Hg(II) within aquatic systems is the dominant source of MeHg, at least for freshwater lakes, wetlands (e.g., Florida Everglades), and for estuarine systems (e.g., Long Island Sound and the Chesapeake Bay).
- Mercury deposited to the terrestrial portions of watersheds is slow to move to sites of methylation via erosion or runoff.
- Data from one study suggested that methylation may also occur in estuarine and coastal areas, perhaps in deep waters, sediments, or hydrothermal vents where mercury concentrations are not greatly affected by human activities.
- There is some indication from studies in the Adirondacks that the retention capacity of watersheds for mercury has decreased over the last century, although possible reasons remain obscure.

- STAR grant studies also demonstrated the importance of subsurface transport and transformation of Hg into MeHg in overall mercury cycling. The interface between ground water and streams appears to be an important methylation site and source of MeHg, and may be a more important source of MeHg from forested ecosystems to surface waters than expected.
- Transport of MeHg through watersheds may be strongly mediated by the transport of colloids.

(4) Bioavailability and bioaccumulation of mercury in aquatic systems.

Several STAR grants investigated factors that influence the bioavailability of inorganic mercury to SRB for methylation and transport up the food chain. Some of these factors have been noted briefly above. These and other findings are described below.

- Newly deposited mercury can be more bioavailable than “older” mercury.
- Mercury appears to be less bioavailable to algae in surface waters with higher DOC levels, perhaps because mercury complexed with DOC is less bioavailable to SRB for methylation.
- Mercury concentrations in biota in lakes are generally higher in the spring than summer, a trend that might result from bio-dilution by growing phyto- and zooplankton during the summer.
- Studies showing higher concentrations of methylmercury in zooplankton from surface waters than deeper waters suggest that mercury in surface waters deposited from the atmosphere may be more bioavailable than mercury in deeper waters.
- In a study of fish in an Adirondack lake, bioconcentration factor (BCF) values of fish increased with each trophic level, indicating bioaccumulation through the food chain consistent with previous studies.
- When sulfide levels are high, neutral mercury-sulfide complexes, which are the bioavailable forms, are more likely to form if the pH is low than if the pH is high. This relationship may help explain why fish tend to have higher tissue mercury residues in waters of lower pH.
- Bioavailability of inorganic mercury varies depending on its chemical form and solubility, with substantial variation apparent across mining sites in different geographic regions.
- Sorption of Hg(II) onto mineral particles may effectively sequester mercury in mineral soils, particularly at mining sites. Iron and aluminum (hydr)oxides are particularly effective in sequestering Hg(II) in colloids.
- Mixing zones between two water masses (e.g., river/lake interfaces, estuaries) demonstrate enhanced bioaccumulation. Although coagulation and settling of larger suspended particles occur in these zones, increased concentrations of smaller particles (with sorbed methylmercury) are available for ingestion by zooplankton.

Major Remaining Tasks/Uncertainties

Future research needs related to mercury fate and transport were identified by comparing the STAR research results to the goals outlined in the *ORD Mercury Research Multi-Year Plan (MYP)*. The STAR research summarized in this report identifies fate and transport issues and provides information on mercury cycling in complex ecosystems.

Other *ORD Mercury MYP* Research Goals and Measures that are related to the grants described here, but may require further work to fully accomplish, include development of a model for mercury in fish, identification of sources of mercury emissions, and the eventual creation of an integrated multimedia modeling framework for mercury in the environment.

The research provides information that relates to all three of the STAR mercury REA questions, but it is most responsive to parts of Question 1 and Question 2 by identifying variables that control partitioning of mercury in the environment and transformation of mercury to methylmercury as well as transformations between inorganic species of mercury. Further research, which builds on the findings presented here, into the relationship between mercury in the watershed to mercury in biota (Question 1) may be necessary to close information gaps regarding uptake by fish and other organisms. Also, further research into how mercury cycling and transformation processes vary by region and ecosystem (Question 3) is needed to support regional modeling of mercury in the environment.

The STAR grant investigators also identified general areas where follow-up work would be beneficial as well as specific tasks that would advance the science addressed by their projects. Some of the topics identified as important for follow-up work include processes such as demethylation and photooxidation and factors affecting methylation such as sulfate concentration, DOC, intracellular sequestration of mercury, and other bacterial processes, as well as observations that newly deposited mercury contributes more substantially to production of methylmercury than “older” mercury.

1. INTRODUCTION



1.1 Purpose of this Report

In 1999, the U.S. Environmental Protection Agency (EPA) published a Request for Applications (RFA) entitled “Mercury: Transport and Fate through a Watershed” under the Science to Achieve Results (STAR) program. The purpose of the RFA was to solicit proposals to research fate, transport, and transformation of mercury (Hg) in aquatic and terrestrial environments. Nine grants were awarded in 1999 based on this RFA, and the work under these has recently concluded. The purpose of this report is to summarize the important scientific findings from these and two related grants, to describe how these findings have improved understanding of mercury behavior in the environment, and to convey remaining data gaps and research needs on this topic. This report is designed to provide EPA program managers and staff, as well as state environmental agencies,

Alignment of ORD’s Mercury Research with EPA’s Strategic Goals

Directly contributes to:

Goal 4: Healthy Communities and Ecosystems

Supports achievement of:

Goal 1: Clean Air and Global Climate Change

Goal 2: Clean and Safe Water

Goal 3: Land Preservation and Restoration

Goal 5: Compliance and Environmental Stewardship

Source: EPA 2003a

researchers, and the public, with an overview of advances in science achieved through these grants and a description of areas where additional research may be needed.

This report is not intended to be used directly for environmental assessments or decision making. Readers with these interests should instead consult the peer reviewed publications produced by the STAR grantees and conduct necessary data quality evaluations as required for their assessments.

1.2 Background

As part of its mission to improve public health and increase the reliability with which risks to public health and the environment are identified and measured, EPA’s Office of Research and Development (ORD) funds extramural research through its STAR program. The program is managed by ORD’s National Center for Environmental Research (NCER). It provides grants and fellowships to scientists to address research goals in various environmental science and engineering disciplines through a competitive solicitation process and independent peer review. Many of these research goals are outlined in ORD’s Multi-year Plans (MYPs), which ORD develops to communicate research proposed for the next five to eight years. The STAR program engages the nation’s best scientists and engineers in targeted research that complements EPA’s own intramural research program and research of EPA’s partners in other federal agencies.

NCER issues RFAs for topics based on ORD’s *Strategic Plan* (EPA 2001) and, more specifically, on the research goals described in the MYPs. These RFAs are prepared in cooperation with other parts of the Agency and concentrate on areas of special significance to EPA’s mission. For example, ORD’s mercury research directly contributes to meeting one strategic goal “Goal 4: Healthy Communities and Ecosystems” in the EPA *Strategic Plan* (2003a) and supports achievement of the four other goals (see text box).

1.3 Organization of this Report

This report describes the research performed under each of the nine grants awarded under this RFA as well as research performed under two additional, closely related STAR grants¹. Section 2 provides a brief overview of mercury fate and transport, identifies the STAR research grants that addressed this topic, and describes the research themes covered by their results. Section 3 describes key findings from these grants according to research theme, emphasizing how they have advanced general understanding of mercury fate and transport. Section 4 describes how this information can be practically applied to address EPA’s goals. Section 5 discusses outstanding research needs and data gaps identified by the grantees and other sources. Section 6 lists the cited references, and the Appendix to this report provides the lists of publications derived from the research conducted under these grants.

¹ Two research grants lead by Mae S. Gustin are presented here because they involve mercury fate and transport although they were not funded under the FY99 mercury RFA. These grants were instead funded under the Exploratory Research - Air Chemistry & Physics (1996) and Experimental Program to Stimulate Competitive Research (1998) STAR RFAs.

2. OVERVIEW OF STAR MERCURY GRANTS



This section first provides a brief overview of issues and information needs concerning mercury in the environment at the time ORD issued its RFA on this topic (Section 2.1). It then describes the 1999 STAR program mercury RFA and lists the nine STAR grants awarded under this RFA in 1999 and two other related STAR grants awarded under two other RFAs (Section 2.2). The relationship of those grants to ORD's MYPs is highlighted next (Section 2.3). Finally, the overarching research themes covered by the results of the grants are described (Section 2.4).

2.1 Overview of Mercury in the Environment

As summarized in the introductory material included in the original solicitation for these 1999 STAR grants, the presence of mercury in the environment poses potential risks to human health and wildlife. Both natural and anthropogenic sources contribute to mercury in the environment, with a substantial increase in the contribution from anthropogenic sources since the beginning of the industrial age. Mercury can cycle between various environmental media, including air, land, water, and biota, through deposition, volatilization, and other fate and transport processes (see Exhibit 1). It is a metal with complicated chemistry and can transform between different chemical species, including elemental mercury liquid and vapor, inorganic salts, and organic forms (e.g., methylmercury), through a series of complex chemical and physical

transformations. Methylmercury is toxic and can bioaccumulate in the tissues of animals. Consumption of contaminated fish is a predominant exposure pathway for human and wildlife populations. A number of adverse effects have been linked to mercury exposure, including behavioral abnormalities, impaired growth and development, reduced reproductive success, and death. Of particular concern are the potential neurotoxic effects of methylmercury exposure on the developing fetus.

As required under section 112(n)(1)(B) of the Clean Air Act, as amended in 1990, EPA has prepared the *Mercury Study Report to Congress* (EPA 1997a), which summarizes the magnitude of mercury emissions in the United States, the health and environmental effects of the emissions, and the cost and availability of control technologies. This and other major EPA reports (e.g., the *Great Waters Second Report to Congress* (EPA 1997b), the *Utility Air Toxics Report to Congress* (EPA 1998)) stress the adverse effects of mercury exposure on humans and wildlife. Those and other publications indicate that additional research is needed to better understand mercury fate and transport in the environment.

EPA has taken and is planning different actions to address the health and environmental concerns about mercury, and the STAR research results should be useful to the Agency in these important and high-profile efforts. For example, most of the

research results from these STAR grants have been published in time to be considered as the Agency finalized its regulations to reduce mercury emissions from coal-fired power plants.

2.2 FY99 STAR Mercury Grants

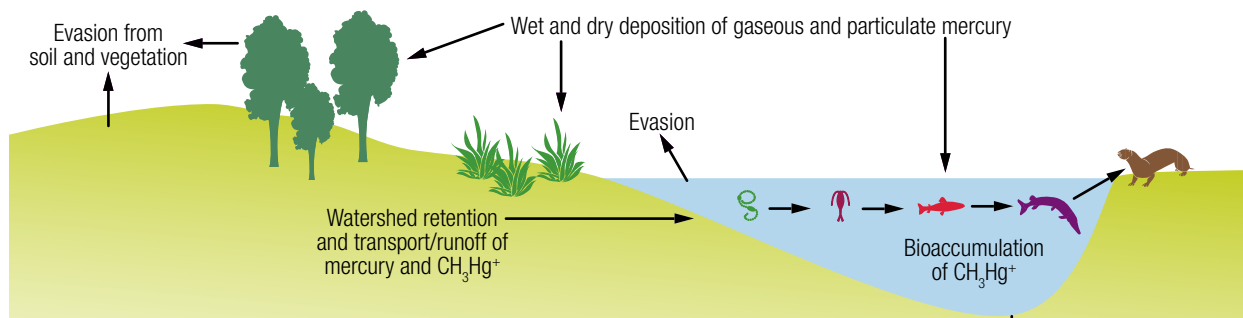
The “Mercury: Transport and Fate through a Watershed” RFA was issued to fund fundamental research on the complex chemical and physical transformations and movement of mercury through the environment. The outcome of this research was intended to increase EPA's ability to trace mercury from its entrance into an ecosystem through its biogeochemical cycling to the concentration of methylmercury in fish tissues in particular. The *overall goal* of the research solicited on mercury transport in a watershed context was summarized in the original RFA as follows:

“The goal of this solicitation is to develop a better understanding of terrestrial and aquatic fate and transformation processes (especially microbial) that mediate ecological and human exposures to mercury. The development of improved models of the fate of mercury in aquatic and terrestrial systems in order to estimate ecosystem response to decreased anthropogenic inputs of mercury is also needed.”

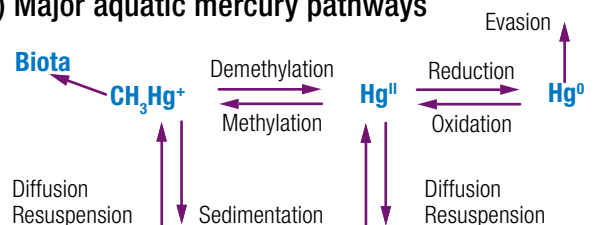
The RFA specifically invited grant applications addressing the following *critical research questions*:

EXHIBIT 1: MAJOR ROUTES INTO THE ENVIRONMENT

(a) Major ecosystem inputs and outputs of mercury



(b) Major aquatic mercury pathways



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- (1) For a given amount of mercury transported into a watershed, what is the predicted concentration of methylmercury in fish? How do mercury and methylmercury spatially distribute across the terrestrial and aquatic components of a watershed? What controls bioavailability of mercury in the food chain?
- (2) What environmental and biochemical variables control transformation of mercury to methylmercury? What environmental variables control the reduction of divalent mercury to elemental mercury in soils, sediments, and surface waters?
- (3) How does mercury cycling vary within different geographic regions of the United States (e.g., south Florida, Great Lakes, northeast, or west)? How might the variability be accounted for (e.g., resource types (wetlands), temperature regimes, microbial communities)?

Finally, the RFA presented three specific research objectives:

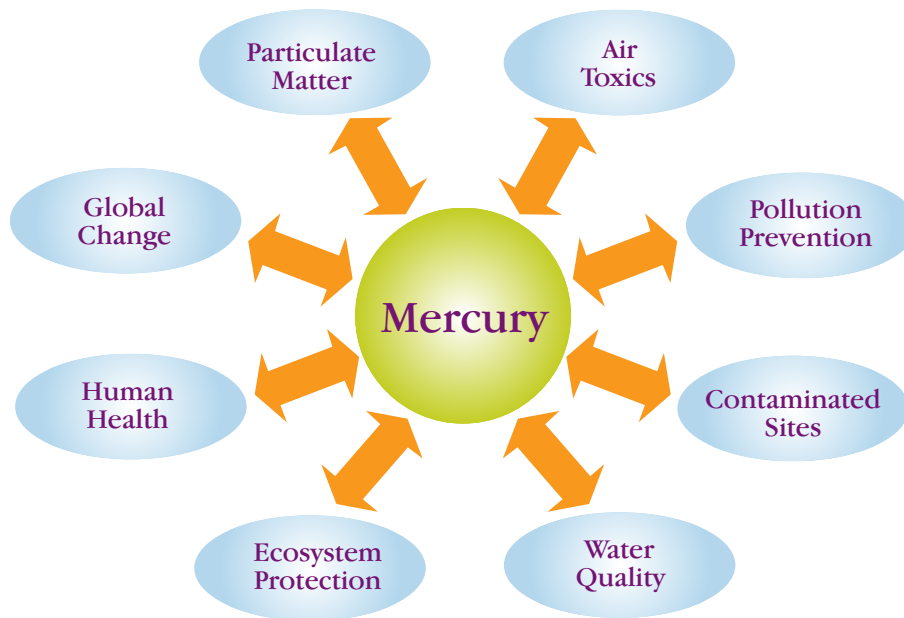
- (1) The performance of theoretical and laboratory investigations focused on understanding the behavior of mercury in the environment, including mercury cycling models; the role of biogeochemistry, especially mercury sulfide complexes; interactions among nutrients, carbon, and sulfur on methylation processes; the role of microorganisms; and the role of macrophytes, periphyton, and their interactions with hydrological processes.
- (2) The development and evaluation of biogeochemical models of the microbial transformations of mercury in ecosystems in order to interpret the sources and distributions of total mercury and methylmercury in terrestrial and aquatic systems.
- (3) Investigation of hypotheses about the regional behavior of mercury, extrapolating microbiological and biogeochemical process data from experimental scales to ecologically meaningful scales and time periods.

EPA awarded nine STAR grants under this solicitation. The grant titles and principal investigators are listed in Table 1 along with the information for two additional grants related to this topic. This document describes the results of these 11 research projects. Throughout this report, we use the last name of the principal investigator to refer to a specific research project or research team and/or the grant reference number that is designated in the first column of Table 1.

2.3 Relationship of 1999 Mercury STAR Grants to ORD MYPs

As described in Section 1, one of the primary purposes of the STAR program is to provide grants and fellowships to scientists for research that addresses the goals outlined in the ORD MYPs. The mercury fate and transport STAR grants pertain primarily to the Mercury Research Multi-Year Plan (EPA 2003b). The research results obtained from these STAR grants relate most directly to Long-term Goal (LTG) number two of the Mercury Research MYP, which states:

EXHIBIT 2: MERCURY MYP RESEARCH ASSISTS OTHER MYPS



“to understand the transport and fate of mercury from release to the receptor and its effects on the receptor.”

There are seven general Annual Performance Goals (APGs) defined by ORD under this LTG, with several specific Annual Performance Measures (APMs) for each APG. Specific laboratories and centers within ORD are designated as the lead for each APM. One of the APMs assigned to NCER under LTG number 2, “hold workshop/state-of-the science on mercury with emphasis on fate and transport in watersheds and ecosystem impacts,” was accomplished by NCER when it held the STAR Mercury Fate and Transport Final Progress Review Workshop in November 21, 2003, which was attended by all FY99 mercury STAR grant recipients and other scientists.

In addition, results from these STAR grants will support four key APGs and three key APMs from the *Mercury MYP* (as listed in Table 2).

Research directed by the *Mercury MYP* will influence and advance the goals in other multi-year plans (see Exhibit 2). For example, the results of the mercury STAR research should also play a role in accomplishing the general goal of the *Air Toxics Multi-Year Plan* (EPA 2003c) of reducing the uncertainty associated with risk assessment of air emissions of an important toxic air pollutant, mercury.

2.4 Research Themes

Several overarching research themes were embodied by the specific research questions and objectives listed in the original RFA and presented in Section 2.2. Each investigator developed preliminary objectives for their proposed research that could be linked to one (or more) RFA research objective(s). The *actual research results* generated through the funded projects are more easily discussed according to their contributions to four somewhat more specific research areas or themes, which are described below. The first three of these relate to *critical research*

question 2, while the last one relates to *critical research question 1*.

- (1) **Biogeochemical controls of mercury transformations.** Research on factors that influence transformations among mercury species, including biologically and chemically mediated processes involving both organic (i.e., methylation and demethylation) and inorganic forms of mercury (i.e., reduction and oxidation of inorganic mercury).
- (2) **Biogeochemical controls of mercury cycling in the environment.** Research on factors that affect phase partitioning and inter-media transport of mercury in both aquatic and terrestrial systems, such as transfer between sediment and surface water, surface water and the atmosphere, soil and the atmosphere, and interchange between the atmosphere and plants through various processes.

TABLE 1. FY99 STAR GRANTS ON TRANSPORT AND TRANSFORMATION OF MERCURY IN AQUATIC AND TERRESTRIAL ENVIRONMENTS

Grant Ref. No. in this Report	EPA STAR Grant No.	Grant Title ^a	Principal Investigator	Co-investigators ^a
[1]	R827629	Watershed influences on transport, fate, and bioavailability of mercury in Lake Superior	Hurley, James P., Univ. of Wisconsin	D. E. Armstrong, Richard C. Back, M. M. Shafer, Helen Manolopoulos
[2]	R827630	Methylmercury sources to lakes in forested watersheds: has enhanced methylation increased mercury in fish relative to atmospheric deposition	Swain, Edward B., Minnesota Pollution Control Agency	Jim Almendinger, Jim Cotner, Daniel Engstrom, Jeff Jeremiason, Edward Nater
[3]	R827631	Responses of methylmercury production and accumulation to changes in mercury loading: a whole-ecosystem mercury loading study	Gilmour, Cynthia C., Academy of Natural Sciences and Univ. of Maryland	Andrew Heyes, Robert P. Mason, John M. Rudd
[4]	R827632	Cycling of mercury in Saginaw Bay Watershed	Nriagu, Jerome, Univ. of Michigan	Gerald J. Keeler, John Lehrnan, Steve Lindberg, Xia-Qin Qang, Hong Zhang
[5]	R827633	Chemical and biological control of mercury cycling in upland, wetland, and lake ecosystems in the northeastern United States	Driscoll, Charles T., Syracuse University	Ronald Munson, Robert Newton, Joseph Yavitt
[6]	R827634	Processes controlling the chemical speciation and distribution of mercury from contaminated mine sites	Brown, Gordon Jr., Stanford University	Daniel Grolimund, Mae Sexauer Gustin, Trevor R. Ireland, Christopher S. Kim, James J. Rytuba, Greg Lowry, Samuel Shaw, Stephen B. Johnson, Aaron S. Slowey
[7]	R827635	Mercury and methylmercury cycling in the coastal/ estuarine waters of Long Island Sound and its river-seawater mixing zones	Fitzgerald, William F., Univ. of Connecticut	Pieter T. Visscher, Prentiss H. Balcom, Chad R. Hammerschmidt, Carl H. Lamborg
[8]	R827653	Understanding the role of sulfur in the production and fate of methylmercury in watersheds	Mason, Robert P., Univ. of Maryland	Cynthia C. Gilmour
[9]	R827915	The redox cycle of mercury in natural waters	Morel, Francois M., Princeton Univ.	N/A
[10] ^b	R825249	Light induced mercury volatilization from substrate: Mechanisms responsible and <i>in situ</i> occurrence	Gustin, Mae S., Univ. of Nevada-Reno	N/A
[11] ^b	R827622E02	Determining the role of plants and soils in the biogeochemical cycling of mercury on an ecosystem level	Gustin, Mae S., Univ. of Nevada-Reno	Ray Alden, James Coleman, Dale W. Johnson, Steve Lindberg

^a The grant title and co-investigators listed in this table correspond to the information provided in the final summary report for each project and may differ from the title and staff listed on the original grant proposal.

^b The two grants lead by Gustin were funded under different RFAs (Exploratory Research - Air Chemistry & Physics (1996) and Experimental Program to Stimulate Competitive Research (1998)).

(3) **Sources and distribution of mercury in terrestrial and aquatic systems.** Research on sources of inorganic mercury and methylmercury as well as factors influencing their distribution in the environment that are not already covered under the first or second themes (e.g., inputs via atmospheric deposition, inputs from runoff and erosion).

(4) **Bioavailability and bioaccumulation of mercury in aquatic systems.** Research on the availability of mercury for uptake by aquatic organisms and the factors that influence this availability and accumulation.

In addition, STAR grant researchers developed several new analytical methods for measuring total or speciated mercury to facilitate their major research objectives. These

new methods are discussed as a fifth research theme.

Table 3 presents a crosswalk of the 11 STAR grant projects and these five research themes. Project results as they relate to the aforementioned themes are described in the next section.

TABLE 2. CROSSWALK OF STAR GRANT CONTRIBUTIONS TO ORD'S MERCURY RESEARCH GOALS AND MEASURES

Annual Performance Goals and Measures under LTG 2 of the <i>Mercury MYP</i> (EPA 2003b; target year, assigned lab/center for APMs)	Mercury Fate and Transport STAR Research Grants									
	Hurley [1]	Swain [2]	Gilmour [3]	Nriagu [4]	Driscoll [5]	Brown [6]	Fitzgerald [7]	Mason [8]	Morel [9]	Gustin [10 and 11]
APG: Provide an assessment of key fate and transport issues for tracking the fate of mercury from sources to concentrations in fish tissue (2004)	●	●	●	●	●	●	●	●	●	●
APM: Hold workshop/SOS on mercury with emphasis on Fate and Transport in watershed(s) and ecosystem impacts (2004)	●	●	●	●	●	●	●	●	●	●
APM: Evaluate mercury cycling in complex ecosystems; including, air/water interface to accurately assess TMDLs for mercury and predict methylmercury concentrations in water and fish. Focus is on human exposure as the ecological endpoint (2004, NCER)	●	●	●	●	●	●	●	●	●	●
APG: Develop a model for tracking mercury from deposition to concentrations in fish tissues (2006)	●	○	●	○	●		○	○	○	○
APG: Develop information on sources of mercury emissions including the regional/global atmospheric fate and transport of such emissions (2008)				●		●	●			○
APG: Produce an integrated multimedia modeling framework for understanding mercury fate from source to fish concentrations (2010)	○	○	○	○	○	○	○	○	○	○
APM: Develop an integrated multimedia modeling framework for the complete scientific understanding of mercury fate/transport and atmospheric chemistry/processes (2010, NERL, NMRL, NCER) ^a	○	○	○	○	○	○	○	○	○	○

Key: ● = significant contribution based on available results; ○ = results provide background knowledge that may be useful in meeting goal/measure.
^a This APM pertains most directly to the 2001 RFA; although as stated the FY 99 RFA grants provide supporting materials.

TABLE 3. CROSSWALK OF RESEARCH THEMES AND MERCURY STAR GRANT RESEARCH PROJECTS

Research Themes	Mercury Fate and Transport STAR Research Grants									
	Hurley [1]	Swain [2]	Gilmour [3]	Nriagu [4]	Driscoll [5]	Brown [6]	Fitzgerald [7]	Mason [8]	Morel [9]	Gustin [10 and 11]
Biogeochemical controls of mercury transformations (see Section 3.1)	●	●	●	●			●	●	●	
Biogeochemical controls of mercury cycling in the environment (see Section 3.2)	●			●	●	●	●	●		●
Sources and distribution of mercury in terrestrial and aquatic systems (see Section 3.3)	●	●	●		●	●	●		●	
Bioavailability and bioaccumulation of mercury in aquatic systems (see Section 3.4)	●	●	●		●	●	●	●		
New methods for mercury analysis (see Section 3.5)	●					●	●	●		●

Key: ● = Research results applicable to research theme.

3. STUDY RESULTS



The important results of the 11 STAR research projects on mercury fate and transport are described in this section. This discussion is organized according to the five research themes described in Section 2.4. In general, this section focuses on the study results, but details regarding the study approach are also included to facilitate interpretation of the results. Detailed descriptions of the research conducted under each individual grant can be found in the final summary reports prepared by the principal investigators and in the references listed in the Appendix.

Throughout this report, the principal investigator's name and/or grant reference number presented in Table 1 are used to identify research conducted under the different grants, even when co-investigators may have led the specific part of research that contributed to the result. This format is used to simplify the presentation of the grant findings. The primary sources used to compile this report were the final reports prepared by researchers and submitted to NCER. Presentation materials from the November 21, 2003, STAR Mercury Fate and Transport Final Progress Review meeting were also used.² In addition, Dr. Robert Mason of the University of Maryland, one of the grant principal investigators, provided an informal summary of what he believes to be the most important findings of the nine grants, and his input is reflected in this synthesis report as well.

3.1 Biogeochemical Controls of Mercury Transformations

STAR grant research included several studies that investigated the processes by which mercury transforms from one species to another. These ranged from ecosystem-level studies, in which the overall speciation of mercury was analyzed, to laboratory-scale experiments, in which the mechanisms of transformation were investigated. Results described here include new information on factors affecting the methylation/demethylation of mercury and inorganic transformations between elemental mercury (Hg(0)) and divalent mercury (Hg(II)).

Methylation/Demethylation

Net MeHg production in aquatic ecosystems is a complex process because there is rapid recycling between inorganic Hg (Hg(II)) and MeHg, as Hg is effectively methylated in low oxygen environments by sulfate reducing bacteria (SRB) in sediments, but MeHg is also efficiently demethylated in both anoxic and oxic environments. The recent STAR research suggest that the turnover time of MeHg in aquatic sediments is on the order of days to weeks and that Hg is likely recycled many times by these processes between the two forms before being bioaccumulated into fish as MeHg, or lost from the system as Hg(II), elemental Hg(Hg(0)) and MeHg by other processes.

STAR grant research demonstrated that rates of mercury methylation and demethylation are affected by a variety of factors that influence both the availability of environmental mercury and the activity of SRB that are known to methylate inorganic mercury. Results from methylation-related research performed under STAR grants include information on factors that increase methylmercury production rates, the pathway of reaction in SRB methylation, and demethylation rates of methylmercury.

In general, there has been more study of methylation than of demethylation, and much of the STAR research conducted in this area also focused on factors that affect methylation of inorganic mercury. Study results showed that methylation rates *increase* with:

- Increased bacterial metabolic rates in summer [7];
- Higher concentrations of inorganic mercury in sediment pore water [7];
- Increased levels of bioturbation by benthic infauna [7];
- Increased mercury load to the ecosystem [3]; and
- Increased sulfate load to a wetland [2, 8].

² One exception is noted. Information on research conducted by Hines and Brezonik under Swain's STAR grant that was not included in the final summary report was obtained from separate pre-publication drafts of journal articles.

Additionally, research demonstrated that methylmercury production rates decrease with:

- Increased concentrations of organic matter in sediments (which binds inorganic mercury, limiting its bioavailability) [7];
- Higher sediment distribution coefficient (K_D) values for inorganic mercury [7]; and
- Increased sulfide loads in the ecosystem [2, 7, 8].

STAR grant research also showed that methylmercury demethylation can occur via photolytically-induced reactions [2], and that demethylation is a major removal process of methylmercury, along with burial [1]. Additionally, researchers measured biological demethylation in sediments and related it to the net methylation rate [3, 8]. The research supporting these findings are described below.

Fitzgerald et al. [7] performed multiple experiments in Long Island Sound using mercury isotope tracers to identify factors that increase methylation in sediments. Methylation rates were enhanced in August relative to March and June, illustrating the importance of methylating bacteria in utilizing available substrate, Hg(II). In areas where organic matter was lower, there were higher Hg(II) concentrations in the porewater and correspondingly higher rates of methylation. Conversely, the presence of organic matter (i.e., dissolved organic carbon, or DOC) resulted in decreased methylation rates by binding available inorganic mercury and making it less available to the bacteria. Sediment-water partition coefficients (K_D s) for inorganic mercury also were measured, and higher coefficients were correlated with lower methylation rates. Additionally, increased levels of bioturbation by benthic infauna appear to extend the zone of active mercury methylation in sediment and

might move buried mercury to the active methylating zone.

Other STAR research demonstrated that increasing mercury or sulfate loads to an ecosystem can increase methylmercury formation. Gilmour et al. [3] report their study to be the first *direct* set of whole ecosystem-level experiments to show the rapid and linear increase in methylmercury production in an aquatic ecosystem in response to increasing surface loading of inorganic mercury. Response time (i.e., time between increase in mercury load and a measured change in methylmercury production) varied with environmental conditions. For shallow, warm sites in the Florida Everglades, response time was days to weeks, depending on temperature. Response time for the Experimental Lakes Area in Canada ranged from weeks for small, shallow enclosures, to about a year for the whole lake. Time to reach a new equilibrium for the increased mercury loading rate (about four times higher than normal mercury loading) in Experimental Lakes Area is expected to be at least three years.

Gilmour et al. [3] noted that the magnitude of the change in methylmercury production due to mercury loading depended on when and where the loading occurred. Mercury added to the lake surface was readily methylated in lake sediments. Mercury loaded to uplands and wetlands was slow to move to sites of methylation (i.e., subsurface areas near the water table). Mercury mass budgets calculated from isotope measurements suggest that most of the methylmercury in the lake was formed in the lake rather than being transported to the lake from other parts of the watershed.

Sulfate concentrations influence environmental methylation rates because SRB require sulfate to break down organic matter to yield sulfide, carbon dioxide, and energy, with

concomitant methylation of Hg(II). Swain et al. [2] applied sulfate to the surface of a naturally sulfate-poor wetland and to lake sediment samples. Sulfate sprayed onto half of a 2-ha peatland at the Marcell Experimental Forest in northeastern Minnesota increased the annual sulfate load by approximately four times relative to the control half of the wetland. Measurements of sulfate and methylmercury in the wetland two weeks after the first application indicated that methylmercury porewater concentrations had increased three-fold. Three subsequent sulfate additions that year did not further increase methylmercury porewater concentrations; methylmercury concentrations in the treated portion of the wetland remained elevated relative to the control. Methylmercury concentrations in the outflow from the wetland increased following each addition. Based on these results, Swain et al. [2] concluded that methylmercury production in sulfate-poor wetlands is as much a function of atmospheric deposition of sulfate as of mercury.

The addition of sulfate to lake sediment samples in the laboratory, however, reduced mercury methylation rates [2]. Addition of glucose and ammonium to those sediment samples also reduced net mercury methylation rates. Swain et al. [2] suggested that these additions probably reduced the bioavailability of mercury through the binding of sulfides, reduced pH, increased formation of mercury-Cl species, or a combination of these factors. Pyruvate treatments were the only additions to the lake sediment samples that increased net mercury methylation rates. Swain et al. [2] suggested that this occurred because the SRB were fermenting pyruvate instead of sulfate and were not producing the sulfides that reduce mercury bioavailability. In a set of sediment cores taken across a transect in the lake, methylmercury concentrations were negatively cor-

related with total inorganic sulfides. Swain et al. [2] proposed that bioavailability of mercury, which can be reduced by binding with sulfides (see Section 3.2), may control the distribution of methylmercury in the lake sediments.

Mason et al. [8] designed their experiments to evaluate how different types of mercury-sulfide complexes affect the rate of mercury methylation by SRB. In the presence of dissolved sulfide, mercury forms both neutral complexes (e.g., HgS^0 , $\text{Hg}(\text{SH})_2^0$) and charged complexes (e.g., $\text{Hg}(\text{SH})^+$, HgS_2^{2-}). Mason et al. [8] hypothesized that SRB bioconcentrate neutral mercury-sulfide complexes via passive diffusion, but do not bioconcentrate charged mercury-sulfide complexes. Thus, the neutral mercury-sulfide complexes are believed to be the bioavailable form by which inorganic mercury can enter these bacteria cells and undergo methylation. Mason et al. [8] measured a relatively high octanol-water partition coefficient (K_{ow}) for two neutral mercury sulfide complexes. Based on estimated cell membrane permeability for compounds with similar K_{ow} values, Mason et al. [8] estimated that SRB could uptake these complexes at rates that are more than sufficient to achieve observed methylation rates in cultures, both pure and field cultures.

The fraction of mercury-sulfide complexes in sediments that are neutral is a function of the sulfide concentration in the medium. Chemical complexation modeling by others has shown that the speciation of mercury tends to shift toward charged complexes as sulfide levels increase. Mason et al. [8] conducted mesocosm experiments in various locations in the Florida Everglades and observed that as sulfide concentrations increased, methylation rates decreased. The investigators also compared modeled uptake rates,

assuming passive diffusion of neutral mercury-sulfide complexes (HgS^0 and HOHgSH^0), and compared them to observed methylation rates in pure cultures of the SRB *Desulfobulbus propionicus*. Uptake and methylation rates both increased with increasing HgS^0 concentration with similar slopes. Mason et al. [8] believe that these findings confirm that speciation of mercury in the medium surrounding methylating bacteria is a key factor affecting mercury methylation rates in sediments.

Mason et al. [8] also observed that sulfate levels affect mercury methylation rates in sediments. Mason et al. studied sediment cores taken from various regions of the Florida Everglades that differ in sulfate concentrations. When the investigators added sulfate to cores with low sulfate levels, they observed an induction of SRB activity and increased mercury methylation, even though that activity increased sulfide levels. Confirming previous findings, they found that adding sulfide alone inhibited methylation. Overall, the results of both the laboratory and field studies indicated that the balance between sulfate levels, which affect SRB activity, and sulfide production and accumulation, which reduce mercury bioavailability (see Section 3.2), affects net mercury methylation rates.

One STAR grant indicated that bacterial community structure also can affect mercury methylation rates. Previous research had shown that the acetyl-coenzyme A pathway is key for producing methylmercury in several SRB strains. Morel et al. [9] hypothesized that some methylation can also occur via different pathways in other strains. In a series of laboratory experiments on seven strains of SRB, Morel et al. used carbon monoxide dehydrogenase (CODH) activity to indicate activity of the acetyl-CoA pathway and chloroform to inhibit the acetyl-CoA pathway. They found

four incomplete-oxidizing SRB strains that clearly do not utilize the acetyl-CoA pathway for mercury methylation and, therefore, might not require vitamin B_{12} as a coenzyme.

Demethylation of methylmercury is important in determining the net formation of methylmercury in an ecosystem. In Spring Lake in northern Minnesota, Hines and Brezonik [2] measured methylmercury photodegradation rate constants of 0.0025 hr^{-1} in the field. They estimated that photolytically-induced demethylation accounts for twice as much removal of methylmercury from surface waters as does methylmercury burial in sediments. The depth profile of methylmercury photodegradation showed loss of methylmercury up to 50 to 60 cm, which corresponded to the depth of 90 percent attenuation of PAR (photosynthetic active radiation). Using a mass-balance approach to estimate the distribution and cycling of mercury species in Lake Superior, Hurley et al. [1] concluded that both sediment burial and photo-demethylation are major removal processes for methylmercury in surface waters.

In addition to photodemethylation, biological demethylation is also an important process, as demonstrated by Mason et al. [8] and Gilmour et al. [3]. Results showed that methylmercury speciation and bacterial activity influence the rate of demethylation in sediments and thus also affect the overall net production of methylmercury in the system. Therefore, demethylation rates vary across ecosystems. The researchers concluded that studies should measure both methylation and demethylation rates to properly understand the rate of net methylmercury production.

Inorganic Transformations

STAR research also focused on transformations between inorganic species of mercury via redox reactions,

with a particular focus on photo-induced reactions as an important pathway. These redox transformations can affect the fate and transport of mercury by converting mercury to chemical species that are more or less mobile in the environment. This section presents STAR grant findings related to rates of transformation, chemical mechanisms, and factors affecting these transformations.

Research focused more on the overall transfer of mercury between media (including transfers that might occur due to redox reactions involving inorganic mercury transformation) are covered in the Section 3.2.

STAR grants showed that oxidation of Hg(0) to Hg(II):

- Occurs via photo-oxidation, perhaps indirectly via hydroxy radicals and other reactive chemical intermediates [2, 9];
- Can at times account for the majority of Hg(0) lost from surface waters [9]; and

STAR grants also demonstrated that reduction of Hg(II) to Hg(0):

- Can occur via photoreduction [2];
- May require the Hg(II) to be bound to organic matter [7]; and
- Can occur at a higher rate than photooxidation [2].

In some experiments, however, both oxidation and reduction were observed under similar conditions [4]; additional research is needed to understand such reactions.

Both Morel et al. [9] and Hines and Brezonik [2] found photooxidation of Hg(0) to be a significant means of Hg(0) removal from surface waters. In laboratory and field studies on the St. Lawrence River, Morel et al. [9] found the rate of loss of Hg(0) to photooxidation to be about two orders of magnitude greater than

its loss via volatilization to the air. Through treatment with heat, chloroform, and filtration to eliminate SRB activity, Morel et al. [9] confirmed that the oxidation is chemically mediated chiefly by UV radiation rather than biologically mediated. Their data suggested that factors other than photon flux, however, are rate-limiting. They proposed that hydroxy radicals and reactive halogen and oxygen intermediates may favor Hg(0) oxidation.

In water samples from Spring Lake in northern Minnesota, Hines and Brezonik [2] calculated a pseudo-first order rate constant of 0.58 h^{-1} for the photooxidative loss of Hg(0). Measurements of air and water Hg(0) concentrations indicated that lake water was supersaturated with Hg(0). Fluxes of Hg(0) from the lake to the air were greatest in warmer, sunnier months, but correlation with solar radiation was weak. The loss of Hg(0) by photooxidation may have exceeded loss by volatilization to air at times. Other losses of Hg(0) from the lake water were reaction with ozone, hydroxyl radical, and possibly singlet oxygen. Burial was also a major loss of total mercury.

In studies of the photoreduction of Hg(II), Fitzgerald et al. [7] concluded that it must be bound to organic material to be reduced by abiotic processes in natural waters. Their research demonstrated that the addition of humic acid to synthetic seawater increases the rate of Hg(II) reduction to Hg(0), as has been reported by others. However, Fitzgerald et al. also observed that adding ethylenediaminetetraacetic acid (EDTA) and chlorine (Cl^-) as competitive ligands at concentrations that are high enough to outcompete the humic acid as a ligand resulted in reduction rates falling to almost zero. Fitzgerald et al. [7] concluded that higher Hg(0) concentrations in surface water in the summer are supported by the higher

summer concentrations of DOC and other ligands that enhance reduction of Hg(II). However, they also concluded that DOC may sometimes be high enough to prevent reduction to Hg(0) and that mercury-organic associations can explain the reduction that was measured below the photic zone (i.e., dark reductions of mercury may be abiological and organically mediated). Their data suggest that organic ligands and DOC affect the speciation of dissolved inorganic mercury complexes in anoxic low-sulfide sediments such as those in Long Island Sound. That conclusion appears to contrast with existing chemical speciation models that indicate sulfide to be the major ligand of both dissolved methylmercury and Hg(II) in natural porewaters.

Data collected by Nriagu et al. [4] also suggest that photoreduction of Hg(II) to Hg(0) is important in surface waters. They measured diurnal cycles of dissolved gaseous mercury (DGM; dissolved gaseous Hg(0)) concentrations in Great Lakes water to correlate with solar radiation both temporally and spatially. Their calculations indicated that the Hg(0) was supersaturated at most locations, a finding consistent with those of Hines and Brezonik [2]. In addition, Nriagu et al. [4] investigated the photoreduction of Hg(II) by examining the role of amino acids in the redox cycle of mercury. Preliminary experiments demonstrated that Hg(II) was photo-reduced in the presence of eight amino acids, but not photo-reduced in the presence of at least four other amino acids. Hines and Brezonik [2] also measured photoreduction of Hg(II) in the lake and found the rate constant to be 1.1 h^{-1} , which was twice the rate constant for photooxidation. They concluded that redox reactions between Hg(0) and Hg(II) readily occur, providing a source of ionic mercury to the system that can be methylated.

These STAR results indicate that both oxidation and reduction of inorganic mercury species appear to occur readily in natural waters under the right conditions. Additionally, in surface water samples spiked with Fe(III) and exposed to sunlight, Nriagu et al. [4] found that DGM increased in some samples and decreased in others. Nriagu et al. estimated a rate constant for the reduction and proposed chemical mechanisms for both reduction and oxidation. It is not entirely clear why both oxidation and reduction were observed under similar conditions. Experimental conditions introduced by the investigators were proposed as one explanation; however, further research is necessary.

3.2 Biogeochemical Controls of Mercury Cycling in the Environment

Mercury cycling (i.e., phase partitioning and inter-media transport) is key to the distribution of mercury in the environment. Most of the STAR research in this area focused on processes controlling mercury transfer between surface water and the atmosphere or surface water and sediment as summarized in the subsections below.

Sediment—Surface Water Transfers

As MeHg formation appears to occur primarily in sediments, the processes responsible for its transport from the sediment into the water column are very important in determining its rate of bioaccumulation into fish. Partitioning of mercury between dissolved and solid phases in surface water determines the mechanisms by which it can be transferred to other media (e.g., mercury bound to particles in the water column will be subject to deposition and to resuspension from the benthic sediment, whereas dissolved mercury complexes will not; some dissolved complexes may be bioavailable whereas other are not).

Fitzgerald et al. [7] found that most of the ionic inorganic mercury dissolved in the Long Island Sound water column is complexed with dissolved organic matter with a high affinity, given that the conditional stability constants were very high (log K' of about 21 to 24). Principal sources of organic ligands in Long Island Sound appear to be influx from river water as terrestrial organic matter (47 percent) and phytoplankton exudation (31 percent). The primary loss of organic ligands is via tidal exchange with low DOC/low ligand waters of the continental shelf. The Connecticut River is the primary source of organic matter to Long Island Sound, which is reflected in the seasonal variation in the ligand abundance (highest in summer/spring, lowest in winter).

Fitzgerald et al. [7] studied factors affecting the fraction of mercury in more labile forms which can potentially increase the rates of methylmercury formation. In the mixing zone of the Connecticut River and the Long Island Sound, Fitzgerald et al. found that the fraction of mercury present as reactive mercury increased from levels present in river water upstream of the mixing zone. The reactive fraction was primarily in the particulate phase. On the basis of field measurements and a simple competitive ligand model, Fitzgerald et al. concluded that the enhanced reactive mercury in the estuary is a result of dilution of the dominant organic ligand class (characteristic of fresh water mercury) and competition with chloride (from Long Island Sound) in the mixing zone, followed by coagulation/adsorption onto suspended particles.

Fitzgerald et al. [7] found both sedimentary organic matter and acid-volatile sulfide to affect partitioning of methylmercury and Hg(II) between particulate and dissolved phases in waters of Long Island Sound. As expected on the basis of bioavailabil-

ity of Hg(II) to SRB, Fitzgerald et al. [7] found mercury methylation rates to vary inversely with the K_D of Hg(II) and positively with the concentration of Hg(II) in porewater (which exists mostly as HgS^0).

Mason et al. [8] also explored how mercury partitioning to sediment particles impacts mercury concentration and bioavailability in sediment pore waters. They developed a model accounting for adsorption and sulfide concentration to predict Hg(II) concentrations in sediment pore water and sorbed to particles. The model was applied to two ecosystems, the Patuxent River and the Florida Everglades, and the results were validated with measurements. The model's predictions of neutral mercury-sulfide complexes correlated well with the methylmercury concentrations for the samples.

Binding of mercury to dissolved organic carbon (DOC) in surface waters has been found to be important, but the findings of Mason et al. [8] suggest that the influence of DOC on mercury partitioning in sediments is more complex. Their research suggested that binding of mercury to DOC is less important in sediment pore waters under typical DOC levels and when there is greater than 0.01 micromolar sulfide. Mercury binding with DOC in the solid phase is important, and these studies [8] suggest that in aerobic sediments, binding with the organic fraction of sediments is more important than binding with methyl oxide phases.

Surface Water—Atmospheric Transfers

Deposition of mercury from the atmosphere to surface waters (and soils and plants) occurs via both wet and dry deposition. Dry deposition is less well studied than wet, and includes deposition of atmospheric particulate Hg and gas phase Hg. Gas phase Hg consists of both Hg(II), often called reactive gaseous mercury (RGHg), and Hg(0). Dry deposition

of RGHg depends on its chemical composition (e.g., HgBr₂, HgCl₂), wind speed, and other factors. Less well studied is the loss of mercury from surface waters via volatilization of Hg(0) to the atmosphere. Several STAR grants investigated the relative importance of Hg(0) volatilization from surface water in the total mercury mass balance.

Estimating net dry deposition of Hg(0) to surface water (and soils) is complex because Hg(0) is constantly degassing (i.e., volatilizing) from the surface. As described above, Hines and Brezonik [2] and Nriagu et al. [4] found Hg(0) concentrations in lakes typically to be above saturation with respect to the atmosphere, indicating that dry deposition of Hg(0) will not occur; rather, Hg(0) will escape from the surface water into the atmosphere. Both Hurley et al. [1] and Fitzgerald et al. [7] found volatilization of Hg(0) from surface water to be a major process by which Hg(0) leaves surface water. Based on a mass balance of mercury derived for Lake Superior, Hurley et al. suggested that volatilization of Hg(0) is one of the main removal processes for total mercury from that ecosystem, followed by sediment burial. Fitzgerald et al. found volatilization of Hg(0) to be important in removing Hg(0) from Long Island Sound as well, and noted that this transfer is a potentially important source of atmospheric Hg(0). Fitzgerald et al. estimated annual emissions of Hg(0) from Long Island Sound to be 80 kg in total. This corresponds to 35 percent of the annual input of mercury to Long Island Sound being remobilized into the atmosphere as Hg(0). Fitzgerald et al. concluded that volatilization competes with sediment methylation of mercury as a mechanism of removal of Hg(0) from surface water.

Results from a short-term study of a Tobico marsh at the coast of Saginaw Bay suggested to Nriagu et al. [4] that loss of Hg(0) from that marsh

resulted primarily from volatilization of Hg(0). They estimated a “lifetime” of about one hour for DGM in the marshlands. Volatilization of Hg(0) may be more or less important than other processes that remove Hg(0) from surface waters in other types of ecosystems. As stated earlier, results from Nriagu et al. indicate that mercury cycling between surface water and air varies diurnally and seasonally, with rather large daily variations in DGM in surface water of Saginaw Bay. Bay waters were generally supersaturated with Hg(0) relative to the partial pressure of Hg(0) in the atmosphere. Distinct diel variations in DGM concentrations were observed that indicate a high dependence on the intensity of solar radiation. In their research, Nriagu observed a maximum DGM in surface water samples around noon, with DGM levels generally highest in June. These variations seem to indicate that the dissolved mercury pool is being actively recycled in the water column.

Soil—Atmospheric Transfers

Deposition of mercury from the atmosphere to surface soils, which occurs via both wet and dry deposition, has been extensively studied. Less well studied is the transfer of mercury from soils back into the atmosphere. Several STAR grants investigated factors affecting the emission of mercury from soils to the atmosphere.

Gustin et al. [10] performed laboratory, field, and mesocosm experiments to investigate light-enhanced mercury volatilization. In laboratory experiments, a well-mixed single pass gas exchange chamber was used to test various hypotheses about mercury volatilization from soil. All mercury species and mercury-containing substrates constantly emitted mercury to the air. However, of the pure phase mercury species, only mercury sulfide exhibited light-enhanced emissions. In a test of whether mercury adsorbed to iron oxides

and organic matter would exhibit light-enhanced emissions, iron oxide amended with mercury chloride, and organic material amended with Hg(0) and mercury chloride exhibited light-enhanced emissions.

At various mining, Superfund, and geothermal sites in Nevada and California, Gustin et al. [10] used chamber and micrometeorological flux measurements to assess light-enhanced mercury emissions. At all sites, light-enhanced emissions of mercury were observed with little increase in soil temperature. A rapid increase in emissions was observed in the morning (e.g., at New Idria, CA, emissions from soils doubled as morning light irradiated the soil), and on cloudy days the flux would mimic the shadowing and lighting of the sites. A 100-fold increase in emissions was observed by artificially lighting tailings at night at the Carson River Superfund site. Gustin et al. [10] also calculated the activation energy for the mercury flux in dark and light conditions. The activation energy was lower for the nighttime flux, indicating that the light energy in the day is being used for a process in addition to volatilization, perhaps to generate elemental mercury by photoreduction.

In follow-up field work, Gustin et al. (under the Brown et al. [6] grant) compiled data on mercury emissions from mine wastes and surrounding mercury-enriched terrains by measuring fluxes at 18 areas of mining activity. They studied the different emissions under light versus dark conditions and determined the speciation of the mercury sources at each site. Overall, the researchers found that mercury-contaminated mining sites with higher concentrations of soluble mercury-containing species emit more mercury to the atmosphere than those containing less soluble mercury-containing species. Specifically: (1) as particle size decreases, mercury concentration,

mercury emissions, and light-to-dark emission ratio increase; (2) metacinnabar-bearing samples exhibit higher light-to-dark emission ratios than those containing cinnabar; and (3) the presence of more soluble mercury species also correlates positively with higher light-to-dark emission ratios.

Gustin et al. [11] used large mesocosms (Ecologically Controlled Lysimeter Laboratories (EcoCELLs)), smaller plant-exposure chambers (ecopods), and a single-plant gas-exchange system to further study the role of soils (and plants, see next section) in controlling the fate and transport of mercury in the environment at the ecosystem level. Measurements of mercury emissions from the soil were made in the EcoCELLs. Dominant factors driving mercury emissions from soil were incident light, precipitation, and the presence of vegetation. Soil temperature and moisture also influenced flux. Data indicated that soil gas efflux is not a diffusion-driven process, except during certain periods of the day (particularly midday). Therefore, soil gas concentrations are not an effective predictor of soil mercury flux.

Plant Transfers

In the EcoCELL experiments, Gustin et al. [11] found that nearly all the mercury in plant foliage was derived from the atmosphere, as opposed to the soil. Mercury concentrations in the foliage of trees grown in mercury-enriched soil (concentration of 12.3 $\mu\text{g/g}$) was similar to the foliage of trees grown in soil with a background mercury concentration (0.03 $\mu\text{g/g}$). These results indicate that foliage may act as a significant sink for atmospheric mercury, and that the mercury content in litterfall would represent a significant mercury input to terrestrial ecosystems, consistent with the findings of Driscoll et al. [5] described below. Additionally, experiments (using leaf washing) showed that less than three percent of mercury would be

removed with precipitation. Gustin et al. concluded that litterfall may be an effective way to estimate mercury deposition in deciduous forests. Ecopod and gas exchange chamber experiments supported these results by showing that mercury concentration in foliage increased with increasing air concentrations of mercury, and that mercury soil concentrations either did not significantly influence foliar concentration or influenced it much less than the air concentrations. Experiments in the gas exchange chamber indicated that some mercury is transported from the soil via the transpiration stream, because there was a pulse in water vapor and mercury emitted when the chamber was first illuminated.

In their study of two upland forest sites (one deciduous, one coniferous) in the Sunday Lake watershed, Driscoll et al. [5] also found forest vegetation to be very important in mediating the inputs of mercury to the forest floor. They found that the flux of mercury to the forest ecosystem was dominated by dry deposition (70 percent of total deposition, including both litter fall and throughfall). Ten-fold higher levels of total mercury were reported for the throughfall (i.e., deposition passing through tree canopy) at the coniferous plot, however, than at the deciduous plot. The major pathway for dry deposition in the coniferous plot was throughfall, while the major pathway in the deciduous plot was litterfall, which is consistent with the conclusions from Gustin et al. [11] regarding litterfall being an effective measure of deposition in deciduous forests.

Studies by Nriagu et al. [4] indicate that plants are contributing in a minor way to the release of mercury from soils to the air. Mercury flux measurements over soybean plants (3 $\text{ng/m}^2\text{-hr}$) were higher than mercury flux measurements over soil with no plants that had previously been sown with corn

seed dressed with mercury (from < 0.1 to 1.7 $\text{ng/m}^2\text{-hr}$). Results of these measurements indicated that the mercury in the soil from the seeds was a minor source of mercury to the atmosphere, but that vegetation could play a role in transferring mercury from soil to the atmosphere.

3.3 Sources and Distribution of Mercury in Terrestrial and Aquatic Systems

Several STAR grants identified the major sources and means of distribution of mercury in a given study area. Researchers identified and investigated important processes influencing movement of mercury throughout a watershed (e.g., production of methylmercury, predominant mercury fate and transport processes). In addition, several researchers performed general mass balance studies to quantify sources and inputs within a given watershed. Relevant results are summarized here.

Mass Balance Studies

Using data from open water cruises and GIS-based studies, Hurley et al. [2] developed a mass balance model of mercury in Lake Superior. They reported that total mercury inputs were dominated by atmospheric deposition (58 percent), followed by tributary inputs (21 percent) and contributions from particulate remineralization (19 percent), while sources of methylmercury were somewhat evenly divided between the atmosphere, tributaries, groundwater, remineralization, and *in-situ* methylation. Elevated concentrations of mercury in nearshore waters appeared to be the result of tributary inputs. Hurley et al. [2] estimated volatilization of $\text{Hg}(0)$ to be the principal removal process of total mercury from the surface water, followed by sedimentation, while they estimated methylmercury to be removed primarily by sedimentation and photo-demethylation. Based on trace amounts of methylmercury detected in open surface waters

(about 1 percent of total mercury in the lake), Hurley et al. [2] concluded that wet deposition may be a small but measurable source of methylmercury to surface water in the lake. They found the proportion of total mercury as methylmercury to be maximum at the thermocline in open surface waters of the lake, probably because plankton, with their accumulated methylmercury, aggregate at the thermocline. Using their data, Hurley et al. [2] developed a simple model to relate annual tributary loading from a watershed to the lake based on land use/type in the watershed.

Driscoll et al. [5] performed mass balance calculations on mercury cycling in the Sunday Lake watershed of the Adirondacks. Results from this study indicate that overall, the watershed and lake are sinks for total mercury, while the wetlands and the lake are sources of methylmercury. At both coniferous and deciduous upland plots, mass balance calculations indicated that the soil acts as a net sink for inputs of total mercury and methylmercury. Discrepancies in these calculations suggest that mercury is either accumulating in the forest floor or is lost by volatilization or both. As a part of this study, total mercury concentrations were measured in soil horizons. The concentrations were highest in the surface layer, lowest in the next layer, peaked slightly in the third layer, and then decreased in the lowest layer analyzed. In measurements taken in soil water, fluxes of total mercury decreased with depth, which coincided with decreases in DOC. Driscoll et al. [5] concluded that mercury is immobilized in the mineral soil by the deposition of organic matter.

Swain et al. [2] performed a mass balance study of mercury in the Spring Lake watershed in northern Minnesota. They concluded that atmospheric deposition is the main source

of total mercury to the lake, methylation in the lake is the main source of methylmercury, demethylation and photodegradation consume most of the methylmercury in the lake, and Hg(0) is lost from the lake mostly by photooxidation and volatilization.

In Situ Methylmercury Production

As studies described thus far indicate, although atmospheric deposition and watershed inputs are important sources of methylmercury (MeHg), *in situ* production within the aquatic system is the dominant source of MeHg, at least for freshwater lakes (except for those that have a large watershed or extensive abridging wetlands) and for estuarine systems (e.g., Long Island Sound and the Chesapeake Bay). Hines and Brezonik [2] performed mercury mass balance calculations for Spring Lake in northern Minnesota (a lake with little wetland coverage in the watershed) and found that *in situ* methylation is the main source of methylmercury, accounting for 76 percent of input). In Long Island Sound, Fitzgerald et al. [7] concluded that *in situ* production is also the major source of methylmercury. The calculated diffusive sediment-water flux of methylmercury in Long Island Sound (11 kg/yr) is higher than methylmercury inputs to the Sound from external sources (estimated at 5.2 kg/yr). Results from both a model developed by Driscoll et al. [5] (i.e., the Mercury Cycling Model for Headwater Drainage Lake Systems) and the mercury mass balance calculations for the Sunday Lake watershed in the Adirondacks indicate that both the surrounding wetlands and Sunday Lake itself are the dominant sources of methylmercury to the lake.

Gilmour et al. [3] studied methylmercury sources in both the Everglades and the Experimental Lake Area in Canada. Calculations of mercury mass balance based on mercury

isotope measurements in the systems suggested that most of the methylmercury found in both systems is formed *in situ*. Mercury added to surface water was readily methylated in the sediments, while mercury loaded to uplands and wetlands was slow to move to sites of methylation. The major locations for new methylation in both the shallow, warm sites in the Everglades and the deeper, cooler Experimental Lakes Area were saturated surface peats and sediments, and for the Experimental Lakes Area, also anoxic bottom waters. The newly deposited mercury was more readily methylated than existing mercury at those sites (i.e., sediments and soils), suggesting that older mercury deposits are less bioavailable for methylation.

In Lake Superior, Hurley et al. [1] measured sediment-water partition coefficients ($\log K_D$) for total mercury and methylmercury in sediment that were relatively low compared to other lakes, suggesting that mercury is more mobile in Lake Superior sediments than in other lakes. The highest concentrations in sediment were observed in spring and near tributary inputs. They proposed several factors as likely to control methylmercury concentrations in sediments, but did not acquire quantitative data on those factors during this study.

Morel et al. [9] conducted a statistical analysis of methylmercury concentrations in marine fish tissues and a simple modeling exercise of the Pacific Ocean. Statistical analyses of methylmercury concentrations in yellowfin tuna caught off of Hawaii in 1971 and 1998 indicated no statistically significant change in methylmercury concentrations over this time period. By contrast, a simple, three-layer box model of the ocean over this time span indicated an increase in methylmercury concentrations in surface waters if methylmercury were formed in the thermocline or the mixed layer (and

therefore were susceptible to changes in mercury deposition from the atmosphere). Based on this contrast, Morel et al. [9] suggested that methylation is occurring in deep waters, sediments, or hydrothermal vents where mercury concentrations are not greatly affected by human activities.

Inputs via Atmospheric Deposition

As mass balance studies indicate (e.g., Hurley et al. [1] and Swain et al. [2] results described above), atmospheric deposition can be a major source of total mercury to an ecosystem and can have a direct effect on surface water mercury concentrations. Based on studies in Spring Lake in northern Minnesota, Hines, and Brezonik [2] reported that atmospheric deposition is the primary input of total mercury to the lake. Likewise, Hurley et al. [1] found that atmospheric deposition accounts for 58 percent of the total mercury input to Lake Superior. In a direct ecosystem-level experiment (see Section 3.1 and previous section), Gilmour et al. [3] observed a rapid and linear increase in methylmercury production within the aquatic ecosystem in response to changes in mercury load by surface application designed to simulate elevated atmospheric deposition. Findings from that study also indicate that the newly deposited mercury was more bioavailable than existing mercury at these sites and contributes substantially to methylmercury production and bioaccumulation (Section 3.4).

As described in Section 3.2 under Plant Transfers, Driscoll et al. [5] analyzed mercury deposition in two upland forest sites in the Sunday Lake watershed and found 70 percent of the total mercury deposition to be via dry deposition.

Driscoll et al. [5] also sampled sections of sediment cores from eight lakes in the Adirondacks for total mercury to quantify the increase in mercury deposition in that area over

the last 200 years. Sediment samples were dated using ^{210}Pb to measure changes in sediment deposition throughout this period. On average, sites showed a 5.8-fold increase in sediment mercury deposition from background values (before 1900) to peak values (which occurred from 1973 to 1995). Current mercury sediment deposition has decreased from the peak to a level approximately 3.5 times the background values. Driscoll et al. [5] also estimated rates for current and pre-anthropogenic mercury deposition in a perched seepage lake. Using the sediment deposition data, Driscoll et al. concluded that retention of mercury in Adirondack lakes has decreased over the past 200 years, but the mechanism for this decrease is unclear.

Inputs from Runoff/Erosion

As described in Section 3.3, mass balance calculations by Hurley et al. [1] indicate that tributary loading is a significant input of total mercury to Lake Superior, suggesting that runoff and erosion can be major sources of mercury to a water body. In their watershed study of Lake Superior involving primarily groundwater sampling in the basin, Hurley et al. [1] found (among other results) that forested areas in a watershed basin can be a significant source of methylmercury, apparently generated by *in situ* methylation. Measurements of methylmercury in groundwater and surface water samples of the Sunday Lake watershed indicated to Driscoll et al. [5] that the riparian wetland was a net source of methylmercury to the lake and presumably a site for methylation. Furthermore, Driscoll et al.'s mass balance calculations indicated that fluxes of methylmercury were elevated in waters draining riparian wetlands, and that the entire watershed and the lake were net sources of methylmercury to downstream surface waters. However, the mass balance calculations did suggest that the upland forest floor may be an active zone of demethylation.

On the other hand, mass balance calculations by Gilmour et al. [3] using measured mercury isotope concentrations from their whole-ecosystem study in the Experimental Lakes Area of Canada show that most of the mercury loaded to uplands has been slow to move to sites of methylation in the lake and wetlands. Only a small fraction of the mercury loaded to upland areas had migrated to the lake after two years; much of the deposited mercury remained on surface vegetation. Mercury loaded to the wetland surface has been slow to move to subsurface areas near the water table where methylation occurs. The differences between these observations and those of Hurley et al. [1] and Driscoll et al. [5] may indicate the site-specific nature of inorganic mercury mobility in the environment.

Subsurface Transport

As noted above, Hurley et al. [1] sampled ground water along a stream passing through wetlands and forested area in the Lake Superior basin. A strong link between methylmercury concentrations in subsurface samples and the hydrologic cycle was observed, indicating that subsurface transport and/or production of methylmercury can be an important source of methylmercury to surface waters. Hurley et al. [1] proposed that the source of the methylmercury from the forested areas may be the hyporheic zone of streams (i.e., the subsurface interface occurring between groundwater and stream water).

Brown et al. [6] studied how mercury from mining activities has entered watersheds. The researchers performed column experiments to evaluate the fate of $\text{Hg}(0)$ introduced via dredge tailings during gold mining and subsequent restorations (such as the Clear Creek tributary to the Sacramento River in Redding, CA). Varying influent ionic strengths and low molecular weight organic acids were applied to columns filled with tailings

containing mercury in an attempt to simulate infiltration through the rooting zone of revegetated mine waste. Significant concentrations of mercury leached from the tailings in dissolved and particle-associated forms. Chemical extractions indicated that Hg(0) was transformed into readily soluble species such as mercury oxides and chlorides (3-4 percent), intermediately extractable phases that likely include sorption complexes and amalgams (75-87 percent), and fractions of highly insoluble forms such as mercury sulfides (6-20 percent; e.g., cinnabar and metacinnabar). These results imply that Hg(0) is transformed into other forms of mercury (soluble mercury and insoluble mercury sulfides) during its transport from placer gold mining regions to major wetlands such as the San Francisco Bay Delta. Also the results indicate that colloid-associated mercury from revegetated mercury mine tailings sites may be of potential environmental concern, and that the gradual infiltration of even very low concentrations of organic acids into mine tailings will eventually instigate conditions where colloid mobilization can occur.

Brown et al [6] also attempted to measure the variation of different mercury isotopes from a variety of natural mining samples to determine if any natural variations in the ratios may be useful as a mercury source indicator. No significant variation was found (above the experimental error), but further studies were suggested.

3.4 Bioavailability and Bioaccumulation of Mercury in Aquatic Systems

Bioavailability

Several STAR grant findings related to factors that affect the bioavailability of mercury to SRB have been discussed in the preceding sections on mercury transformations and mercury cycling in the environment. Additional find-

ings on the topic are described here.

STAR grant researchers found that newly deposited mercury is more bioavailable than "older" mercury and that DOC levels in a water body appear to affect bioavailability. In both the Florida Everglades and the Experimental Lakes Area in Canada, Gilmour et al. [3] found that newly deposited mercury was more readily methylated than existing mercury. In the Everglades, Gilmour et al. demonstrated that sulfate and DOC have a much larger effect on the methylation of newly deposited mercury than on the methylation of mercury already present in soils. Additionally, new methylmercury production from mercury isotope spikes added during the experiments was a good predictor of total methylmercury concentrations in surface sediments. After two years of mercury loading, Gilmour et al. [3] found that about 25 percent of the mercury in perch in the Experimental Lakes Area lake originated from the isotopically-labeled spike. Partitioning of methylmercury to biota appeared to decrease with time in Hurley's study. Hurley recorded the uptake of methylmercury by *Selenastrum* over time; a partition factor of 10^5 was measured through 24 hours. After this time, the factor decreased to 10^4 . The reason for this change is unclear, but may reflect the increased algal growth rate.

Hurley et al. [1] found that mercury concentrations in biota in Lake Superior are generally higher in the spring than summer, a trend that might result from bio-dilution by growing phyto- and zooplankton during the summer. Their results also showed higher concentrations of methylmercury in zooplankton from the epilimnion. These observations suggest that mercury in surface waters deposited from the atmosphere may be more bioavailable than mercury in deeper waters.

Hurley et al. [1] also reported that samples of water from Lake Superior with higher DOC had lower algal

concentrations of methylmercury, suggesting that DOC may be complexing mercury and making it unavailable for uptake. That observation agrees with those of Fitzgerald et al. [7] (discussed in Section 3.1) that increasing DOC reduces methylation rates.

Driscoll et al. [5] found that bioconcentration factor (BCF) values of fish in Sunday Lake in the Adirondacks increased with each trophic level. Total mercury concentrations in yellow perch were also higher than values measured in many remote regions (locations not specified). However, BCF values were generally lower for yellow perch in Sunday Lake than values for this species in other Adirondack lakes. Driscoll et al. suggested that this may occur because methylmercury in Sunday Lake is less bioavailable due to binding with the high concentrations of DOC.

Mason's team [8] evaluated the role of pH in mercury-sulfide complexation, given that a number of studies have shown an inverse relationship between lake water pH and mercury contamination of fish tissues. Mason et al. modeled mercury-sulfide speciation with changing pH and found that at low pH, as sulfide levels increase, the tendency for speciation of mercury to shift toward charged complexes is not as strong as it is at higher pH. In other words, when sulfide levels are high, neutral mercury-sulfide complexes, which are the bioavailable forms (see Section 3.1), are more likely to form if the pH is low than if the pH is high. This relationship may help explain why fish tend to have higher tissue mercury residues in waters of lower pH.

The bioavailability of mercury at mining sites could vary based on the mercury speciation at the site and presence of ions such as chloride and sulfate. Brown et al. [6] took samples from multiple mining locations in California Coast Range mercury mineral belt, the placer gold mining

belt in the Sierra Nevada foothills, and Nevada and found significant variations in mercury speciation from site to site. Highly soluble forms of mercury, such as the minerals corderoite, montroydite, schuetteite, egglesonite, and terlinguite, found at some sites are potentially much more bioavailable than highly insoluble forms of mercury, such as cinnabar and metacinnabar. Therefore, bioavailability may vary from site-to-site with mine waste contamination.

However, Brown et al. [6] also found that sorption of Hg(II) onto mineral particles may effectively sequester mercury in mine tailing and aquatic environments if the sorption complexes are strongly bonded to the particle surfaces. An assessment of Hg(II) sorption complexes that form on mineral particles in mercury-mine waste environments showed that Hg(II) forms dominantly inner-sphere sorption complexes on these common mineral particles. An important result of this study is the finding that iron and aluminum (hydr)oxides can play a significant role in the uptake of Hg(II) through direct inner-sphere sorption processes. Additionally, the sorption of Hg(II) on these particles was examined in the presence of chloride and sulfate ions as a function of pH. The presence of chloride reduced Hg(II) sorption (through the formation of HgCl₂ complexes), and the presence of sulfate enhanced Hg(II) sorption (through the reduction in electrostatic repulsion at positively-charged particle surfaces).

Bioaccumulation

Hurley et al. [1] and Fitzgerald et al. [7] studied the river/lake interfaces (i.e., the riverine mixing zones) of Lake Superior and Long Island Sound, respectively, and observed that the concentration of mercury

bound to the particulate phase increased in the mixing zones relative to the river water, which can affect bioavailability and bioaccumulation. Hurley et al. [1] measured mercury and methylmercury concentrations at the riverine mixing zone in Lake Superior. The methylmercury concentration on particles increased within the mixing plume with distance from the interface; in other words, the methylmercury content of particles is enriched at the outer edge of the plume. Larger particles (and the methylmercury associated with these particles) settle out closer to the mouth of the river; smaller particles remain in solution and carry their load further offshore. Therefore, methylmercury in the particulate phase enters the lake water column from the river associated predominantly with small particles, which can be ingested by zooplankton. The result is enhanced bioaccumulation of methylmercury in plankton in the mixing zone.

3.5 New Methods for Mercury Analysis

Several new analytic methods for measuring total and speciated mercury in the environment were developed under the STAR grants:

- A batch culture bioassay using *Selenastrum capricorutum* was developed to measure bioaccumulation of methylmercury by algae [1].
- Refined methods to measure methylation rates in sediments at near ambient mercury levels were developed using individual stable mercury isotopes and ICP-MS analysis [1, 8]. These methods also allow tracking of both the *in situ* mercury methylation and the fate of the added mercury. Using these techniques, methylation and demethylation were measured in the same sample concurrently [8].
- Synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy was used to determine the molecular-level speciation of Hg in many different mining localities in California [6]. This method was compared to sequential extraction methods and solid phase mercury thermodesorption in a collaborative study [10].
- An *in vitro* reducible-mercury titration approach was developed to determine the concentration and conditional stability constants of dissolved organic matter towards mercury [7].
- A semi-automated dissolved elemental mercury analyzer (DEMA) was developed for measuring Hg(0) concentrations in laboratory samples of surface water [7].
- A method was refined to estimate the bioavailability of mercury at environmental levels through measurement of the octanol-water partitioning of mercury [8]. Previous measures were effective only for high concentrations of mercury. Clean techniques and other modifications allowed detection of mercury at picomolar levels.
- A new technique for measuring low levels of sulfide in natural waters was developed to detect at nanomolar to micromolar levels of mercury [8].
- EcoCELLs were used for investigating the biogeochemical cycling of an environmental contaminant [11].

4. APPLICATIONS OF FINDINGS FROM STAR GRANTS



In this section, the findings presented by research theme in Section 3 are summarized in three ways according to their potential application in future mercury research and modeling. First, results are grouped according to how they may be used in the development or improvement of mercury fate and transport models. Second, key variables studied here that affect the fate and transport of mercury in the environment are cross-walked with mercury cycling processes that are influenced by these variables. Finally, information about how these research results broaden our understanding of variation across ecosystems and regions is presented.

4.1 Potential Improvements to Mercury Fate and Transport Models

This section summarizes new models developed as a part of the STAR research and groups key findings that will be useful in the refinement of existing mercury fate and transport models.

New Models

Work under two of the STAR grants included developing models that incorporated the observations made by the investigators in their ecosystem studies. Methods and algorithms from these models could potentially be used in the development of other models as well. Driscoll et al. [5] constructed the Mercury Cycling Model for Headwater Drainage Lake Systems (MCM-HD) to simulate

mercury interactions in headwater drainage lakes and the adjacent watersheds, including wetlands, and found that results from the model were generally in agreement with mass balance calculations. Hurley et al. [1] developed a simple model that related annual tributary loading from a watershed to the lake based on watershed composition (i.e., land use/type). The model was applied to the entire lake watershed. Data from that study [1] also are being incorporated into the Lake Superior dynamic Mercury Cycling Model (D-MCM) to elucidate the effects of mercury loads in specific nearshore regions.

New Data

STAR grant investigators gained new understanding of various processes that affect mercury fate and cycling in the environment that can be incorporated into existing or new mercury models. Findings are summarized according to their relevance to methylation, inorganic transformations, and mercury transport.

Factors Affecting Methylation

Several investigators studied mercury methylation and the factors that enhance or inhibit it. Fitzgerald et al. [7] demonstrated that methylation rates increase with elevated bacterial metabolic rates and higher concentrations of inorganic mercury. Factors affecting methylation studied by other researchers can be grouped into these same two categories.

Bacteria methylation rates influence the total amount of methylmercury that is formed. Three important factors that influence bacteria methylation rates were studied, including:

- **Time of year/temperature.** Methylation rates are higher during the warmer summer months [7].
- **Sulfate levels.** Increasing sulfate levels can increase methylation in sulfate-poor systems [2, 8].
- **Availability of Hg(II).** Increasing inorganic mercury loading to a watershed increases methylation rates [3].

The STAR grant investigators demonstrated the effect of several factors on the availability of inorganic mercury for methylation. Many of these factors would be important in mercury fate models.

- **Organic Matter.** Increasing organic matter concentrations decreases the concentration of methylmercury, probably because inorganic mercury forms complexes with DOC, making it unavailable for uptake by methylating bacteria [1,7].
- **Sulfide Concentration.** The addition of sulfide can decrease the rate of methylation [8]. The effect of sulfide on methylation depends on whether neutral or charged sulfide mercury complexes form. Neutral complexes enhance methylation, while charged complexes inhibit it [8].

- **Particulate Binding.** Inorganic mercury binding to sediment and particulate matter will decrease methylation. Higher sediment-water distribution coefficients for inorganic mercury are associated with lower methylation rates [7].
- **Mixing Zones.** The fraction of reactive mercury increases in the mixing zones of rivers with lakes or sounds, thereby increasing the amount available for methylation and bioaccumulation [1,7].
- **Bioturbation.** Increased bioturbation of benthic infauna in the sediment can increase available mercury and increase methylation [7].
- **“Newness” of Mercury.** In some environments, newly deposited mercury contributes more substantially to production of methylmercury than “older” mercury [3]. Sulfate and DOC have a much larger effect on the methylation of newly deposited mercury than of mercury already present in soils [3].

Factors Affecting Inorganic Mercury Transformations

Transformations between Hg(II) and Hg(0) also were studied by STAR grant investigators, and their results include key information that could be incorporated into mercury environmental fate models. Reduction of Hg(II), photooxidation of Hg(0), and volatilization of Hg(0) are all important processes in the mercury cycle that can ultimately affect the availability of mercury for methylation and subsequent accumulation in the food chain, as indicated below.

- **Photochemical Reduction.** Hg(II) is readily reduced to Hg(0) in aquatic surface waters by photochemical reduction; as a result, Hg(0) formation and subsequent volatilization display a diurnal cycle [4].
- **Organic Matter.** Some data indicate that Hg(II) must be bound to organic material to be reduced by abiotic processes in natural waters. However, excess ligands can result in significantly lower reduction rates of Hg(II) [7].
- **Photooxidation.** Photooxidation is responsible removing much of the Hg(0) in surface waters. In some cases, photooxidative flux can exceed volatilization as a loss mechanism for Hg(0) in an aquatic system [2, 9].

Factors Affecting Transport

Some data points collected on the major transport processes for mercury through a watershed could be incorporated into fate and transport models.

- **Volatilization.** Volatilization is an important process for removing Hg(0) from surface waters and a potentially significant source of Hg(0) to the atmosphere [1, 2, 4, 6, 7]. For example, Fitzgerald et al. [7] estimated annual emissions of Hg(0) from Long Island Sound to be 35 percent of the input of mercury to Long Island Sound. Volatilization of mercury from soils, which has been shown to vary based on light, could also be an important source of mercury to the atmosphere [10, 11].
- **Deposition and Plant Transfers.** Several studies confirmed that atmospheric deposition is the key pathway for emitted mercury to enter watersheds [1, 2, 5], and some provided quantitative data on this relationship (e.g., dry deposition was 70 percent of the total deposition of mercury to the forest floor [5]). Additionally, plant foliage may be a significant sink of mercury from the atmosphere, and consequently may be a large source of mercury to watershed via litterfall and deposition [11].
- **Runoff/Erosion.** Results were mixed regarding the extent to which uplands and wetlands func-

tion as a source of methylmercury to downstream water bodies. The rate of transport and methylation in a watershed depends on ecosystem-specific properties [1, 3, 5] as well as sorption onto mineral particles and availability of complexing ligands [6].

4.2 Understanding Key Variables Affecting Mercury Fate and Transport

Several specific variables that affect mercury fate and transport in the environment were identified and studied in the STAR mercury research projects. Key variables are summarized in Table 4. The applicability of each variable to mercury transport, availability, or speciation (as determined by these studies) is indicated.

4.3 Understanding Variation in Key Variables by Ecoregion and Ecotype

The STAR grant research on mercury was performed in a variety of ecosystems across North America, including an Adirondack lake, Long Island Sound, the Experimental Lakes Area in northwestern Ontario, Canada, the Florida Everglades, Lake Superior, the Patuxent River in Maryland, the St. Lawrence River, the Saginaw Bay watershed in Michigan, the Marcell Experimental Forest in northeastern Minnesota, and mining and other mercury source locations in California and Nevada. Some regional differences were noted by researchers; however, no study attempted to systematically identify regional characteristics affecting mercury fate and transport in the environment.

Regional differences are expected for processes that are affected by temperature and solar radiation. For example, Gilmour et al. [3] performed similar experiments in the Florida Everglades and the Experimental Lakes Area in Canada and observed differences in methylmercury response to mercury surface

TABLE 4. VARIABLES AFFECTING MERCURY FATE AND TRANSPORT

Variable	Processes Affected by Variable		
	Transport between media	Availability to methylating bacteria	Transformation between Hg species ^a
Deposition rate / mercury load	✓	✓	✓
Sulfate load			✓ ^b
Sulfide concentrations and charge of mercury-sulfide complexes		✓	
Dissolved organic carbon (DOC)	✓	✓	✓
Suspended particulate matter	✓	✓	
Sediment burial	✓	✓	
Temperature	✓		✓ ^b
Bacterial activity			✓ ^b
“Newness” of mercury		✓	✓
Phase partitioning of mercury between solid and liquid in sediment and surface water	✓	✓	✓
Bioturbation of sediments		✓	
pH		✓	
Photo-demethylation of methylmercury			✓
Oxidation of Hg(0)			✓
Reduction of Hg(II)		✓	✓
Volatilization of Hg(0) (phase partitioning between water and air)	✓		
Vegetation	✓		

^a For reasons other than availability to methylating bacteria, which is covered in the previous column.

^b Principally due to effects on bacteria methylation rates.

application at these two locations, with shorter response times measured in the shallow, warm sites of the Everglades. Both photooxidation of Hg(0) and photoreduction of Hg(II) will be more prevalent in areas with less cloud cover and, during the summer, at lower latitudes with more intense solar radiation. The balance between those two processes is likely to be affected by more localized factors, however.

Ecosystem differences are expected for processes that are affected by DOC and particulate matter in surface waters, which can vary substantially depending on the type of water body and characteristics of the watershed. The effects of these factors on mercury bioavailability, methylation,

and bioaccumulation are complex, and will need to be considered in conjunction with other factors. In freshwater systems, high levels of suspended sediment particles tend to result in lower dissolved Hg(II) concentrations as the mercury sorbs to the particles and may become buried in the benthic sediments. Where rivers meet large lakes or the ocean, on the other hand, the smaller suspended sediment particles might enhance transfer of mercury through aquatic food chains as the mercury-containing particles are consumed by zooplankton in the mixing zone. DOC can affect mercury cycling in aquatic systems by binding dissolved inorganic and organic mercury in complexes limiting its bioavailability to methylating bacteria and to

other aquatic organisms, by limiting UV light penetration and photolytic processes, and by generating reactive molecules that assist in Hg(II) reduction. The affinity of DOC for mercury varies across ecosystems as well. Given the importance of these localized factors, differences in mercury distribution can occur within relatively small geographic regions. For example, Driscoll et al. [5] compared measured BCF values in Sunday Lake in the Adirondacks to values measured in other Adirondack lakes and observed that BCF values were lower in Sunday Lake. He suggested that the methylmercury in Sunday Lake may be less bioavailable due to binding associated with high concentrations of DOC.

5. FUTURE RESEARCH NEEDS



Several overarching future research needs related to mercury fate and transport were identified by comparing the STAR research results for these eight projects to the goals outlined in the ORD Research Plan and the original STAR Mercury RFA (see Section 2.2). Additionally, areas of further research that were specifically identified by investigators as follow-up to the work completed under these STAR grants are summarized below.

Topics Included in ORD Research Plan

The research summarized here contributes new data and analyses that improve general understanding of processes and factors that affect the fate and transport of mercury in the environment. Thus, these research projects have contributed significantly to the first two ORD goals/measures listed in Table 2. Specific ORD research goals and performance measures that are related to the grants described here (see Section 2.3), but may require further work to fully accomplish, include development of a model for mercury in fish, identification of sources of mercury emissions, and the eventual creation of an integrated multimedia modeling framework for mercury in the environment. The research covered by the eight STAR grants described here will help EPA accomplish these broader, long-term goals; however, it is expected that other ORD-related research will also play a role in ultimately meeting those goals (especially the long-term goal of an integrated multimedia framework).

Topics of STAR RFAs

The specific research questions posed in the original RFA are listed in Section 2.2. The majority of the STAR grant research projects described in this report focused on Question 2 (i.e., variables controlling mercury transformations). Specific variables were identified that control the transformation of mercury to methylmercury as well as transformations between inorganic species of mercury.

Question 1 (i.e., bioavailability and fish concentrations of mercury) was addressed by some investigators (e.g., Hurley et al. [1] and Driscoll et al. [5]). Further research into the relationship between mercury in the watershed to mercury in biota, however, may be necessary to close information gaps regarding uptake by fish and other organisms.

The STAR research described here was performed in a range of locations; however, follow-up research systematically analyzing the differences between results for these different ecosystems would be required to comprehensively answer Question 3 (i.e., how mercury cycling varies in different geographic regions). In addition to further analyzing the existing results across regions, studies that conduct research in parallel in more than one region (similar to the Gilmour et al. [3] study in Canada and Florida) may be useful in clearly identifying how mercury cycling varies by region. The focus for most of the research presented

here was on freshwater ecosystems; therefore, further investigation into the differences between freshwater and estuarine or coastal ecosystems would be beneficial, especially because research presented here (Fitzgerald [7]) indicates that processes may be different in the estuary environment than in freshwater.

Topics Specified by Researchers

Many of the STAR grant final reports list areas where further research is warranted. Investigators have reported both general subjects worthy of future consideration and more specific research topics that follow directly from work completed to date. Both types of recommendations are summarized here.

General areas for continued or future research identified by the STAR grant investigators include the following.

- **Effects of sulfate on methylation.** Driscoll et al. [5] suggested developing a new formulation for the response of methylation to changes in sulfate concentrations in a wetland environment. Other research mentioned by Driscoll et al. has shown a greater-than-linear response in methylation when sulfate is added; however, the current model, based on data for lakes, does not predict that type of response.
- **Intracellular sequestration of mercury.** Mason et al. [8] noted that not all of the mercury entering a sulfate-reducing bacterium

in neutral sulfide complexes is methylated. Methylating bacteria carry out both methylation processes and competing processes that sequester mercury and render it unavailable for methylation. It has been hypothesized that differences in cell physiology (e.g., size and membrane composition) and in mercury partitioning within the cell cause the variation in methylation rates observed among bacterial strains. Further work is needed to understand the mechanisms and kinetics of these intracellular sequestration pathways.

- **Demethylation.** Mason et al. [8] also observed that the factors influencing demethylation processes are not well understood and deserve further study.
- **“Newness” of mercury.** Mason et al. [8] further suggested that more work is needed to elucidate the differences in methylation rates of newly added mercury compared to *in situ* mercury. It is difficult to assess the pool of mercury available for methylation, and this information is also necessary to accurately estimate methylation rates.
- **Photooxidation.** Morel et al. [9] recommended further research in different types of water bodies to determine if more of the Hg(0) in surface waters is converted to Hg(II) via photooxidation or is lost to the atmosphere via volatilization of Hg(0).
- **SRB studies.** Morel et al. [9] suggested additional research on bacterial methylation by SRB, including: the role of vitamin B₁₂ and other methyl-transferring coenzymes in methylmercury production by SRB; the role internal mercury speciation plays in methylation; the pathways responsible

for methylation; and the biomechanical mechanism of bacterial methylation.

- **Mercury in seafood.** Morel et al. [9] and Nriagu et al. [4] both noted that more research is needed to determine the ultimate sources of mercury in seafood.

Specific research needs noted by investigators that relate to sites or topics studied in STAR grants include the following.

- Gilmour et al. [3] suggested follow-up research in the Experimental Lakes Area in Canada to determine time to equilibrium for increased mercury loading at Experimental Lakes Area; to determine the time course for mercury movement through uplands and wetlands; to investigate bioavailability of mercury from uplands and wetlands for methylation and bioaccumulation; to investigate biogeochemical parameters that affect bioavailability; and to more fully investigate “aging” of dosed mercury (including ligand exchange of mercury).
- Hurley et al. [1] listed several specific next steps for research in Lake Superior, including the investigation of atmospheric deposition (i.e., effects of local urban sources on nearshore regions and direct deposition of methylmercury in the basin), mixing zones/watershed influences (i.e., mechanisms for algal and zooplankton uptake and fate of colloidal methylmercury), and in-lake processes (i.e., fate of changing anoxia on methylmercury dynamics in Lake Erie, mechanisms of bioaccumulation in offshore zones, and methylation in deep sediments).
- Nriagu et al. [4] observed associations between photosynthetically

active radiation and indicators of biological activity (e.g., chlorophyll-a). They plan to use those data to further explore the interaction of biological processes with the mercury cycle in the Saginaw Bay.

- Brown et al [6] saw in laboratory experiments that organic acids may affect mercury transport from mining sites, and suggested further field studies into the potential impact of revegetation on the mobilization of colloidal materials from mine tailings. Additionally, Brown et al. [6] suggested further studies into the question of whether ratios of mercury isotopes could be used to determine the source of mercury. Specifically, measurements of the isotope ratios need to be made with more precision (using more sensitive multi-collector, inductively coupled plasma mass spectrometer).
- Gustin et al. [11] follow-up research has already begun and includes using the EcoCELLS to study mercury cycling associated with tall grass prairie vegetation and soils from Oklahoma.

In addition, these STAR grant results have provided a wealth of data that merits further analysis and comparative review. For example, the research of Nriagu et al. [4] could be analyzed for additional patterns and reasons for reduction of mercury and other transformations. Measured mercury concentrations in environmental media at the different locations studied by the STAR grant investigators could be tabulated, and ratios of total mercury, Hg(0), Hg(II), and methylmercury, could be compared to identify regional and temporal trends or patterns of mercury distribution in the environment.

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APPENDIX: GRANT PUBLICATION LISTS



[1] Hurley, EPA Grant Number: R827629

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[2] Swain, EPA Grant Number: R827630

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[3] Gilmour, EPA Grant Number: R827631

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[4] Nriagu, EPA Grant Number: R82763201

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[8] Mason, EPA Grant Number: R827653-01-0

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[9] Morel, EPA Grant Number: R827615

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[11] Gustin, EPA Grant Number: R827622E02

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