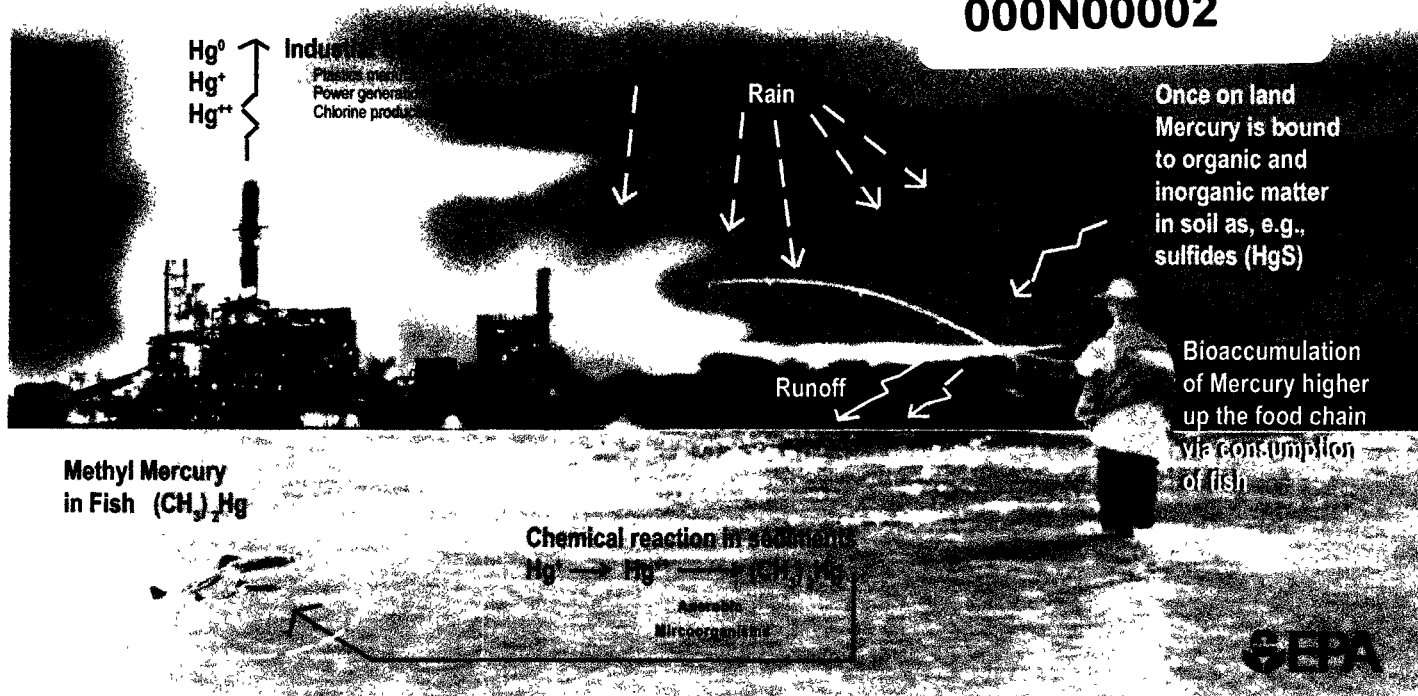


MERCURY TRANSPORT AND FATE IN WATERSHEDS

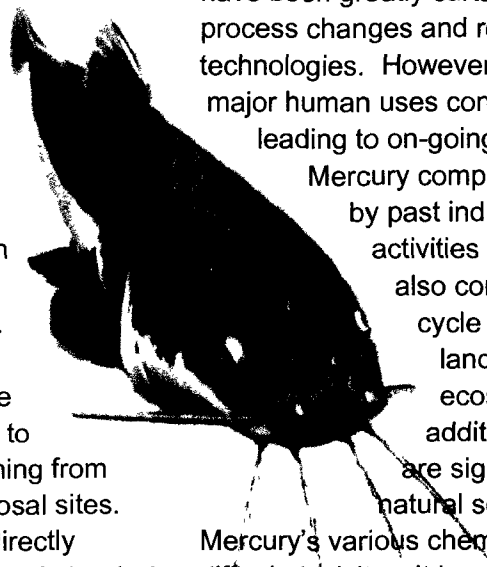
In December 1997, EPA's Mercury Study Report to Congress identified mercury as a critical human health and environmental problem needing additional scientific and technical research. Mercury poses risks to humans and wildlife, particularly because it concentrates in the tissues of animals as it moves up through a food chain. Observed adverse effects in mammals, fish and birds have included behavioral and neurological abnormalities, impaired growth and development, reproductive abnormalities such as fetal deformities, and in some

cases complete reproductive failure. Fish consumption is the dominant exposure pathway for humans and wildlife. In some cases, mostly in the past, wildlife were killed by extreme environmental concentrations of mercury, for example from seed grains treated with mercury, or from unusually severe instances of waste release. But the most pervasive wildlife effects involve reduced breeding success, which now poses severe consequences for water birds throughout North America and some endangered species, including panthers, in the Florida Everglades.

Sources & Paths of Mercury in the Environment



More U.S. waters are closed to fishing because of mercury contamination than any other toxic contamination problem. Because fish consumption can be a significant route of human exposure to toxic chemicals, the U.S. Food and Drug Administration (FDA) issues guidelines to states on fish contamination levels that warrant closures of fishing waters to commercial or recreational fishing. The principal sources of fish contamination, perhaps surprisingly, are air emissions of mercury from coal burning power plants, municipal waste incinerators and other industrial sources. The emitted mercury compounds readily settle, either directly on water, or on land from which they runoff to water bodies. Additional significant amounts reach surface and ground water due to urban runoff and leaching from mines and waste disposal sites. Mercury can also be directly discharged in inadequately treated municipal or industrial wastewaters. A number of biological and chemical processes that are partially understood occur in soils, water bodies and sediments that cause mercury to react with organic matter to form methyl mercury (MeHg), the most toxic form of Hg, which is readily taken up by plants and animals. A principal focus of the research studies described in this report is to achieve a better understanding of



the rates at which formation or transformation of such compounds occurs in watersheds and waterbodies and how these are affected by releases of various forms of mercury from natural sources, from residues left by historic human activities, and from current human activities.

Many human sources of mercury have been eliminated or much reduced by laws and regulations. Its use in paints and pesticides has been banned, and industrial and municipal emissions have been greatly curtailed through process changes and recovery technologies. However, some major human uses continue, leading to on-going emissions.

Mercury compounds left by past industrial activities and mining also continue to cycle through land and water ecosystems. In addition, there are significant natural sources.

Mercury's various chemical forms differ in toxicity. It is readily changed from one form to another in passing from air to land to surface waters, wetlands and sediments, and then released back again to the atmosphere. It is a highly challenging problem for environmental managers and scientists to understand the potential risks posed by mercury to wildlife and humans, and to determine what regulatory and non-regulatory approaches will most effectively eliminate those risks.

STAR MERCURY TRANSPORT AND FATE RESEARCH PROJECTS

In 1999, EPA's STAR program funded a set of studies to develop a better understanding of mercury's terrestrial and aquatic fate and transformation processes that influence ecological and human exposures. In several projects, there is a particular focus on microbial processes, which are at present poorly understood. Another area of focus is model development. Improved models are needed to predict ecosystem responses to changes in anthropogenic inputs of mercury that could result from various emission reduction options and scenarios.

Whole-Ecosystem Studies

A research team from **Syracuse University, Cornell University** and **Smith College** is studying chemical and biological control of mercury cycling in upland, wetland and lake ecosystems in the Adirondack region of New York. Many Adirondack lakes have elevated mercury concentrations in water and fish tissue, and health advisories warning against freshwater fish consumption have been mandated throughout the region.

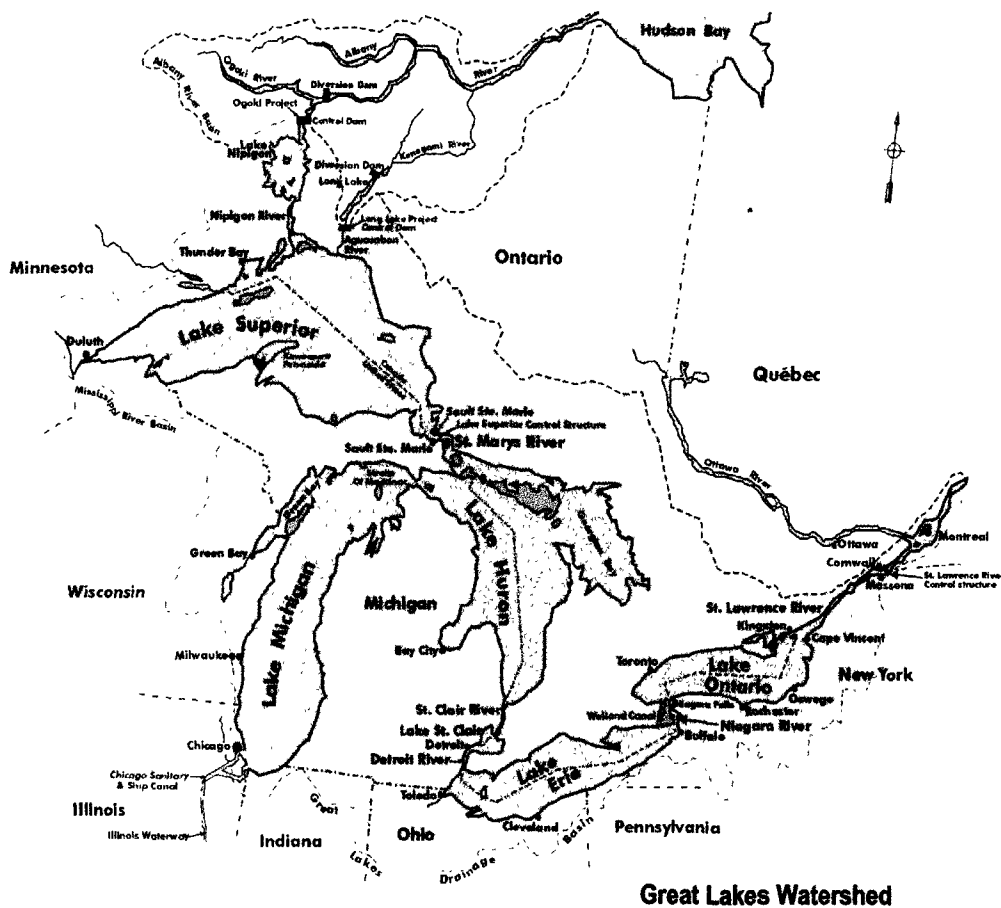
The concentration of mercury in fish tissue has been found to be higher in more acidic water bodies. High acidity can occur naturally, but is exacerbated by acid deposition from coal-burning power

plants, mine drainage and other pollution sources. Conversely, high levels of dissolved organic carbon, resulting from the decay of organic matter such as plants, can decrease mercury uptake by fish. Consequently, lakes that receive substantial drainage from wetlands are often characterized by relatively low levels of mercury in fish. Recent lake sediment studies in the Northeast have shown more than threefold increases in mercury deposition since 1850, suggesting the degree to which industrial pollution has contributed to regional mercury contamination. Moreover, for reasons that are not yet understood, these studies suggest that watershed retention of

atmospheric mercury has decreased markedly over the last 60 years, from 95% retention in the 1930s to 75% retention today. The Syracuse-led team is gathering data on transport and transformation patterns of mercury compounds in an Adirondack forest, wetlands and surface water. They will focus on mechanisms controlling MeHg levels and transport in wetland pore waters and open waters. Based on these findings and other current data, and on historic patterns of mercury transport and fate, they will develop a lake/watershed mercury cycling model. This will be used to predict impacts on ecosystem mercury levels that might result from emis-

sion reductions in the Adirondack region.

The opportunity to fully track and quantify MeHg production, transport and fate in two large ecosystems is offered by a study in the Experimental Lakes Area of northwestern Ontario, and by extensive work in the Florida Everglades. An international research team from the **University of Maryland's Chesapeake Biological Laboratory**, the **Academy of Natural Sciences Estuarine Research Center**, and the **Freshwater Institute of the Canada Department of Fisheries and Oceans** is conducting comparative studies on these large systems. They are assessing mercury methylation in a catchment (large watershed) that includes uplands, wetlands and a lake. This STAR-funded work is one portion of a larger scale, whole-ecosystem experiment in which all mercury fate, transport, transformation and uptake, from atmospheric loading through fish mercury concentrations, is being traced. The STAR study component focuses on how MeHg changes in response to changes in mercury loading. Stable isotope tracing methods will be used to measure accumulation, production and degradation rates of MeHg in upland and wetland soils and lake sediments, together with key biogeochemical parameters that affect mercury methylation and bioavailability. The tracer method will allow them to track the fate of "new" mercury deposits vs. "old" mercury stored in sediments and soils, and to track the bioavailability



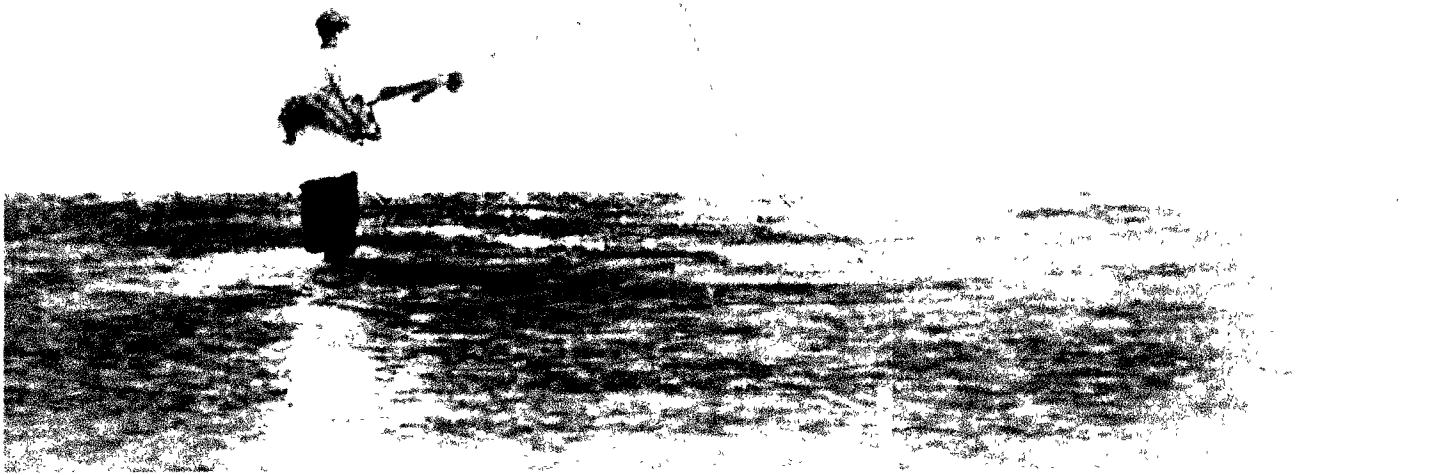
of new mercury over time across the components of the watershed.

The Experimental Lakes Area (ELA) is representative of north central and northeastern US ecosystems affected by mercury. To provide a comparison in a very different ecosystem and region, this team will conduct parallel mercury tracing studies in the Florida Everglades. Here, mercury addition experiments will be conducted within wetland enclosures. Additional field work, together with transport and fate data from other Everglades studies, will support estimates of MeHg fate in this warm, highly organically enriched system. Taken together, these two studies will provide data that bracket the most likely conditions in most U.S. watersheds impaired by mercury pollution and provide information on regional and landscape variability in methylation and subsequent mercury accumulation in fish. Results should provide the ability to predict changes in levels of various forms of mercury in the environment

caused by reduced mercury emissions.

Fish consumption advisories have been issued for Lake Superior due to mercury contamination. Transport, fate and bioavailability of mercury in the whole Lake Superior Basin ecosystem are being studied by a team from the **University of Wisconsin at Madison, Lake Superior State University**, and the **Wisconsin Department of Natural Resources**. Preliminary studies of several rivers in the area have found that wetland- and forest-dominated watersheds attenuate total mercury transport in the Basin. And, very importantly, these watershed types enhance the production of the MeHg, the most bioaccumulative, toxic form of mercury. Preliminary estimates suggest that while air deposition provides about 75% of the total mercury input, inputs from watersheds provide more than 80% of the MeHg. Furthermore, while atmospheric inputs are distributed across the vast surface area of the

Lake, watershed influences are concentrated in certain nearshore zones. The specific physical and chemical factors regulating bioavailability are not known. For instance, perhaps the MeHg produced in some components of watersheds is largely unavailable for bioconcentration due to its association with certain high molecular weight organic materials, or specific soil types. This study will investigate sites where it is hypothesized that enhanced bioaccumulation may occur, including sub-watersheds, river-lake mixing zones and open waters. Field work will be supplemented with lab studies of processes influencing fate, transport and bioavailability of MeHg and total mercury under similar conditions. Results will be incorporated into models predicting the influence of each part of the ecosystem on the ultimate delivery of the more toxic and bioaccumulative forms of mercury to the Lake's waters and aquatic life.



The Re-emission Problem

Recent national mercury emissions inventories estimate that re-emission of previously deposited mercury from historic human sources is similar in magnitude to industrial emissions. U.S. industrial emission is approximately 240 tons per year, while estimates of re-emission from soils, sediments and terrestrial and aquatic vegetation range from 150 to 600 tons per year. The role of soils, water bodies and vegetation as mercury sources will affect the success of any program aimed at reducing mercury loading in and from watersheds. Processes that convert mercury to the elemental form, which is highly volatile, also diminish its availability for methylation and uptake by living organisms. The **University of Michigan** is examining an important hypothesis: that the processes through which monovalent and divalent mercury are converted to the elemental form are enhanced by sunlight. If true, it indicates that when there is strong light penetration into water bodies, the monovalent and divalent forms of mercury associated with the organic matter abundant in wetlands and some lakes may be preferentially converted to readily released elemental mercury. It would thus be far less likely to form the bioavailable MeHg that accumulates in food chains. Lab and shipboard experiments will assess the following and other factors in the Saginaw Bay/Lake Huron system: 1) what

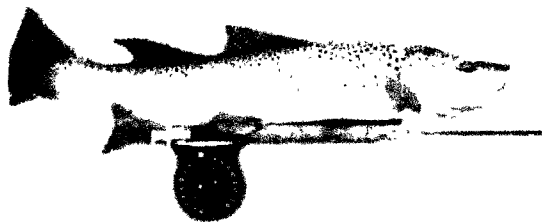
degradation products, containing what forms of mercury, are created when locally typical organic matter decays in different amounts of light?; 2) what intracellular or extracellular pathways in organisms can result in methylation of these compounds?; 3) whether conversion of monovalent and divalent mercury to its elemental form is activated in solid phases in soils and wetlands; and 4) what effect does oxidation of elemental mercury have on its tendency to be released? Results will help distinguish which components of the watershed are the most likely sources of mercury re emission. For example, perhaps clear lakes could be identified as less serious sources of mercury re-emission than wetlands with murky waters, and thus with less light-induced conversion of mercury into the less bioavailable forms. This will help in modeling likely successes of decreasing mercury contamination in fish and other organisms for given watershed if new mercury emissions are decreased.

Emission from Water to Air

The natural chemical processes of reduction and oxidation, called the "redox" cycle, control the proportions of mercury present in various forms. This in turn affects rates of mercury exchange between water bodies and the atmosphere. **Princeton University** is performing a comprehensive analysis of all components of this cycle. Some water bodies release

mercury in large amounts to air, while others do not, resulting in major differences in the amounts of mercury in the water, sediments and organisms. A series of lab and field experiments will study the chemical and biological redox mechanisms that transform mercury between its divalent form, Hg(II), and the volatile elemental form, Hg(0). The forms differ in the electron charges of the mercury atoms. The experiments test three complementary hypotheses: 1) biological reduction of Hg(II) to Hg(0) normally occurs through a two-electron transfer reaction mediated by certain enzymes in two groups of photosynthetic microorganisms, phytoplankton and cyanobacteria; 2) chemical reduction of Hg(II) occurs in two distinct one-electron transfer reactions, first the reduction of Hg(II) to Hg(I) which requires a high energy reducing agent (typically formed in light) such as the superoxide anion or an organic radical (probably a semiquinone), followed by the reduction of Hg(I) to Hg(0) by organic matter typically present in natural waters; and 3) oxidation of elemental mercury requires first oxidation of Hg(0) to Hg(I), likely caused by the same radicals, superoxide or semiquinones, and then oxidation of Hg(I) to Hg(II) by oxygen, which is facilitated by chloride complexation of the ionic mercury species.

Starting with simple modeled systems and building up to complex lab situations more like those of natural waters, the lab experiments are designed to establish the



mechanisms and rates of these processes and to provide techniques and probes for field work. Field experiments will include a range of values for the key parameters, and are designed to establish the actual occurrence of the mechanisms in nature and to provide data on process rates. Results should let us understand how factors including solar irradiation, dissolved organic matter concentration, pH and biological productivity control rates of mercury loss from water bodies to the atmosphere, and hence why water bodies with similar mercury inputs end up with different mercury levels in water, sediments and fish.

Sulfur-Mediated Microbial Effects

Sulfur, in all its chemical forms, plays important roles in the methylation of mercury by naturally occurring sediment and soil bacteria. Researchers from the University of **Maryland's Chesapeake Biological Laboratory** and the **Academy of Natural Sciences Estuarine Research Center** are using lab and field studies to investigate the hypothesis that high levels of sulfide (a reduced form of sulfur) diminish methylation by lessening the degree to which mercury is taken up by methylating bacteria. The scientists

also hypothesize that when there is little sulfur present as sulfate (an oxidized form), little methylation occurs because many methylating bacteria need sulfate as a nutrient. Also, they will investigate the role of some sulfate-using bacteria in the converse process of demethylation, together with assessing rates under various conditions of abiotic demethylation, a purely chemical process with no bacteria or other organisms involved. Results will provide a comprehensive picture of the soil and sediment processes leading to greater or lesser production of the more toxic and bioaccumulative forms of mercury.

Mercury from Mine Wastes

Mercury mining has left a legacy of contaminated wastes throughout the mining belts of the United States. The problem is compounded by weathering, which transforms the mercury into additional chemical forms, redistributes it in watersheds and through the air, and may increase bioavailability to organisms. Mine wastes can have significant regional environmental impacts, since airborne mercury sometimes reaches uncontaminated ecosystems far from point sources. **Stanford University** and **the University of Nevada at Reno** are studying the physical and chemical processes that control chemical transformation, release and distribution of mercury from mine wastes, with the overall objective of assessing risks to local and regional ecosystems.

The researchers will determine the mix of mercury compounds in environmental samples, and use lab experiments to examine sorption processes of mercury on mineral particles typical of sediments downstream from mine sites, transport on colloidal particles, and the effects of sulfate and chloride on sorption processes. They will also monitor atmospheric emissions from mine waste sites representing different weathering and climatic regimes, and compare emission levels of each type of mercury with the distribution of types (the "speciation") in the mine wastes. This will test the hypothesis that emissions of mercury to the atmosphere are closely linked to mercury speciation in mine wastes, and are influenced by the amount of available elemental mercury, the other mineral components of the wastes, and weather. Based on these results, they will develop an area emission model by incorporating the speciation data into a Geographic Information System. With this they will "scale up," to estimate mercury emissions over entire contaminated mine sites. If this research increases our understanding of the contributions of various mercury sources to local and regional mercury budgets, results will help assess whether particular control options for various point sources will be effective in reducing local and regional risks. Results will also provide information useful in global mercury modeling efforts.

Mercury in a Coastal Environment

When polluted freshwater mixes with saline coastal water chemical processes typically lead to precipitation (settling out) of many toxic pollutants, including mercury compounds. Estuarine water bodies are thus major repositories for riverborne/watershed derived mercury. The **University of Connecticut** is studying microbiological, chemical and physical aspects of mercury cycling in Long Island Sound. For decades the Sound and its river tributaries served as the receiving water for discharges associated with older industrial facilities. Many of these facilities

no longer exist, but in some cases a legacy of contamination remains, particularly in sediments associated with freshwater and saltwater interfaces. Preliminary work has found large emissions of elemental mercury from the waters of the Sound to the atmosphere. At present it is not known how rates of historic and new mercury inputs and deposition compare to rates at which it is being released to the air. This research team will test the following hypotheses: 1) that the principal influences on mercury distributions are the amount that is present from place to place in bioavailable forms and the levels of chemical reducing agents, bacterial activity and solar radiation from place to place; (2) that organic matter production, reflected in the difference between net primary production and bacterial consumption, can serve as a surrogate for the amount of active organic substances that influence the biogeochemical fate of mercury; (3) that estuarine reactions (i.e., mixing of riverborne mercury with seawater high in chlorine and positively charged ions) increase the proportion of bioavailable mercury available for reduction; 4) that direct sewage discharge into contained brackish waters leads to enhanced localized production of elemental mercury; (5) given the availability of reactive mercury species, and the limited light penetration in coastal waters, elemental mercury is the predominant mercury cycling product of bacterial activity in the zone of well oxygenated waters; and 6) net synthesis of MeHg is

most significant in redox "transition zones", primarily the shallower sediments and waters in basins that experience seasonal low oxygen conditions (i.e., the western and central Sound). Results of these studies will be incorporated into a biogeochemical mercury cycling and mixing model, aspects of which will be relevant to other coastal regions. Such a model can be used to predict water quality and fish mercury levels that may result from alternate pollution abatement strategies.

Historic Analysis of Sources and Environmental Conditions

Efforts to reduce mercury emissions tend to have been based on the assumption that in most water bodies, particularly lakes, mercury accumulation in fish would be more or less proportional to atmospheric deposition. Given the strong evidence that mercury deposition is now about 3 to 4 times greater than natural rates, a first estimate would be that fish should be 3 to 4 times more contaminated than natural levels. But a team of Minnesota researchers has determined, based on comparing modern fish to fish preserved in the 1930s, that mercury concentrations in fish may have increased by a factor of 10 in the low alkalinity lakes that are common in their region. It is possible that enhanced bioaccumulation could be caused by changes in the biological community. For example, there could be



higher levels in food chains, and thus more biomagnification, if there have been changing prey abundances. However, recent sediment cores from sixteen Minnesota lakes demonstrate that, beginning about 1940, MeHg was an increasingly large percentage of the total. This suggests a fundamental change in methylation efficiency, weakening support for the competing hypothesis of longer food chains.

Researchers from the **University of Minnesota**, the **Minnesota Pollution Control Agency** and the **Science Museum of Minnesota** are investigating the anthropogenic

ecosystem changes that have become widespread since World War II to assess which are the most likely contributors to enhanced methylation. The changes include increased sulfate deposition, increased nutrient loads and increased loading of mercury to wetlands because of soil disturbance. The study will establish the relative importance of atmospheric, in-lake, and various wetland sources of MeHg to a lake in a forested watershed. They will determine mercury retention and release in different wetland types and conduct experiments to deter-

mine which methylation-enhancing processes are occurring. Finally, they will add a hydrologically-based wetland geographic information system module to a widely used Mercury Cycling Model, so the findings can be applied to other lakes. The model will be, among other applications, relevant to states' needs to develop the total maximum daily load estimates required to support water quality protection actions.

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