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Mercury and Monomethylmercury: Present and Future Concerns

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Global atmospheric changes carry the potential to disrupt the normal cycling of mercury and its compounds. Acid rain may increase methylmercury levels in freshwater fish. Global warming and increased ultraviolet radiation may affect the global budget of methylmercury, including its formation and degradation in both biotic and abiotic environments. In this article we review current knowledge on mercury and monomethylmercury with regard to their environmental fate and the potential for human health effects. Recent findings indicate that atmospheric Hg deposition readily accounts for the total mass of Hg in fish, water, and sediment of Little Rock Lake, a representative temperate seepage lake in north-central Wisconsin. It is strikingly evident that modest increases in atmospheric Hg loading could lead directly to elevated levels in the fish stock. It is doubtful, given the experimental limitations in many recent studies, that the temporal pattern for Hg emissions, for background atmospheric Hg concentrations, and for changes in Hg depositional fluxes has been identified. Thus, the present and future questions of whether the environmental impact is of local, regional, or hemispheric significance remain. Contemporary investigations must address these important questions. Human exposure to methylmercury in the United States is probably increasing due to increased consumption of fish and fish products. A recent epidemiological investigation indicates high susceptibility to brain damage during prenatal exposures to Hg. An important objective for future investigation is to establish the lowest effect level for human exposure to methylmercury.

Introduction

Mercury and a variety of its compounds have been in use for several millennia. The applications range broadly from cosmetics, medicinal treatments, and dentistry to paints, electrical apparatus, and batteries. Despite the utility of a metal that is a liquid at room temperature, elemental Hg (Hg^0) and many Hg compounds are toxic, volatile, and readily dispersed through the atmosphere. Indeed, the principal exchange of Hg between terrestrial sources and the marine environment occurs at the air–sea interface, rather than by river input. The dominance of atmospheric transport and dispersion of Hg at the surface of the earth is well established (*1–9*). Recent investigations place the total annual Hg flow through the atmosphere in the 5 to 6 x 10^9 g range (*6,10–12*). We emphasize that this refined estimate is significantly smaller than the erroneous estimates for natural or "pre-industrial" fluxes, which, unfortunately, were common in earlier mass balance simulations of the global Hg cycle. Thus, the impact from human-related emissions on the natural cycling of Hg in the atmosphere and aqueous reservoirs should be greater than initial modeling suggested. Approximately two-thirds of the total world's yield of Hg has been produced during the twentieth century, and anthropogenic inputs of Hg to the environment have increased about 3-fold since 1900 (*13*). The dominant Hg fluxes to the atmosphere are associated with coal and oil combustion, incineration of solid wastes (includes Hg volatilized from discarded batteries), and smelting processes for the production of copper and zinc (*14*).

During the past decade, we have learned much about the global atmospheric cycling of Hg, particularly its interactions at the air–water interface. Our work has produced the reasonably well-constrained model for the mobilization of Hg in the environment that is presented in Table 1 (*11,15*). This analysis suggests conservatively that 30 to 40% of the present total annual flow of Hg to the atmosphere could result from human-related emissions. It should be noted that the Nriagu and Pacyna (*14*) assessment using median values would put the interference from anthropogenic Hg emissions at about 60% of the total. Our work also suggests that the oceans may be important natural contributors of Hg in the form of Hg^0 to the atmospheric cycle (*17,19*). We are finding a similar water–air partitioning of Hg^0 for freshwater lakes in north-central Wisconsin. We have suggested that production and eventual evasional losses of Hg^0 across the water surface to the atmosphere can provide a potential buffering and /or amelioration role in the biogeochemical cycling of Hg in aquatic systems (*20*).

Interferences from human-related Hg emissions within the biogeochemical cycle of Hg in natural waters have presented a complex environmental problem. Not only must we worry about the direct impact of certain poisonous Hg compounds, but we must be alert to the potential for Hg species to transform biologically and chemically to the more lethal forms, particularly monomethylmercury (MMHg). Oddly, MMHg, which is more toxic than either Hg^0 or other Hg^{2+} species, is the principal form of Hg in fish (*3,21*). The grave results from localized MMHg contamination in natural waters have been tragically demonstrated by the mass poisonings at Minamata and Niigata, Japan.

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Table 1. Global atmospheric mercury budget.

Sources	Mercury fluxes, units of 10^9 g/year	Reference
Atmospheric Hg deposition	5–6	(*11*)
	6	(*6*)
Atmospheric Hg emissions		
Anthropogenic	2	(*16*)
Natural	3.6	(*14*)
Volcanic	0.06	(*11*)
Other continential sources	1–2	
Crustal degassing		
Forest fires		
Biological mobilization		
Oceanic sources		
Equatorial Pacific	0.2	(*17*)
World ocean	2	(*17*)
Fluvial Hg input	0.2	(*18*)

The bioaccumulation of Hg in freshwater and marine biota (*3,22*) is well known, with elevated Hg concentrations (<0.5 μg/g wet weight) common in both freshwater and marine organisms, particularly large predators (*9,23–26*). There have been numerous studies concerned with the environmental cycling of Hg and particularly with the sources and mechanisms leading to the accumulation of Hg in aquatic food chains. Much work has been flawed by inadequacies in analytical technique and the lack of ultra-clean, trace-metal-free protocols that are necessary to properly examine trace constituents in the environment (*27–29*). Although many of the essential details remain unclear, it is evident that atmospheric deposition can be an important vector for Hg contamination in natural waters (*18,30,31*). Björkland and coworkers (*30*), for example, reported that elevated Hg levels found in pike from southern and central Swedish lakes appear to be related to increases in atmospheric Hg deposition as inferred from the temporal imprint preserved in the vertical distribution of Hg in lake sediments.

Atmospheric Mercury Deposition

It is probable that small increases in Hg depositional fluxes could yield Hg levels in organisms that are of ecological and perhaps toxicological concern. We have shown that even the present yearly remote oceanic deposition of Hg at approximately 4 to 7 μg/m²/year (*18,31*) would introduce an annual amount of Hg comparable to the total Hg burden present in the water and biota of many freshwater lakes. Recently, for example, we presented a preliminary model from an ongoing study of the biogeochemical Hg cycling in temperate lakes of north-central Wisconsin showing that the estimated atmospheric Hg deposition could readily account for the total mass of Hg in fish, water, and sediment of a representative lake (*28,32,33*). High levels of Hg are present in piscivorous fishes from low alkalinity lakes in the rural, north-central Wisconsin environs. Interestingly, atmospheric Hg deposition to this region may have increased by a factor of 3 or 4 since precolonial times as deduced from sediment core analyses (*34*). Furthermore, the current geographically broad pattern (e.g., Canada, United States, Sweden) of elevated Hg in fish even in watersheds far from anthropogenic sources suggests that increases in atmospheric Hg deposition are occurring on a hemispheric scale (*35*).

The prominence of atmospheric mobilization and deposition within the biogeochemical cycle of Hg can be illustrated on a global basis. For example, the annual pluvial input of Hg to the marine environment appears to be about a factor of 10 greater than the estimated fluvial flux (*18,31*) (Table 1). Moreover, the impact of aeolian fluxes to the oceans is manifested clearly by the higher concentrations of Hg in North Atlantic waters relative to the Pacific (*18*). This distribution is consistent with our estimate of a large, modern interference of anthropogenic emissions on the global Hg cycle (Table 1), as well as the temporal pattern of modern Hg usage and environmental discharges. Atmospheric transport of Hg from the continents should be most pronounced in the Atlantic Ocean because of the proximity of terrestrial sources to the open ocean atmosphere. The observed geographically wide pattern of elevated Hg levels in gamefish is a further suggestion that relatively subtle but long-term increases in atmospheric Hg deposition could lead directly to enhanced levels in fish stock. Watson's (*16*) projections for the world trends in human-related Hg discharges as summarized in Figure 1 are of additional concern. Current worries about Hg and MMHg in the environment and in fish for human consumption will be exacerbated over the next 25 or 35 years if the forecast for increased discharges is correct.

Global Mercury Cycle

A brief overview of the global biogeochemical cycling of Hg is necessary to provide the proper scaling and perspective to illustrate both the complexities and the potential low-level, insidious sources leading to the bioaccumulation of MMHg in fish. The relationship between atmospheric Hg deposition and MMHg present in biota will be further demonstrated and assessed using our current investigations into the atmospheric cycling, air–water transfer, and exchange of Hg in fresh waters of the rural, north-central environs of Wisconsin as a case study.

Marine Biogeochemical Cycling of Mercury

The marine biogeochemical cycle of Hg has presented a formidable analytical challenge. Thus, the accumulation of reliable oceanographic data on the amounts and distribution of Hg in sea water and the determination and understanding of fundamental aspects of the marine biogeochemistry of Hg have been modest (*18,27,29,36*). Mercury concentrations in the low picomolar range (<20 pM) have been reported for the North Atlantic Ocean and Pacific Ocean (*18,27,29,36–40*), for surface waters of the North Sea (41), and for the coastal northeast Pacific (42). These concentrations are much lower than most earlier studies, which suffered from a variety of contamination problems.

Moreover, it is becoming increasingly evident that Hg concentrations in other natural waters such as lakes approach the small concentrations found in sea water (*28*). Furthermore, recent oceanographic studies (*18,27,29,36,39,40*) are beginning to reveal patterns consistent with the large atmospheric depositional fluxes and significant particle-reactive behavior predicted for Hg species in sea water. Vertical profiles for Hg from the North

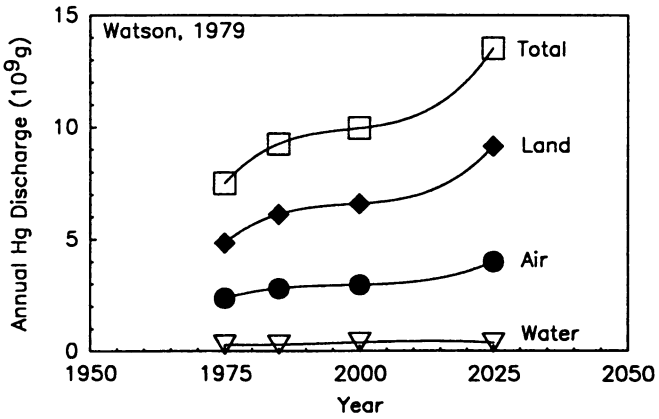

FIGURE 1. Estimates of world trends in human-related Hg discharges to the environment (*16*).

Atlantic and North Pacific Ocean illustrate major features of the marine biogeochemical cycle of Hg (*18,36,39*). The surface water concentrations of Hg from the northwest Atlantic Ocean (2.6–6.5 pM) are generally higher than those in the northeast Pacific Ocean (0.95–2.8 pM), consistent with an enhanced atmospheric supply of Hg in the northwest Atlantic Ocean. In the northeast Pacific profiles, there is striking evidence of atmospheric inputs and temporal variability in surface water concentrations.

Further evidence of the reactive nature of Hg in sea water is found in the productive waters of the central equatorial Pacific Ocean. Reactive Hg was found depleted in surface waters due most probably to the combined interactions of biologically mediated particulate scavenging and gas transfer of volatile Hg (Hg^0) from the surface water to the atmosphere (*18,19*). A more recent investigation of the partitioning of gaseous Hg between the atmosphere and surface waters in the equatorial Pacific revealed a general pattern of supersaturation with respect to Hg^0 (*17,43*). The highest concentrations of Hg^0 occurred in cooler, nutrient-rich waters that characterize equatorial upwelling and support biological productivity. A significant flux of Hg^0 to the atmosphere is predicted for this marine region. We have also observed the production of volatile Hg in association with phytoplankton blooms developed in coastal sea water mesocosms using flow-through tanks designed to simulate a near-shore ecosystem (*44*).

In summary, oceanic distributions of Hg appear to be governed by a competition between the local source strengths (e.g., atmospheric deposition) and the intensity of water-column scavenging and removal processes that include the production of Hg^0, which is eventually lost at the sea–air interface. Most recently, Mason and Fitgerald (*40*) reported the first reliable determinations of methylated Hg species in the open ocean. Based on this equatorial Pacific Ocean investigation, they hypothesized that MMHg in pelagic fish was derived from the biologically mediated *in situ* production at the base of the food chain. In addition, a linkage between atmospheric deposition of reactive inorganic Hg species and the *in situ* synthesis of methylated Hg compounds as well as Hg^0 was proposed. This biogeochemical situation occurs in lacustrine regions as well. Moreover, the rather delicately poised state of natural waters to current Hg inputs can be most clearly illustrated with a lake system (see "Mercury Cycling in Temperate Lakes").

Atmospheric Cycling of Mercury

Most of the atmospheric Hg species in the marine boundary layer over the open ocean are in the vapor phase (>99%). Even in a coastal/urban region such as Long Island Sound, greater than 97% of the total Hg in the near-surface atmosphere is in the gaseous state. This physical speciation has been established by our laboratory (*7,45*) and by others (*6*). A study of Long Island Sound atmosphere showed that Hg^0 accounts for 95 to 100% of the total Hg (*46*). Our most recent mid-continental studies in north-central Wisconsin are showing a similar partitioning with the Hg^0 fraction generally >99%. MMHg is much more soluble in water than Hg^0, and we do find small quantities in precipitation. For example, during 1989, MMHg ranged between 59 and 224 picograms (pg)/L in rain and from <5 to 80 pg/L in snow (*33*). The source of these small quantities of MMHg in the atmosphere is not known.

Total gaseous Hg, which consists almost entirely of Hg^0, decreases in the near surface atmosphere between the Northern and Southern Hemisphere over the Pacific and Atlantic Oceans (see Figure 2 for our Pacific data). This interhemispheric distribution is characteristic of a trace atmospheric gas whose primary sources, on a unit area basis, are continental and include anthropogenic and natural sources. An average tropospheric residence time of total gaseous Hg, assumed to be Hg^0, of about 1 year is obtained by modeling Hg as a trace gas (*10*). This relatively long average residence time, which is corroborated by our estimates of annual Hg deposition to the earth's surface using a steady-state model for the global Hg cycle (Table 1), indicates that Hg^0 emissions from both natural and anthropogenic sources are readily mixed intrahemispherically and can be transferred interhemispherically. Thus, Hg emissions from the Northern Hemisphere will be transported to the atmosphere of the Southern Hemisphere. Although this broad dispersion of Hg has probably reduced some local impacts from high-temperature, human-related processes that volatilize Hg, it also may have led to a geographically expansive problem of elevated Hg levels in fresh and marine fish.

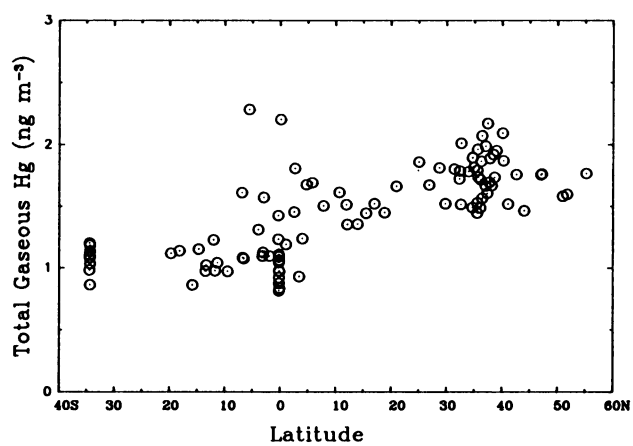

FIGURE 2. Latitudinal distribution of total gaseous Hg (TGM; ng/m³) over the Pacific Ocean between 1980 and 1986. Adapted from Fitzgerald (*15*).

Biogeochemical Cycling of Mercury in Natural Waters: Conceptual View

Atmospheric transport and air/sea exchange are preeminent pathways in the global cycling of Hg. A simplified physicochemical picture of the biogeochemical cycle of Hg near the air/aqueous boundary is presented in Figure 3. A proposed chemical composition is illustrated, as well as generalized examples of chemical and physical reactions associated with biological uptake and incorporation, phase transformations, regeneration processes, and transfer at the water surface. This model is derived principally from marine studies conducted by the University of Connecticut group (e.g., *7,11,15,17–19, 33,36,40,43,45,46*). Analogous physicochemical representations of the Hg cycle in natural waters have been offered (*11,15,47–50*). In sea water, thermodynamic chemical equilibrium modeling indicates that the inorganic speciation of dissolved Hg consists principally of chloride and mixed halide complexes [e.g., $HgCl_4^{2-} > HgCl_3Br^{2-} > HgCl_3^- > HgCl_2Br^- > HgCl_2^0$ (*51*)]. In fresh waters the hydroxide species can prevail. Sulfide species may also be important, even in oxygenated waters (*52*). Organically bound Hg (e.g., carbon-Hg species as CH_3Hg^+), Hg associations with organosulfur compounds, and Hg complexes with representative organic ligands such as free amino acids or "dissolved humic material" should be significant contributors to the dissolved fraction.

A sense of the expected high biogeochemical activity of Hg in natural waters is provided by the multiple routes and reactions available for the interconversion of dissolved Hg species, Hg^0, methylated Hg compounds, and other organo-Hg species. Although many of the transformations are reversible, a fraction of the total Hg will eventually remain fixed in inorganic and organic solid phases to be carried to the bottom with fecal material or other settling debris. Sedimentary diagenetic processes aided by bacterial mediators will recycle much of this Hg as the organic substrates are destroyed and inorganic carriers dissolve. The final immobilization and accumulation of Hg in freshwater and coastal marine sediment will involve sulfidic phases. In pelagic ocean oxygenated sediments, Hg will be associated with refractory organic matter, hydrous oxides of Fe and Mn, calcareous oozes, or siliceous deposits.

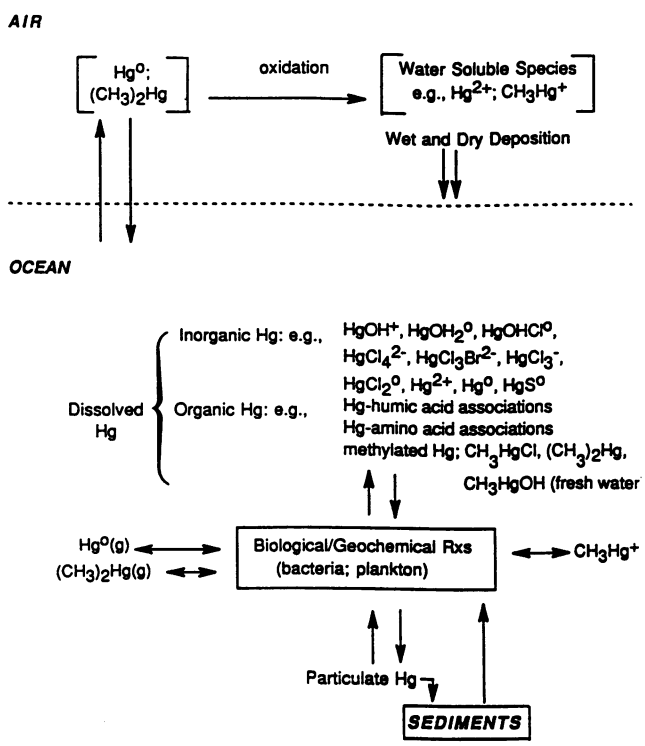

FIGURE 3. Physicochemical view of the biogeochemical cycling of Hg with emphasis on the water–air interface. Adapted from Fitzgerald (*15*).

Species such as Hg^0 and $(CH_3)_2Hg$, which are volatile, can evade to the atmosphere. Little is known about gas-phase reactions involving Hg species in the atmosphere. This conceptual model proposes a photochemical oxidation route whereby sparingly soluble, volatile Hg forms as exemplified by Hg^0 and $(CH_3)_2Hg$ are converted to more soluble species [e.g., $Hg^0 \rightarrow Hg^{2+}$; $(CH_3)_2Hg \rightarrow CH_3Hg^0$]. Mass-balance estimates suggest that Hg^0 is slowly oxidized in the atmosphere, whereas laboratory studies by Niki et al. (*53*) suggest that rapid OH-radical-initiated oxidation of $(CH_3)_2Hg$ might take place in the atmosphere. These hypotheses are consistent with the widespread findings showing that Hg^0 is the principal atmospheric species. No significant amounts of atmospheric methylated Hg species have been reliably reported. We are finding small quantities of MMHg in terrestrial precipitation (*33*).

The reality of this conceptual model for the biogeochemical cycling of Hg in natural waters has been amply demonstrated for the marine environment by the recent work of Mason and Fitzgerald (*40*). As noted, these authors reported the first unequivocal evidence for MMHg and DMHg (dimethylmercury) in the open ocean. More importantly, the alkylated species, as well as reactive Hg, total Hg, and Hg^0, were distributed in an oceanographically consistent manner. The authors advanced a biogeochemical explanation in the form of a preliminary model containing many aspects of the aquatic Hg cycle proposed in Fugure 3. They suggest that labile inorganic Hg is the most probable substrate for *in situ* biologically mediated methylation reactions that are favored in low-oxygen environments. Similar distributional and speciation patterns are evident in fresh waters as shown by the ongoing multidisiciplinary studies in the Mercury in Temperate Lakes Program in Wisconsin (e.g., *54–60*). Moreover, the suggested biogeochemical explanations show some similarities. One striking difference, however, between lacustrine and oceanic Hg speciation is the lack of evidence for DMHg in fresh waters.

Mercury Cycling in Temperate Lakes

As discussed previously, high levels of Hg are present in piscivorous fishes from low alkalinity lakes in the rural, north-central Wisconsin environs. Concentrations of Hg (i.e., MMHg) exceeding the state health guidelines of 0.5 μg/g (wet weight) have been reported in gamefish from about 30% of the 300 lakes examined (Wisconsin Department of Natural Resources and Division of Health, 1987, personal communication). Many of these bodies of water are remote from obvious sources of Hg contamination. There is evidence suggesting a linkage between Hg bioaccumulation and lake chemistry, especially pH, alkalinity, and dissolved calcium (*25,35,58,61–63*). A correlation between the Hg concentrations for three age/size classes of walleye pike

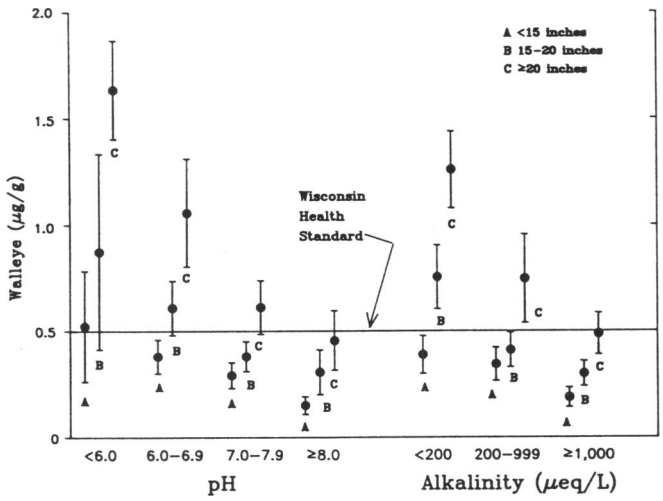

FIGURE 4. Walleye Hg concentration means and 95% confidence intervals for fish-length classes in Wisconsin lakes of different pH and alkalinity categories (means were derived from individual lake mean concentration of walleyes). Adapted from Lathrop et al. (*64*).

with lake pH and alkalinity is illustrated in Figure 4. Increases in the Hg accumulation in walleye were inversely related to pH and alkalinity in these lakes. The widespread situation with elevated Hg in fish has created a human health concern and economic dilemma for the sportfishing industry. We are currently participating in the Mercury in Temperate Lakes Program. The multidisciplinary program is examining the processes regulating the aquatic biogeochemistry of Hg in the temperate mid-continent lacustrine environs of north-central Wisconsin. This study, which is supported by the Electric Power Research Institute and the Wisconsin Department of Natural Resources, has enabled us to extend our investigations of the tropospheric chemistry and oceanic cycling of Hg to terrestrial aquatic systems. We are investigating the atmospheric cycle, air–water transfer, and exchange of Hg in these natural waters. Trace-metal-free procedures are used to measure Hg and alkylated Hg species at the picomolar level in air, water, and precipitation.

These aquatic systems have Hg concentrations similar to remote, open ocean regions. The total atmospheric Hg deposition of approximately 11 $\mu g/m^2$/year (wet deposition at 70% and dry deposition at 40%) determined during the first 2 year's (October 1988–September 1990) readily accounts for the total mass of Hg in fish and water in Little Rock Lake (LRL), clear-water seepage lake that is being acidified experimentally (*28,32,33*). Moreover, the budget is well constrained because the estimated yearly accumulation of Hg in fish, water, and sediments is balanced by atmospheric Hg deposition. Further, this model reveals that the approximate annual net Hg accumulation in LRL biota of 0.06 g can be supplied using <10% of the yearly Hg deposition (*33*). This scaling demonstrates the significance of atmospheric Hg deposition to the biogeochemical cycling of Hg in temperate seepage lakes. It further illustrates how modest increases in atmospheric Hg loading could lead directly to enhanced levels of Hg in biota. This budget, which is illustrated in Figure 5, has been modified from the initial budget published by Fitzgerald and Watras (*28*).

The cycling of volatile Hg is quite important, and the evasional fluxes (as noted in Fig. 5) are geochemically significant. The volatile fraction in the temperate lakes study consists principally of Hg^o under all sampling conditions, with no significant contribution from volatile organic Hg species (detection limit of 10 femtomolar). This situation is different in the equatorial Pacific, where significant levels of DMHg were observed (*40*). Atmospheric gaseous Hg, which is principally Hg^o, was measured and the air–water partitioning determined. As Vandal et al. (*20*) report, the lake waters generally have been supersaturated with Hg^o relative to the atmosphere. The flux of Hg^o due to gas evasion is significant, estimated at approximately 7% (treatment basin) and 14% (reference basin) of the annual atmospheric input of Hg to LRL (*20*). The evasional fluxes of Hg^o across the lake surface can diminish the Hg substrate for methylation, thereby providing a potential buffering and /or amelioration role in the biogeochemical cycling of Hg in lakes.

Analogous modeling for MMHg is as yet limited. However, preliminary data for the atmospheric deposition of MMHg suggest that this flux is insufficient to account for the amounts of MMHg observed in biota. In-lake synthesis of MMHg is implicated.

Human Exposure and Health Risks from Methylmercury

Human exposure to methylmercury compounds is almost exclusively from the consumption of fish and fish products (*65*). Consumption of marine mammals is an important source for certain populations.

Estimated intakes of methylmercury for the U.S. population are given in Figure 6 based on population survey of the 1960s and 1970s. Given the increasing popularity of fish for dietary and other health reasons, these figures probably underestimate current consumption levels. What is strikingly apparent is the extreme range of consumption. In distinction to lead or cadmuim where these metals are present in virtually all food, methylmercury is restricted to only one class of foodstuffs. Thus, the wide range in consumption basically reflects the wide range in individual fish-eating habits.

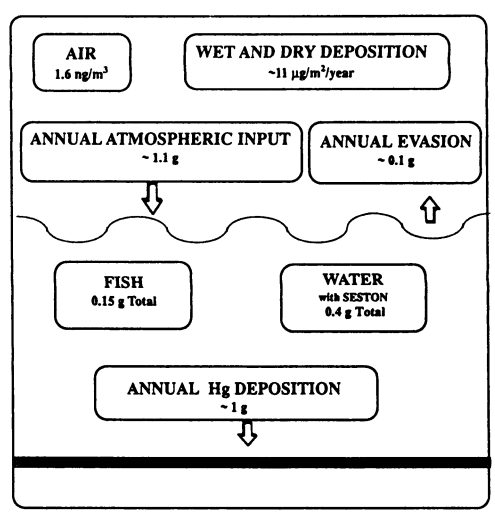

FIGURE 5. Mercury budget, Little Rock Lake treatment basin. Adapted from Fritzgerald and Watras (*28*) and Wiener et al. (*31*).

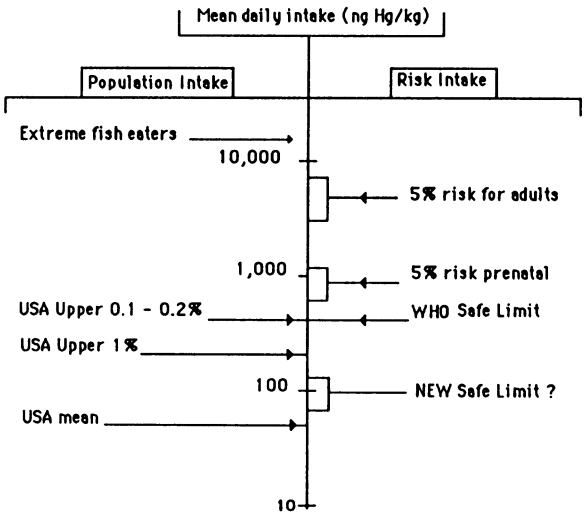

FIGURE 6. A comparison of population intakes of methylmercury with intakes associated with risks to health. Adapted from Clarkson (*66*).

The associated health risks for a given intake are also indicated in Figure 6. Methylmercury affects primarily the central nervous system. In severe cases in adults, specific anatomical areas of the brain are damaged. Neuronal cells are destroyed, so the damage is irreversible. The first symptom at the lowest doses are complaints of paresthesias, an abnormal sensation or loss of sensation in the extremities of the hands and feet and circumorally (*65*). These effects also are believed to be due to damage to the central nervous system. As indicated in Figure 6, such effects in nonpregnant adults occur only in the range of extreme intakes. An epidemiological study of Cree Indians in Quebec who were extreme fish consumers suggested that mild neurological changes may have been caused by methylmercury in freshwater fish (*67*).

The intake associated with a 5% risk of mild neurological effects as indicated in Figure 6 is, in practice, a lowest effect intake. The limitations of the epidemiological studies were such that a risk level below 5% was not detectable above background variation in the control groups. Thus, a World Health Organization expert group, following current procedures at that time, applied a safety factor of 10 to the lowest effect level to estimate a "tolerable" intake for the general population (*68*). As indicated in Figure 6, the "WHO limit" would be exceeded by about 0.1% of the U.S. population—about 250,000 people.

Prenatal life is more susceptible to brain damage from methylmercury as compared to the adult. Methylmercury is believed to inhibit cellular processes basic to cell division and neuronal migration [for review, see Clarkson (*69*)]. Cases of severe exposure prenatally can result in massive disruption of the developing brain (*70*). A follow-up study of the population in Iraq exposed to methylmercury added as a fungicide to wheat indicated more subtle effects in prenatally exposed children (*71*). These effects manifested themselves as delayed achievement of developmental milestones and abnormal reflexes. These effects appeared at intakes 5 to 10 times lower than those intakes associated with adult exposure (Fig. 6). If a 10-fold safety factor is applied to estimate a new acceptable or tolerable human intake, it is clear from Figure 6 that a substantial fraction of the U.S. population would exceed such a limit.

The Iraqi studies were on people exposed to methylmercury in homemade bread prepared from wheat treated with a fungicide. A critical question is whether or not findings in the Iraqi population can be extrapolated to fish-eating populations. Two epidemiological studies, one on consumers of freshwater fish (*72*), the other on consumers of ocean fish (*73*), have produced findings that tend to support Iraqi data on prenatal exposure. However, all these studies suffer from a small population size so that an accurate lowest effect intake cannot now be established. There is, therefore, a great need for an extensive study on a fish-eating population covering the range of methylmercury intakes associated with the lowest effect levels estimated from the Iraq outbreak.

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REFERENCES

1. Garrels, R., Mackenzie, F., and Hunt, C. Chemical Cycles and the Global Environment: Assessing Human Influences. W. Kaufman, Los Altos, CA, 1975.
2. Wollast, R., Billen, F., and MacKenzie, F. T. Behavior of mercury in natural systems and its global cycle. In: Ecological Toxicology Research, NATO Science Committee Conference on Ecotoxicology (A. D. McIntyre and C. F. Mills, Eds.), Plenum Press, New York, 1975, pp. 145–166.
3. National Academy of Sciences. An Assessment of Mercury in the Environment. NAS, Washington, DC, 1978.
4. Lerman, A. Geochemical Process: Water and Sediment Environments. John Wiley and Sons, New York, 1978.
5. Lantzy, R., and MacKenzie, F. Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta 43: 511–527 (1979).
6. Slemr, F., Seiler, W., and Schuster, G. Latitudinal distribution of mercury over the Atlantic Ocean. J. Geophys. Res. 86: 1159–1166 (1981).
7. Fitzgerald, W. F., Gill, G. A., and Hewitt, A. Air-sea exchange of mercury. In: Trace Metals in Seawater (C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton, and E. D. Goldberg, Eds.), NATO Conference Series IV, Marine Science, Vol. 8, Plenum Press, New York, 1983, pp. 297–316.
8. Slemr, F., Schuster, G., and Seiler, W. Distribution, speciation and budget of atmospheric mercury. J. Atmos. Chem. 3: 407–434 (1985).
9. Lindqvist, O., and Rodhe, H. Atmospheric mercury—a review. Tellus 337B: 136–159 (1985).
10. Fitzgerald, W. F., Gill, G. A., and Hewitt, A. D. Mercury, a trace atmospheric gas. In: Abstracts, Symposium on the Role of the Ocean on Atmoshperic Chemistry. IAMAP Third Scientific Assembly, Hamburg, Federal Republic of Germany, August 17–18, 1981.
11. Fitzgerald, W. F. Cycling of mercury between the atmosphere and oceans. In: The Role of Air-Sea Exchange in Geochemical Cycling (P. Buat-Menard, Ed.), NATO Advanced Science Institutes Series, Reidel Publishing Co., Dordrecht, The Netherlands, 1986, pp. 363–408.
12. Nriagu, J. O. A global assessment of natural sources of atmospheric trace metals. Nature 338: 47–49 (1989).
13. Andren, A., and Nriagu, J. O. The global cycle of mercury. In: The Biogeochemistry of Mercury in the Environment (J. O. Nriagu, Ed.), Elsevier-North Holland, Amsterdam, 1979, pp. 1–21.
14. Nriagu, J. O., and Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333: 134–139 (1988).
15. Fitzgerald, W. F. Atmospheric and oceanic cycling of mercury. In: SEAREX Volume of the Chemical Oceanography Series (J. P. Riley and R. Chester, Eds.), Academic Press, London, pp. 151–186.

16. Watson, W. D. Economic considerations in controlling mercury pollution. In: The Biogeochemistry of Mercury in the Environment (J. O. Nriagu, Ed.), Elsevier-North Holland, Amsterdam, 1979, pp. 42–77.
17. Kim, J. P., and Fitzgerald, W. F. Sea-air partitioning of mercury in the equatorial Pacific Ocean. Science 231: 1131–1133 (1986).
18. Gill, G. A., and Fitzgerald, W. F. Mercury in surface waters of the open ocean. Global Biogeochem. Cycles 1: 199–212 (1987).
19. Fitzgerald, W. F., Gill, G. A., and Kim, J. P. An equatorial Pacific Ocean source of atmospheric mercury. Science 224: 597–599 (1984).
20. Vandal, G. M., Mason, R. P., and Fitzgerald, W. F. Cycling of volatile mercury in temperate lakes. International Conference on Mercury as an Environmental Pollutant, Gavle, Sweden, June 11–13, 1990. J. Water Air Soil Pollut., in press.
21. Westoo, G. Determination of methyl mercury compounds in food stuffs. I. Methylmercury compounds in fish, identification and determination. Acta Chem. Scand. 20: 2131–2137 (1966).
22. Huckabee, J. W., Elwood, J. W., and Hildebrand, S. G. Accumulation of mercury in freshwater biota. In: The Biogeochemistry of Mercury in the Environment (J. O. Nriagu, Ed.), Elsevier-North Holland, Amsterdam, 1979, pp. 277–302.
23. Bernard, M., and Renzoni, A. Mercury concentrations in Mediterranean marine organisms and their environment: natural or anthropogenic origin. Thalassia Jugosl. 13: 265–300 (1977).
24. Eisler, D. Trace Metal Concentrations in Marine Organisms. Pergamon Press, New York, 1981.
25. Lindqvist, O., Jernelov, A., Hohansson, K., and Rodhe, H. Mercury in the Swedish Environment: Global and Local Sources. National Swedish Environment: Global and Local Sources. National Swedish Environment Protection Board, Solna, Sweden, 1984, p. 105.
26. Barber, R. T., and Whaling, P. J. Mercury in marlin and sailfish. Mar. Pollut. Bull. 14: 395: 395–396 (1983).
27. Gill, G. A., and Fitzgerald, W. F. Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. Marine Chem. 20: 227–243 (1987).
28. Fitzgerald, W. F., and Watras, C. J. Mercury in the surficial waters of rural Wisconsin lakes. Sci. Total. Environ. 87/88: 223–232 (1989).
29. Gill, G. A., and Fitzgerald, W. F. Mercury sampling of open ocean waters at the picomolar level. Deep Sea Res. 32: 287–297 (1985).
30. Bjorklund, I., Borg, H., and Johansson, K. Mercury in Swedish lakes—its regional distribution and causes. Ambio 13: 118–121 (1984).
31. Fitzgerald, W. F., and Gill, G. A. Depositional fluxes of mercury to the oceans. In: International Conference on Heavy Metals in the Environment, Vol. 1 (T. O. Lekkas, Ed.), CEP Consultants, Edinburgh, 1985, pp. 79–81.
32. Weiner, J. G., Fitzgerald, W. F., Watras, C. J., and Rada, R. G. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. Environ. Toxicol. Chem. 9: 909–918 (1990).
33. Fitzgerald, W. F., Mason, R. P., and Vandal, G. M. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. International Conference on Mercury as an Environmental Pollutant, Gavle, Sweden, June 11–13, 1990. Water Air Soil Pollut., in press.
34. Rada, R. B., Wiener, J. G., Winfrey, M. R., and Powell, D. E., Recent increases in atmospheric deposition of mercury to northcentral Wisconsin lakes inferred from sediment analyses. Arch. Environ. Contam. Toxicol. 18: 175–181 (1989).
35. Wiener, J. G. Metal contamination of fish in low-pH lakes and potential implications for piscivorous wildlife. Trans. N. Am. Wild. Natl. Resource. Conf. 52: 645–657 (1987).
36. Gill, G. A., and Fitzgerald, W. F. Vertical mercury distributions in the oceans. Geochim. Cosmochim. Acta 52: 1719–1728 (1988).
37. Dalziel, J. A., and Yeats, P. A. Reactive mercury in the central North Atlantic ocean. Marine Chem. 15: 357–361 (1985).
38. Olafsson, J. Mercury concentrations in the North Atlantic in relation to cadmium, aluminum and oceanographic parameters. In: Trace Metals in Seawater (C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton, and E. D. Goldberg, Eds.), NATO Conference Series IV, Marine Science, Vol. 9, Plenum Press, New York, 1983, pp. 475–468.
39. Gill, G. A., and Bruland, K. W. Mercury in the northeast Pacific. EOS Trans. Am. Geophys. U. 68: 1763 (1987).
40. Mason, R. P., and Fitzgerald, W. F. Alkylmercury species in the equatorial Pacific. Nature 347: 457–459 (1990).
41. Freiman, P., and Schmidt, D. Determination of mercury in sea water by cold vapor atomic absorption spectometry. Fres. Z. Anal. Chem. 313: 200–202 (1982).
42. Bloom, N. S., and Crecelius, E. A., Determination of mercury in seawater at subnanogram per liter levels. Marine Chem. 14: 49–59 (1983).
43. Kim, J. P., and Fitzgerald, W. F. Gaseous mercury profiles in the tropical Pacific Ocean. Geophys. Res. Lett. 15: 40–43 (1988).
44. Kim, J. P., and Fitzgerald, W. F. Volatile mercury in the equatorial Pacific Ocean. EOS Trans. Am. Geophys. U. 65: 84D (1984).
45. Fitzgerald, W. F., and Gill, G. A. Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. Anal. Chem. 51: 1714–1720 (1979).
46. Bloom, N. S., and Fitzgerald, W. F. Determination of volatile mercury species at the nanogram level by low temperature gas chromatography with an ultrasensitive cold-vapor atomic fluorescence detector. Anal. Chim. Acta 51: 1714–1720 (1988).
47. Wood, J. M. Biological cycles for toxic elements in the environment. Science 183: 1049–1052 (1974).
48. Beijer, J., and Jernelöv, A. Methylation of mercury in aquatic environment. In: The Biogeochemistry of Mercury in the Environment (J. O. Nriagu, Ed.), Elsevier-North Holland, Amsterdam, 1979, pp. 203–210.
49. Stumm, W., and Morgan, J. Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley and Sons, New York, 1981.
50. Brosset, C. The mercury cycle. Water Air Soil Pollut. 16: 253–255 (1981).
51. Dyrssen, D., and Wedborg, M. Major and minor elements. In: Biogeochemistry of Estuaries (E. Olausson and I. Cato, Eds.), John Wiley and Sons, New York, 1980, pp. 71–119.
52. Dyrssen, D. Sulfide complexation in surface seawater. Marine Chem. 24: 143 (1988).
53. Niki, H., Maker, P. D., Savage, C. M., and Breltenbach, L. P. A long-path fourier transform infrared study of the kinetics and mechanism for the HO-radical initiated oxidation of dimethylmercury. J. Phys. Chem. 87: 4987–4991 (1983).
54. Bloom, N. S., Watras, C. J., and Hurley, J. P. Impact of acidification of the methylmercury cycling of remote seepage lakes. Water Air Soil Pollut, in press.
55. Bloom, N. S., and Watras, C. J. Seasonal and vertical variability in the mercury speciation of an acidified Wisconsin lake. In: Heavy Metals in the Environment: International Conference, Vol. 2 (J. P. Vernet, Ed.), CEP Consultants, Geneva, 1989, pp. 349–352.
56. Hurley, J. P., and Watras, C. J. Identification of bacteriochlorophyll in lakes using reverse-phase HPLC. Limnol. Oceanogr., in press.
57. Hurley, J. P., Watras, C. J., and Bloom, N. S. Distribution and flux of particulate mercury in temperate seepage lakes. Water Air Soil Pollut, in press.
58. Lathrop, R. C., Rasmussen, P. W., and Knauer, D. K. Walleye mercury concentrations in Wisconsin lakes. Water Air Soil Pollut., in press.
59. Watras, C. J., Bloom, N. S., Fitzgerald, W. F., Hurley, J. P., Krabbenhoft, R. G., Rada, R. G. and Wiener, J. G. Mercury in temperate lakes: a mechanistic field study. Verh. Int. Verin. Limnol., in press.
60. Weiner, J. G., Fitzgerald, W. F., Watras, C. J., and Rada, R. G. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. Environ. Toxicol. Chem. 9: 909–918 (1989).
61. Scheider, W. A., Jeffries, D. A., and Dillon, P. J. Effects of acidic precipitation of Precambrian freshwaters of southern Ontario. J. Great Lakes Res. 5: 45–51 (1979).
62. Hakanson, L. The quantitative impact of pH, bioproduction and Hg accumulation on the Hg content of fish (pike). Environ. Pollut. Ser. B. 285–304 (1980).
63. Sloan, R., and Schofield, C. L. Mercury levels in brook trout (*Salvellinus fontinalis*) from selected acid and limed Adirondack lakes. Northeast. Environ. Sci. 2: 165–170 (1983).
64. Lathrop, R. C., Noonan, K. C., Gunther, P. M., Brasino, T. C., and Rasumussen, P. W. Mercury Levels in Walleyes from Wisconsin Lakes of Different Water and Sediment Chemistry Characteristics. Technical Bulletin No. 163, Department of Natural Resources, Madison, WI, 1989, p. 23.
65. WHO. WHO Environmental Health Criteria 1: Mercury. World Health Organization, Geneva, 1976.
66. Clarkson, T. W. Health risks from methylmercury in fish. Environ. Toxicol. Chem. 9(7): 957–961 (1991)
67. MeKeown-Eyssen, G. E., and Ruedy, J. Prevalence of neurological abnormality in Cree Indians exposed to methylmercury in northern Quebec. Clin. Invest. Med. 6: 161–169(1983).

68. WHO. Evaluation of Certain Food Additives and the Contaminants Mercury, Lead and Cadmium. Sixteenth report of the Joint FAO/WHO expert committee on food additives. Technical Report Series No. 505, World Health Organization, Geneva, 1972.
69. Clarkson, T. W. Metal toxicity in the central nervous system. Environ. Health Perspect. 75: 59–64 (1987).
70. Choi, B. H., Lapham, L. W., Amin-Zaki, L., and Saleem, T. Abnormal neuronal migration, deranged cerebral cortical organization and diffuse white matter astrocytosis of human fetal brain. A major effect of methylmercury poisoning in utero. J. Neuropathol. Exp. Neurol. 37: 719–733 (1978).
71. Marsh, D. O., Clarkson, T. W., Cox, C., Myers, G. J., Amin-Zaki, L., and Al-Tikriti, S. Fetal methylmercury poisoning: relationship between concentration in single strands of maternal hair and child effects. Arch. Neurol. 44: 1017–1022 (1987).
72. McKeown-Eyssen, G. E., Ruedy, J., and Neims, A. Methylmercury exposure in northern Quebec. II. Neurological findings in children. Am. J. Epidemiol. 118: 470–479 (1983).
73. Kjellstrom, T., Kennedy, P., Wallis, S., Stewarts, A., Friberg, L., Lind, B., Wutherspoon, T., and Mantell, C. Physical and Mental Development of Children with Prenatal Exposure to Mercury from Fish. Stage 2: Interviews and Psychological Tests at Age 6. National Swedish Environmental Protection Board Report 3642, Solna, Sweden, 1989.