Critical Review

The Case for Atmospheric Mercury Contamination in Remote Areas

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Elevated levels of mercury in aquatic environments remote from industrial sources have been broadly attributed to long-range atmospheric transport and deposition of anthropogenic Hg. Evidence in support of this prevailing scientific view—global biogeochemical Hg models, sedimentary archives of historic Hg fluxes, and geographic trends in soil Hg—have been challenged as being insufficiently rigorous to rule out the alternative explanation that natural geologic sources are the principal contributors of Hg in remote locations. In this review, we examine the weaknesses in interpretation and the choice of information that has been used to argue against atmospheric Hg contamination. Analytical advances in measuring trace levels of environmental Hg have greatly narrowed estimates of natural Hg fluxes, providing a clear measure of the relative magnitude of anthropogenic Hg emissions and deposition. Recent experimental results indicate that diagenetic processes cannot explain the mounting number of lake sediment and peat profiles showing substantial increases in Hg flux during the past century. Geologic sources of Hg may be important in specific localities but cannot explain corresponding geographic trends in soil Hg and industrial emission sources. Despite uncertainties in current understanding, there is a broad and geochemically consistent data base indicating that, over large regions of the globe, human-related Hg emissions have increased relative to natural sources since the onset of the industrial period.

Introduction

Human exposure to monomethylmercury (MMHg) through the consumption of freshwater and marine fish is the principal public health concern with Hg in the environment.

Alkylated Hg species such as MMHg and dimethylmercury (DMHg) are integral components of the Hg cycle. Their distribution and fate at the earth's surface will be affected by natural and anthropogenic sources and processes. Elevated MMHg concentrations in fish are common even in the oceans and terrestrial waters distant from point sources. Long-range atmospheric transport and deposition of anthropogenically-derived Hg has been implicated (e.g., refs 1–4). Much of the recent work appears in the conference volumes from three international conferences on "Mercury as a Global Pollutant" (5–7).

However, in a recent *Environ. Sci. Technol.* critical review of the subject, Rasmussen (8) argues that the underlying assumptions linking anthropogenic Hg emissions to the atmosphere and to subsequent Hg deposition in remote continental and oceanic settings "deserve careful scrutiny" because the "conclusions hold serious implications to both government and industry". In Rasmussen's view, recent investigations suggesting that atmospheric transport and deposition of human-related Hg emissions dominate the cycling and bioaccumulation of Hg in systems distant from anthropogenic point sources underestimate the influence of natural geological sources. Evidence in support of anthropogenic interruption of the global Hg cycle such as historic records of Hg accumulation in lake sediments and peat cores or geographic gradients in soil Hg concentrations are dismissed as diagenetic artifacts or the product of underlying geologic variation.

The purpose of this review is to provide the "careful scrutiny" that such controversial conclusions demand. It is our contention that the case for atmospheric Hg contamination in remote areas is stronger than ever, having been advanced by worldwide improvements in analytical methods, sampling techniques, and experimental design over the past decade. Much of the earlier uncertainty regarding Hg contributions from natural sources has been replaced by a convergence of data that points unequivocally toward significant human-related Hg emissions and deposition over large regions of the globe.

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In contrast to previous views, it has become evident that atmospheric and aquatic cycling of Hg and the bioaccumulation of MMHg in aquatic systems are driven by complex chemical and biological reactions involving exceedingly small quantities of Hg. Accordingly, environmental investigations of Hg require an ultraclean trace metal analytical approach that was rarely used during the 1960s to the mid-1980s. Thus, one must carefully evaluate the Hg literature for analytical quality and the assurance that the findings are geochemically consistent. In the following review, we address the weaknesses in interpretation and the choices of information used to support the contention that geological sources of Hg are the principal contributors of Hg in remote locations. We consider first the geological fluxes associated with the global cycle of Hg, then examine the reliability of lake sediments and peat cores as recorders of past Hg deposition, and finally explore geographic gradients in soil Hg relative to industrial emission sources.

Global Hg Cycle

The global biogeochemical cycling of Hg has been described often using mass balance formulations (e.g., refs 1−3 and 9−18). These simulations, in general, show the prominent role of the atmosphere in mobilizing and depositing Hg at the earth's surface and indicate that anthropogenic Hg emissions to the atmosphere represent a significant interference in the modern Hg cycle. Environmental assessments of source strengths for natural and anthropogenic processes have often been in error due to the inclusion of inaccurate published information and the limited availability of accurate data for important aspects of the Hg cycle. The geochemical picture of the global mercury cycle has improved significantly during the past decade. Present estimates for mercury fluxes to the earth's surface and for the mercury content of active reservoirs (e.g., natural waters; atmosphere) are converging. Continued improvements are expected from the large number of on-going high-quality studies concerning the emissions, chemical speciation, and reactivity of Hg in the environment. Indeed, the field is so active that a fourth international conference on "Mercury as a Global Pollutant" (since 1990) was held in Hamburg in August 1996.

A scrupulously critical approach must be employed in evaluating environmental Hg measurements, especially those obtained prior to the mid-1980s. Unfortunately, Rasmussen (8) was not discriminating in her tabulation of global estimates of annual Hg emissions from natural sources. By including results from the early work by Lantzy and MacKenzie (12) and alluding to others, she concludes that estimates for natural global Hg emissions to the atmosphere vary by orders of magnitude. While modern values for average annual natural Hg flows to the air range from 8 to 20 Mmol (1, 2, 18), the estimate of 29 325 Mg yr^{-1} (150 Mmol yr^{-1}) reached by Lantzy and MacKenzie (12) is much larger and certainly wrong. This value, which is derived using a global Hg model developed by MacKenzie and Wollast (11), is in gross error because it is based on inaccurate Hg measurements of the Hg content of Greenland ice that were published by Weiss and co-workers (19) in 1971. Weiss et al. reported that the average Hg concentration in ice between 800 BC and 1952 was 60 ± 20 pg g^{-1} and 130 ± 50 pg g^{-1} for the period between 1952 and 1965. The enhanced levels were attributed to anthropogenic Hg emissions, which were determined by Lantzy and Mackenzie (12) to be 15 800 Mg yr^{-1} (79 Mmol yr^{-1}), which is also an erroneously large value.

The Greenland Icesheet studies illustrate the need for scrupulous attention to analytical methodology and field sampling protocols in ultratrace studies of Hg. They also show clearly the need to evaluate critically the literature for accuracy and geochemical consistency. Historically, Hg measurements in the Greenland Icesheet range from <1 to 880 pg g^{-1}, approximately 3 orders of magnitude. The highest levels were reported by Weiss and co-workers in 1971 (19) and in 1977 (20). These concentrations reflect gross contamination acquired during sample collection, processing, and analysis. Using improved techniques, later work by investigators from the Danish Isotope Center (21) reported Hg concentrations between 2 and 19 pg g^{-1} over the time period of 1727−1971. Most recently, Vandal et al. (22) found a range in between (<1−1.5 pg g^{-1}) for samples within any one year for the past 30 years that have been analyzed thus far. These collections were made using extraordinarily careful and ultratrace metal free techniques developed especially for depositional studies in polar regions by C. Boutron and co-workers at the Laboratoire de Glaciologie et Géophysique de l'Environnement, France (see refs 23 and 24 for technical details). These latter results are the order of magnitude consistent with recent measurements of Hg in snows from the mid-continental lakes region in northcentral Wisconsin, which show concentrations between 2.3 and 8.2 pg g^{-1} (25, 26). Thus, an estimate of natural Hg emission to the atmosphere of 150 Mmol is not supported by modern data. Indeed, using modern data, Mason et al. (2) have applied a model similar to the one developed by Lantzy and MacKenzie (11) to assess the role of anthropogenic emissions within the global cycle of Hg. Their estimate for annual average Hg emissions from natural sources at 8 Mmol is nearly 20-fold lower.

Geological Hg Fluxes to the Oceans

Global tectonic theory may provide a useful framework for evaluating natural Hg fluxes. However, the suggestion (in Table 3, ref 8) that there are extraordinarily large geothermal Hg fluxes from ocean ridges and oceanic crust at 9.3−18.6 Mmol yr^{-1} (1860−3720 Mg yr^{-1}) and 36.7−73.4 Mmol yr^{-1} (7340 −14 680 Mg yr^{-1}) respectively, that affect the oceanic concentration of Hg is not supported by oceanic profiles of Hg. Deep ocean profiles (e.g., ref 27) do not show any significant increase in concentration with depth, which would be expected if inputs from the ocean floor exceeded the rate of vertical mixing. Thus, this source cannot exceed the rate of vertical mixing. Use of a vertical mixing coefficient of 3 m/yr (28) and 2 pM Hg concentration (a conservatively high value) yields a flux of 6 nmol m^{-2} yr^{-1}. Eddy diffusion calculations yield a value of the same order. This is equivalent to a (maximum) flux of 1.8 Mmol yr^{-1} or 360 Mg yr^{-1}. These field data negate the heat flow-based flux estimate suggesting that a geothermal Hg input to the oceans that would be 20−40 times larger (8). Furthermore, many trace metals such as Hg are scavenged by precipitating hydrous oxides of Fe and Mn and trapped close to their hydrothermal entry points. Accordingly, elevated concentrations of Hg are found in hydrothermally derived metal-rich sediments of the East Pacific Rise (29) and the Gorda Ridge (30).

Unfortunately, erroneous data from the literature were published by Camargo (31). He gives a value of 100 ng/L or 500 pM as the ocean concentration. Oceanic concentrations of Hg range between <1 and 10 pM (<0.2 and 2 ng/L) (27, 32−34; see recent review in ref 35). This gross error invalidates arguments that the ocean reservoir is so large that anthropogenic inputs are undetectable. It also ignores ocean mixing processes and the rapid recycling of mercury to the atmosphere due to volatilization (2). Estimates for the annual volatilization of Hg from the oceans are large ranging between 6 (3) and 10 Mmol (2). Moreover, a substantial fraction of these oceanic emissions represents the recycling of Hg that entered the marine environment from anthropogenic sources.

Lake Sediments and Peat Bogs as Historical Archives

Lake-Sediment Records. Anthropogenic Hg emissions on a global scale have been increasing for at least 100−150 years, which is a short period as compared to processes occurring over geological time. For example, it takes about 500−1000 years to mix the oceans (28, 36). Indeed, geological sources of Hg have varied very little during this modern industrial interval because large-scale geologic processes associated with plate tectonics are essentially constant over such short time intervals. In contrast, there is much evidence from the tabulation of various emission sources and from the historical record of Hg as preserved in lake sediments and peat bogs that indicate that significant human-related Hg interferences have been impressed on the Hg cycle over a broad geographic area.

An estimate of the potential impact from human-related Hg emissions to the atmosphere on a national basis can be developed for the United States. In an extensive recent effort, the Environmental Protection Agency (EPA) determined the overall annual fluxes (1990) of Hg from U.S. anthropogenic sources to the atmosphere to be ca. 1 Mmol (205 t yr^{-1}; 37). These amounts are considerably smaller (50−70%) than Watson's (38) estimate of 2.4 Mmol for the year 1975. Nevertheless, even 1 Mmol from the United States alone appears as a very large interference (ca. 20%) as compared to the annual worldwide natural terrestrial Hg emissions, which were estimated to be about 5 Mmol (2).

Lake-sediment records provide the most compelling evidence thus far that remote regions receive significant inputs of anthropogenic Hg by long-range atmospheric transport. Although numerous studies from European (39−42) and North American (43−51) sites show consistently elevated Hg levels (and fluxes) in recent sediments as compared to deeper preindustrial strata, Rasmussen (8) suggests that many (if not all) such profiles are generated by post-depositional diagenesis and diffusion (or advection) of Hg. As we argue elsewhere, such assertions, in general, are clearly not supported by recent experimental studies. Moreover, the lake-sediment records themselves show a pattern of recent Hg enrichment that is spatially and temporally coherent and not easily explained by either diagenetic processes or local geological sources.

In almost every well-dated sediment core from the midwestern United States, Hg concentrations (or fluxes) increase above background in the mid-19th century, shortly after the start of the industrial period (48, 52, 53). These sediment profiles range in length from <20 cm (Thrush L.) to more than 90 cm (Wirth L.), yet the timing of the increase is the same. Although Hg levels rise somewhat later in cores from northern Canada and Scandinavia (40, 42, 51), the chronology is again consistent among lakes within each geographic area. In lakes where multiple sediment cores have been analyzed, Hg increases are likewise synchronous, though sediment depth may vary by a factor of 2 or more (54). It seems highly improbable that temporally concordant patterns of Hg accumulation could be generated in numerous sediment profiles of varying thickness by post-depositional sedimentary processes.

Not only is the timing of Hg increase synchronous among sites, but also the magnitude of the change is remarkably similar across a large geographic area. In mid-continental North America, four studies of 40 U.S. and Canadian lakes (45−48) show modern Hg concentrations (or fluxes) elevated over background values by a ratio of 2.7 ± 0.9 (SD). A similar range of enrichments (modern/background) has been reported for northern Canada (2.3 ± 0.6, $n = 10$) (51) and Scandinavia (mean = 2.0−2.6) (39, 41), although ratios become higher for sites closer to industrialized areas of eastern Europe (mean = 5.0−6.3) where direct measurements of atmospheric Hg deposition are also higher (55). It is difficult to imagine how sediment diagenesis and Hg diffusion could generate such a convergence of enrichment ratios or the north−south increase that parallels measured Hg deposition in the Nordic countries. There is clearly variability in Hg loading among lakes [in some cases attributable to differences in local geology; e.g., Coker et al. (56)], but the similar timing and magnitude of recent increases and a concordance with spatial trends in measured Hg deposition argue strongly that long-distance transport of anthropogenic Hg is the cause of increasing Hg concentrations and fluxes in the sediments of lakes in sparsely populated regions that are not impacted by localized human-related sources of Hg.

A particularly convincing case for the utility of lake sediments in preserving the anthropogenic perturbation to the background Hg pattern is found in the work of Swain et al. (48) and Fitzgerald et al. (25, 57). Swain and co-workers (48) employed an innovatively simple but effective multiple core mass-balance approach to obtain modern and historical Hg flux information from the sediment record of seven "relatively undisturbed" lakes in Minnesota and Wisconsin. Regression analysis using the seven lakes yielded an average value for present atmospheric deposition of 12.5 μg m^{-2} yr^{-1} and a preindustrial value of 3.7 μg m^{-2} yr^{-1}. This represents an average enrichment ratio of 3.4. The recent depositional determination is similar to the estimate for atmospheric Hg deposition of 11.5 ± 3.8 μg m^{-2} yr^{-1} for the period of 1988−1990 (57). This estimate was established by Fitzgerald and co-workers for the Little Rock Lake region (one of the study lakes in the Swain et al. work) in Wisconsin. The good agreement between these two independent measures of modern Hg deposition is a strong indication that the Hg accumulating in lake sediments is not significantly affected by diagenetic processes and the anthropogenic signal is preserved.

An additional example of the utility of lake sediments to preserve the Hg accumulation signal is evident at a relatively unusual core site in Clay Lake, Northwestern Ontario. This lake received inputs of a chloralkali plant at Dryden, Ontario, during the 1960's, but Hg emissions ceased in 1970. A core was taken in 1971 by Armstrong and Hamilton (58), and it showed a peak at the surface of the sediment, consistent with recent inputs. In 1978, another core was taken by Rudd et al. (59), which showed the peak a few centimeters deeper, consistent with cleaner recent inputs. The latest core was obtained in 1995, and it shows the peak several centimeters lower than observed in 1978 (60).Thus, the three cores preserved accurate records of mercury consistent with known history. This is similar to the experience of Smith and Loring (61), but the availability of three cores from Clay Lake provides convincing evidence that diagenetic factors are not major influences on the Hg accumulation pattern in lake sediments.

Geological Context. High variability in background Hg concentrations in lake sediments has been offered as evidence that local geology, not long-distance atmospheric transport, controls the natural distribution of Hg in Canadian lakes (8). However, much of this variability may be explained by differences in sediment flux among lakes and by spatial variability in Hg sedimentation within lakes. Most of the Hg data in the studies Rasmussen (8) cites are based on single sediment collections from which Hg concentrations are calculated on a dry-weight basis (62). Concentration data, however, are very sensitive to differences in dilution by the flux of the sediment matrix, which is known to vary considerably among and within lakes (63−66). Mercury concentrations are also highly variable (by a factor of 10 or more) within lake basins because of density-dependent particle settling (focusing) (44, 54, 67). When these factors (sediment flux and focusing) are taken into account, either by the calculation of Hg flux ratios for individual cores or by

multiple-core studies of whole-basin Hg accumulation (*54*), much of the between-lake variability evident in raw concentration data vanishes. Variations of Hg concentrations in surface sediments do not automatically imply local differences in geological Hg supply as some have claimed (*8*, *68*).

Diagenetic Questions. The main argument against the use of sediments as historical records of atmospheric pollution is that diagenetic processes may bring Hg up to the sediment surface (as organo-mercury complexes, mercury organosulfide complexes, or vapor-phase Hg), followed by adsorption on oxides and hydroxides (Fe, Mn) with higher redox potential (*8*). Support for this view is contained in a study of Hg in slowly accumulating deep lake sediments and porewaters of four depositional environments in Lake Superior and Lake Michigan (*69*). However, if this were generally true, we should find (1) approximately the same kind of profiles for Fe, Mn, and Hg, (2) a probable correlation of Hg with Fe and Mn in surface sediments when comparing several lakes, and (3) no clear geographical pattern for Hg. None of these points are valid in several studies conducted by Verta and co-workers in Finland (*40, 41, 70*).

These researchers studied 25 lake profiles from 16 lakes for all major elements including Fe, Mn, Hg, Cu, Zn, Pb, and Cd (*40, 41, 70*). They found that the geographical patterns for Pb, Cd, Hg, and Zn in surface sediments (uppermost 5−10 cm) were very similar with the higher concentrations in the southern more industrialized areas. This distribution is preserved at depth in sediments deposited after the late 1800s (and shows an earlier increase in Pb deposition than other elements). In general, no such geographical or vertical pattern was found for Fe or Mn. Large variations in Fe and Mn occurred among lakes, and in most lakes a surface or subsurface maximum for Fe was found with no increase in Hg (*70*). There was also a positive correlation of sulfate in lake water with surface sediment Hg concentrations.

These observations are consistent with the measured higher atmospheric Hg deposition rates in southern Scandinavia (including one station in Finland) than in the north and with positive correlation of rainwater sulfate and rainwater Hg in the area (*55*). They do not support indications of any major effects of diagenetic processes on Hg partitioning and vertical movement in sediments.

Lucotte and co-workers (*51*) studied Hg in 12 oligotrophic lakes in northern Quebec, where the redox boundary layer lies at or very close to the water−sediment interface. Below this sharp redox gradient, sedimentary iron is reduced and liberated in pore waters and diffuses upward toward the water column. Only in rare cases could they identify a layer of iron re-precipitation at the very interface between the water column and the sediment (*71, 72*). Along with these early diagenetic reactions, loss of detrital organic matter through biodegradation does not appear to be measurable within the sediments as all profiles of organic carbon remain fairly constant below the immediate surface of the sediment (*51, 71, 72*). At the same time, all mercury profiles decrease progressively with depth to baseline concentrations in sediments older than about 1940. These trends appear totally decoupled from the iron or the carbon profiles (*51, 71, 72*) and thus clearly contrast with the Hg profiles reported for marine sediments (*73*). On the other hand, Dmytriw et al. (*71*) demonstrated that most Hg in a lake sediment (85%) was bound to NaOH-extractable organic matter. As the organic matter load remains fairly stable in the sampled sediments, the surficial increases of mercury concentrations in the sedimentary profiles thus represent larger Hg fluxes in the recent years.

It can also be argued that the inference of historic Hg fluxes from sediment cores requires that there has been no loss of Hg to pore water during the decomposition of humic material, no transport within the sediment column, and no Hg transfer between the sediment pore water and overlying waters. However, recent experimental studies indicate that these restrictions are overstated. Because gross sedimentation of Hg to the sediment surface exceeds net accumulation, there is likely to be recycling of Hg prior to incorporation in the permanent sediment record. The important factor is the depth of the zone of recycling. Gobeil and Cossa (*73*) found that post-depositional migration of Hg in pore waters in estuarine environments could not account for the surface enrichment. Similarly, and in lacustrine experiments, Hurley et al. (*52*) observed K_d values between sediments and pore waters to be about 10^4, suggesting a strong affinity for the particulate phase. Additionally, in long-term (12 and 27 month) sediment mixing−incubation experiments, Henning (*74*) and Hurley et al. (*75*) found little post-depositional redistribution of Hg due to diffusion in pore water. Hurley et al. (*75*) reported little or no diffusion below 2−4 cm, concluding that any pore water release to overlying waters must occur above the 2 cm sediment depth.

If deep pore water release were important in regulating hypolimnetic increases in anoxic lakes, pore water Hg concentrations of several hundred nanograms per liter would be necessary to create a diffusion gradient in sediments (*52*). No such levels have been reported by researchers using ultratrace metal clean techniques. Montgomery et al. (*76*) in their northern Quebec study, for example, report the absence of gradients in the profiles of dissolved Hg in sediment pore water, and the concentrations were found to be in equilibrium with the water column.

The work of Krabbenhoft and Babiarz (*77*) can be considered as an example where advection obscures Hg profiles in sediments. However, it must be stressed that the Krabbenhoft and Babiarz (*77*) study was not one designed for interpretation of historical profiles, but was rather a study of transport of Hg through a sandy, shallow aquifer. A sediment core for use in evaluating historical accumulation would never be taken in shallow, sandy sediments. In deep, high organic matter sediments (where cores for historical evaluation are commonly taken), advective processes are usually minimal.

Peat Bogs. The use of ombrotrophic peat bogs as depositional archives of Hg has been criticized on the basis of potential *in situ* diagenetic remobilization of Hg and contributions to the peat record that may be derived from localized gaseous evasion of elemental Hg from soils (*8*). However, a number of studies on the adsorptive capacity of mosses suggest high retention of Hg in peat (*78−82*). Speciation calculations for Fe, Al, and Mn show that the vertical distribution of metals in ombrotrophic bogs can be explained by the redox potential gradient in peat and seasonal fluctuations in water table depth (*83*). A geochemical model for metal mobility indicates that the Hg (and Pb) profiles in peat cores cannot readily be explained by redistribution processes but that they probably reflect changes in deposition to the bog over time (*83*). In this study, total Hg inventories (μg m^{-2}) for the past several hundred years were extremely consistent among hummocks, which indicates no significant horizontal movement of Hg as water drains laterally through the surface peat. Similarly, Urban et al. (*82*) found that Pb-210 inventories from Minnesota peatlands were similar to that expected from atmospheric deposition and that there was little evidence of transport of Pb from hummocks to hollows.

With respect to local gaseous evasion of Hg from soils, we note that the residence time of Hg^0 in the atmosphere is about 1 yr (*2, 13, 14, 84*). This long residence time allows for hemispheric-scale mixing of this gas before it is returned to the soil via precipitation and dry deposition. Furthermore, there is no evidence of large-scale temporal changes in the

magnitude of soil degassing of Hg^0 over time. This is analogous to the gaseous evasion of ^{222}Rn from soils. The deposition of ^{210}Pb (derived from ^{222}Rn), which has remained fairly constant over the past several hundred years, indicates that ^{222}Rn emissions from soils have also been relatively stable with time (85).

The discussion of peat cores from ombrotrophic bogs in Rasmussen's (8) review uses the Scandinavian study of Jensen and Jensen (86) as a case study. It is implied that soil Hg concentrations varying from one geological setting to another may partly explain the variability of Hg shown in these bogs. If instead another Scandinavian study (87; also referenced in ref 8) had been chosen to discuss the origin of Hg in these bogs, a different conclusion would have seemed more reasonable. Data from that study showed a uniform Hg level of 31 ± 8 ng g^{-1} (mean $\pm$ SD) at 50 cm depth in 13 ombrotrophic bogs distributed all over Norway, reflecting a general pre-industrial level. In recent peat layers, the Hg concentration had increased to 169 ± 32 ng g^{-1} in four bogs along the southern coast where the general impact of long-range atmospheric transport of pollutants from Europe is considerable (88). In central Norway (which is much less exposed to air pollution), the corresponding figure for four bogs was 66 ± 10 ng g^{-1}. These figures are very difficult to explain on the basis of soil-derived Hg, which might be expected to vary considerably with geological setting but not so much with time.

As documented, Hg accumulation trends in surface sediments are similar in a great variety of biological and geographical settings and seem independent of local geological conditions. For example, chronologies for Hg from lower latitude subtropical Florida wetlands (89) corresponded well with reported trends in lacustrine systems in Scandinavia, the northern United States, and Canada. Rood and co-workers (89) studied a total of 18 sediment cores from four major hydrologic units in the Florida Everglades and a dynamic linear wetland system along Florida's Atlantic coast (Savannas Marsh). The field sites varied from organic peat to predominantly marl spanning a wide range of geological conditions. Post-1985 Hg accumulation rates averaged 53 $(23-141)$ μg m^{-2} yr^{-1} with pre-1900 rates generally below 10 μg m^{-2} yr^{-1}. Recent Hg fluxes were an average of 4.9 times higher than those of ca. 1900 and appeared to be unrelated to geochemical conditions. Rates increased starting about 1940, coinciding with mid-century alterations of the hydrology of these wetlands and increased regional agricultural and urban development.

Geographic Gradients in Soils

Nater and Grigal (90) inferred a regional gradient in atmospheric Hg deposition and anthropogenic impact based on observation of a gradient in Hg burdens in forest floor (a partially-decomposed surficial organic layer) and surface mineral soils $(0-25$ cm depth) along a transect from northwestern Minnesota to northeastern Michigan. Rasmussen (8) has questioned the assumption that Hg in soil organic matter originates from the atmosphere and argues for the possibility that "... geological variations override regional deposition effects".

Concerning these objections, we note that atmospheric Hg deposition directly to soils, complexation of Hg by organic matter (91), and atmospheric inputs to leaves $(92-94)$ and hence to surface soils are well-documented processes (95). Significant plant uptake of Hg directly from deeper geological materials is unlikely because of limited root uptake of Hg (96) and the lack of a trend in Hg burdens in subsoils $(75-100$ cm depths) along the transect (90). Deeper geological materials are beyond the rooting zone. Consequently, for deeper geological sources to affect the Hg accumulation in soil, as discussed by Rasmussen (8), there must be an indirect

pathway requiring (1) volatilization/emission of Hg from the geological substrate as Hg^0; (2) diffusion to the soil—atmosphere interface; (3) Hg^0 uptake and/or Hg^0 oxidation and capture by leaves; (4) leaf senescence and deposition of Hg to the soil surface; and (5) retention by soil.

Such an indirect pathway may exist, and while we agree with Rasmussen (8) that it is possible that deep geological sources may be responsible for part of the Hg trends observed in forest litter and surficial mineral soils, the magnitude of this geological contribution would be small as compared with that from other atmospheric sources. The 155 study sites from Nater and Grigal (90) were located across a large region on a wide variety of bedrock and surficial materials, where the distributional pattern for Hg corresponded well with similar trends for Cd and Pb that were found in the same samples (97, 98). Pb and Cd are elements known to be atmospheric deposition products of anthropogenic activity. In addition, the metal distribution corresponded with known patterns of acid sulfate deposition across this region (99, 100) and with a general increase in anthropogenic activity toward the southeast. The high correspondence between Hg and other known atmospheric pollutants in this region strongly supports a regional gradient in anthropogenic atmospheric Hg deposition rather than undetermined trends in deep geological sources. The statistically significant trend produced by the 155 samples measured, by definition, shows that the regional trend was sufficiently clear to override local scale variability.

Summary

In summary, there is much published literature on the Hg cycle. While the quality of the data has improved dramatically over the past decade, one must be most diligent in evaluating the quality of published data for the cycling of Hg in the environment. Inaccurate results plague the Hg literature and mislead the unwary researcher. There has been much recent research on Hg in nature that has been reported and published especially in association with the 1990, 1992, 1994, and 1996 international conferences on "Mercury as a Global Pollutant". Nevertheless, critical information is lacking concerning natural and anthropogenic emissions, chemical speciation, and reactivity of Hg in the environment. This discussion stresses appropriately that, while our understanding of the biogeochemical cycling of Hg and assessments of the impact from anthropogenic Hg releases are as yet limited by many "uncertainties" in current knowledge, there is a broad and geochemically consistent data base indicating that, over large regions of the globe, human-related emissions and deposition during the past century have increased relative to natural sources $(5-7)$. Moreover, the signal is evident in remote regions. The results demonstrate that (carefully selected) lake sediments, bogs, and soils can be used as indicators of airborne Hg pollution.

We have noted that the critical concern associated with Hg in the environment is human exposure to MMHg through the consumption of fish and fish products. Current studies show the insidiously complex nature of the biogeochemical cycle of Hg. The production and bioaccumulation of MMHg in aquatic systems (especially piscivorous fish) and the resultant exposure to humans and wildlife are driven by chemical reactions and biologically-mediated transformations involving ultratrace amounts of Hg in the atmosphere and natural waters. It is apparent from the modern high quality work we have summarized that human-related Hg emissions are significant and that plausible linkages between the releases of Hg to the atmosphere from anthropogenic sources and the exposure to humans and wildlife to MMHg can be drawn. At present, however, a comprehensive quantitative assessment of the relationship between anthropogenic Hg releases to the atmosphere and the potential

exposure to people, wildlife, and terrestrial and aqueous systems is not possible. For example, deposition is critically dependent on the chemical form of Hg. Yet, there are few data on the physical and chemical species of Hg emitted from various sources (e.g., refs 101 and 102); near-source contamination is most likely related to the emission of ionic and particulate forms of Hg, while the farther field effects are associated with elemental Hg (*2*, *103*, *104*). There is much research to be done. Modern studies are providing a scientifically reasonable blueprint to use in designing and conducting experimental research on Hg in the environment. It does not appear that large natural sources of Hg have been missed, and there is evidence for the impact of atmospherically transported human-related Hg emissions in remote regions of the globe.

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