



ATMOSPHERIC MERCURY—AN OVERVIEW

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Abstract—This paper presents a broad overview and synthesis of current knowledge and understanding pertaining to all major aspects of mercury in the atmosphere. The significant physical, chemical, and toxicological properties of this element and its environmentally relevant species encountered in the atmosphere are examined. Atmospheric pathways and processes considered herein include anthropogenic as well as natural sources of Hg emissions to the atmosphere, aerial transport and dispersion (including spatial and temporal variability), atmospheric transformations (both physical and chemical types), wet and dry removal/deposition processes to Earth's surface. In addition, inter-compartmental (air–water/soil/vegetation) transfer and biogeochemical cycling of mercury are considered and discussed. The section on numerical modelling deals with atmospheric transport models as well as process-oriented models. Important gaps in our current knowledge of mercury in the atmospheric environment are identified, and suggestions for future areas of research are offered. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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1. OCCURRENCE, PHYSICAL, CHEMICAL AND TOXICOLOGICAL PROPERTIES OF MERCURY

More than 25 mercury-containing minerals are known to occur in Earth's mantle, yet the average crustal abundance of this element is only about 0.5 ppm ($\mu\text{g g}^{-1}$). Its principal ore is the mineral cinnabar (HgS), which has been known and used by humankind for more than 2300 years. Major mercury deposits are located at Almadén (Spain), Idria (Slovenia) and Monte Amiata (Italy). In North America, significant cinnabar deposits occur in California (Almadén) and British Columbia (Pinchi Lake).

Mercury (Hg) is found among the transition elements of the Periodic Table, in Group IIB along with zinc and cadmium. As can be seen from their oxidation potentials (E° for $\text{M} = \text{M}^{2+} + 2e^-$ is 0.762, 0.402 and -0.854 V for Zn, Cd, and Hg, respectively), zinc and cadmium are fairly electropositive, whereas mercury is relatively inert. Hg° readily combines with noble metals (Au, Ag, Pt, Pd) to form alloys ("amalgams"). Amalgamation with gold provides the basis for pre-concentration of Hg from samples of ambient air prior to analytical determination.

Hg is the only metal which is a liquid at STP. Other unique and/or technologically important physico-chemical properties include: high surface tension (Hg° does not wet glass), high specific gravity (13.55 at 20°C), low electrical resistance, and a constant volume of expansion over the entire temperature range of its liquid state. Because of its many useful properties, its economic importance in commerce, industry, mining, metallurgy, manufacturing, medicine and dentistry increased rapidly during the Industrial Revolution.

There are seven stable isotopes of mercury (yielding a characteristic isotope pattern easily identifiable in mass spectrometric investigations) plus four unstable (radioactive) isotopes, two of which (^{197}Hg with a half-life of 64.1 h and ^{203}Hg with a half-life of 46.6 d) are valuable in instrumental neutron activation analysis, as well as in radio-labelled compounds of mercury, owing to their decay by emission of readily detectable γ rays.

Mercury is capable of existing in three oxidation states: 0, +1 and +2. In the atmospheric environment, mercury exists predominantly in the elemental form (oxidation state 0) and in the +2 oxidation state, with the +1 oxidation state being very rare, if it exists at all. The chemical and physical properties of mercury and its compounds dominate their behavior in the atmosphere and their significance as environmental contaminants. Selected physical and chemical

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properties of some environmentally relevant mercury species are summarized in Table 1. Inspection of Table 1 reveals the extremely wide range of physico-chemical properties (ranging many orders of magnitude in the case of vapor pressure, water solubility and Henry's law coefficients) which characterizes elemental mercury and its environmentally significant inorganic and organic compounds.

As originally shown by the seminal work of Jernelöv in Sweden, inorganic forms of mercury released into the environment can be converted, by naturally occurring biological processes, into the highly toxic methyl mercury (MeHg) species. The ability of MeHg to bio-concentrate more than a million-fold in the aquatic food chain is the main reason for concern about emissions/mobilization of mercury into the biosphere. This has resulted in regulatory fish consumption guidelines and health advisories in Scandinavia, North America and elsewhere in the industrialized world. Like polychlorinated biphenyls (PCBs), methyl mercury can cross the blood-brain barrier, which normally protects the human brain from toxins in the blood stream, and is also able to penetrate the placenta, thus, exposing the fetus to this potent neurotoxin. Methyl mercury and mercuric chloride are listed on USEPA's Integrated Risk Information System (IRIS) as "Class C" or "Possible Human Carcinogen" substances.

2. ATMOSPHERIC PATHWAYS AND PROCESSES

Once released into the atmosphere (usually the planetary boundary layer within the troposphere), mercury is subjected to a variety of physical and/or chemical or photochemical processes/interactions. This paper will build on a conceptual framework of atmospheric pathways and processes—the atmo-

spheric "emission-to-deposition cycle"—shown in Fig. 1. In this scheme, the specific pathway(s) actually taken and the fate experienced by a given species of mercury depend upon many factors, both its own physical/chemical characteristics, as well as the prevailing environmental/meteorological conditions existing at any given time and place.

The most important characteristics of mercury that set it apart from the other metals commonly found in the atmosphere, are its tendency to be readily re-emitted to the air once deposited to surfaces, and the fact that mercury exists in ambient air predominantly in the vapor phase whereas the other metals are almost exclusively present in the solid phase, being associated with airborne particulate matter (aerosols). Being in the vapor phase, relatively inert to chemical attack by other air constituents/contaminants and only sparingly soluble in (pure) water, imparts to elemental mercury an atmospheric residence time of the order of 1 yr (Slemr *et al.*, 1985; Lindqvist and Rodhe, 1985), thus, supporting the concept of mercury as a "global pollutant". Even allowing for an uncertainty factor of 2 (i.e. a global atmospheric residence time of Hg⁰ in the range of 1/2–2 yr), the low end of the resultant estimate is still quite long when compared with other metals since they are preferentially associated with airborne particulate matter which typically has an atmospheric residence time of the order of days or, at most, a few weeks (depending on, *inter alia*, aerosol size/characteristics, prevailing meteorology).

2.1. Sources and emissions

2.1.1. *Natural sources and emissions.* Mercury is released or re-emitted into the atmosphere by a number of natural processes/emission sources, including outgassing of the earth's mantle/crustal material,

Table 1. Physical/chemical properties of mercury and some of its compounds

| Property | Hg ⁰ | HgCl ₂ | HgO | HgS | CH ₃ HgCl | (CH ₃) ₂ Hg |
|---|--|--|------------------------------------|-----------------------------------|---|--|
| Melting point (°C) | -39 | 277 | dcomp. @ + 500°C | 584 (sublim.) | 167 (sublim.) | --- |
| Boiling point (°C) | 357 | 303 | --- | --- | --- | 96 |
| Vapor pressure (Pa) | @ 1 atm 0.180 @ 20°C | @ 1 atm 8.99 × 10 ⁻³ @ 20°C | 9.20 × 10 ⁻¹² @ 25°C | n.d. | 1.76 @ 25°C | 8.30 × 10 ³ @ 25°C |
| Water solubility (g/l) | 49.4 × 10 ⁻⁶ @ 20°C | 66 @ 20°C | 5.3 × 10 ⁻² @ 25°C | ~ 2 × 10 ⁻²⁴ @ 25°C | ~ 5–6 @ 25°C | 2.95 @ 24°C |
| Henry's law coefficient [Pa m ³ mol ⁻¹] | 729 @ 20°C 0.32 ^a @ 25°C 0.18 ^a @ 5°C | 3.69 × 10 ⁻⁵ @ 20°C | 3.76 × 10 ⁻¹¹ @ 25°C | n.d. | 1.6 × 10 ⁻⁵ @ 15°C and pH = 5.2 | 646 @ 25°C 0.31 ^a @ 25°C 0.15 ^a @ 0°C |
| Octanol-water partition coefficient | 4.2 ^a | 0.5 ^a | --- | n.d. | 2.5 ^a | 180 ^a |

Sources: Schroeder *et al.* (1991) and references cited therein; Wallschläger (1996) and references cited therein.

^aDimensionless units.

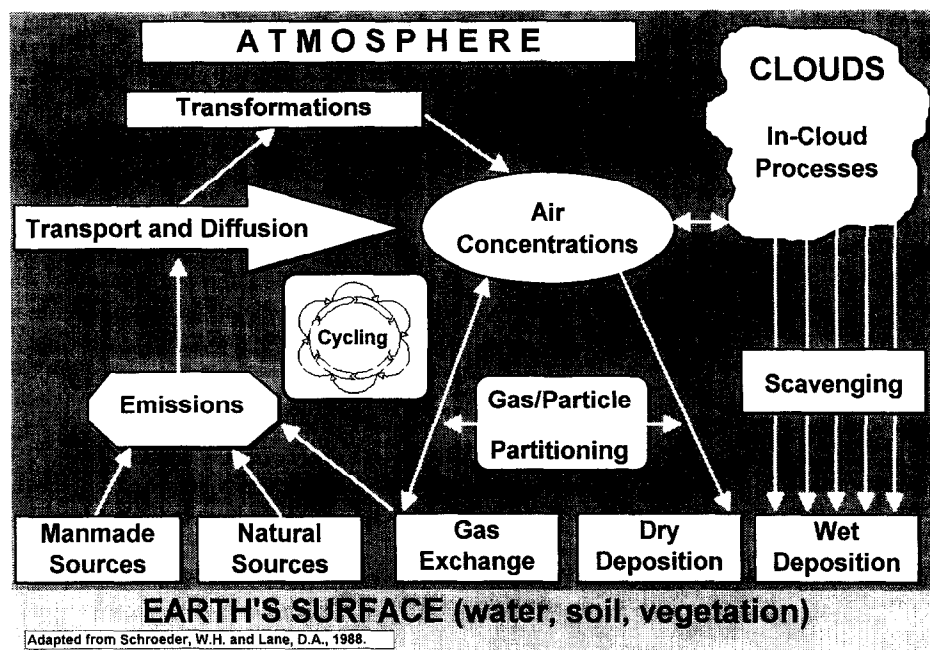


Fig. 1. Conceptual framework of the atmospheric emissions-to-deposition cycle for mercury.

Note: "emissions" also include re-emission of previously deposited Hg, so called "recycled" mercury.

evasion from surficial soils, water bodies (both fresh- and salt-water), vegetation surfaces, wild fires, volcanoes, and geothermal sources. Re-emission involves gaseous evasion of previously deposited Hg° . Only a limited number of published measurements/estimates exist of Hg emission rates ("fluxes") from natural surfaces (e.g. Schroeder *et al.*, 1989). The reader is referred to Section 2.4 for details. More definitive data are urgently required to better constrain current estimates of Hg emissions from natural sources/surfaces, and it is of critical importance to separate these aggregated emissions into primary emissions from natural surfaces or geological sources and re-emitted Hg originally released by or discharged from anthropogenic sources.

Mercury is thought to be released from natural sources mainly as Hg° vapor, but mercury bound to particulate matter/aerosols may originate from some types of natural sources or processes (e.g. volcanoes or soil erosion). Although Hg° is likely to be the predominant chemical species of mercury emitted from natural sources, emissions of other species, e.g. dimethyl mercury (DMM), or volatile inorganic Hg compounds, cannot be ruled out. Albeit DMM, if released into the atmosphere from any source (natural or anthropogenic), is expected to be rather short-lived due to rapid oxidation by ubiquitous hydroxyl radicals in the atmosphere (Niki *et al.*, 1983a).

Estimates of mercury emissions from natural sources which were published between 1970 and 1982 have been reviewed by Lindqvist *et al.* (1984). Confronted

with values that ranged from 2 500 to 30 000 tonnes yr^{-1} for natural Hg emissions globally, these authors considered the lower end of the given range as the most reliable. Since then, Nriagu and Pacyna (1988) and Nriagu (1989) have estimated global natural mercury emissions to be approximately 3 000 ton per annum. According to Lindqvist *et al.* (1991), this would correspond to an average global flux for natural mercury emissions of about $6 \text{ g km}^{-2} \text{ yr}^{-1}$ ($0.7 \text{ ng m}^{-2} \text{ h}^{-1}$). Recent estimates of the natural (pre-Industrial Revolution) mercury budget and inter-compartmental environmental fluxes are contained in the global mercury model proposed by Mason *et al.* (1994).

2.1.2. *Anthropogenic sources and emissions.* Prior to the 1970s, chlor-alkali plants were the single largest source category of anthropogenic Hg emissions to the environment in many industrialized countries. Since then, the implementation of regulatory controls or guidelines on this as well as other sources of anthropogenic mercury emissions—coupled with, for example, changes in the mix of fossil fuels used to generate power and heat for industrial, commercial and residential use—has substantially changed the ranking among the remaining source categories. Coal combustion, waste incineration (of municipal refuse, medical waste, and sewage sludge) as well as metal smelting, refining and manufacturing are currently major source categories in the industrialized world. The relative ranking of the various source categories will vary from one jurisdiction to another, depending upon socio-economic, demographic and other factors.

Properly gridded (i.e. spatially resolved) emission inventories are one of the most important input parameters for numerical models currently used to simulate the atmospheric pathways and behavior of mercury within the framework illustrated in Fig. 1. However, considerable time and effort are required to compile emission inventories given the continually changing nature of usage patterns and losses to the environment of metallic mercury and its industrially significant compounds (for example, due to the introduction of various control technologies). Therefore, emission inventories are almost always outdated before they are available to the scientific and regulatory communities who rely upon them.

Using emission factors for the release of mercury from 7 source categories, Nriagu and Pacyna (1988) estimated world-wide anthropogenic mercury emissions for the year 1983 to have been in the range of 910–6200 tonnes, with a median value of 3560 ton. An inventory of historical anthropogenic mercury emissions to the air in Sweden (for the period from 1860 to 1987) and estimates for the mid to late 1980s, broken out into point and diffuse source categories, are contained in Lindqvist *et al.* (1991). Anthropogenic mercury emissions for 1987 and 1988 were compiled by Axenfeld *et al.* (1991) for 27 European countries and came to a total of 726 ton per annum.

The previous two years have seen a veritable flurry of activities by industry and regulatory agencies in Europe and North America to update anthropogenic emission inventories for mercury (and a number of other heavy metals). These activities were prompted by efforts of UN-Economic Commission for Europe (ECE) member nations, including the United States and Canada, to prepare draft Protocols for heavy metals and for Persistent Organic Pollutants (POPs) under the Convention of Long-Range Transport of Air Pollutants (LRTAP). This effort should result in the publication of an up-to-date, authoritative data base for Hg emissions in much of the industrialized Western world. Although little information is available, anthropogenic Hg emissions in the Southern Hemisphere exist and may be substantial in some regions (e.g. the Amazon).

In the United States, the Clean Air Act Amendments of 1990 also stimulated a great amount of research into environmental aspects of mercury, including inventories of anthropogenic sources of mercury. Some references to recent literature on this topic include: US EPA, 1993, 1996; Porcella *et al.*, 1996; Pirrone *et al.*, 1996. Estimated values (ton a^{-1}) for 1990 from the major U.S. anthropogenic source categories are: fossil-fuel combustion (62.1), municipal and medical waste incineration (56.6), manufacturing/smelting (27.7) and other sources (7.7) for a total of 154.1 ton a^{-1} . It should be recognized that there can be large variations in the geographic distribution of anthropogenic sources both in the Northern and Southern Hemispheres. A discussion of uncertainties

associated with current anthropogenic mercury emission estimates can be found in Pai *et al.* (1997).

Canadian anthropogenic mercury emissions for the year 1990 were estimated to be 38.8 tonnes (Environment Canada and Natural Resources Canada, 1996). At that time, the three largest contributions came from the primary base metals sector (77.4%), followed by coal-fired power plants (10.3%) and then municipal solid waste and sewage sludge incineration (8.4%). Since then, process improvements made at a number of Canadian base-metal smelters may have resulted in a significant reduction of mercury emissions from that industrial sector.

2.1.3. Physical and chemical speciation of emissions. So far, estimates of natural emissions of mercury have not paid much attention to either physical or chemical speciation of the emissions. Hopefully, this situation will be remedied in the future. Similarly, inventories for anthropogenic mercury emissions produced prior to the 1980s generally considered only the total amount of mercury released to the atmosphere. However, most (if not all) of the more recent anthropogenic source inventories recognize the importance of differentiating between mercury emitted in different physical and/or chemical forms.

Because of their significantly different atmospheric behavior, at least three species of mercury should be explicitly dealt with in emission inventories: elemental mercury (in the gas phase), gaseous divalent inorganic mercury compounds, and particulate-phase Hg (see Section 2.2.1). A new technique for measuring gaseous water-soluble Hg(II) species in ambient air has been reported (Stratton and Lindberg, 1995). The importance of mercury speciation on mercury transport and deposition was demonstrated in a modelling study by Petersen *et al.* (1995). The atmospheric deposition of mercury to the North Sea and the Baltic Sea was calculated using the EMEP-Hg model. The model was run using two different emission scenarios: with all emissions as Hg^0 , and with a given fraction of the emissions in the form of Hg(II). The total emissions of mercury were the same in both cases. With Hg(II) emissions corresponding to 10–60% of the total amount emitted (depending on source category), the total deposition to the two sea areas is increased by more than a factor of 2, clearly demonstrating the importance of Hg(II) species on deposition.

An important aspect of speciation of mercury is the possibility of emissions of methylated mercury forms, i.e. monomethyl mercury or DMM. Both species have been shown to be present in air at pgm^{-3} levels (Bloom *et al.*, 1993; Brosset and Lord, 1995) and MeHg has also been found in precipitation (Bloom and Watras, 1989; Lee and Iverfeldt, 1991; Hultberg *et al.*, 1994; Munthe *et al.*, 1995a, b). The source(s) of the atmospheric methylated mercury forms is/are not well known. Degassing of DMM from the ocean in upwelling areas, followed by chemical degradation to MeHg has been suggested (Prestbo and Bloom, 1996).

Further studies of potential sources of atmospheric DMM and MeHg are clearly needed (see Section 2.4.2).

2.2. Atmospheric transport and dispersion

2.2.1. *Spatial variability.* Atmospheric dispersion/transport of mercury is generally considered to be an environmental phenomenon on global, regional and local scales (Expert Panel, 1994). The spatial scale will depend on the chemical and physical forms of the mercury and the rate of interconversion among species. The three predominant mercury species exhibit different transport characteristics. Hg^0 is capable of being transported aerially for very long distances (tens of thousands of kilometers), Hg(II) species in the gas phase can be expected to be removed in the vicinity of a few tens to a few hundreds of kilometers from their source, and particulate-phase mercury, Hg(p) , species are likely to be deposited at intermediate distances, depending on aerosol diameter/mass.

Few studies have been designed to identify spatial gradients in atmospheric Hg. A network of eight sampling sites across the Nordic countries revealed a factor of three increase in annual wet deposition of Hg toward the southwestern part of the region, which is closer to probable source areas on the European continent (Iverfeldt, 1991a). For a network of three sites in Michigan, annual wet deposition of mercury differed by nearly a factor of two between the northern and southern parts of the state (Hoyer and Keeler, 1995). Regional differences in precipitation amount accounted for only part of these spatial differences in annual deposition.

Spatial differences in gas- and particle-phase mercury measurements were less definitive in these studies. Gas-phase mercury for the Nordic network was measured at only three sites, and the annual average concentration for the southern site was approximately 15% higher than the northern and central sites, which both had the same average concentration (Iverfeldt, 1991a). Annually averaged concentrations of particle-phase Hg varied even less between these sites, although episodic events with higher gas- and particle-phase mercury concentrations occurred more frequently at the southern site which was nearest to continental source areas (Iverfeldt, 1991a). In Michigan, annually averaged concentrations of gas-phase Hg were approximately 15% different between the northern and southwestern Michigan sites, but annually averaged Hg(p) concentrations were higher by a factor of two at the southern sites compared to the northern site (Keeler *et al.*, 1995).

2.2.2. *Temporal variability.* Seasonal variations in atmospheric mercury concentrations have been observed; albeit, few studies have adequately sampled across multiple seasons. For total gaseous mercury (TGM), a seasonal trend was observed at the Nordic network sites, with somewhat higher concentrations during the winter (Lindqvist *et al.*, 1991). Seasonal

differences in TGM were not significant at rural locations in the Great Lakes region nor in Vermont (Burke *et al.*, 1995). Nevertheless, TGM concentrations in ambient air can exhibit a strong diel cycle under certain meteorological conditions, especially in layers of air near the earth's surface (Kvietkus and Sakalys, 1994; Schroeder *et al.*, 1995). In general, the degree of variability observed at a given location is influenced largely by the proximity or absence of strong Hg-emitting point- or area sources. Seasonal differences in Hg(p) tend to be significant, with higher concentrations in winter (Iverfeldt, 1991a; Keeler *et al.*, 1995), whereas mercury concentrations in precipitation and wet deposition fluxes of Hg are higher in summer compared to winter (Lamborg *et al.*, 1995). For more information on this topic, the reader is directed to the report prepared by the Expert Panel on Mercury Atmospheric Processes (1994). American and Canadian scientists are collaborating on a new bi-national network for Hg wet-deposition monitoring. The Mercury Deposition Network (MDN) operates ~25 sites in North America with the objective of quantifying spatial and temporal trends in Hg and MeHg wet deposition (Lindberg and Vermette, 1995; Vermette *et al.*, 1995).

2.3. Atmospheric transformations and removal processes

Mercury is removed from the atmosphere through both wet and dry processes acting on Hg^0 , Hg(II) and Hg(p) species. It is not possible to select one of these processes as the most important since the actual deposition flux at a specific site will depend on the individual concentrations of the different mercury species (which is highly variable for Hg(II) and Hg(p)), the presence of other atmospheric constituents involved in the removal processes (i.e. aerosols, ozone), and the type of land use/cover/surface.

Nevertheless, some important statements about the relevance of different removal processes can be made (see discussions below):

- In air containing high concentrations ($> \sim 100 \text{ pg m}^{-3}$) of Hg(II) and/or Hg(p) , these species will dominate the deposition of mercury, both wet and dry.
- In air containing moderate or low concentrations of Hg(II) and Hg(p) , the wet deposition of mercury will mainly depend on the oxidation of Hg^0 in gas and/or aqueous phase processes involving ozone or other oxidants.
- In forested areas, dry deposition is of equal or greater importance than wet deposition.

2.3.1. *Atmospheric reactions.* Only a few chemical reactions of mercury, under conditions relevant to the atmosphere, have been studied in laboratory investigations. Oxidation processes for Hg^0 involving ozone have been identified in the gas phase (Hall, 1995) and in the aqueous phase (Munthe, 1992). Both gaseous- and aqueous-phase processes are potentially important for the overall atmospheric cycling of mercury.

Field observations of apparent interactions between TGM, O₃ and water vapor have been published recently (Poissant, 1997). Oxidation of Hg⁰ may, to some extent, be balanced by reduction processes occurring simultaneously in the atmosphere. To date, only one such process has been identified: the aqueous-phase reduction of Hg(II) by S(IV) (Munthe *et al.*, 1991). On a global scale the importance of this specific reaction is probably limited, but other reduction processes may exist (for example, photochemically initiated reduction of Hg(II) species).

Atmospheric processes may also play a key role in the formation of particulate mercury species, Hg(p). Several investigators have proposed mercuric oxide, HgO, as the primary product of gas-phase oxidation of Hg⁰ by O₃, NO₃ and other oxidants (Schroeder *et al.*, 1991; Hall, 1995; Sommar, 1997). The vapor pressure of HgO is very low and, if produced in the atmosphere, it will most likely be transformed into the solid state. A condensation of pure HgO is unlikely given the low concentrations in ambient air, so it will probably be sorbed by available aerosol surfaces.

Current knowledge of the atmospheric chemistry of MeHg and DMM is limited to the results of investigations of DMM reactions with different radical species. DMM has been shown to react with OH and Cl (Niki *et al.*, 1983a, b), O(³P) (Lund-Thomsen and Egsgaard, 1986) and NO₃ (Sommar *et al.*, 1996). Of the above processes, the reactions with OH and Cl are of potential importance since they lead to the formation of MeHg, known to be present at low concentrations in air and precipitation. The nitrate radical reaction, on the other hand, is reported to yield only inorganic forms of mercury and could provide a competing reaction during night-time conditions.

2.3.2. Deposition to forested ecosystems. Atmospheric deposition of Hg on forest canopies is reflected in the chemical composition of throughfall—precipitation after it falls through a forest canopy (Lindberg *et al.*, 1994). Iverfeldt (1991b) and Lindberg *et al.* (1991) have shown that wet deposition cannot account for all the mercury reaching the forest floor via throughfall and litterfall. Dry deposition to the

forest canopy is the most likely explanation: dry deposited Hg may be washed off plant surfaces, elevating concentrations of Hg in throughfall over those in precipitation. Dry-deposited Hg reaches plant surfaces through 3 processes: adsorption and oxidation of gaseous Hg⁰ (Munthe *et al.*, 1995); uptake of Hg⁰ by stomata (Lindberg *et al.*, 1992); or adsorption of Hg(II) and Hg(p) (Lindberg *et al.*, 1994). The Hg may then be either washed off by precipitation, or retained by the leaves and eventually deposited as litterfall to the forest floor where it could be absorbed by the roots of trees, along with water-soluble Hg species already present in the soil. Various studies suggest, however, that the absorbed mercury is not translocated from roots to leaves in significant amounts relative to those available in the root zone (Gilmour and Miller, 1973; Lindberg *et al.*, 1979; Godbold and Huttermann, 1988; Lodenius, 1995). Hg⁰ re-emission through plant/tree leaves has been investigated recently (Hanson *et al.*, 1995; Lindberg, 1996).

Mercury in throughfall and litterfall has been studied in 3 forested ecosystems: a boreal forest at Lake Gårdsjön in southwestern Sweden (Iverfeldt, 1991b; Hultberg *et al.*, 1994; Munthe *et al.*, 1995a, b); two temperate forests: an oak-hickory forest at Walker Branch Watershed, Tennessee (Lindberg *et al.*, 1994; Lindberg, 1996), and a mixed-hardwood forest in the Lake Champlain Watershed, Vermont (Rea *et al.*, 1996). The Swedish studies revealed that dry deposition of methyl mercury is as important as its wet deposition and that atmospheric deposition of MeHg may contribute significantly to the total load of methyl mercury to aquatic ecosystems in that region. The deposition of mercury and methyl mercury in precipitation, throughfall, and litterfall from these forests are summarized in Table 2. This table clearly shows that deposition of Hg in throughfall is significantly greater than deposition in precipitation. Similarly, the amount of Hg deposited in litterfall is much greater than that deposited in throughfall. The few available foliage and litterfall Hg concentration measurements suggest that atmospheric mercury may accumulate on or be absorbed by leaves (or needles)

Table 2. The deposition of mercury and methyl mercury in precipitation, throughfall, and litterfall from forested watersheds

| Location | Precipitation ($\mu\text{g m}^{-2}$) | | Throughfall ($\mu\text{g m}^{-2}$) | | Litterfall ($\mu\text{g m}^{-2}$) | | Reference |
|-----------------------|---|------|---|------|--|---------|-----------|
| | Hg | MeHg | Hg | MeHg | Hg | MeHg | |
| Lake Gårdsjön 1987-88 | 12 | — | 17-19 | — | 25 | — | 1 |
| Sweden 1990-92 | — | 0.41 | — | 0.18 | — | 0.6 | 2 |
| 1991-94 | 9.7 | 0.34 | 15.4 | 0.20 | 10.4 | 0.24 | 3 |
| Walker Br. Watershed | 13.5 | — | 16.5 | — | (6 mo.) | (6 mo.) | 4 |
| U.S.A. 1991-95 | 10 | — | 14 | — | 30 | — | 4 |
| Lake Champlain | 7.9 | — | 11.7 | — | 13 | — | 5 |
| U.S.A. 1994 | — | — | — | — | — | — | 5 |

Note. ¹Iverfeldt (1991b); ²Hultberg *et al.* (1994); ³Munthe *et al.* (1995a); ⁴Lindberg (1996); ⁵Rea *et al.* (1996).

and is later deposited to the forest floor in litterfall (Lindberg, 1996; Rea *et al.*, 1996). The latter authors estimated that $\sim 80\%$ of the increase in the Hg content of foliage and litterfall was due to accumulation and absorption of dry-deposited atmospheric mercury.

2.4. Air-surface exchange of gaseous species

In comparison to the other heavy metals, one of the major distinguishing features of Hg is the great extent to which it is re-circulated in the environment via the atmosphere. Since 1890, $\sim 2 \times 10^5$ tonnes of Hg have been deposited to terrestrial soils (Expert Panel, 1994). The re-emission of mercury from this large pool may represent a significant global flux to the atmosphere. During the last 10 years, there have been a considerable number of scientific studies which have focused on air-surface exchange of Hg. These investigations have arisen out of a growing recognition of the importance and extent of intermedia transfer processes and environmental cycling involving Hg^0 (and possibly methylated-Hg species also).

Wet deposition (of "dissolved" Hg(II) species) and dry deposition (of particulate Hg) are generally considered to be uni-directional processes involving transfer of mercury from the atmospheric compartment to the earth's surface. However, air-surface exchange of Hg^0 can occur bi-directionally, allowing re-emission or recycling of this trace element from a given surface to the atmosphere. If oxidized forms of Hg, i.e. Hg(II) species, are deposited on water, soil or vegetative surfaces they will tend to remain non-volatile and hence relatively immobile unless chemical, photolytic or biological reduction to the elemental form (or to DMM) occurs. In this section we will deal specifically with Hg^0 since it is the major Hg species involved in extensive environmental cycling. DMM, even if it is released into the atmosphere from certain environmental media (Wallschläger, 1996), is not likely to be extensively recycled owing to its rapid degradation and short lifetime in the atmosphere. Facilitated by its remarkable volatility and its chemical persistence, it is the pronounced tendency of Hg^0 mobilized into the environment to participate easily and repeatedly in air-surface exchange/global distillation processes that results in its dispersion in the environment on regional, continental and global scales.

2.4.1. *Air-water exchange.* The most widely employed paradigm describing mass transfer (i.e. flux) of chemicals across the air-water interface was derived by Liss and Slater (1974). At equilibrium (as predicted by Henry's law) there is no net transfer of Hg^0 in either direction and the system is in a dynamic steady state. Thus, in principle, at least, there should exist a "point of reversal" (analogous to the "compensation point" proposed by Hanson *et al.* (1995) for foliar exchange of Hg^0 vapor) at which the direction of flux changes from evasion to deposition or vice versa, corresponding to the aquatic system going from an "oversaturated" state to an "undersaturated" state relative

to the Hg^0 concentration in the layer of air above the water surface. It is curious that the large majority of aquatic ecosystems studied so far have been found to contain dissolved gaseous mercury (thought to be mainly Hg^0) at concentrations which are supersaturated relative to the equilibrium values predicted by Henry's law. Indeed, evasion of Hg^0 has been suggested to occur both from the oceans (Fitzgerald *et al.*, 1983; Kim and Fitzgerald, 1986; Fitzgerald, 1986) and from inland waters (Schroeder and Fanaki, 1988; Schroeder *et al.*, 1989; Xiao *et al.*, 1991; Vandal *et al.*, 1991; Fitzgerald *et al.*, 1991; Schroeder *et al.*, 1992; Vandal *et al.*, 1993, 1995), but has only been measured directly in a few cases (Schroeder *et al.*, 1989; Xiao *et al.*, 1991; Lindberg *et al.*, 1996). Whereas the earlier estimates for gaseous-Hg evasion from aquatic systems were based on model calculations, or were derived from field measurements with flux chambers, more recent work has invoked micro-meteorological methods for direct, ambient air (vertical concentration gradient) flux measurements (e.g. Meyers *et al.*, 1996; Lindberg *et al.*, 1996).

On a global scale it is estimated (Mason *et al.*, 1994) that the oceans release ~ 2000 tonnes of $\text{Hg} \text{ yr}^{-1}$, which is in balance with the total deposition flux to the marine environment. In the global Hg model of these authors, the ocean flux is one-half as large as the total annual anthropogenic emissions and twice the "natural" evasion flux of Hg from all terrestrial sources. The relative importance of Hg emitted from freshwater systems compared to evasion from soils or other terrestrial emission sources is still largely unknown, but could make a significant contribution to Hg budgets and the biogeochemical cycling of mercury on regional and/or global scales.

2.4.2. *Air-soil exchange.* Soils, especially the humus layer of forest soils, are often viewed as a "net sink" for the Hg pool ("source") present in the atmosphere (Lindqvist *et al.*, 1984; 1991; Johansson *et al.*, 1991). The studies by Lindberg and co-workers of biogeochemical cycling of Hg in the forest at Walker Branch Watershed (Tennessee) have shown that (at least for this forest ecosystem) the largest Hg pool resides in the soil (similar to the situation for most nutrients and other trace elements) and, furthermore, that about 75% of the total Hg soil pool is concentrated in the organic-rich A horizon. Nevertheless, some volatilization of mercury does occur — at least during the warmer times of the year — from boreal forest soils (Schroeder *et al.*, 1989; Xiao *et al.*, 1991), from soil lysimeters (Schlüter *et al.*, 1995a, b; 1996) and from "background" forest soils in more temperate climatic regions (Lindberg *et al.*, 1992; Kim *et al.*, 1995) at emission rates on the order of $1\text{--}10 \text{ ng m}^{-2} \text{ h}^{-1}$. The first quantitative measurements of MeHg and inorganic Hg^0 emissions from soil amended with municipal sewage sludge yielded daily average emission flux values of $12\text{--}24 \text{ pg m}^{-2} \text{ h}^{-1}$ and $\sim 100 \text{ ng m}^{-2} \text{ h}^{-1}$, respectively (Carpi *et al.*, 1997).

This overview will concentrate on some recent studies, especially those in which volatilization fluxes have been experimentally determined in the field. The work of Schroeder *et al.* (1989) and Xiao *et al.* (1991) revealed that Hg was deposited to soil surfaces in the Swedish boreal forest during the winter and was emitted or re-emitted during the rest of the year. Volatilization fluxes measured over boreal forest soil were generally less than $5 \text{ ng m}^{-2} \text{ h}^{-1}$ and exhibited both daily and seasonal variability. By comparison, background forest soils in eastern Tennessee, U.S.A., during the summer and fall of 1993 exhibited emission fluxes as high as $30 \text{ ng m}^{-2} \text{ h}^{-1}$ with a mean value and standard deviation of $7.5 \pm 7.0 \text{ ng m}^{-2} \text{ h}^{-1}$. Even higher Hg evasion flux values ($> 50 \text{ ng m}^{-2} \text{ h}^{-1}$) have recently been reported over contaminated flood plain soils (Lindberg *et al.*, 1995a, b; Wallschläger *et al.*, 1997), and over contaminated mill tailings as well as over naturally enriched ("mercuriferous") soils in Nevada, U.S.A. (Gustin *et al.*, 1996). Studies involving field measurements of mercury volatilization fluxes over a variety of soils have been summarized in Table 3. This table is not intended to be comprehensive, but rather indicative of the general magnitude of volatilization fluxes associated with different types of soils or solid waste deposits. The reader is referred to Schroeder *et al.* (1989) for a review of the substantial body of earlier literature dealing with deposition and emission processes of Hg from soil surfaces (both natural and contaminated).

2.4.3. Air-vegetation exchange. Any discourse on the biogeochemical cycling of Hg in terrestrial and aquatic ecosystems would not be complete without consideration of the exchange (uptake and release) of mercury by vegetation. Direct uptake of Hg^{2+} via stomata is controlled by stomatal and mesophyll resistances (Lindberg *et al.*, 1991). Relatively few data have so far been published in the open literature on air-vegetation exchange (rates, mechanisms) of mercury in natural or anthropogenically contaminated systems and thus, the amount of Hg removed from, or released to, the atmosphere by vegetation regionally or globally is virtually unknown. Nevertheless, the potential importance of air-vegetation exchange in the biogeochemical cycling of mercury is now being recognized. In contrast to the situation pertaining to persistent organic pollutants (POPs) in the environment (e.g. Bacci *et al.*, 1990; Calamari *et al.*, 1991; Simonich and Hites, 1994), in the case of mercury no estimates exist, for example, of the magnitude of the Hg pool currently residing in plant biomass globally or on a regional basis, even though the amount involved could be very significant in environmental budgets.

Results from, and references to, earlier studies on the uptake and/or emission of mercury from various types of vegetation can be found in Lindberg *et al.* (1979), Lindberg (1986), Schroeder *et al.* (1989) and in Johnson and Lindberg (1995). This overview emphasizes the more recent (post 1990s) scientific

publications. Lindberg and co-workers have conducted extensive studies on the biogeochemical cycling of mercury, including measurements of gas-phase Hg fluxes over tree canopies and other vegetative surfaces as well as numerical modeling of dry deposition processes, in the temperate, deciduous forest at Walker Branch Watershed in the southeastern United States. Concentration gradient measurements over the forest canopy during 1993 indicated the existence of bidirectional fluxes. Out of a total of 23 successful gradient measurements conducted under a wide range of atmospheric conditions, 14 indicated emission while 9 indicated net deposition of mercury. Observed canopy-emission rates ranged from $7\text{--}290 \text{ ng m}^{-2} \text{ h}^{-1}$ with a mean and standard deviation of $\sim 100 \pm 80 \text{ ng m}^{-2} \text{ h}^{-1}$, whereas deposition events occurred during about 40% of the measurement period and had an average flux of $\sim 50 \pm 70 \text{ ng m}^{-2} \text{ h}^{-1}$ (Lindberg, 1996). Another important observation made in this work was that dry-deposition was the dominant process under conditions in which the canopy was wet with rain, fog or dew. In the original data set of 35 observations, 8 of the 10 periods with a wet canopy exhibited dry-deposition fluxes. The resultant dry-deposition velocity (derived from TGM concentration gradient measurements) to the wet canopy averaged $1.3 \pm 1.8 \text{ cm s}^{-1}$, while that to the dry canopy averaged $0.4 \pm 0.3 \text{ cm s}^{-1}$. The latter values are comparable to the model-predicted values of $0.2\text{--}0.3 \text{ cm s}^{-1}$ reported previously (Lindberg *et al.*, 1992). Finally, the data obtained for the deciduous forest at Walker Branch Watershed suggest that (re-)emission/volatilization may be the dominant flux direction over the forest canopy, and that these fluxes can be an order of magnitude higher than those over background soils.

2.4.4. Environmental cycling. Once they are released into the environment, persistent chemicals, such as mercury, with relatively high Henry's law coefficients are expected to cycle between air and water/soil/vegetation media (Schroeder *et al.*, 1989). Since, unlike all the other heavy metals, mercury exists in the atmosphere predominantly in the vapor phase it may be more appropriate to look to volatile or semivolatile persistent organic pollutants for model compounds or chemical surrogates for the purpose of rationalizing or predicting the atmospheric behavior of Hg^{2+} (Mackay *et al.*, 1995).

In the case of semivolatile organic compounds such as PCBs, HCB and organochlorine pesticides (e.g. HCHs, DDT, chlordane, toxaphene) there exists strong scientific evidence (Mackay *et al.*, 1986; Schroeder and Lane, 1988; Kurtz, 1990; Wania and Mackay, 1996) that these chemicals participate in a "global distillation" phenomenon. This phenomenon effectively transfers chemical emissions from equatorial/tropical or subtropical and temperate regions of the earth to the polar regions via the so-called "grasshopper effect". It is intriguing to consider the possibility that mercury may also be participating in similar environmental behavior. Climatic

Table 3. Mercury volatilization fluxes from soil surfaces

| Location | Site or soil type | Msmt. period/ duration | Day/night (D/N) | Soil/air temp. (°C) | Type of measurement ^a | Hg flux (ng m ⁻² h ⁻¹) | [Hg] air (ng m ⁻³) | Literature reference |
|---|------------------------------------|----------------------------|--------------------|------------------------|--|---|---|--------------------------------|
| Sweden (near Göteborg) | Forest: deciduous coniferous | 87-08-04 | D | 10/15 | FC | 1.4 ± 0.5 | Range: ~2-4 | Schroeder <i>et al.</i> (1989) |
| | | 87-08-06 | D | 10/19 | FC | (0.3-0.6) ± 0.2 | ~2-4 | |
| | | 13 87-08-11 | D | 11/19 | FC | (0.1-1.2) ± 0.3 | ~2-4 | |
| Sweden (near Lake Gårdsjön) | Forest: coniferous | 87-12-17 to 89-06-12 | D; N | (-5)-13/ (-10)-20 | FC | 1.0 ± 1.1 (n = 5) -1.1 ± 0.7 (n = 7) | mean ± s.d. | Xiao <i>et al.</i> (1991) |
| | | 88-04 to 89-03 | D; N | -/0-30 | MM (MBR) | Model values: 10 and 50 (upper & lower bounds) | Annual mean 5.8 ± 3.6 Range 0.8-15 | Lindberg <i>et al.</i> (1992) |
| Same as above | Forest: deciduous | 93-05 to 93-11 | D; N | 12-36/ 7-34 | MM (MBR) | 7.5 ± 7.0 (n = 30) -2.2 ± 2.4 (n = 9) | Range: 1.5-3.7 | Kim <i>et al.</i> (1995) |
| Tennessee, U.S.A. (East Fork Poplar Creek) | Contam flood plain soil | 93-03-29 to 93-10-15 | D | 5.3-24.2/ 2.7-26.3 | MM (MBR) | 53 ± 59 | Range: 3.48 ± 1.56 | Lindberg <i>et al.</i> (1995) |
| | | 94-04-23 | D; N | — | — | 86 ± 72 (n = 6) | Range: 3.8-4.3 | |
| Nevada, U.S.A. (Central western Nevada) | b | 93-10 to 94-09 | D; N | —/ 8-57 | Air conc. (1994); at 7 locations | — | 1.9 ± 0.8 (n = 8) to 152 ± 18 (n = 46) | Gustin <i>et al.</i> (1996) |
| | | 95-04 | D; N | 5-12/ 7-13 | Conc. grad.; K-theory flux calculation | 15(65 ^d)- 125(15 ^d) | 248-1625 ^e 145-866 ^f 143-312 ^g | |
| | c | 95-06 | D; N | 15-34/ 11-31 | flux calculation | 3(239 ^d) 116(9 ^d) | 109-716 ^e 70-740 ^f 46-698 ^g | |

^aFC = Flux Chamber; MM = Micrometeorological Method.^bNaturally enriched and anthropogenically contaminated sites.^cContaminated mill tailings (Bessels Mill site).^dCoefficient of variation.^{e,f,g}Air concentration at a height of 0.43; 0.89; and 1.8 m, respectively.

characteristics (warm and humid conditions) existing in tropical and subtropical regions of the earth enhance the volatilization and emission or re-emission of such substances from the Earth's surface into the atmosphere. The atmosphere, in turn, constitutes an efficient medium for their dispersal and systematic accumulation in colder climates—cold condenser effect (Mackay *et al.*, 1995). The temperature difference between the hottest place on earth (usually near the equator; $T > 40^{\circ}\text{C}$.) and the coldest place on earth (usually at the South Pole; $T < -60^{\circ}\text{C}$.) can easily (and indeed frequently does) exceed 100°C ., thus, creating the conditions necessary for a global fractionation/cold-condensation process.

3. NUMERICAL MODELLING

Numerical models of atmospheric transport and deposition are essential tools for the interpretation of field measurement data and as guidelines for the establishment of abatement strategies and measures for pollution control. Modeling of atmospheric mercury has undergone rapid development during the last decade and a number of large-scale models are in operation today. Further advancement of Hg modeling is in many aspects limited by a lack of quantitative knowledge of the atmospheric behavior of mercury. Many of the key processes involved in the transformation and deposition of atmospheric mercury remain unidentified or unquantified.

3.1. Long-range transport models

The first comprehensive atmospheric model for mercury was the modified EMEP model (Petersen *et al.*, 1995). This Lagrangian-type model uses a highly parameterized approach for calculating the deposition of mercury based on wash-out ratios of Hg^0 , Hg(II) and Hg(p) . The wash-out ratio of Hg^0 is, in turn, based on the rate of aqueous-phase oxidation by ozone and an empirically derived relation between mercury in precipitation and soot-particle concentrations. Despite its simple approach, this model was quite successful in simulating long-range transport of mercury from the European continent to Scandinavia. Similar approaches have since then been applied in a number of different long-range transport models with varying success (Galperin *et al.*, 1995; Shannon and Voldner, 1995; Bullock *et al.*, 1997). Currently, development of comprehensive Eulerian models is underway (e.g. Bloxam *et al.*, 1991; Petersen, 1996), but the models are still limited by a lack of independently determined process parameters. Key processes that need to be independently quantified and described are

- Adsorption/desorption of mercury species on atmospheric aerosol surfaces
- Formation of Hg(II) and Hg(p) species in air
- Sources of atmospheric MeHg and DMM

Of equal importance are the improvement of speciated emission inventories and a better understanding of natural emissions/re-emissions from land, vegetation, and water surfaces.

3.2. Process-oriented models

Two types of process-oriented models have been presented in recent years. Chemical process models with detailed chemical descriptions but with limited meteorological parameterization (Seigneur *et al.*, 1994; Pleijel and Munthe, 1995a, b) and hybrid models describing atmospheric behavior of mercury during specific events (Pirrone *et al.*, 1995). These models are useful for evaluation of local to small regional scale processes and for investigations of the importance and environmental significance of specific processes. As is the case for the long-range transport models, these process models are also limited by the lack of quantified process information.

4. KNOWLEDGE GAPS

Notwithstanding the impressive advances that have been made in all areas of science relating to Hg in the atmosphere, there are still many important gaps in our current knowledge and understanding of the wide spectrum of atmospheric Hg issues covered in this overview. For example, we require better data for the most significant natural sources of mercury, their spatial distribution, and their contemporary as well as historical emission fluxes. This will constrain published estimates of natural emissions (which differ by several orders of magnitude) and clarify their relative importance vis-a-vis anthropogenic atmospheric sources/emissions. There is, at present, considerable discussion and controversy regarding the possibility that the strength of natural emission sources may have been significantly underestimated in natural emission inventories published in recent years (Rasmussen, 1994). Substantially improved levels of accuracy are associated with the current generation of anthropogenic Hg emission inventories, at least those recently produced for North America and Europe (resulting from incremental refinements to the methods and procedures used). By comparison, a much greater level of uncertainty is attached to most of the published estimates of mercury emissions from natural sources. Part of the problem (especially for diffuse sources) is the fact that, once mercury has been released into the atmosphere and has become incorporated into the global biogeochemical cycle, its original source (whether natural or anthropogenic) can no longer be discerned (unlike the situation for lead where isotope ratios have been utilized successfully for source apportionment; e.g. Sturges and Barrie, 1989). Because of its persistence in the environment and its proclivity to cycle (through successive processes of evaporation/condensation/re-emission) a large portion of the mercury in the atmosphere

today may consist of recycled mercury stemming from previous releases from both natural and anthropogenic sources.

It is also extremely important to obtain reliable data on the physical/chemical speciation of both natural and anthropogenic emissions, since the physical and chemical properties of the species emitted by a given source are a major determinant, along with the prevailing meteorology/climatology, of their atmospheric behavior and fate. Long-term speciated mercury measurements in industrial, urban and rural locations are lacking. Whereas current methods for measurement of "TGM" in ambient air or "total Hg" in rain or snow are now quite mature, the same cannot be said for measurements of particulate-phase Hg, divalent ("reactive") gaseous mercury, or of mono- or dimethyl-mercury species in air or precipitation samples. Work is urgently required to bring results for the latter types of determinations up to the same level of reliability and comparability as the "total Hg" methods.

Much more work needs to be carried out to obtain a more solid understanding of the processes driving the air-soil exchange of Hg and the relative magnitude of emissions from different types of soils under a variety of environmental conditions and during different times of the year (i.e. seasonal variability of volatilization fluxes). One of the major challenges yet to be addressed is how to differentiate Hg re-emitted by natural surfaces/processes, from Hg released for the first time by natural surfaces/processes or geological sources/processes. Also, given the apparently large heterogeneity of Hg concentrations found in natural and in anthropogenically contaminated soils or other matrices, viable procedures need to be found for scaling up (extrapolating) the results from the limited number of site-specific studies conducted so far. This is essential to gain insight into, and to be able to draw conclusions about, the influence and possible effect which air-surface exchange fluxes have on the atmospheric budget of mercury on local, regional, and global scales.

5. RECENT DEVELOPMENTS

Over the last decade, since the atmospheric mercury review paper by Lindqvist and Rodhe (1985) was published, there has been an explosive growth in knowledge relating to all aspects of elemental Hg (and some of its compounds) in the atmospheric environment which are dealt with in this overview paper. A much deeper understanding exists now than ever before of local, regional and global aspects of the atmospheric emissions-to-deposition cycle and the ultimate fate of mercury and its environmentally relevant species.

The development and present commercial availability of at least 3 automated mercury-vapor analyzers now allows near-real-time continuous measurements

of atmospheric TGM concentrations to be made. This significant technological advancement can be expected to lead to gradual replacement of traditional manual methods of sampling and analysis for total gaseous mercury. This quantum leap in measurement methodology has opened the door to many new research opportunities, such as: aircraft measurements of vertical concentration profiles of mercury which are characterized by hitherto unattainable temporal and spatial resolution (extremely important for estimation of the Hg burden of the troposphere, which is a central component in regional/global budgets and mass balances, as well as for establishing horizontally advected atmospheric fluxes of mercury from densely populated and industrialized coastal regions to adjoining water bodies); long-term, remote/unattended monitoring; and micrometeorological, or chamber-type, mercury air-surface exchange flux measurements with unprecedented temporal resolution. To name just a few.

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