

CHAPTER 8

Emission and Deposition of Atmospheric Mercury Vapor

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ABSTRACT

The global biogeochemical cycle of mercury is complicated by the fact that the atmospheric burden is dominated by various forms of mercury vapor, not all of which have been identified. We have studied three of the most important industrial sources of atmospheric mercury: the chloralkali, cinnabar mining, and electric power generation industries. These studies are reviewed here in the light of more recent work on the global cycle of mercury.

Our work at a commercial coal-fired power plant in the United States involved collection of samples in the stack, plume, and ambient air. Mercury vapor was the dominant form of mercury in all samples, accounting for 92–99% of the total, and was not converted to particle-associated forms during plume interactions. Because of these characteristics, mercury is inefficiently removed by conventional means during fossil fuel combustion, with nearly 99% of the feed coal mercury being discharged to the atmosphere.

Contamination of aquatic environments by direct discharges from chloralkali plants is well known. Our work at a non-operating plant in the United States identified a previously unrecognized source of mercury to the environment, atmospheric emission of the vapor from stored waste deposits. Our studies indicated that atmospheric and aquatic emissions were comparable, and that losses from defunct plants could approach those from active plants. The legacy of continued mercury pollution from such sites must be considered.

Studies at the Almadén mercury mine in Spain indicated that mercury vapor is also emitted from mercury-rich soils, and that the emission rates are temperature dependent and influenced by vegetation cover. Plants grown on these soils accumulate mercury by two means: the roots from soil mercury, and the leaves by direct absorption of emitted mercury vapor.

Predominance of the vapor form of mercury is conducive to long range transport,

global dispersion, and direct uptake by plants and animals. On a global scale, precipitation scavenging appears to be the major removal process, but dry deposition measurements are virtually non-existent. Recent reports of relationships between mercury in fish and lake acidification suggest that air pollution may be having an indirect effect on the biogeochemical cycle of mercury.

INTRODUCTION

Reports of potential relationships between acidic deposition, lake acidification, and concentrations of Hg in fish (Brouzes *et al.*, 1977; Brosset and Svedung, 1977) have prompted a recent resurgence of interest in the environmental behavior of Hg. This has been demonstrated by recent publications on global Hg cycling (Nriagu, 1979; Slemr *et al.*, 1981; Fitzgerald *et al.*, 1983; Lindqvist *et al.*, 1984). In the early 1970s, the amount of Hg discharged to the environment from anthropogenic sources was estimated to be comparable with quantities derived from continental weathering processes (Klein and Goldberg, 1970). Following new regulations, most large industrial sources in the developed countries were identified and the aquatic discharges of Hg reduced to amounts that were negligible relative to natural sources. However, current anthropogenic emissions of Hg to the atmosphere exceed direct releases to surface waters by more than an order of magnitude (Harriss and Hohenemser, 1978), and are considered to be of the same order of magnitude as atmospheric emissions from natural processes (Lindqvist *et al.*, 1984). Mercury released from both high- and low-temperature processes enters the atmosphere primarily as a vapor. Ultimately, atmospheric deposition processes return airborne Hg to the Earth's surface, where it undergoes the same reactions as Hg discharged directly into aquatic and terrestrial environments.

This chapter is not intended to be a comprehensive review of the biogeochemical cycle of Hg, which has been published elsewhere (Nriagu, 1979). Rather, it addresses the implications of the fact that vapor-phase Hg dominates the atmospheric pool of Hg by summarizing several of our own and other recent field studies in the areas of atmospheric emission, deposition, and plant uptake of Hg vapor. The reader is referred to more extensive reviews of the behavior of Hg in the environment by Lindqvist *et al.* (1984) and reviews of recent developments in analytical methods for speciation of airborne Hg by Schroeder (1982) and Schroeder and Jackson (1983).

EMISSION AND DEPOSITION

Estimates of global anthropogenic emissions of Hg to the atmosphere are on the order of 2000 to 3000 metric tons/year (Harriss and Hohenemser, 1978; Fitzgerald *et al.*, 1984; Lindqvist *et al.*, 1984). The major contributors to this

flux are mining and smelting of Hg ores, industrial processes involving mercury compounds, and fossil fuel combustion (particularly coal). Over the past several years we have studied the mechanisms of release of Hg vapor from three of the most important industrial sources: electric power generation, chlorine/caustic soda production, and cinnabar mining. The details of these studies and analytical/sampling methods used are in the literature (Lindberg and Turner, 1977; Lindberg *et al.*, 1979; Lindberg, 1980).

Coal Combustion

Our research on Hg emission from power generation involved an investigation of Hg partitioning between particle and vapor forms in the plume of a modern utility coal-fired power plant (Lindberg, 1980). Based on samples collected in the stack and in the combustion plume, we determined the relationship between plume age and atmospheric Hg (Figure 8.1). As expected, Hg collected in the plume 0.25 km from the stack was dominated by the vapor phase, most likely Hg° (elemental mercury vapor). Approximately 92% of the total Hg at this point in the plume was present as Hg° at a measured concentration of 1700 ng/m^3 . During plume travel from 0.25 to 7 to 22 km, the measured concentrations of Hg° decreased to 1000 ng/m^3

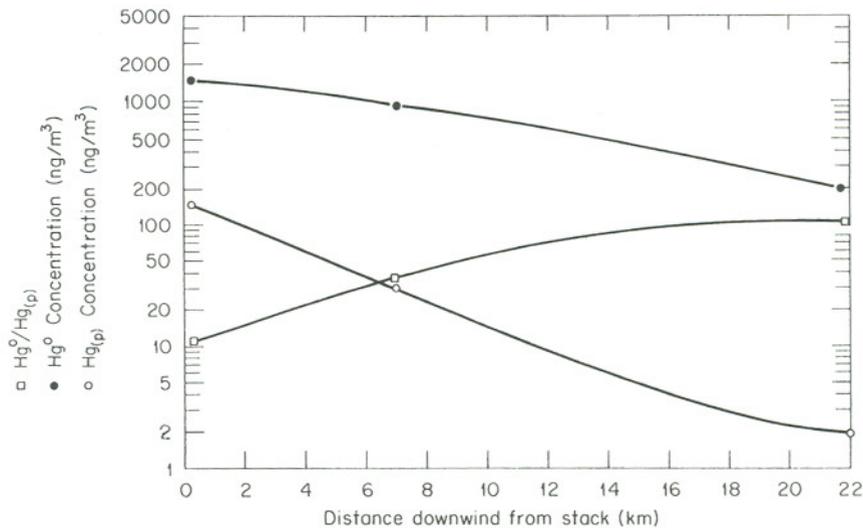


Figure 8.1 Concentration of mercury vapor (Hg°), particulate mercury [$\text{Hg}_{(p)}$], and Hg vapor to particulate Hg concentration ratio [$\text{Hg}^{\circ}/\text{Hg}_{(p)}$] in the plume of a coal-fired power plant. \square , $\text{Hg}^{\circ}/\text{Hg}_{(p)}$; \bullet , Hg° concentration (ng/m^3); \circ , $\text{Hg}_{(p)}$ concentration (ng/m^3) (from Lindberg, 1980)

at 7 km and 200 ng/m³ at 22km. (Background concentrations were on the order of 10–20 ng/m³.) Because of some uncertainty in the plume dimensions, the absolute concentrations of airborne Hg in the plume itself should be regarded cautiously, particularly at the point closest to the smokestack. It is best to consider the ratios of the measured concentrations.

If significant adsorption or condensation of Hg⁰ vapor onto particles were occurring as the plume cooled and mixed with ambient air, as suggested elsewhere (Williston, 1968; Staff, *Environmental Magazine*, 1971; Billings and Matson, 1972; Lockeretz, 1974), the vapor to particle ratio should decrease, assuming little settling loss for particles in the size range encountered in the plume (mass median diameters of ~0.1 to 0.5 μm, Lindberg and Harriss, 1980). However, this ratio increased with distance from 11 at 0.25 km, to 33 at 7 km, to 100 at 22 km. Similarly, the fraction of the total Hg present as a vapor increased to 97% at 7 km and 99% at 22 km. This increase in the vapor to particle ratio indicates not only the absence of any measurable gas-to-particle conversion but also the loss of some fraction of the initial particulate Hg population. Considering the measured concentrations of Hg⁰ and that the vapor pressure of Hg at ambient temperatures is ~20 mg/m³, one would not expect gas to liquid phase condensation to influence the gas-phase concentrations. The loss of particulate Hg could be the result of desorption or displacement of Hg vapor from the aerosol, or physical removal of some fraction of the particles during plume travel. Because settling of these particles is negligible over these distances, displacement is more likely. This displacement may be the result of reactions between various mercury species (e.g. HgO) on the suspended particulate matter and gaseous oxides of S and N in the plume. Reactions between SO₂, for example, and surfaces of metal-containing particles are well known (Fennelly, 1975), although the effects of these interactions on adsorbed species have not been documented. Reactions between HgO and SO₂ to yield Hg⁰ vapor have been recently suggested as an important Hg reduction process in the atmosphere (Stevens *et al.*, 1982). Such interactions could explain the observations in our plume study.

The fraction of the total incoming feed coal Hg which is discharged to the atmosphere from the power plant and the source strength can be estimated by using the 0.25-km downwind plume data to represent the maximum particle to vapor concentration ratio and by knowing the coal feed rate (4.8 × 10⁵ kg/hour), the precipitator efficiency (99%), the composite coal Hg content, and the precipitator ash Hg concentration (Lindberg, 1980). Less than 1% of the initial feed coal Hg is retained in the plant (in collected ash), and the remainder is released in the stack emissions, ~7% in particulate form and 92% in vapor form. The estimated source strength for the unit sampled was ~3.5 kg Hg/day as a vapor and ~0.3 kg Hg/day in particulate form. Because nearly all of the feed coal Hg is emitted from the

stacks, total Hg emission rates should be proportional to coal usage rates of power plants as reflected by megawatt capacity. As shown in Table 8.1 this is generally true, thus providing a simple method of estimating total Hg emissions from coal-fired power plants. Estimates of total atmospheric emissions from coal burning for the early 1970s were on the order of 100 metric tons per year (Harriss and Hohenemser, 1978; National Research Council, 1978). Our 'model' (atmospheric Hg loss $\approx 5 \times 10^{-3}$ kg/day per MW of electricity generated, determined from the mean ratio of the MW and emission values in Table 8.1), combined with statistics for the United States (National Coal Association, 1980), suggests that there has been an increasing emission trend as coal use has increased (values in metric tons Hg/year): 1976 = 190, 1978 = 200, 1980 = 230.

Table 8.1 Emission rates of Hg from modern coal-fired power plants. Generally, more than 90% of the Hg emitted was in a vapor phase in each case

Electric generating capacity (MW)	Atmospheric Hg emission rate (kg/day)	Reference
200	1.5	Anderson and Smith, 1977
1000	4.3	Lockertez, 1974
1300	3.8	Lindberg, 1980
2100	7.5	Billings and Matson, 1972
United States	270	Harriss and Hohenemser, 1978
World	1700	Harriss and Hohenemser, 1978

Chloralkali Wastes

Our research on the emission of Hg from the chloralkali industry involved measurement of the loss of Hg vapor from solid wastes stored near an inactive Hg-cell chloralkali plant in a rural area of the eastern United States (Lindberg and Turner, 1977). Although estimates have been published on the emission of Hg vapor from production processes in active plants (Caban and Chapman, 1972; Van Horn, 1975; Wallin, 1976; Högström *et al.*, 1979), none have considered the problem of atmospheric emissions from waste products stored in ponds or otherwise stored near either active or inactive plants. Based on laboratory studies, field data, and plume dispersion models, we estimated the emission rate of Hg vapor from solid wastes and the influence of these emissions on local air quality near two solid waste ponds of 4×10^5 m² surface area (Hildebrand *et al.*, 1980).

The volatility of elemental Hg and many of its compounds suggests that its presence in large-scale waste deposits such as these might have an influence on local air quality. In laboratory experiments, the emission of Hg vapor

from the waste material was clearly related to surface temperature, as expected (Figure 8.2). The relationship is similar to that between temperature and the saturation concentration of Hg^0 in air (Wallace *et al.*, 1971), suggesting that the mercury occurs in the waste material to some extent in the elemental state. The mean total Hg content of these wastes was $150 \mu\text{g}/\text{gm}$, but that present as Hg^0 was not specifically determined. Estimates of natural degassing rates of Hg on regional or global scales and even measured rates for mineralized soils are one to three orders of magnitude lower than those we have measured for the waste material (Table 8.2).

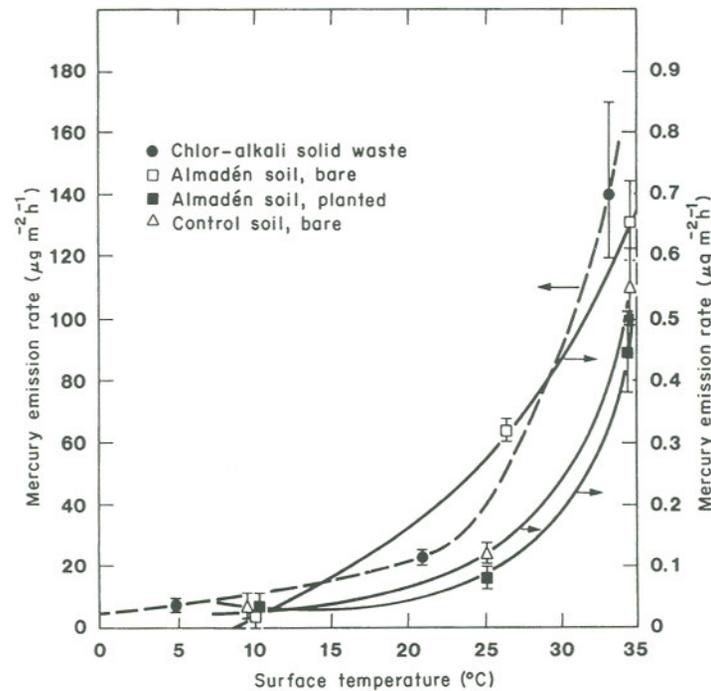


Figure 8.2 Relationship between emission of vapor phase mercury and surface temperature for chloralkali waste material ($155 \mu\text{g Hg}/\text{gm}$) and for mercuriferous soils ($97 \mu\text{g Hg}/\text{gm}$) and control soils ($2.3 \mu\text{g Hg}/\text{gm}$) with and without plant cover (from Lindberg and Turner, 1977; Lindberg *et al.*, 1979)

We used a Gaussian diffusion model (Gifford, 1968) to estimate 24-hour mean concentrations of Hg^0 vapor in the ambient air downwind of the waste area, based on emission rates measured under controlled conditions (Figure 8.2) and local meteorological measurements (Hildebrand *et al.*, 1980). For comparison, air sampling stations near the ponds measured Hg^0 in air and

Table 8.2 Natural emission rates of Hg vapor from solid materials

Material	Method	Hg emission rate ($\mu\text{g}/\text{m}^2 \cdot \text{hour}$)	Reference
Global land area	Input/output models	0.02–0.03	Weiss <i>et al.</i> , 1971; Kothny, 1973
Bedrock	Rock volatility	0.04–0.08	Desaedeleer and Goldberg, 1978
Soils 15 km from cinnabar mine	Chamber measurements	0.12–0.14	Lindberg <i>et al.</i> , 1979
Soils 1 km from cinnabar mine	Chamber measurements	0.32–0.34	Lindberg <i>et al.</i> , 1979
Mercuriferous soils	Chamber measurements	0.2–1.7	McCarthy <i>et al.</i> , 1969
Chloralkali wastes	Chamber measurements	35–40	Lindberg and Turner, 1977

total Hg on suspended particles, wind speed and direction, air temperature, and bulk deposition. At temperatures from 6 to 30°C, the measured and calculated air concentrations agreed to within ~30% (Lindberg and Turner, 1977), suggesting that the entire surface area of the waste pond was emitting Hg⁰ vapor at a rate comparable with that measured in controlled experiments.

The levels of Hg⁰ in air measured near the pond at 6°C (60 to 90 ng/m³) were slightly elevated above those reported for large US cities and areas near active chloralkali plants (Table 8.3). However, these concentrations decreased to rural background levels within ~2 km of the waste area. At temperatures near 30°C the concentration of Hg measured in the pond vicinity approached the US Environmental Protection Agency guideline level for total Hg in ambient air (1000 ng/m³) (*Federal Register*, 1973). This is comparable with levels in air over natural Hg deposits and near geothermal emissions (Table 8.3).

The concentration of particulate Hg during this sampling period was very low and comparable with that reported for urban areas. The indication that essentially 100% of the Hg in air is in vapor form agrees with reported results for ambient air in remote and urban areas (Johnson and Braman, 1974; Fitzgerald *et al.*, 1983; Lindqvist *et al.*, 1984).

The bulk deposition of Hg was also measured during one 24-hour period of air monitoring, during which it rained for 1 hour (0.25 cm of precipitation). The concentrations of Hg in replicate bulk precipitation samples were 1.1 and 1.4 $\mu\text{g}/\text{litre}$, comparable with values reported for urban areas (see the review by Galloway *et al.*, 1980) but considerably higher than concentrations of Hg in precipitation collected in generally rural areas (~0.01–0.1 $\mu\text{g}/\text{litre}$)

Table 8.3 Concentrations of Hg vapor and particulate Hg in various atmospheres

Study area	Hg concentration (ng/m ³)		Reference
	Vapor	Particle	
Remote marine	1-3	0.0004-0.002	Slemr <i>et al.</i> , 1981; Fitzgerald <i>et al.</i> , 1983
Rural	3-10		Kothny, 1973; Brosset, 1982; Lindberg and Turner, 1977
Urban	2-30	0.2-0.3	Ferrara <i>et al.</i> , 1982
Large cities	5-50		Johnson and Braman, 1974; Van Horn, 1975
Industrial	10-50		Högström <i>et al.</i> , 1979
Chloralkali waste ponds	60-1000	0.2-0.4	Lindberg and Turner, 1977
Cinnabar deposits	30-1600		Kothny, 1973
Power plant plume	200-1700	2-150	Lindberg, 1980
Volcanic and geothermal vents	10-40 000		Siegel and Siegel, 1975

(see the review by Lindqvist *et al.*, 1984). The bulk deposition rates of Hg during this period were 7.4 and 9.0 $\mu\text{g}/\text{m}^2$ per day, which are comparable with values measured near active chloralkali plants but much higher than those in rural areas not influenced by local emissions (Table 8.4).

Using regression equations and air temperature records, we estimated the total annual surface emission of Hg vapor from the waste area. The calculated flux is 36 ± 4 kg Hg/year (mean and SE). Interestingly, one estimate of annual aquatic loss of Hg by leaching and runoff from the waste ponds into the adjacent river was similar (39 ± 2 kg Hg/year; Turner and Lindberg, 1978). The estimated total annual flux of Hg from this inactive plant, 75 ± 5 kg/year, is less than 10% of the US Environmental Protection Agency standard for emission of Hg to air and water from active chlorine plants, but it is ~25% of the emission measured from active European plants (Högström *et al.*, 1979).

Emission of Hg vapor from waste deposits is likely to increase in relative importance because of modernization of the chloralkali industry. Reduction of direct losses results in an increase in landfill waste Hg; 60 to 90% of current Hg used by the industry is deposited in waste ponds ($>10^5$ kg Hg/year in the United States, Harriss and Hohenemser, 1978). In addition, conversion to the non-Hg diaphragm process suggests that existing waste ponds will be the major source of Hg vapor from this industry in the future. Because of the rate of generation of these wastes ($>10^9$ kg/year in the

Table 8.4 Atmospheric deposition rates of Hg at diverse locations

Study area	Hg deposition rate ($\mu\text{g}/\text{m}^2\cdot\text{d}$)	Reference
Remote marine	0.02–0.06	Fitzgerald <i>et al.</i> , 1983
Rural	0.2–3	Schlesinger <i>et al.</i> , 1974, Galloway <i>et al.</i> , 1980
500–50 000 m from active chloralkali plant	0.5–1	Jernelöv and Wallin, 1973; Högström <i>et al.</i> , 1979
50–500 m from active chloralkali plant	1–40	Jernelöv and Wallin, 1973; Högström <i>et al.</i> , 1979
Chloralkali solid waste ponds	7.4–9.0	Lindberg and Turner, 1977

United States) and the residence time of Hg in such deposits (>100 years, Hildebrand *et al.*, 1980), these areas will continue to be sources of Hg vapor well into the future.

Since we completed our research at this plant, and in part because of our findings, considerable effort has been expended to seal the waste deposits to prevent continued losses. However, these efforts have been aimed primarily at reducing leaching rates of dissolved Hg into nearby ground and surface waters (Rucker, 1983). Because of the size of the waste ponds, complete sealing of the surface was considered to be impossible. Hence, although direct leaching of dissolved mercury should be reduced, the atmospheric source will be unaffected, allowing mercury vapor to continue to enter the atmosphere.

Mercuriferous Soils

Emissions of Hg to the atmosphere from ore-rich areas by mining and refining operations have been estimated to contribute ~12% of the global anthropogenic emissions of Hg to air (Van Horn, 1975). Local emissions can further increase the Hg burden of vegetation growing on mercuriferous soils; however, there are few measurements of Hg emission rates from such soils or of plant uptake of the emitted Hg. Our study of this industry examined agricultural soils and alfalfa (*Medicago sativa*) plants near the Almadén, Spain, mercury mine and smelter, the largest and oldest mercury mining/refining operation in the world. Emission rates and plant uptake of Hg vapor were measured in controlled chamber experiments as described elsewhere (Lindberg *et al.*, 1979).

Proximity to the mine had an obvious influence on the surface soil Hg

levels, which ranged from 68 to 97 to 263 $\mu\text{g Hg/gm}$ at points 0.5, 1.0, and 2.0 km downwind from the mine, respectively. Wind direction effects were also apparent further from the mine; the Hg concentrations at 15 km downwind decreased to 2–5 $\mu\text{g/gm}$, while those 15 km upwind were 0.3–0.5 $\mu\text{g/gm}$. All of these concentrations are elevated above the average crustal abundance of Hg of 0.07 $\mu\text{g/gm}$ (Vinogradov, 1959) and above uncontaminated topsoils collected around the world (~ 0.02 – $0.07 \mu\text{g/gm}$), but are comparable with soils collected near other mercury sources [2.5–10 $\mu\text{g/gm}$ (US Geological Survey, 1970)].

Two of these soils (Almadén, $\text{Hg} = 97 \pm 7 \mu\text{g/gm}$, and control, $2.3 \pm 0.4 \mu\text{g/gm}$) were used for detailed chemical analysis, plant uptake studies, and emission rate experiments. The soils were comparable in characteristics known to influence soil Hg behavior, such as pH, organic content, and cation exchange capacity. In addition, density gradient fractionation indicated that a major portion of the Hg in each soil (40% in Almadén, 80% in control) was associated with the most dense inorganic soil fractions, and likely represented cinnabar. The least dense soil fraction, including organo-clay complexes and surface deposited Hg^0 , comprised 50% of the Almadén soil Hg (or 48 $\mu\text{g/gm}$), but only 10% of the control (0.2 $\mu\text{g/gm}$).

The results of some of our Hg emission experiments are shown in Figure 8.2. The emission rates were clearly related to surface temperature, as expected, and were also related to soil Hg content, as noted for soils experimentally amended with Hg (Landa, 1978). The measured Hg emission rates for bare Almadén and control soils at 25°C exceeded natural rates measured for non-mineralized regions by factors of 4 to 10, but were within the range reported for mineralized soils (Table 8.2). At 25°C, the emission rate of Hg from bare Almadén soils was significantly greater ($P < 0.05$) than the rate from these soils planted with alfalfa. Alfalfa cover may reduce mixing of Hg-rich air at the soil surface with air above the alfalfa canopy. However, because of the flow rate used, duration of the experiments, and small amount of plant cover present (Lindberg *et al.*, 1979), we believe this effect to be minor. A more likely possibility is direct absorption of emitted Hg^0 by foliage.

Our measurements of Hg accumulation in alfalfa grown on these soils suggest two mechanisms of Hg uptake by plants under these conditions: the first controlling above ground, foliar levels of Hg, which is independent of soil Hg levels; and the second influencing root uptake, which is related to soil concentrations. The Hg concentrations in alfalfa foliage grown on both soil types were similar (pooled mean = $1.4 + 0.6 \mu\text{g/gm}$, $n = 18$) and exceeded world average levels in grasses by an order of magnitude (Wallace *et al.*, 1971). On the other hand, concentrations of Hg in well-washed Almadén roots ($8.0 \pm 0.1 \mu\text{g/gm}$) far exceeded those in control roots ($0.38 \pm 0.08 \mu\text{g/gm}$) and represented 80% of the total Hg accumulated by

plants in Almadén soils, while for control soils 80% of the accumulated Hg occurred in above ground foliage.

The ability of plants to absorb Hg vapor from the atmosphere is well known (Hitchcock and Zimmerman, 1957; Huckabee, 1973; Wallin, 1976; Lodenius and Laaksorvirta, 1979). Our alfalfa plants were exposed to elevated levels of Hg vapor emitted from the soils throughout the uptake experiments. In the plant growth chamber containing several pots of control and Almadén soils, the air concentration ranged from 50 to 220 ng/m³, averaging 80 ng/m³ during the 16-week plant uptake studies (compare background levels in Table 8.3). To quantify foliar uptake of Hg vapor a duplicate set of alfalfa plants was grown from seed on an inert silicate substrate in the same growth chamber and exposed to Hg vapor emitted from Almadén and control soils. Although the silicate contained essentially no Hg (<0.0005 µg/gm), the alfalfa grown on it exhibited a foliar Hg concentration of 2.0 ± 0.1 µg/gm, but a root level of only 0.35 ± 0.01 µg/gm. Hence, foliar Hg was comparable among plants grown on all three substrates, while root concentrations differed in the order Almadén > control ≈ silicate. Translocation of foliar Hg to the roots, or direct deposition of Hg vapor to the silicate followed by root absorption, may explain why the silicate-grown roots had a higher Hg concentration than the silicate itself.

Previous plant uptake studies support the hypothesis of direct foliar absorption (and emission) of Hg vapor (Ross and Stewart, 1962; Gilmour and Miller, 1973; Kozuchowski and Johnson, 1978). Mechanisms of foliar uptake in wheat were studied by Browne and Fang (1978) using labeled Hg vapor. They found that: uptake was controlled by the stomata, but not influenced by air temperature; surface adsorption was negligible; uptake rates increased with increasing air concentration; total uptake increased with duration of exposure; and the absorbed Hg was confined solely to leaves.

IMPLICATIONS AND GLOBAL CYCLING

The activated charcoal adsorption traps used to sample airborne Hg in all our studies collect both elemental and chemically bound Hg vapor (Lindberg, 1981). However, our data and that of others suggest that the major or predominant species of airborne Hg vapor is elemental Hg, the source of which is thought to be direct industrial emissions plus chemically or biologically reduced mercury compounds in soil and water (Frear and Dills, 1967; Gilmour and Miller, 1973; Johnson and Braman, 1974; Nriagu, 1979; Fitzgerald *et al.*, 1984). Organic and inorganic Hg compounds react with soil organic matter to release Hg⁰ (Hitchcock and Zimmerman, 1957). Direct, abiotic methylation of divalent Hg in soils has been reported by Rogers (1977) and by Rogers and MacFarlane (1979), who found that Hg⁰ (not methyl Hg) was the predominant vapor species (~70%) emitted from these

soils. Based on tests with autoclaved soils Landa (1978) suggested that soil micro-organisms mediate the volatilization of Hg^0 . Following the reduction of various Hg compounds and organo-Hg complexes to Hg^0 in soils, sediments, and surface waters, the vapor is lost to the atmosphere, where it apparently remains in this same form (Slemr *et al.*, 1981; Fitzgerald *et al.*, 1983).

Current estimates suggest that natural and anthropogenic emissions of Hg to air are of the same order of magnitude (Fitzgerald *et al.*, 1984; Lindqvist *et al.*, 1984). However, when emission rates are normalized to a unit surface area basis, it is apparent that atmospheric fluxes from the combustion of coal dwarf those from other sources (Figure 8.3). Despite the wide range in measured fluxes, the compositions of these emissions have one characteristic in common with the global atmosphere: dominance of total airborne Hg by vapor species. There are many important implications of this vapor-phase dominance. As discussed earlier, crop plants have been shown to absorb and retain Hg through leaf uptake, while the incorporation of particulate forms is considered less likely (Hosker and Lindberg, 1982). In addition, inhaled metallic Hg vapor is able to diffuse much more extensively into blood cells and various tissues than inorganic particle-associated Hg (Magos, 1968).

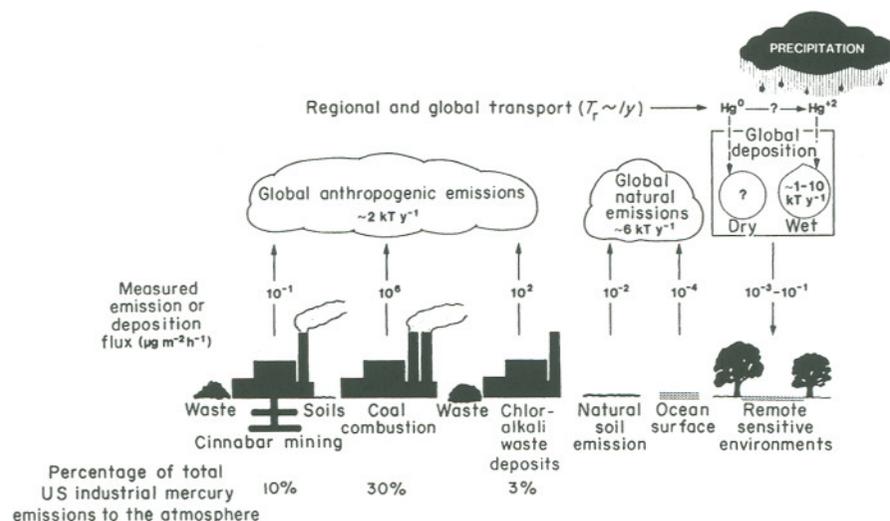


Figure 8.3 Schematic representation of the relative magnitude of Hg vapor emission fluxes from several sources and the general atmospheric cycle of Hg vapor leading to deposition in remote environments (values compiled from references cited in the text). The unit kT is 10^3 metric tons: T_r represents the global mean residence time of Hg vapor in the atmosphere

Other important implications involve atmospheric transport, residence time, and deposition. The occurrence of airborne Hg as a vapor is conducive to long-range transport from the source and a long atmospheric residence time. Several studies of the dispersion and deposition of Hg near point sources have confirmed this hypothesis (Jernelöv and Wallin, 1973; Lockeretz, 1974; Anderson and Smith, 1977; Crockett and Kinnison, 1979; Högström *et al.*, 1979). Slemr *et al.* (1981) recently reappraised earlier estimates of the mean global tropospheric residence time of atmospheric Hg, based on numerous measurements of Hg in the atmosphere over the Atlantic Ocean. Using box model calculations and the relationship between average residence time and the variability of gas concentrations in the troposphere proposed by Junge (1974), these authors calculate residence times in the range of 0.7 to 2 years, considerably larger than values of 0.03 to 0.1 year proposed earlier (Weiss *et al.*, 1971; Kothny, 1973; Wollast *et al.*, 1976; Andren and Nriagu, 1979). More recent estimates based on oceanic measurements (Fitzgerald *et al.*, 1983) and theoretical calculations (Lindqvist *et al.*, 1984) support these longer times. However, it should also be noted that recent analyses of some lesser known atmospheric reactions of Hg⁰ (with O₃ for example) suggest that under certain conditions its half life could be on the order of minutes (Stevens *et al.*, 1982). Clearly more work in the area of atmospheric reactions of mercury and its compounds is needed.

Minimal data exist on the rates and mechanisms of Hg removal from the atmosphere, particularly by dry deposition. Theoretical estimates of the contribution of dry deposition to the overall flux of Hg to the Earth's surface are as follows: (1) 4 to 40% within 2 km of a power plant and 40 to 90% at 20 km from this same source (Lockeretz, 1974); (2) ~99% within 0.2 km of a chloralkali plant and 94% at 5 km from the plant (Högström *et al.*, 1979); (3) <20% to a forest canopy in the eastern United States (Andren and Lindberg, 1977); (4) 50% to the sea surface in the north Pacific (Fitzgerald *et al.*, 1983), and to the globe as a whole (Lindqvist *et al.*, 1984); and (5) from <1% to 'possibly significant' on the global scale (Lantzy and Mackenzie, 1979, and National Research Council, 1978, respectively). Clearly, empirical data on dry removal rates of atmospheric Hg are needed. A comparison of total global emission and deposition rates confirms the degree of uncertainty in dry fluxes (Figure 8.3).

Once Hg is dispersed from the source, precipitation scavenging may favor greater removal rates for the vapor than for the particles. We have found particulate Hg to be concentrated in the 0.6- to 1.1- μm size range in ambient air (Lindberg, unpublished data), a size range for which precipitation scavenging efficiencies are at a minimum (Beard, 1977). Because precipitation scavenging of particles is largely a physical process, a captured particle may or may not release Hg to solution. Thus, the initial composition of the raindrop has little influence on the scavenging efficiency for particulate

Hg, although it will influence the ultimate dissolved Hg concentration in the droplet. However, scavenging of the vapor is highly dependent on its solubility in the rain-drop, and any characteristic of the initial drop which increases the solubility of vapor-phase Hg can enhance the removal rate.

Reported solubilities of Hg^0 in pure water are 30 to 60 $\mu\text{g/litre}$, for a saturated atmosphere (Onat 1974; Sanemasa 1975). Concentrations of Hg in precipitation (0.001 to 1.0 $\mu\text{g/litre}$) (Nriagu, 1979; National Research Council, 1978) do not approach these levels, suggesting that the solubility of Hg vapor in the raindrop is not a limiting factor in its removal from the atmosphere (McCarthy *et al.*, 1969). However, the equilibrium solubilities for ambient air concentrations of Hg^0 are much lower ($\sim 3 \times 10^{-5}$ $\mu\text{g/litre}$ for a background air concentration of 10 ng/m^3 , Fogg and Fitzgerald, 1979). Hence, even at the highest air concentrations measured in our studies (1700 ng/m^3 ; Table 8.3), the equilibrium concentration of Hg^0 in pure water (0.005 $\mu\text{g/litre}$) is considerably below reported levels in precipitation. Possible explanations for these discrepancies include the following: (1) Hg^0 solubility is greatly enhanced by the presence of oxidants and H^+ in rain, (2) Hg^0 is rapidly transformed into considerably more soluble vapor species in an oxidizing atmosphere saturated with water vapor (i.e. during precipitation), and (3) most of the Hg in rain originates from particle removal from the air. The last hypothesis seems least likely because of the low particle/gas Hg concentrations in air and the low particle removal efficiency by rain. Although testing of the other hypotheses awaits further analytical and field data, the existence of highly soluble vapor-phase molecular species [e.g. $\text{Hg}(\text{OH})_2$] has been suggested (Brosset, 1982; Lindqvist *et al.*, 1984).

The global wet deposition of Hg from the atmosphere has been estimated to be from 10^6 to 10^8 kg/year (Weiss *et al.*, 1971; Garrels *et al.*, 1975; Fitzgerald, 1976; Slemr *et al.*, 1981); more recent estimates are in the range of 10^6 to 10^7 kg/year (Lindqvist *et al.*, 1984), indicating considerable uncertainty in wet removal rates. Lack of measurements of dry deposition rates of Hg hinders the assessment of the importance of this process as a removal mechanism. However, precipitation scavenging of the vapor appears to be the major removal process on a global scale and theoretically should increase in efficiency as precipitation acidity and airborne oxidant concentrations increase. Thus, enhanced atmospheric deposition of Hg should be considered as a possible contributing factor to recent reports of relationships between acid precipitation and elevated Hg levels in fish from remote locations, previously ascribed to regional soil/watershed acidification (Brouzes *et al.*, 1977; Brosset and Svedung, 1977; see also the review by Lindqvist *et al.*, 1984).

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