

## Atmospheric mercury—a review\*

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### ABSTRACT

An attempt is made to assess present knowledge about atmospheric mercury: its occurrence in air and precipitation, chemical transformations taking place in the atmosphere, and mercury fluxes to and from the Earth's surface. Tentative budgets are estimated for mercury in the global atmosphere and in the atmosphere over Europe and Sweden.

Major features revealed by this include the following:

For the global atmosphere, current anthropogenic emissions are comparable to emissions by natural processes (pre-industrial). The present background fluxes are probably significantly augmented by anthropogenic emissions during the industrial era.

A dominant fraction ( $\approx 80\%$ ) of the total mercury in the atmosphere consists of a volatile gaseous mercury form, presumably elemental mercury,  $\text{Hg}^0$ . This mercury has an atmospheric residence time of at least a few months, maybe even one or two years, and is uniformly distributed throughout the troposphere ( $1\text{--}2 \text{ ng m}^{-3}$ ).

The volatile mercury vapour ( $\text{Hg}^0$ ) is oxidized in the atmosphere to unknown forms that are soluble and can be scavenged by precipitation or dry deposited at the surface. The oxidation process is not known but photochemical oxidants (including ozone) are likely to be important. The atmospheric residence time of the water soluble (non-volatile) mercury is in the range of a few days to a few weeks, corresponding to a characteristic transport distance of up to a few thousand kilometers.

Even if a dominant fraction of the mercury emitted from an individual source, such as a chlor-alkali plant, is dispersed regionally or globally, a small fraction ( $< 10\%$ ) is deposited locally. Increases by a factor of 10 to 100, above background deposition rates, have been measured within the nearest km of such plants. At a distance of 10–50 km, the deposition normally approaches the background value. Around a large Swedish smelter, mercury levels in lake sediments are significantly augmented even beyond 50 km from the plant.

The contribution to current mercury deposition in Sweden from anthropogenic mercury emissions in other European countries is most likely larger than the contributions from current Swedish emissions.

Measurements of mercury in lake sediments and peat bogs show that in southern Scandinavia, the rate of mercury deposition has increased by a factor of about 5 during the last hundred years. The increase in northern Scandinavia is significantly less, at most a factor of two. These increases are caused, most likely, by anthropogenic emissions into the atmosphere mainly within the European region.

### 1. Introduction

Many of the environmental aspects of mercury have been reviewed in the monograph of Nriagu

(1979). During recent years, new analytical techniques have become available and the understanding of mercury chemistry and biochemistry in natural systems has also improved. The aim of the present review is to evaluate data on the occurrence of mercury in air and precipitation, on relevant transformation processes that may take place in the atmosphere, and on mercury emissions

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from and deposition to the earth's surface. Regional and global budgets are also assessed. This study was undertaken as part of a more comprehensive investigation of mercury in the environment, reported elsewhere by Lindqvist et al. (1984).

Mercury can exist in a large number of different physical and chemical forms with a wide range of properties, which is of fundamental importance for its environmental behaviour. Conversion between these different forms provides the basis for mercury's complex distribution pattern, for local and global cycles, and for its biological enrichment and effects. The three most important chemical forms known to occur in the environment are: elemental mercury ( $\text{Hg}^0$ ), which has a high vapour pressure and a relatively low solubility in water; divalent inorganic mercury ( $\text{Hg}^{2+}$ ) which has a strong affinity for many inorganic and organic ligands, especially those containing sulfur; and methyl mercury ( $\text{CH}_3\text{Hg}^+$ ), which is resistant to environmental degradation, rapidly enriched by but only slowly destroyed by living organisms, and capable of passing through important biological barriers such as blood/brain barriers and the placenta.

Mercury participates in a number of complex and interwoven environmental cycles that involve conversion between the different forms. Two of the most important of these cycles are the atmospheric cycle and the aquatic-biological cycle. The atmospheric cycle is derived from conversion in soil and water of divalent inorganic mercury,  $\text{Hg(II)}$ , to gaseous elemental mercury ( $\text{Hg}^0$ ) and/or  $(\text{CH}_3)_2\text{Hg}$ , and subsequent atmospheric re-oxidation of elemental mercury to water-soluble forms, which are then deposited. The atmospheric cycle entails a retention in the atmosphere for long periods, and consequently, transport over very long distances.

Major features of the aquatic-biological cycle of mercury are the formation of methyl mercury, its enrichment in organisms and nutritional chains, and finally, destruction (demethylation) of methyl mercury. Although methyl mercury is the dominant form of mercury in higher organisms, it represents only a very small amount of the total mercury in an aquatic ecosystem and in the atmosphere. The rates of formation and destruction of methyl mercury are therefore of prime importance for the amount of mercury which can be enriched by aquatic organisms and thus for the concentration of mercury in these organisms.

## 2. Sampling, storage and analytical procedures

Techniques for sampling, storing, and determining low concentrations of mercury ( $<0.1 \mu\text{g kg}^{-1}$ ), normally occurring in ambient air and natural waters, have only recently become available and are still under development (Lindqvist et al., 1984). A number of different techniques for determining total mercury may be used depending on the nature of the sample (National Academy of Sciences, 1978; Schroeder, 1979, 1982). A frequently applied and sensitive method for determining elemental mercury in environmental samples is the cold-vapor atomic-absorption technique (CVAA) (cf. Olafsson, 1982). Techniques with even lower detection limits than CVAA, are various types of atomic emission spectrometry (AES) (Braman and Johnsson, 1974; Schroeder, 1982). The detection limit for plasma-AES is better than  $0.005 \text{ ng}$  (Iverfeldt, 1984).

With low background concentrations ( $0.5\text{--}5 \text{ ng m}^{-3}$ ) of gaseous mercury in ambient air, accumulative sampling is necessary. After a particle filter, various gas collection methods have been applied, mainly involving acidic oxidative solutions or adsorption on gold and silver (Schroeder, 1982). At present, gold traps are most widely used for sampling of total gaseous mercury in air, allowing safe storage for up to a week or longer.

Due to the high affinity of mercury for gold, certain adsorbed mercury compounds may be stripped to  $\text{Hg}^0$  and amalgamated with the gold (Jagner, personal communication, 1982). The trapping kinetics appear to be different for different mercury compounds, being slower for oxidized forms than for  $\text{Hg}^0$ , which may lead to breakthrough at high gas velocities through the gold trap (Slemr et al., 1979; Iverfeldt and Lindqvist, 1982).

Water samples are generally reduced to  $\text{Hg}^0$  by  $\text{SnCl}_2$  or  $\text{NaBH}_4$  and transferred to the gas phase for analysis. In rainwater samples, the low mercury concentrations are sensitive to storage errors (Lindqvist et al., 1984). Therefore, the analysis has to be performed as soon as possible after sampling, or alternatively, the mercury content may be immediately transferred to gold traps. When water samples have to be conserved for longer periods, an accepted method is to add concentrated  $\text{HNO}_3$  and seal the sample in Pyrex or quartz glass. Parallel storage of blanks is essential (Slemr et al., 1981; Olafsson, 1982; Seritti et al., 1982).

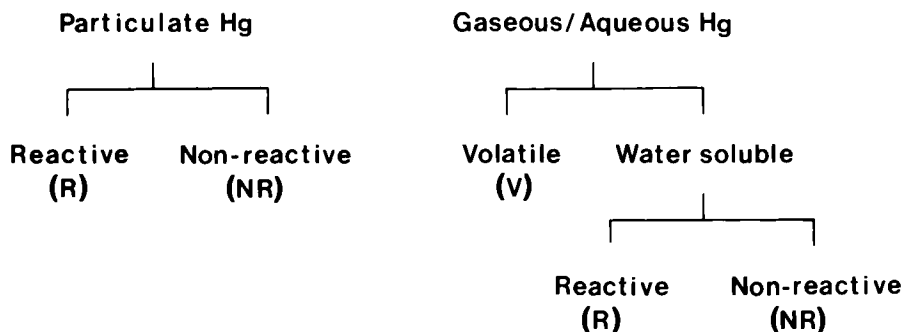


Fig. 1. Classification of mercury compounds according to appearance in nature, but also with respect to possible separation with available sampling and analytical methods.

Since it is generally not possible to achieve complete speciation of the different mercury forms in natural systems, the classification in Fig. 1 has been found useful.

The volatile mercury compounds are those having a relatively high Henry's law constant (cf. Table 5), i.e.  $\text{Hg}^0$  and  $(\text{CH}_3)_2\text{Hg}$ , while examples of less volatile, water-soluble compounds are  $\text{CH}_3\text{HgCl}$  and  $\text{HgCl}_2$ . In the future, other compounds of intermediate volatility may be found to be important. The volatile fraction in water samples has to be bubbled immediately into gold traps.

Particulate mercury is normally collected on filters. The chemical form of the particulate mercury in air is not known. During sampling, some of the particulate mercury initially trapped on the filter may be transferred to the subsequent sampler, causing analytical problems.

Separation of different compounds of gaseous atmospheric mercury is difficult and methods are still being developed. In general, attempts to utilize chromatographic properties of commercially available polymers, or the different affinity of mercury compounds for silver and gold, have not yet been successful. The obvious way to separate water soluble and volatile mercury compounds in air (i.e., to connect a wash bottle with pure water before the gold traps) has been utilized in some recent measurements (Brosset, 1985; Iverfeldt, 1984).

The classification into reactive and non-reactive compounds in particulate or aqueous samples may be defined in different ways according to the analytical treatment (cf. Fig. 1).

(a) Reactive compounds are reduced to  $\text{Hg}^0$  by  $\text{SnCl}_2$  in acid solution, while non-reactive compounds are reduced to  $\text{Hg}^0$  by  $\text{NaBH}_4$  in alkaline

solution or freshly prepared  $\text{NaBH}_4$  (Oda and Ingle, 1981; Brosset, 1982; Iverfeldt, 1984).

(b) Reactive compounds are reduced to  $\text{Hg}^0$  as in (a), while non-reactive compounds are transformed to reactive forms after treatment with concentrated  $\text{HNO}_3$  (cf., Kaiser et al., 1978; Slemr et al., 1981; Olafsson, 1982; Seritti et al., 1982; Fitzgerald et al., 1983).

Two additional treatments, to ensure the release of non-reactive mercury in water or solid samples, are UV irradiation (Olafsson, 1983) or ultra-sonic shocking (Brosset, 1985).

### 3. Occurrence of mercury in nature

The methods generally used to enrich air and water concentrations before analysis make it difficult or impossible to maintain and determine the original chemical composition of the mercury compounds sampled. Most data available are thus unspicated, i.e., given as total mercury concentrations. As described in Fig. 1, it is possible to separate volatile (V) and water-soluble or particle-born reactive (R) or non-reactive (NR) compounds, but only a few measurements with these forms separated have been published.

Components of probable importance in air and natural water systems are:

- V:  $\text{Hg}^0$ ,  $(\text{CH}_3)_2\text{Hg}$ ;  
 R:  $\text{Hg}^{2+}$ ,  $\text{HgX}_2$ ,  $\text{HgX}_3^-$  and  $\text{HgX}_4^{2-}$  with  $\text{X} = \text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ ;  $\text{HgO}$  on aerosol particles;  $\text{Hg}^{2+}$  complexes with organic acids;  
 NR:  $\text{CH}_3\text{Hg}^+$ ,  $\text{CH}_3\text{HgCl}$ ;  $\text{CH}_3\text{HgOH}$  and other organomercuric compounds,  $\text{Hg}(\text{CN})_2$ ;  $\text{HgS}$  and  $\text{Hg}^{2+}$  bound to sulfur in humic matter.

It is generally assumed that the main volatile form in air is elemental mercury, but dimethyl mercury may also occur (Slemr et al., 1981).

Uncharged complexes, such as  $\text{HgCl}_2$ ,  $\text{CH}_3\text{HgOH}$  etc., occur in the gaseous phase, but are also relatively stable in fresh water, i.e., in precipitation, lakes, and rivers.  $\text{HgCl}_4^{2-}$  is the dominating form in sea water (cf. Table 6).

Mercury bound to particles in the aquatic systems is most probably bound to sulphur. During degradation of humic matter, mercury may be released to the aqueous phase with water-soluble humic or fulvic acids.

### 3.1. Air

A wide range of concentrations of total mercury in air has been reported in the literature. In view of the difficulties in obtaining reliable data, we have chosen to consider only some of the most recent data. These observations are summarized in Table 1. Fig. 2 shows the latitudinal distribution of total

gaseous mercury in surface air over the Atlantic (Slemr et al., 1985). These data indicate the existence of a background level of about  $2 \text{ ng m}^{-3}$  in the lower troposphere of the northern hemisphere and just over  $1 \text{ ng m}^{-3}$  in the southern hemisphere, at least in an oceanic environment. The few measurements in the upper troposphere of the northern hemisphere give only slightly lower concentrations (mainly between 1 and  $2 \text{ ng mg}^{-3}$ ). At remote locations in Europe, like the rural parts of southern Sweden and Italy, concentrations most often lie in the range 2 to  $3 \text{ ng m}^{-3}$  in summer and 3 to  $4 \text{ ng m}^{-3}$  in winter (Brosset, 1981b; Ferrara et al., 1982). In urban air, the concentrations can be still higher. In the plume of a coal-fired power plant, Lindberg (1980) measured concentrations of total gaseous mercury in excess of  $1000 \text{ ng m}^{-3}$  within a few km from the source ( $5\text{--}10 \mu\text{g m}^{-3}$  are normal concentrations in the flue gas).

Few reliable speciation measurements have been made of the gaseous mercury found in the

Table 1. Measured concentrations of total (gaseous) Hg in air

Location	Season	Sampling time	Range (ng/m <sup>3</sup> )	Mean (ng/m <sup>3</sup> )	Ref.
S. Sweden, rural	All year	24 h	2–6	3.3	a
S. Sweden, 1–3 km height	Mar.–July	30 min	1.6–3.1	2.1	a
Remote land areas			2–9		b
Hokkaido, Japan			0.7–6.2		c
Mainz, FRG		20 min		9.9	d
Atlantic Ocean	Oct.	2–4 h	1–11	2.8	e
Atlantic Ocean			1–3	2 in N.H.	f
Tropical pacific	April–Aug.		0.8–3.2	1.7	g
N. Atlantic	July		1–1.9	1.6	g
Long Island Sound, USA			1.6–7.2	2.9	g
Upper troposphere			0.6–2.6	1 in S.H.	e
Florida, rural	Aug. & Nov.	30 min	3–300		h
Italy, over sea			0.9–3.6	2.1	i
Italy, rural area			1.2–4.1	3.2	i
Italy, urban area			2.2–31.5	10.1	i
Italy, "mineralized area"			8.2–86.3	12.4	i
Italy, industrial area			12.1–35.5	22.2	i
Canada, rural area	Summer	~10 h		3	j
Canada, suburban area				8	j
S. Sweden, urban	May–June	30 min	0.8–13.2	4.0	k

(a) Brosset (1981b)

(b) Matheson (1979)

(c) Matsunaga and Goto (1976)

(d) Slemr et al. (1979)

(e) Seiler et al. (1980)

(f) Slemr et al. (1985)

(g) Fitzgerald et al. (1983)

(h) Johnson and Braman (1974)

(i) Ferrara et al. (1982)

(j) Schroeder (1981)

(k) Iverfeldt (1984)

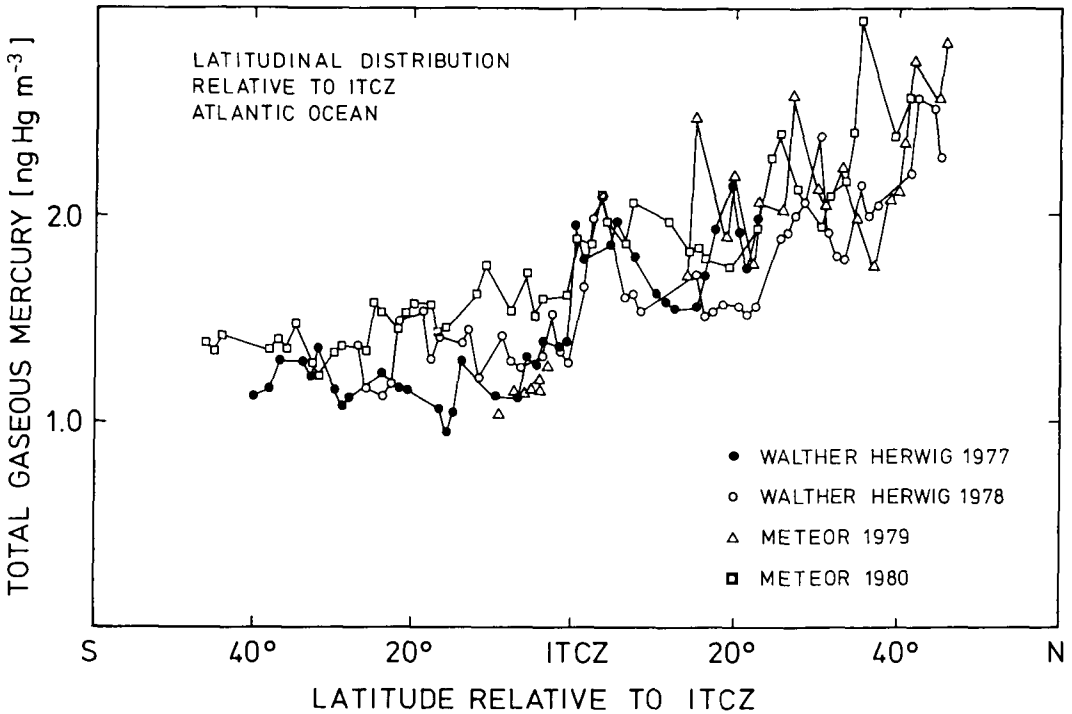


Fig. 2. Latitudinal distribution of total gaseous mercury in surface air over the Atlantic (Slemr et al., 1985). The mid-point represents the position of the Intertropical Convergence Zone (ITCZ); the northern hemisphere is to the right.

atmosphere. Generally, elemental mercury seems to be the dominant form. However, Slemr et al. (1981) found dimethyl mercury to make up over 30% of the total gaseous mercury over the European continent.

The corresponding figure for oceanic air was about 5%. Later measurements by the same group (Slemr et al., 1985) indicate that the above figures may have been too high. They also found that monomethyl mercury could make up several % of the total gaseous mercury, particularly in continental air.

Brosset (1981b) distinguished between a water-soluble fraction and a non-soluble fraction, presumably metallic mercury,  $\text{Hg}^0$  (although, for example, dimethyl mercury might also contribute). For rural air in southern Sweden, Brosset (1981b) found the soluble fraction to make up on the average 5–10% of the total gaseous mercury in winter. The fraction was smaller in summer.

Mercury associated with aerosol particles normally makes up only a small fraction of the total

airborne mercury. However, the rôle of the particulate mercury in the atmospheric part of the mercury cycle is important, since its residence time is considerably shorter than that of the gaseous mercury. Average concentrations of particulate mercury at remote locations are normally below  $0.1 \text{ ng m}^{-3}$  (cf. review by Matheson (1979); Millward and Griffin (1980)). Fitzgerald et al. (1983) measured concentrations as low as about  $0.001 \text{ ng m}^{-3}$  in oceanic air and around  $0.01$  to  $0.06 \text{ ng m}^{-3}$  (average  $0.02$ ) at Long Island Sound in northeastern USA.

### 3.2. Precipitation

Since deposition by precipitation is a major removal process for atmospheric mercury and is relatively easily estimated from measurements, it is worthwhile to review carefully the available data on mercury in precipitation. In Table 2 we have summarized the pertinent data. The lowest concentrations in rain water (around  $1 \text{ ng L}^{-1}$ ) have been reported from a coastal site in Japan and from Samoa Island. Most other values lie in the range

Table 2. Measured concentrations of Hg in precipitation and in ice cores

Location	Season	Precip. type	Range (ng/l)	Mean (ng/l)	Ref.
Onsala, Sweden	Aug	rain	10–75	20	a
Gothenburg, Sweden	Nov.	rain	10–25		b
Vemdalen, Fredrika Sweden	Nov. (2 samples)	snow		~1	b
Onsala, Sweden	Nov.	rain	21–52	37	b
Rural sites, Denmark	Whole year	rain	5–300	80	c
Liverpool, UK		rain	6–30	17	d
Göttingen, FRG			23–75		f
Italy, polluted		early rain	30–85	66	g
Italy, polluted		late rain	10–26	18	g
Italy, remote		rain		~20	g
Hokkaido, Japan (coastal site)	May–Aug.	rain	0.7–1.5	~1.0	h
(coastal site)	Dec.	rain	1.0–1.5	~1.0	h
(coastal site)	Dec.–March	snow	0.6–3.4	~1.0	h
Southern New England (coastal site)	Sept.–Nov.	rain	2–21	10	i
Northern New England (mountain site)	March	rain		60	j
Canada, several sites		snow	20–200		k
Quebec, Canada		rain and snow	20–100		l
North Sea		rain	17–58	30	m
North Pacific Ocean		rain	10–50		n
Tropical Pacific	July	rain	1.7–2.3	2.0	o
Samoa Island	Nov.	rain		0.8	i
Alaska		snow	<5–26		p
Greenland		icecores	7–13		q
Greenland		icecores	2–17	~10	r

(a) Brosset (1981b)

(b) Brosset (1982)

(c) Anonymous (1979)

(d) Airey (1982)

(f) Ruppert (1975)

(g) Ferrara et al. (1982)

(h) Matsunaga and Goto (1976)

(i) Fogg and Fitzgerald (1979)

(j) Schlesinger et al. (1974)

(k) Quoted in Matheson (1979)

(l) Tomlinson et al. (1980)

(m) Cambray et al. (1979)

(n) Nishimura (1979)

(o) Fitzgerald et al. (1983)

(p) Weiss et al. (1975)

(q) Appelqvist et al. (1978)

(r) Boutron and Delmas (1980) (review)

5–100 ng L<sup>-1</sup>. Some of the snow samples contained very low concentrations. The Greenland ice core samples have concentrations around 10 ng L<sup>-1</sup>. These values represent total deposition, i.e., with dry deposition included. It is important to point out that some earlier measurements from Greenland ice cores gave significantly higher concentrations (pre-industrial averages of about 60 ng L<sup>-1</sup>), but that these high values later proved to be wrong (Appelqvist et al., 1978). Most of the estimates of fluxes through the atmosphere made

during the middle and late 1970s have been based on these erroneously high Greenland data, and therefore must be modified.

It is of interest to compare concentrations of mercury in rainwater with those in air for those few studies where both have been measured. We define a washout ratio  $W$  as

$$W = C(\text{rain})/C(\text{air})$$

with the concentrations expressed in ng m<sup>-3</sup> in both air and rainwater. The washout ratio is thus a

Table 3. *Rough estimates of mercury washout ratios (concentration in rainwater divided by concentration in air)*

1	2	3		
$\text{Hg}_{\text{tot}}, \text{rain}$	$\text{Hg}_{\text{tot}}, \text{rain}$	$\text{Hg}_{\text{tot}}, \text{rain}$		
$\div$	$\div$	$\div$		
$\text{Hg}_{\text{tot}}, \text{air}$	$\text{Hg}_{\text{sol}}, \text{air}$	$\text{Hg}_{\text{part}}, \text{air}$	Location	Ref.
$\sim 10^4$	$\sim 10^5$	—	rural Sweden	a
$\sim 10^4$	—	—	rural Italy	b
$\sim 10^3$	—	—	urban UK	c
$\sim 3 \cdot 10^3$	—	—	urban Japan	d
—	—	$\sim 10^6$	tropical Pacific	e

(a) Brosset (1981b)

(b) Ferrara et al. (1982)

(c) Airey (1982)

(d) Matsunaga and Goto (1976)

(e) Fitzgerald et al. (1983)

measure of removal efficiency of mercury by precipitation. For a gaseous compound,  $W$  corresponds to the solubility, at least to the extent that equilibrium can be assumed to exist between raindrops and the surrounding air.

Table 3 shows very rough estimates of washout ratios defined in 3 different ways. The values in column 1 are considerably lower than those for other metals that occur mainly in accumulation mode particulate matter. For Pb and V, for example, Slinn et al. (1978) give values of  $6 \times 10^4$  and  $16 \times 10^4$ , respectively. If only the water-soluble mercury fraction is considered for the gas phase, the washout ratio is closer to that of these other metals. Because of the many different mercury forms that may exist in the atmosphere and the large differences in their solubilities (cf. Table 5), it is difficult to draw any firm conclusions regarding atmospheric mercury speciation from the washout ratios presented in Table 3. It is likely that both particulate mercury and water-soluble gaseous forms contribute significantly to the mercury content in precipitation.

### 3.3 Natural waters

Fitzgerald (1979) reviewed concentration measurements of mercury in natural waters performed during the period 1971–1978. The wide variation (0–1000 ng L<sup>-1</sup>), with location, depth, and analytical laboratory, causes difficulties in defining an average value useful for budget calcula-

tions. Previous intercalibrations of mercury in seawater have demonstrated the analytical problems. In the ICES study (Olafsson, 1982), 32 laboratories obtained values within the range 0.7–94 ng L<sup>-1</sup>, which shows that it is necessary to be very careful when using literature data of mercury concentrations.

It is important to distinguish between dissolved mercury and mercury bound to suspended matter, especially in polluted waters. Seritti et al. (1982) found ranges of 0.3–80 ng L<sup>-1</sup> on the particles and 1.7–12.2 ng L<sup>-1</sup> in the dissolved phase along the Italian coast.

Recent measurements of mercury in aquatic systems have given lower values than previously assumed (Table 4). The following concentration ranges may be considered representative for dissolved mercury:

open ocean 0.5–3 ng L<sup>-1</sup>;

coastal sea water 2–15 ng L<sup>-1</sup>;

rivers and lakes 1–3 ng L<sup>-1</sup>.

Local variations from these values are of course considerable, especially in coastal seawater and in lakes and rivers where mercury associated with suspended matter may also contribute to the total load. Generally, there are increased levels of mercury if the waters contain elevated amounts of organic matter like humic acids.

The relatively low background levels given for lakes and rivers compared to coastal sea water are consistent with the fact that Hg(II) is not stabilized as  $\text{HgCl}_4^{2-}$  in fresh water as it is in seawater. Of the total concentration of 2–3 ng L<sup>-1</sup> in the North Atlantic, Olafsson (1983) found that more than 80% occurred as reactive Hg, i.e. mainly as inorganic Hg(II) compounds.

Only a few measurements of volatile mercury have been made in aquatic systems: Iverfeldt (1984) found 0.2–3.0 ng L<sup>-1</sup> in the oxic surface water of a Norwegian fjord, and Brosset (1985) found approximately 0.02–0.1 ng L<sup>-1</sup> in lakes in southern Sweden. The higher values are found in productive zones.

## 4. Transformation processes

The biogeochemical cycle of mercury depends not only on concentrations in different reservoirs but also on thermodynamic properties of the

Table 4. *Measured concentrations of dissolved mercury in marine and fresh waters (ng L<sup>-1</sup>)*

Location	Ocean	Coastal	Rivers and lakes	Ref.
Norwegian fjord		3		a
Norwegian fjord, anoxic deep water		7–15		a
South Baltic and Kattegat		9		b
The Sound, SW/Den.		10–15		b
Mediterranean, Tyrrhenian coast		2–12 <sup>1</sup>		c
North sea	1–3	3–10		d
North Atlantic 0–2900 m	0.5–4.5 <sup>2</sup>			e
North Atlantic	1.2–3.2			f
Pacific ocean	0.3–0.7 <sup>3</sup>			f
River, eastern Sweden			2–6	g
Lakes, southern Sweden			1–3	g

(a) Iverfeldt (1984)

(e) Olafsson (1983)

(b) Pedersen and Larsen (1977)

(f) Fitzgerald et al. (1983)

(c) Seritti et al. (1982)

(g) Brosset (1985)

(d) Portman and Topping (1983)

<sup>1</sup> 0.3–80 ng L<sup>-1</sup> were found on suspended particles.<sup>2</sup> Not dependent on depth.<sup>3</sup> Reactive mercury in surface water.

mercury compounds present. Vapor pressures, solubilities, solution equilibria, and air–water distribution (Henry's law) constants of mercury compounds occurring in nature are necessary information for interpretation of the pathways of mercury. Also, kinetic data for the chemical reactions involved are needed for correct estimates of the fluxes. In this section, we discuss mercury speciation, distribution equilibria, and redox reactions. Despite interest in environmental aspects of mercury in recent years, such fundamental data are partly still not available.

#### 4.1. Air/water distribution equilibria

Some of the mercury bound in soil and water may slowly be transformed to volatile species that are emitted (or re-emitted) to the atmosphere. This emission from continents and oceans is probably mainly due to elemental mercury, Hg<sup>0</sup>, and dimethyl mercury, (CH<sub>3</sub>)<sub>2</sub>Hg, both of which can be formed by biochemical processes.

Elemental mercury and dimethyl mercury are defined as volatile from their relatively high air/water distribution constant, both being ~0.3 (dimensionless, cf. Table 5). This magnitude of the constant means that an air concentration of 1 ng m<sup>-3</sup> of either compound is in equilibrium with only ~0.003 ng L<sup>-1</sup> in the water phase (cf. Fig. 3). The

few measurements of volatile mercury that have been made in aquatic systems have given values in the range 0.02–3.0 ng L<sup>-1</sup>. This indicates that these compounds are emitted to the atmosphere.

It is generally assumed that most of the gaseous mercury in the atmosphere is elemental mercury. It is not known which of the two mentioned volatile compounds dominates the evasion process; compounds other than Hg<sup>0</sup> and (CH<sub>3</sub>)<sub>2</sub>Hg may also contribute. Measurements over the European continent and over the Atlantic have indicated that an appreciable amount of dimethyl mercury is emitted, but that a relatively fast degradation to elemental mercury takes place in air (Seiler, personal communication, 1983). Niki et al. (1983) have studied the reaction between OH radicals and (CH<sub>3</sub>)<sub>2</sub>Hg and determined the reaction rate constant to  $k = 2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. For typical concentrations of OH radicals (10<sup>5</sup>–10<sup>6</sup> molecules cm<sup>-3</sup>), this corresponds to an atmospheric lifetime of (CH<sub>3</sub>)<sub>2</sub>Hg of at most a few days.

A number of mercury compounds of probable importance in the environment are defined as water-soluble due to their relatively low air/water distribution constants. Table 5 shows compounds for which such constants have been determined experimentally. Distribution constants can also be calculated from thermodynamic data, e.g. subli-



Table 5. Experimentally-determined distribution constants for some compounds of relevance for the mercury cycle

Compound	$H = \{HgX(g)\}/\{HgX(aq)\}$ (v/v)	Temp ( $^{\circ}C$ )	Cl ionic strength (M)	Ref.
$Hg^0$	0.29	20	0	a
$(CH_3)_2Hg$	0.31	25	0	b
$(CH_3)_2Hg$	0.15	0	0	b
$CH_3HgCl$	$1.9 \times 10^{-5}$	25	0.7	c
$CH_3HgCl$	$1.6 \times 10^{-5}$	15	1.0	c
$CH_3HgCl$	$0.9 \times 10^{-5}$	10	$0.2 \times 10^{-3}$	c
$Hg(OH)_2$	$3.2 \times 10^{-6}$	25	$0.2 \times 10^{-3}$	d
$Hg(OH)_2$	$1.6 \times 10^{-6}$	10	$0.2 \times 10^{-3}$	d
$HgCl_2$	$2.9 \times 10^{-8}$	25	$0.2 \times 10^{-3}$	d
$HgCl_2$	$1.2 \times 10^{-8}$	10	$0.2 \times 10^{-3}$	d

(a) Sanemasa (1975)

(b) Talmi and Mesmer (1975)

(c) Iverfeldt and Lindqvist (1982)

(d) Iverfeldt and Lindqvist (1980)

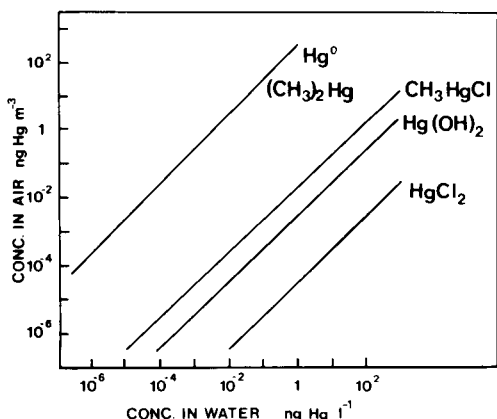


Fig. 3. Equilibrium concentrations in air of some mercury compounds as a function of corresponding concentrations in the water phase obtained from experimentally determined air/water constants at  $25^{\circ}C$  (cf. Table 5). The curves for  $Hg^0$  and  $(CH_3)_2Hg$  coincide.

mation, solvation and complexation energies in a Born-Haber cycle. However, such calculated data may suffer from uncertainties, adding to significant errors in the interpretation of fluxes. Therefore, experimentally determined air/water distribution constants should be used when available (cf. also Graedel et al., 1982).

Of compounds not listed in Table 5, it seems most important to determine the distribution constant for  $Hg(CN)_2$ , as a stable molecular

compound of possible importance for the mercury cycle. Investigations of  $CH_3HgOH$  have resulted in  $H$  values around  $10^{-7}$  (Iverfeldt and Persson, 1985).

It is important to note that only uncharged species are responsible for the distribution equilibria between air and water. When applying distribution or Henry's law constants to natural systems, it is therefore necessary to take the relevant complex equilibria into account when estimating the concentrations of exchangeable molecules in the aqueous system.

Hg speciation in waters of different ionic strength and pH, based on well-established stability constants, is given in Table 6, and also illustrated in Fig. 4 as a function of pH, redox potential, and chloride concentration. Similar and more extensive calculations can be found elsewhere (cf. Lerman, 1979; Stumm and Morgan, 1981).

Accurate calculations of mass transfers between air and water droplets in the atmosphere require not only thermodynamic distribution constants, but also, surface-layer diffusion and mass-transfer constants for the gas and aqueous phases (Liss and Slater, 1974; Stumm and Morgan, 1981), especially for the rapidly changing concentrations that may occur in and around falling rain drops. However, the experimentally determined air/water distribution constants are in most cases sufficient to determine the direction of fluxes between the gas and water phases. If the Hg species are well-mixed

Table 6. % of different inorganic and monomethyl mercury species in natural waters (from Dyrssen and Wedborg, 1980)

Compound	Sea water {Cl} = 0.7 M	Fresh water {Cl} = 0.2 mM				
		pH = 4	pH = 5	pH = 6	pH = 7	pH = 8
<b>Inorganic</b>						
HgCl <sub>4</sub> <sup>2-</sup>	65.8	—	—	—	—	—
HgCl <sub>3</sub> Br <sup>2-</sup>	12.3	—	—	—	—	—
HgCl <sub>3</sub> <sup>-</sup>	12.0	0.2	0.2	0.1	0.1	—
HgCl <sub>2</sub> Br <sup>-</sup>	4.3	—	—	—	—	—
HgCl <sub>2</sub>	3.0	99.6	98.8	91.1	34.1	0.1
HgClBr	1.1	—	—	—	—	—
HgOHCl	0.2	0.1	0.9	8.5	49.4	6.2
HgCl <sup>+</sup>	—	0.2	0.2	0.2	0.1	—
Hg(OH) <sub>2</sub>	—	—	0.002	0.2	16.4	93.7
<b>Monomethyl</b>						
CH <sub>3</sub> HgCl	92.2	97.8	97.1	89.8	33.5	1.9
CH <sub>3</sub> HgOH	5.1	0.1	0.8	8.4	65.8	98.1
CH <sub>3</sub> HgBr	2.7	—	—	—	—	—
CH <sub>3</sub> Hg <sup>+</sup>	—	2.1	2.1	1.9	0.7	0.04

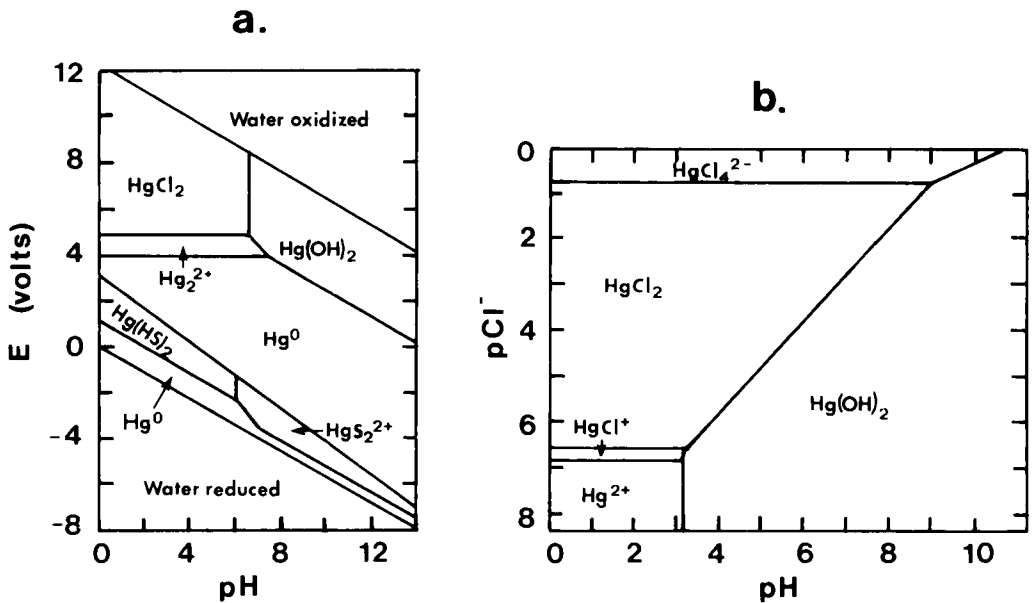


Fig. 4. (a) Predominance diagram for soluble mercury species in water containing  $10^{-3}$  M Cl<sup>-</sup> and  $10^{-3}$  M SO<sub>4</sub><sup>2-</sup> or equivalent total sulphur. The vertical axis represents oxidation potential (*E*). The diagram refers to 25 °C and 1 atm pressure (from Benes and Havlik (1979) and Hem (1970)). (b) Stability ranges from chloro- and hydroxo-complexes of divalent mercury in aqueous solution (from Benes and Havlik (1979) and Lockwood and Chen (1973)). The vertical axis represents the negative logarithm of the chloride concentration.

in the atmosphere, it is usually adequate to assume that equilibrium conditions in raindrops have been achieved. Fig. 3 can thus be used for simple model calculations.

Most of the mercury in the oceans is probably present as inorganic mercury. If one assumes 2 ng L<sup>-1</sup> of inorganic mercury in the normal oceanic background, this would correspond to 0.06 ng L<sup>-1</sup> of HgCl<sub>2</sub> (Table 6), which would be in equilibrium with only  $\sim 2 \times 10^{-6}$  ng m<sup>-3</sup> of HgCl<sub>2</sub> in air (smaller for Hg(OH)<sub>2</sub> and HgOHCl).

The average concentration of non-reactive mercury in ocean water may be estimated to be 0.2–0.4 ng L<sup>-1</sup>. How much of this that is monomethylated mercury is not known. An assumption of 0.1 ng L<sup>-1</sup> monomethyl mercury (probably too high) would correspond to  $2 \times 10^{-3}$  ng m<sup>-3</sup> of CH<sub>3</sub>HgCl in air.

Air concentrations of the inorganic compounds HgCl<sub>2</sub>, Hg(OH)<sub>2</sub> or HgOHCl greater than  $\sim 10^{-6}$  ng m<sup>-3</sup> will thus give a flux from the atmosphere to the ocean, while the corresponding value for mono-methyl mercury is  $\sim 10^{-3}$  ng m<sup>-3</sup>. The few measurements of the water-soluble fraction of mercury in background air indicate concentrations of 0.05–0.2 ng m<sup>-3</sup> of such compounds (Brosset, 1984). This means either that there is a flux of water-soluble compounds from the atmosphere to the ocean, or that some other water-soluble mercury form with a higher air/water distribution constant is of importance. This compound could be Hg(CN)<sub>2</sub>.

At present, it is not possible to decide if the emission of volatile mercury from the oceans to the atmosphere dominates over the wet and dry deposition of water soluble mercury to the oceans.

Typical concentration values for mercury in precipitation in relatively remote parts of Europe are 3 ng L<sup>-1</sup> as reactive and 10 ng L<sup>-1</sup> as non-reactive mercury, while higher values are found in industrialized areas (Ferrara et al., 1982; Brosset, 1985). The composition of the non-reactive part is not known, but it has been shown that it is not monomethyl mercury (Brosset, 1984).

Assuming that HgCl<sub>2</sub> is representative for reactive mercury in rainwater of normal acidity (cf. Table 6), the equilibrium air concentration of reactive, water-soluble mercury is not more than  $\sim 10^{-4}$  ng m<sup>-3</sup>. This is far below the  $\sim 0.1$  ng m<sup>-3</sup> of water-soluble mercury found in air (Brosset, 1985), and leads us to the conclusion that most of the

water-soluble mercury in air is non-reactive with an air/water overall distribution constant of  $\sim 10^{-5}$ . It may be gaseous or associated with small particles ( $\sim 0.1 \mu\text{m}$ ).

Transfer of insoluble compounds or charged complexes from water to airborne particles or vice versa may also occur. Mechanisms responsible for the formation of mercury containing aerosol may be atmospheric oxidation of Hg<sup>0</sup> to Hg(II), evaporation of cloud drops and, probably less important, of sea spray droplets. Charged complexes in air have to be bound to aerosol particles until degassed as neutralized species, redissolved, or deposited. Only a small fraction of the atmospheric mercury has been found in the aerosol particles (cf. Section 3). However, with respect to the sampling difficulties, one should not rule out the possibility that more of the airborne water-soluble mercury is associated with small particles. In an aquatic system, one is more likely to find insoluble mercury compounds bound to organic material or HgS on particles.

#### 4.2. Redox chemistry

The redox stabilities of mercury compounds in natural systems have been reviewed by Benes and Havlik (1979). Two of their diagrams are reproduced in Fig. 4. They show that the oxidized forms are stabilized in oxygenated water and in air, in which the oxidation potential  $E > 0.5$  V.

Elemental mercury occurring in air or dissolved in oxygenated surface water is thus thermodynamically unstable with respect to oxidized species. However, possible oxidation processes seem to be relatively slow, so that Hg<sup>0</sup> formed in water under reducing conditions or in biological processes may pass unchanged through the oxidizing surface water to the atmosphere (cf. Iverfeldt, 1984). Furthermore, Hg<sup>0</sup> in the atmosphere has a rather long life-time, 0.3–2 years (cf. Section 5), also indicating that atmospheric oxidation processes are slow.

It is also possible that mercuric compounds can be reduced by photochemical reactions in the atmosphere. Dimethyl mercury, primarily formed in biochemical processes and emitted to the atmosphere, may, for example, be photolysed to Hg<sup>0</sup> and CH<sub>3</sub> radicals. The photochemical sensitivity of this and other divalent mercury compounds under atmospheric conditions may be of importance for the mercury cycle.

A probable pathway of the mercury cycle, recently proposed by Brosset (1981a), is that  $Hg^0$  is mobilized to the atmosphere where it is subjected to atmospheric oxidation processes that yield water-soluble forms subsequently scavenged by wet or dry deposition. Brosset also proposed that in industrialized areas, other anthropogenic air pollutants could significantly influence the formation rate of oxidized  $Hg$  species.

The atmospheric oxidation processes are not yet fully understood. The ratio  $Q = Hg(II)/Hg(tot)$  has been found to be approximately 0.1 in industrialized areas, and correlations between concentrations of atmospheric oxidants and  $Q$  are presently being investigated (Brosset, 1985).

Early laboratory studies (P'yankov, 1949) have shown that  $Hg^0$  is oxidized by ozone in dry air. High concentrations of mercury ( $7.9 \mu g m^{-3}$ ) and ozone (3 ppm) were used. Applying P'yankov's rate constant to ambient concentrations of  $1 ng m^{-3}$  of  $Hg^0$  and 25 ppbv of ozone would result in a  $Hg^0$  half-life of approximately 0.6 years. This is in agreement with the average residence time estimated in Section 5. However, the oxidation products are not known and the significance of the

homogeneous  $Hg^0$  oxidation with ozone is not yet clear.

Homogeneous gas phase oxidation has also been compared with the oxidation rate in a water phase in equilibrium with a gas phase containing  $500 ng Hg^0 m^{-3}$  and 100–200 ppbv ozone (Iverfeldt, 1984). The reaction was found to be much faster with the water phase present and to be first-order both with respect to ozone and  $Hg^0$ . Elevated reaction rates were also obtained in humid air (71% RH at 20°C), but whether the reaction occurs mainly in the water film adsorbed on the reactor walls or as a gas-phase reaction is not yet resolved.

The oxidation rate constant from the water-phase experiments, extrapolated to ambient concentrations in a cloud (i.e.  $1 ng Hg^0 m^{-3}$ , 25 ppbv  $O_3$  and  $1 g H_2O(aq) m^{-3}$ ) gives a half-life for  $Hg^0$  of approximately 5 days within the cloud. Taking into account the frequency of occurrence of clouds, the corresponding overall half-life would be about two months, roughly consistent with the estimate of average residence time given in Section 6.

Since the presence of water seems to accelerate the  $Hg^0$  oxidation, it is likely that the oxidation mechanism involves a  $Hg-H_2O_2$  complex, and

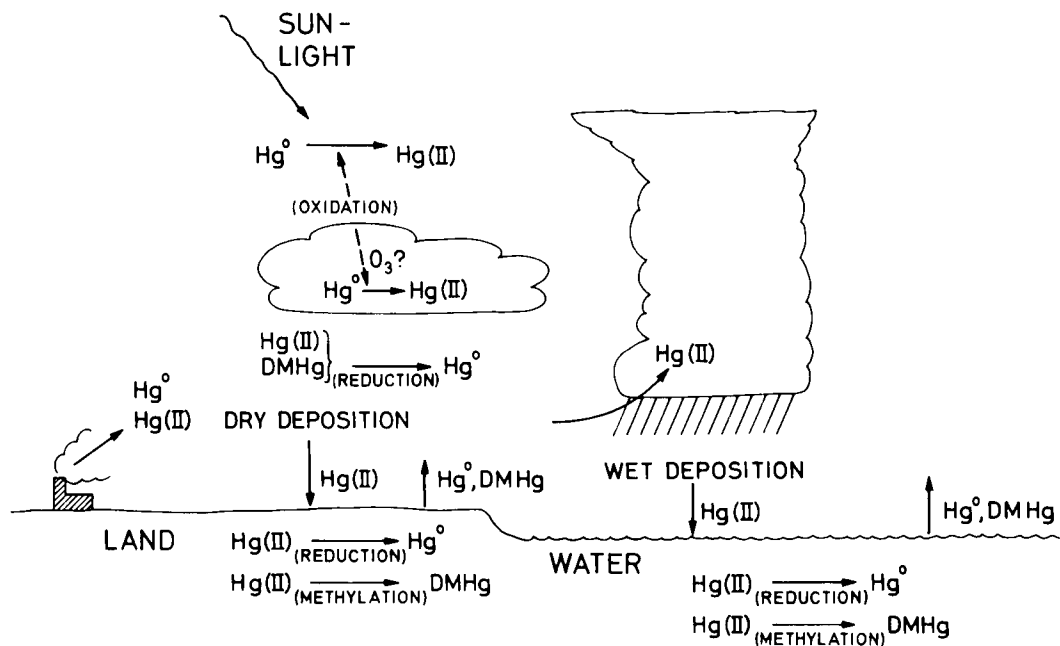


Fig. 5. Schematic representation of transfers and transformations affecting the atmospheric part of the mercury cycle. DMHg represents  $(CH_3)_2Hg$ .

thus, that the primary oxidation product is  $\text{Hg}(\text{OH})_2$ .

The influence of sunlight, temperature, relative humidity and other pollutants on the homogeneous and heterogeneous reaction kinetics of the mercury compounds in ambient air needs further investigations. Some of the transformation and transfer processes discussed above are summarized schematically in Fig. 5.

## 5. Emission processes

It is very probable that past anthropogenic emissions of mercury have significantly increased its present circulation through soils, water and air. It is therefore misleading to refer to present-day fluxes (other than direct anthropogenic emissions) as "natural", even though they may be largely controlled by natural biological processes. We prefer to avoid the word "natural" and rather use the terms "pre-industrial", "present", and "present background". With this terminology, the "present" fluxes through the atmosphere can be viewed as the sum of direct anthropogenic emissions and the "present background" fluxes. The present background fluxes may be substantially larger than the "pre-industrial" fluxes through the atmosphere, the difference representing fluxes resulting from "old" anthropogenic emissions.

### 5.1. Present anthropogenic emissions

Present anthropogenic activities giving rise to mercury mobilization and transfer of mercury to land, water and air include:

- mining and smelting (in particular, zinc and copper smelting);
- burning of fossil fuels (mainly coal);
- industrial production processes (in particular, the mercury-cell chlor-alkali process for production of chlorine and caustic soda);
- agriculture (pesticides);
- consumption-related discharges (including waste incineration).

In Table 7, we summarize some recent estimates of anthropogenic emissions for different parts of the world. The number of significant figures in these numbers does not represent the certainty by which the numbers are known. For example, the estimate of global emissions by Mackenzie and Wollast (1977) gives a value of about 10,000  $\text{ton a}^{-1}$  for air and 9000  $\text{ton a}^{-1}$  for land, i.e. much higher values than cited in Table 7.

A distribution of the global anthropogenic atmospheric emissions, between different countries and continents ascribes about 30% to Europe (without USSR), 20% to USA, and 20% to USSR (Watson, 1979).

The historical development of anthropogenic

Table 7. Present-day anthropogenic emissions of total mercury to air, water and land ( $\text{ton a}^{-1}$ )

	Sweden <sup>1</sup>			USA <sup>2</sup>			Global <sup>2</sup>			Total
	Air	Water	Land	Air	Water	Land	Air	Water	Land	
Mining and smelting	1.2	0.5		70	3	4				2400
Industrial processes	1.5	0.3		40	20	310				
Fossil fuel combustion	0.4	0.0		120	0	10				450
Consumption	1.0	0.2		240	60	750				4650
Total	4.1	1.0		470	80	1070	2400	300	4800	7500
Sweden <sup>3</sup>	4.8	2.5	28							

<sup>1</sup> For the year 1977/78 (SNV, 1981).

<sup>2</sup> For the year 1975 (Watson, 1979). Figures rounded off.

<sup>3</sup> Total for the year (Project KHM, 1983).

emissions has been discussed by Andren and Nriagu (1979). They estimate that emissions have increased by a factor 2 or 3 between 1900 and the 1970s and that the accumulated deposition by the late 1970s corresponds to about 75 years of emissions at the rate prevailing at that time.

All of the above emission estimates refer to total mercury. Very little information is available about the forms of mercury compounds in anthropogenic emissions to the environment. It has generally been assumed that much of the mercury in emissions to air is in the elemental state. Most mercury releases to water are in the inorganic divalent form and to land in any or several of these chemical forms. A few measurements of mercury in the plumes from coal-fired power plants have indicated that between 50% and 70% occurred in a water-soluble form, most of the remainder probably being metallic mercury vapour (Bergström, 1983a,b). An

important fraction may also be associated with particulate matter.

### 5.2. Emissions to the atmosphere by biological and natural physico-chemical processes

The following natural processes contribute to the flux of mercury and its compounds to the atmosphere:

- volcanic emissions;
- windblown dust from dry continental areas;
- emission of gaseous mercury from soils and vegetation;
- emission of gaseous mercury from the ocean and other water bodies.

Very little is known about the magnitude of these fluxes or about the species involved. The volcanic emissions are probably negligible compared to the others (Mackenzie and Wollast, 1977; Buat-Menard and Arnold, 1978; Cadle, 1980). The flux

Table 8. *Previous estimates of pre-industrial emissions of Hg to the atmosphere (ton Hg a<sup>-1</sup>); see text for comments*

Continents to atmosphere	Method of estimate	Ocean to atmosphere	Method of estimate	Ref.
8,300	Based on "old" ice core data (a)	16,700	Based on "old" ice core data (a) This flux was assumed to have increased to 23,300 by now	b, c
8,300	As above	21,000	Present day flux Estimated essentially as above	d
17,800	V <sub>g</sub> = 0.1 cm s <sup>-1</sup> estimated from "old" ice core data (e) Degassing data from USEPA (1975)	2,900	Same as for continents to atmosphere	f
800	Based on "new" ice core data (g)	1,700	Same as for continents to atmosphere	h
(a) Weiss et al. (1971)		(e) Weiss et al. (1975)		
(b) Garrels et al. (1975)		(f) Andren and Nriagu (1979)		
(c) Mackenzie and Wollast (1977)		(g) Appelquist et al. (1978)		
(d) Lantzy and Mackenzie (1979)		(h) Millward (1982)		

associated with dust particles has been estimated by Lantzy and Mackenzie (1979) to be about 25 ton per year, also a negligible amount.

Some attempts have been made to measure soil degassing rates (McCarthy et al., 1969), but most estimates of the global evasion rates rely on indirect arguments, based on deposition rates estimated from concentration of mercury in rainwater and ice-core samples (see e.g. Lantzy and MacKenzie (1979); Andren and Nriagu (1979); Millward (1982)). These and previous estimates of global "pre-industrial" rates of emissions to the atmosphere range from about 2,500 to almost 30,000 ton per year (cf. Table 8). These estimates are extremely uncertain. With the exception of Millward's (1982) estimate, they are based on ice-core data that are likely to be incorrect (i.e. too high, cf., Appelqvist et al., 1978). Furthermore, it is very uncertain to what extent the Greenland ice-core data can be taken to represent global deposition rates. The estimates of "pre-industrial" emissions are discussed further in Section 6.

## 6. Mercury budgets

In this section we summarize some of the information contained in the earlier chapters and attempt to make budget estimates of mercury and its compounds, i.e., systematic comparisons of fluxes and reservoir contents. The aim of these calculations is to compare anthropogenic and pre-industrial fluxes in some reservoirs of different sizes and to obtain some insight into transport patterns and possible areas of influence of specific mercury sources.

### 6.1. Estimates of emission and deposition

Anthropogenic emissions for the European atmosphere are taken from Watson (1979). Pre-industrial emissions into the atmosphere are assumed to be uniformly distributed over all continents and oceans. Deposition from the atmosphere to land or sea surfaces can take place either by precipitation ("wet" deposition) or by direct uptake at the surface ("dry" deposition). Only the former can be directly estimated from available environmental measurements, i.e. concentration of mercury in precipitation samples.

From the (incomplete) data presented in Table 2, we estimate global averages of the concentration of mercury in precipitation to be in the range of 5–30

ng L<sup>-1</sup> over continents and 1–10 ng L<sup>-1</sup> over oceans. For Europe, we use 10–60 ng L<sup>-1</sup> and for Sweden 5–30 ng L<sup>-1</sup>. The total wet deposition is obtained by multiplying these concentration values by the appropriate average amounts of precipitation.

Little direct information is available concerning rates of dry deposition of mercury species. It is true that Greenland ice-core samples represent total deposition (i.e. wet + dry), but it is not possible to apportion the values between wet and dry deposition. It is also very uncertain how representative a snow surface is for dry deposition compared to other types of surfaces, like water, soil, and vegetation.

Peat-bog records of mercury accumulation can also be considered as a measure of total net deposition. Data from Danish peat bogs reported by Pfeiffer Madsen (1981) suggest a rate of total deposition during the 1970s of 30–200 μg m<sup>-2</sup> a<sup>-1</sup>. With present mercury concentrations in rainwater in this region of some 50 ng L<sup>-1</sup> (cf. above), only about half of the estimated deposition can be attributed to wet deposition, thus indicating a significant contribution from dry deposition.

The measurements by Brosset (1981b, 1984) of the water-soluble fraction of atmospheric mercury make it possible to make some rough estimates of dry deposition using the deposition velocity concept (cf. Garland, 1978). We assume that the insoluble gaseous forms—mainly Hg<sup>0</sup>—have a negligible deposition velocity, but that the soluble forms and that the fraction bound to particles have a deposition velocity in the range 0.1–0.5 cm s<sup>-1</sup>. In our budget estimates, we take Brosset's measurements of the soluble fraction (0.1–0.3 ng m<sup>-3</sup>) to be representative of the European atmosphere. For the global atmosphere, we estimate the concentration of soluble mercury to be <0.1 ng m<sup>-3</sup>.

A further considerable difficulty arises, when trying to estimate deposition rates of a volatile and biochemically active element like mercury, since a fraction of the deposited amounts may be re-emitted to the atmosphere (within a relatively short period of time) before it is actually incorporated into soil, water, or vegetation. Several laboratory experiments suggest that a significant fraction of oxidized mercury added to e.g., a soil sample is quickly reduced and volatilized (Andersson, 1979). Such a re-emission probably also takes place in the environment, although no unambiguous data on

this phenomenon seem to exist. It is probable that the character of the surface, for example, its acid/base status, influences the rate of re-emission. Therefore, the relatively high net deposition rates inferred from the Danish peat-bog data need not be representative for other, less acidic surfaces.

### 6.2. Atmospheric transport and transformation

We first try to estimate the average residence time of total mercury in the atmosphere. This can be done in several different ways.

*A comparison between the total content in the atmosphere and the flux through this reservoir.* With an average tropospheric concentration of  $2 \text{ ng Hg m}^{-3}$  in the northern hemisphere and  $1 \text{ ng m}^{-3}$  in the southern hemisphere, the total amount of mercury in the atmosphere is about  $6 \times 10^9 \text{ g}$ . The global rate of deposition is taken to be  $(2-17) \times 10^9 \text{ g a}^{-1}$  (cf. Table 10). Dividing the total atmospheric mercury burden by the total flux gives a turn-over time in the range of 0.4–3 years. If only the water-soluble fraction is considered, the turn-over time is reduced by at least an order of magnitude to a value less than a few weeks. For a reservoir in steady state, the turn-over time defined as above can be shown to equal the average residence time of the element in the reservoir (Bolin and Rodhe, 1973).

*Spatial variability in concentration.* We use the residence time variability relation derived by Junge (1974) and elaborated on by Hamrud (1983) together with the concentration data reported by Seiler (personal communication, 1983), cf. Fig. 2. If all mercury is assumed to originate from direct anthropogenic emission, the observed latitudinal distribution would imply an average residence time of 2–4 years. If, instead, the oceans are assumed to constitute a uniform source for atmospheric mercury, the observed variability in concentration implies a residence time less than or about equal to 0.4 years. Since it is very likely that the anthropogenic emission at least plays an important rôle, these estimates are consistent with the range derived in the previous paragraph. Similar estimates of residence time, using Junge's relation, have been made by Slemr et al. (1981) and Fitzgerald et al. (1983). The results were 0.9 years and 0.5 years, respectively.

*The rate of decrease of the concentration with altitude.* Data from Sweden by Brosset (1982) indicate a decrease in concentration of total

mercury by about a factor of two between the earth's surface and a height of 3 km. In a horizontally homogeneous situation, such a decrease would correspond to a residence time of at most a month or so. Considerably longer residence times are implied by data from the upper troposphere (Seiler et al., 1980), where concentrations as high as 1 to 3  $\text{ng kg}^{-1}$  were measured. This indicates that the mercury has a residence time of at least a month.

*Directional dependence of surface air concentrations.* Daily measurements of total mercury in surface air at several sites in southern Sweden (Brosset, 1981b) show a much smaller directional dependence compared to pollutants such as  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , Pb, V, etc. Since it is extremely unlikely that the sources of the concentration of total mercury affecting this region are more homogeneously distributed in the region than those of the other pollutants, one is led to the conclusion that the residence time of mercury is much longer than that of the other pollutants. This would allow the bulk of the mercury to become reasonably well mixed over at least much of the northern hemisphere. The directional dependence of the concentration of the water soluble fraction in Sweden is more in agreement with that of the other pollutants, with higher concentrations occurring in air coming from the industrial regions on the European continent (Brosset, 1981b). This, again, indicates a shorter residence time for these mercury forms than for the bulk of the volatile part.

The picture that emerges is one where the dominant volatile fraction ( $\text{Hg}^0$ ) has an average residence time in the atmosphere of at least a few months, maybe even a year or two, so that it is rather uniformly mixed throughout the troposphere of the northern hemisphere. Because of higher (present and past) anthropogenic emissions in the northern hemisphere, the concentration in this hemisphere is higher than in the southern hemisphere by about a factor two (cf. Fig. 2). Dimethyl mercury (which may constitute a small but significant part of the volatile fraction) may well have a much shorter residence time, cf. Section 5.

The water-soluble fraction and the fraction associated with particulate matter are much more readily scavenged and have a residence time of perhaps a few days to a few weeks. Their dispersion characteristics probably resemble those of pollutants occurring as soluble gases or associated



with submicrometer-sized aerosol particles (e.g.  $\text{SO}_4^{2-}$  and Pb). This would imply characteristic transport scales of several hundred to a few thousand km for the soluble fraction. Since much of the mercury that is emitted from the earth's surface is in the volatile form (probably mainly  $\text{Hg}^0$ ) and since both dry and wet deposition processes seem to be inefficient in the removal of such mercury from the atmosphere, we are led to postulate the existence of some process that transforms (oxidizes) this mercury to water-soluble forms. Thus, even if most of the mercury in the atmosphere (in particular the insoluble fraction) is transported over long distances, a significantly augmented deposition may well occur close to large point sources. This question is further discussed in Subsection 6.3.

### 6.3. Deposition around point sources

The conclusion that most of the atmospheric mercury has a long residence time—of the order of months—and consequently is dispersed globally does not exclude the possibility that a significant fraction of what is emitted at a particular source is deposited in its vicinity. Actually, several studies of mercury deposition around chlor-alkali plants and other sources clearly show that the deposition is augmented well above the background within 5 to 10 km from the plants, cf. Table 9. Deposition rates—measured as bulk precipitation or as uptake by plants—10 to 100 times higher than the background have been reported within a 1 km radius of the plant. At a distance of 10–50 km, the deposition rate normally approaches the background value. At the Rönnskär smelter in northern Sweden, mercury levels in lake sediments are clearly augmented, even beyond 50 km.

The amount of mercury deposited locally still represents only a small fraction of the emissions. As can be seen from Table 9, at most 10–20% of the emissions can be accounted for by the measured deposition within the nearest 10 km. A dominant fraction is thus carried farther, contributing to the regional and even global background concentration. Model calculations, also presented in Table 9, indicate that if all mercury is emitted in a form that is readily absorbed (and retained) by the surface, the deposition within 10 km could theoretically approach 40% for a low-level source such as a chlor-alkali plant. For an elevated source, the corresponding figure is about 20%.

From a comparison between the model calculations and the measured deposition rates, we are led to the conclusion that the surface absorption in reality is limited. This is naturally so if a large fraction of the emitted mercury occurs as volatile  $\text{Hg}^0$ . Re-emission of the deposited mercury would also contribute to a smaller net deposition. On the other hand, the comparison between observations and model calculations also indicates that a finite, and probably significant, fraction of the mercury from chlor-alkali plants is emitted in a form that is readily deposited. In order to permit more reliable model calculations, it is necessary to acquire a better understanding of the chemical forms of mercury emitted from different sources and of the surface absorption of these different forms.

It cannot be ruled out that a fraction of the emissions, at least under certain conditions, consists of monomethyl mercury and that this may give rise to a local deposition that is very significant from a biological point of view. Since the background deposition rate of monomethyl mercury may well be relatively low (no information is available), the local augmentation above the background could be much higher than the values for total mercury given in Table 9. A search for monomethyl mercury in emissions from different sources is clearly warranted.

### 6.4. A budget for the global atmosphere

From the data presented in the previous sections, we have estimated the global fluxes and their uncertainty ranges as given in Table 10. It is seen that present anthropogenic emissions represent at least 10%, and probably about 30%, of the present global deposition. Compared to the pre-industrial fluxes, the present anthropogenic emission represents at least 20%. Although the sources of the present background emissions have not been well identified, measurements of mercury concentrations in the atmosphere indicate that the continents are more likely to be important sources than the sea (Slemr et al., 1981).

The relative importance of man's contribution within certain regions can also be judged from historical deposition records. The Danish peat bog data (Pheiffer Madsen, 1981) indicate an increase in deposition rate in that region by at least a factor of 5 between the 18th century and the present time (cf. Fig. 6). The most recent ice-core data from Greenland (Appelquist et al., 1978) show no clear

Table 9. *Measurements and calculations of mercury deposition rates near point sources*

Source	Measurement/ calculation	Peak value divided by background (at distance <i>d</i> in km)	Accumulated deposition (within distance <i>d</i> in km) as % of emission	Ref.
<b>A. Measurements</b>				
5 chlor-alkali plants (Sweden)	snow	5–50 (0.5)	2–20 <sup>1</sup> (5)	a
2 chlor-alkali plants (Sweden)	bulk precipitation	~100 (0.1) ~2 (1)	1 (2.5)	b
chlor-alkali plant (Sweden)	mosses	~10 (1) ~1 (10)	1–6 (5) 1–12 (15)	c
chlor-alkali plant (Sweden)	sediments	~2(20)		d
chlor-alkali plant (Thailand)	plant leaves	~40 (0.5)		e
chlor-alkali plant (Finland)	moss bags	~60 (1) ~2 (10)		f
	natural mosses	~15 (1) ~2 (10)		
3 chlor-alkali plants (Finland)	lichens	~100 (0.1)		g
chlor-alkali plant (Finland)	pine needles	<20 (1)		h
chlor-alkali plant (Finland)	fungi	20–300 (0.1)		i
smelter Rönnskär (Sweden)	sediments	~10 (10) ~2 (50)		j
smelter Rönnskär (Sweden)	fish (pike)	~4 (10) ~2 (50)		k
coal-fired power plant (USA)	soil	~2 (1)		l
coal-fired power plant (USA)	soil	~1.5 (10)		m
	fish	<1 (5)		m
<b>B. Model calculations</b>				
chlor-alkali plant incineration	dry deposition		<22 (2.5)	b
	wet deposition		~3 (10)	n
plant (stack height 53 m)	wet deposition		~1 (10)	
	total deposition		~4 (10)	
hypothetical surface source	dry deposition		<35 (10)	o
	wet deposition		<5 (10)	
	total deposition	<40* (1) 0.4* (10)	<40 (10)	
hypothetical elevated source (75 m)	dry deposition		<15 (10)	o
	wet deposition		<5 (10)	
	total deposition	<4* (1) 0.2* (10)	<20 (10)	

(a) Jernelöv and Wallin (1973)

(b) Högström et al. (1979)

(c) Wallin (1974)

(d) Björklund and Norling (1980)

(e) Suckcharoen (1980)

(f) Lodenius and Tulosalu (1983)

(g) Lodenius (1981)

(h) Lodenius and Laaksovirta (1979)

(i) Lodenius and Herranen (1981)

(j) Lithner (1978)

(k) Lithner and Dietrichson (1981)

(l) Crockett and Kinnison (1979)

(m) Anderson and Smith (1977)

(n) Lockeretz (1974)

(o) Persson C. Swedish Meteorological Hydrological Institute, pers. comm. (1983)

\* For a source strength of 100 kg per year.

<sup>1</sup> The upper limit probably too high.

Table 10. *Estimates of fluxes of mercury to and from the global atmosphere ( $10^9$  g Hg  $a^{-1}$ )*

Process	Flux	Range of uncertainty	Method of estimate
Present anthropogenic emissions	2.5	2-10	Watson (1979), Mackenzie and Wollast (1977)
Present background emissions	5.5	< 15	by balance
Total present emissions	8	2-17	assuming balance between emission and deposition
Wet deposition	4	2-10	from estimates of Hg concentration in rainwater
Dry deposition	4	< 7	Average concentration of soluble mercury $< 0.1$ ng $m^{-3}$ ; deposition velocity $< 0.5$ cm $s^{-1}$
Total present deposition	8	2-17	
Pre-industrial deposition (and emission)		2-10	Data from Danish peat bogs and Greenland ice cores

trend but also do not disprove the existence of such a trend. In view of the sparsity of data, we have not attempted to make a separate budget for soluble mercury or specific chemical forms of mercury.

#### 6.5. Budgets for the European and Swedish atmospheres

Because of the relatively long residence time of mercury in the atmosphere, mercury emitted within a limited area such as Europe is not deposited only within this area. Similarly, a large fraction of what is deposited in Europe originates from emissions outside the area. It is nevertheless of interest to compare the magnitudes of emissions and deposition rates for a few areas where some data exist and where the anthropogenic proportion is likely to be more dominant than for the global averages discussed above. Estimates of mercury fluxes in Europe (outside USSR) and Sweden are presented in Table 11. Although the uncertainty ranges are large, it seems very likely that Europe is a net exporter of mercury through the atmosphere. It is also clear that man has had a very significant influence on the total deposition in these regions. Such an impact is indicated not only by the Danish peat bog records (Pheiffer Madsen, 1981), but also by data from sediment cores in freshwater lakes in Sweden (Johansson, 1984; Lindqvist et al., 1984). According to these latter data, the mercury load on forest lakes in southern and central Sweden increased by about a factor of 5 during the 20th century. The increase in northern Sweden is substantially less; at most a factor of 2 in the far north. Thus, it seems very likely that the present

deposition in central Europe and southern parts of Scandinavia is about 5 times higher than the pre-industrial deposition.

In the Swedish mercury budget, it is hardly possible to say whether the present anthropogenic emissions are larger or smaller than the present background emissions. Nor is it possible to say with certainty how much larger the present total deposition is than the pre-industrial deposition.

The fact that the range given for the total present emission agrees quite well with the total present deposition, has no particular significance. As a matter of fact, because of the relatively long residence time of the airborne mercury, a large fraction of the mercury from Swedish emissions will be deposited outside the country. Similarly, much of the mercury deposited in Sweden will have originated from emissions outside the country.

One may make a rough estimate of the contribution of present Swedish anthropogenic emissions to the present deposition within the country by assuming that half of the mercury from anthropogenic emissions occurs as a water-soluble form and that this fraction has a residence time similar to that of anthropogenic sulphur. Calculations of sulphur transport indicate that about 25% of the sulphur emitted in Sweden is deposited within the country (OECD, 1977). Thus, at most one unit ( $10^6$  g) of mercury out of the 5 emitted in Sweden is likely to be deposited within Sweden. In a similar way, we estimate that about 1% of mercury emitted in Europe (outside Sweden) in a water-soluble form is deposited in Sweden. According to the emission figures given in Table 11, this would

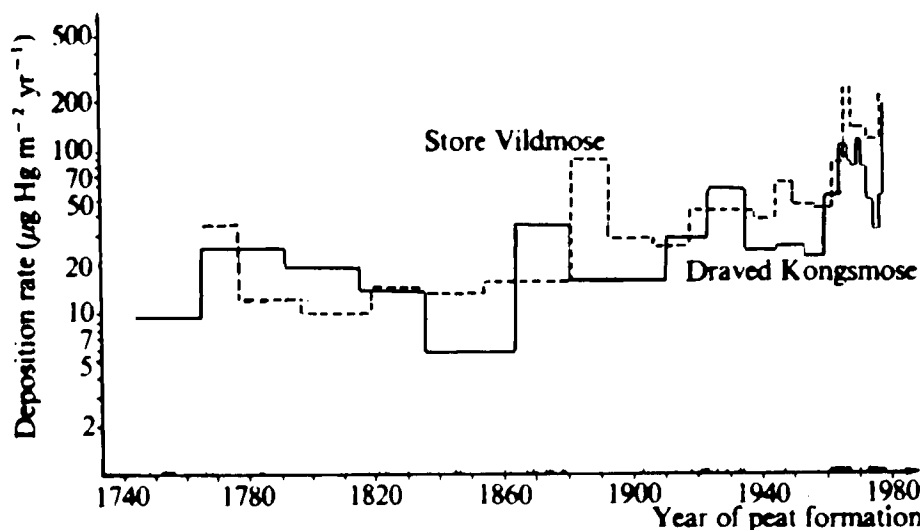


Fig. 6. Accumulation rates of mercury in 2 ombrotropic peat bogs in Denmark (Pheiffer Madsen, 1981). There are good reasons to conclude that these figures represent rates of deposition from the atmosphere. Reprinted with permission from *Nature*, vol. 293, p. 127. Copyright © 1981 Macmillan Journals Limited.

Table 11. Mercury budgets for atmospheres of Europe (outside USSR) and Sweden in the late 1970s ( $10^6 \text{ g a}^{-1}$ )

Process	Flux		Method of estimate
	Europe	Sweden	
Present anthropogenic emissions	500 (300–1000)	5	For Europe: Pacyna (1983) and Watson (1979), for Sweden: Project KHM (1983)
Present background emissions	50 (<150)	5 (<15)	Uniform scaling from global figure in Table 10
Total present emission	550 (300–1200)	10 (5–20)	
Wet deposition	100 (50–200)	5 (2–10)	Rainwater concentration as given in text
Dry deposition	100 (<150)	5 (2–10)	Average concentration of soluble mercury <math><0.2 \text{ ng m}^{-3}</math>; deposition velocity <math><0.5 \text{ cm s}^{-1}</math>
Total present deposition	200 (50–350)	10 (4–20)	
Pre-industrial deposition	50–100	<5	For Europe: $10\text{--}20 \mu\text{g m}^{-2} \text{ a}^{-1}$ , from Danish peat bog records, Pheiffer Madsen (1981), less for Sweden

Values in brackets represent range of uncertainty.

correspond to between 1.5 and 5 units assuming that half of the emission is in a water-soluble form. It seems clear that for the mercury deposition in Sweden as a whole, the emissions on the European continent are more important than those within Sweden. This conclusion about the importance of

long-range mercury transport is supported by Brosset's (1981b) observation of a clear correlation between the concentration of total gaseous mercury (with a background value subtracted) in southern Sweden and transport directions from the south (southeast to southwest). Earlier indications

of the existence of long-range transport of mercury to Scandinavia were reviewed by Johnels et al. (1979).

In the vicinity of individual Swedish sources, the indigenous contribution is relatively more important. Some decades ago, when the Swedish anthropogenic mercury emissions (mainly from chlor-alkali plants) were substantially larger, the deposition in Sweden may have been more significantly influenced by domestic sources.

## 7. Concluding remarks

This study has shown that there are still very substantial gaps in our knowledge about the environmental cycle of mercury in general and about its atmospheric part in particular. Among the questions that need to be resolved are:

How important are methylated mercury compounds in the mercury cycle?

What are the water soluble forms of mercury in rainwater?

What emission and transformation processes represent the sources of these soluble mercury compounds.

To what degree has man influenced such emission and transformation processes?

How large are the present fluxes of mercury through the atmosphere?

To what degree are old anthropogenic emissions still contributing to these fluxes?

The analytical tools needed to address these questions rationally are now becoming available, and systematic measurement programmes and laboratory studies should be undertaken to clarify the biogeochemical mercury cycle. A better understanding of this cycle is a prerequisite for a rational environmental policy related to mercury pollution.

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