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**MERCURY IN THE ATMOSPHERE:  
ESTIMATES OF MODEL PARAMETERS**

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## Introduction

The problem of environmental pollution by mercury at the regional level became evident two decades ago when it was reliably ascertained that mercury content in some ecosystems appreciably increased for the historical period. In a number of cases ecosystems were rather far from sources of anthropogenic emissions and, consequently, the only cause of pollution could be atmospheric transport of mercury and its compounds over considerable distances. Besides experiments showed that atmospheric mercury content significantly exceeds the background levels of the pre-industrial period.

As one of the most toxic heavy metals mercury attracted attention first of all in Europe and North America where specific emission intensity (per area unit) is extremely high. In a number of European countries during the period of industrialization natural mercury input to the atmosphere is exceeded as much as tens-hundreds times. It noticeably impacted parameters of the global atmospheric mercury cycle. At the level of industrial regions such changes were dangerous in terms of ecology.

At present within the framework of Convention on long-range transboundary air pollution transport UN ECE prepares a protocol on heavy metal emission reduction including mercury. Operational and scientific activity under the EMEP programme in particular long-range transport modelling should become an important element for the development of this protocol. Attempts have been made by now to develop regional models. As far as mercury is concerned the problem is complicated by the diversity of its behaviour characteristics in the atmosphere and poor knowledge of a number of key processes.

The goal of this report is an assessment of the level of knowledge on mercury behaviour in the atmosphere, the selection of main parameters of modelling, as well as the estimate of the extent of uncertainties of these parameters and a description of basic model units and performance of tentative calculations. It is presumed that this work makes the ground for MSC-E operational model for calculation of atmospheric mercury transport in European region.

### 1. Chemical forms of mercury occurrence in the environment and their main properties

Mercury as a pollutant belongs to a group of heavy metals. This group also incorporates such toxic substances as lead and cadmium. In view of the position in the periodical system mercury is a transition metal alongside zinc and cadmium. A number of properties put mercury to a special position in the row of other heavy metals. First of all mercury has the lowest melting temperature among all metals existing in nature (it is in a liquid state at the room temperature). It is characterized by high volatility and it is present in the atmosphere in both aerosol and gaseous states. Main mercury properties are presented bellow [Schroeder et al., 1991]:

Melting temperature	-38.8°C
Boiling temperature	+356.7°C
Pressure of saturated vapour	0.246 Pa (at 25°C)
Potential of the first step of ionization	241 kcal/mol (for gold -213, for radon -248)
Saturation concentration in air	13.18 µg/l (at 20°C)
Solubility in water	63.9 µg/l (at 20°C)

The availability of elemental (metallic) (Hg<sup>0</sup>) mercury in the atmosphere above all is explained by a very high ionization potential close to the potential value of inert radon. In

addition to elemental form mercury can be present in the atmosphere and other media as various chemical compounds.  $\text{HgCl}_2$ ,  $\text{Hg}(\text{OH})_2$  are most commonly encountered in solid, liquid and gaseous phases. In the solid state (for example, incorporated in aerosol particles) and in solutions mercury can be present as  $\text{HgO}$ ,  $\text{HgS}$ ,  $\text{HgSO}_4$ ,  $\text{Hg}(\text{NO}_3)_2$  [Schroeder et al., 1991]. Under certain conditions mercury organic compounds are formed of which most common are fully methylated mercury (dimethyl mercury  $(\text{CH}_3)_2\text{Hg}$ ) and partially methylated mercury (monomethyl mercury,  $\text{CH}_3\text{HgX}$ ). Here  $\text{Cl}^-$  or  $\text{OH}^-$  can act as X. Below dimethyl mercury will be designated as DMHg and monomethyl mercury as MMHg. In view of the long-range transport the most important is the fact that like metallic mercury many of its compounds are very volatile and are present in the atmosphere in the gaseous phase.

O.Lindqvist and H.Rodhe [1985] suggested to classify mercury compounds in accordance with their reactivity, volatility and solubility. Their classification can be presented as follows:

Solid phase (aerosols)	Reactive (R)	
	Non-reactive (NR)	
Gaseous and liquid phases	Volatile (V)	
	Water soluble (WS)	- Reactive (R) - Non-reactive (NR)

According to this classification:

(V) =  $\text{Hg}^0$ ,  $(\text{CH}_3)\text{Hg}$ ;

(R) =  $\text{Hg}^{2+}$ ,  $\text{HgX}_2$ ,  $\text{HgX}_3^-$ ,  $\text{HgX}_4^{2-}$  (here X =  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ),  $\text{HgO}$  on aerosol particles, complexes of  $\text{Hg}^{2+}$  with organic acids;

(NR) =  $\text{CH}_3\text{Hg}^+$ ,  $\text{CH}_3\text{HgCl}$ ,  $\text{CH}_3\text{HgOH}$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{HgS}$ ,  $\text{Hg}^{2+}$  (bound with sulphur in humus compounds).

C.Brosset [1987] suggested to consider separately four chemical forms of mercury in the atmosphere, namely:

- elemental  $\text{Hg}^{\text{la}} = \text{Hg}^0$
- fully organic  $\text{Hg}^{\text{lb}} = \text{Org-Hg-Org}$  (for example  $\text{Hg}(\text{CH}_3)_2$ )
- fully inorganic  $\text{Hg}^{\text{lla}} = \text{Inorg-Hg-Inorg}$  (e.g.  $\text{Cl-Hg-Cl}$ )
- partially organic  $\text{Hg}^{\text{llb}} = \text{Org-Hg-Inorg}$  (e.g.  $\text{Cl-HgCH}_3$ ).

Physical-chemical properties of the four forms are drastically different therefore their behaviour in the atmosphere is different and as well as mechanisms of transport between environmental compartments.

Often in literature authors use a concept "total gaseous mercury (TGM)". This concept includes vapour of metallic mercury, gaseous organic and inorganic compounds.

Presumably in the atmosphere mercury and its compounds are tightly sorbed on aerosol particles especially on soot. This process takes place not only in the system "gas-particle" but also in the system "solution-particle", i.e. in drops of clouds, fog, rain [Lindqvist et al., 1991]. Sorption may essentially affect properties of compounds making them interactive though it cannot be completely excluded that heterogeneous chemical process can take place [Seigneur et al., 1996] Therefore with a certain condition we may speak about sorbed mercury as a specific form of inert mercury in chemical terms. Aerosol mercury scavenging from the atmosphere will be determined not by properties of mercury itself but by properties of particles-carriers.

In water solutions mercury can be present in monovalent (Hg(I)) and divalent (Hg(II)) states. Ion(I) properly consists of two ions Hg(II) with one covalent bond. In water solutions there is a mobile equilibrium between these ions at ratio  $\text{Hg(II)}/\text{Hg(I)} \approx 88$  [Fursov, 1983]. It is important that mercury halogenides in water solutions practically do not dissociate and occur as molecules.

In fresh water at pH 5-9 mercury is mainly present in partially methylated form and major compounds should be  $\text{MHgS}^-$ ,  $(\text{MHg})_2\text{S}$ ,  $\text{MHgSR}$  and when sulphur compounds are not present -  $\text{MHgOH}$  and  $\text{MHgCl}$  [Lindqvist et al., 1991]. In lake water >99% of mercury is fixed with humus matter. In river water ~80% of mercury is in a dissolved state and only 15-19% - on particulates [Prokofiev, 1981]. In marine water it should be 12%  $\text{HgCl}_2$ , 23%  $\text{HgCl}_3^-$ , 65%  $\text{HgCl}_4^{2-}$  [Prokofiev, 1981; Lindqvist., 1984] In a large-scale experiment with marine waters (1300 m<sup>3</sup>) it was shown that in 72 days more than 90% of mercury was fixed on bottom sediments. Total mercury content was cut down by 3% every day [Prokofiev, 1981]. It is presumed [Horvat, 1996] that oceanic bottom sediments are the final sink of mercury in the form of practically insoluble sulphide.

Biomethylation process is typical for bottom sediment media and it is not characteristic of plants and soils [Prokofiev, 1981]. In nature biomethylation is accompanied by reverse biodemethylation to  $\text{Hg}^0$  [Prokofiev, 1981] therefore both in water phase and within sediment layer metallic mercury is always present. According to Lindqvist et al. [1991] in slightly acidified fresh water (pH≈4) the most important ligands for binding mercury potentially can be  $\text{SH}^-$ ,  $\text{CN}^-$ ,  $\text{SO}_3^{2-}$ . It is perceived that in water solutions an appreciable part of mercury can be bound with iodine since the stability of iodine compounds is by six orders of magnitude higher than that of chlorine and the accessibility of iodine is sufficient to compete with chlorine [Campos et al., 1996; Dyrssen and Wedborg, 1991; Skotnikova et al., 1997]. The relationship of individual mercury forms in the water media can be varied within wide ranges and as A. Prokofiev [1981] indicated it is unknown to what extent results of calculations of mercury forms in natural waters using the most advanced models reflect the reality.

It is considered that mercury in soils is present as compounds with humus substances. As it was mentioned above biomethylation process is not characteristic of soil therefore the content of methylated forms should not be great. Unfortunately detailed information on mercury forms in soil is not available. Most probably mercury behaviour in soil is controlled by sorption and desorption processes of various complex compounds with  $\text{OH}^-$ ,  $\text{Cl}^-$ , and organic anions [Schuster, 1991]. The rate of these processes is in inverse proportion to the content of organic carbon in soil. A common rule can be as follows the higher organic carbon content the higher is the fraction of divalent sorbed mercury [Yin et al., 1997]

High volatility of mercury conditions its noticeable (contrary to other heavy metals) content in gaseous phase. Mercury vapour air concentration above liquid mercury can be determined with the accuracy  $\pm 2\%$  through formulas [Fursov, 1983]:

$$C = \frac{P \cdot M}{R \cdot T} \quad (1)$$

$$P = 10^{10.5504} \cdot T \cdot 10^{-0.8403} \cdot 10^{-3348/T} \quad (2)$$

where C - air concentration, mg/l; P - saturated vapour pressure, mm Hg; M- molecular mass; R - universal gas constant; P - vapour pressure, mm Hg; T - temperature, °K. At temperature 300°K (27°C) saturated vapour pressure is  $2 \cdot 10^{-3}$  mm Hg (0.27 Pa), and concentration -  $2 \cdot 10^{-2}$  mg/l. In real atmospheric conditions mercury vapour pressure is so low that it cannot exist in

the liquid phase. As it is shown in table 1.1 the most volatile inorganic compounds of mercury ( $\text{HgCl}_2$ ) are in tens - hundreds times less volatile.

**Table 1.1** Vapour pressures (Pa) of metallic mercury and  $\text{HgCl}_2$  at different temperatures [from data of Lindqvist et al., 1991 and Schroeder., 1991]

Temperature, °C	$\text{Hg}^0$	$\text{HgCl}_2$
-30	0.00064 - 0.00067	
-25	0.001	0.00001
0	0.027	0.0008
20	0.160	
25	0.2	0.01
30	0.36 - 0.37	

Earlier it was considered that an appreciable fraction of mercury should occur in the gaseous phase, however, observations of recent years show that the input of aerosol phase at the regional level is several per cent of its total content [Horvat, 1996; Lamborg et al., 1995; Schroeder et al., 1991]. The bulk of tropospheric mercury is in the gaseous phase and consists almost only of  $\text{Hg}^0$  (95-100% in coastal and urban regions of Long Island and Wisconsin). At the global level in the oceanic atmosphere the share of elemental gaseous mercury exceeds 99% [Fitzgerald and Mason, 1996]. The remained fraction of gaseous mercury is represented by monomethyl mercury (MMHg).

From table 1.1 it follows that in the range of normal temperatures for Europe ( $-30^\circ \div +30^\circ\text{C}$ ) vapor pressure value of both  $\text{Hg}^0$  and  $\text{HgCl}_2$  is varied within three orders of magnitude. From this it follows that in different seasons noticeable redistribution of elemental mercury between gaseous and aerosol fractions can be expected but it is not strengthened by experimental data. However, in paper by J.Lu et al. [1997] there are data on records of unusually low concentrations of gaseous mercury and high aerosol concentrations in the Arctic. The authors explain it by the phase redistribution.

Metallic mercury is poorly soluble in water: at  $25^\circ\text{C}$  from 58.8 to 63.9  $\mu\text{g/l}$  are dissolved in water. The solubility is growing from 19.2 to 368  $\mu\text{g/l}$  within temperature range  $5-60^\circ\text{C}$ . The process of solution from the vapour phase follows Henry's law (solution heat 5.3 kcal/mol) [Prokofiev, 1991]. Mercury solubility in marine water also obeys Henry's law and within range  $5-30^\circ\text{C}$  it grows from 17.2 to 69.3 mg/l [Prokofiev, 1981]. In hydrocarbons and esters the solubility is by an order of magnitude higher than in water.

The solubility of various mercury compounds varies within several orders of magnitude.  $\text{HgCl}_2$  is referred to most soluble compounds. Among inorganic compounds sulphide form is the least soluble. Organic compounds with two radicals (like DMHg) are only slightly soluble in water but they are easily soluble in organic substances. Monomethyl mercury (MMHg) take a middle position in terms of solubility. In the temperature range  $0-26^\circ\text{C}$  DMHg solubility in marine water declines from 2.84 to 1.88 g/kg. Data on the solubility of various mercury compounds in water are presented in table 1.2 as Henry's coefficients.

**Table 1.2** Henry's law constants (in brackets - temperature, °C)

Source	Matter					
	$\text{Hg}^0$	DMHg	MHgCl	MHgOH	$\text{HgCl}_2$	$\text{Hg}(\text{OH})_2$
Lindqvist et al., 1984	0.14 (20)	0.13 (25)	2200 (25)		1.4E6* (25)	1.3E4 (25)
		0.30 (0)	2650 (15)		3.6E6 (10)	2.7E4 (10)

			4800 (10)			
Clever et al., 1985	0.112					
Schroeder et al., 1991	0.13 (25) 0.24 (5)					
Fitzgerald et al., 1991				2.5E5 (15)		
Petersen, 1992	0.14 (20) 0.12 (25)	0.13 (25)	2200 (25) 2200 (15)	1.5E5 (25) 2.5E5 (15)	1.4E6 (25) 3.6E6 (10)	
Seigneur et al., 1994	0.11 (20)	0.13 (25)	2200 (25)		1.4E6 (25)	1.2E4 (25)
Schroeder, 1996	0.21 (10)					

\*) - here and below  $1.4E6 = 1.4 \cdot 10^6$

As it follows from table 1.2 solubility to a considerable extent depends on temperature and in the actual range of temperature in the lower atmosphere (from  $-30^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$ ) it can be changed as much as 2-3 times. This fact should be taken into account while operational model development. From the table it also followed that metallic mercury and DMHg are very slightly soluble in water and at the equilibrium in "gas-water" system they should have be present mainly in gaseous phase. On the contrary the rest of mercury compounds ( $\text{HgCl}_2$  in particular) are easily dissolved. If  $\text{HgCl}_2$  gaseous concentration in air is equal to  $0.001 \text{ ng/m}^3$ , equilibrium concentration in water solution at  $25^{\circ}\text{C}$  should be about  $35 \text{ ng/l}$ . It is considered that the dissolution process of mercury compounds in question can be described by Henry law. However, A. Prokofiev [1981] mentions that at practical equality of Henry's coefficients DMHg is evaporated from water solutions in 2.3 times slower than  $\text{Hg}^0$ .

The most important geophysical feature characterizing the behaviour of this or that substance in the environment is its mean life-time in a reservoir. For mercury and its compounds data on their life-time are rather contradictory. The evaluation of half-life time can be made in different ways in particular by the analogy with other substances, physical and chemical properties of which are similar to considered mercury compounds. As a rule assessments for metallic mercury are based on three approaches [Slemr, 1996; Rodhe, 1996]:

- known relationships between life-time and concentration variability in time and space [Junge, 1974; Hamrud, 1983];
- concentration difference in the atmosphere of the South and North Hemispheres [Slemr, 1996];
- chemical and physical transformation rates;
- vertical distribution profiles in the atmosphere.

Life-time of elemental mercury as a rule is estimated to be from several months to 2 years [Lindqvist and Rodhe, 1985; Pacyna et al., 1996; Rodhe, 1996; Slemr, 1996]. But in some papers there are essentially lower estimates. V. Ionov et al. [1976] using data on vertical concentration distribution of radon and gaseous mercury estimated life-time of the latter to be about 10 days. According to [Seignior et al., 1994] in the marine atmosphere rapid chemical process can take place and metallic mercury life-time can be as long as only hours. The life-time of oxidized mercury depends its physical and chemical forms: life-time of aerosol mercury is 3-5 days, for gaseous methylalated mercury - several hours.

## 2. Natural mercury sources

Mercury is one of the most rare and dispersed elements of the Earth. An outstanding geochemist V. Vernadsky reasoning from unique physical-chemical properties of mercury came up with an idea on its quasi-gaseous state in the lithosphere. On the basis of V. Smirnov et al. [1972] mercury content in the Earth's core should be very low but in the mantle - high. According to A. Saukov [1946] mercury percentage in the lithosphere is  $7.7 \times 10^{-6}\%$ . According to estimates of I. Trakhtenberg and M. Korshun [1990] the surface layer of the Earth of 1 km depth contains  $10^9$  tonnes of mercury.

Clearly in the pre-industrial period there was an atmospheric cycle of mercury in which its sources of input to the atmosphere were balanced by the scavenging mechanisms. Rocks, vegetation, soils, seas, oceans, volcanoes and zones of deep fractures were and remained to be natural sources. Due to high mobility (quasi-gaseous state according to V. Vernadsky) mercury diffuses from the mantle to the Earth's surface. At present it is rather difficult to re-establish the pattern of the natural cycle in the past since many environmental compartments to a considerable extent are polluted by mercury of the anthropogenic origin and the separation of natural from secondary anthropogenic fluxes is often impossible. It is possible to make only rough estimates of the emission intensity and its spatial distribution in the past [Pacyna et al., 1996].

As a rule mercury deposits coincide with deep fractures of the Earth forming so-called planetary mercury belts. One of these planetary mercury belts is located in the southern part of Europe. Mercury contained in zones of enhanced concentrations in the upper layer of the Earth's crust volatilizes to the atmosphere. According to V. Fursov data [1983] in the vicinity of mercury deposits its concentration in the atmospheric surface layer are increased in thousands - tens of thousand times. Even over deposits of deep occur mercury anomalies are observed in the atmosphere. For example, in the region of Beregovo (the Ukraine) air concentrations over the deposit are varied from 40 to 150  $\text{ng/m}^3$  exceeding the backgrounds in tens times [Fursov, 1983].

Mercury geochemical anomalies are of a widespread occurrence in southern Europe and adjacent Asian regions. Mainly they are located in Russia, the Ukraine, Italy, Spain. From data of I. Trakhtenberg and M. Korshun [1990] a typical anomaly is characterized by mercury content in soil at the level of 1-10  $\mu\text{g/kg}$ , in water - 0.002-0.3  $\text{mg/l}$  and in air - 7-13  $\text{ng/m}^3$ .

It is important to note that snow cover in Europe does not prevent mercury emission to the atmosphere [Fursov, 1983]. V. Fursov [1983] found that in the snow layer depth above the ore body gaseous halo of dispersion is produced. Actually the snow does not absorb mercury and readily transmit it to the atmosphere

Volcanic activity is a direct source of mercury input to the atmosphere. For example, within Kuril-Kamchatka volcanic region mercury input with gases produces geological formations of mercury mineralization scale [Smirnov et al., 1972] Assessments of volcanic input of mercury to the atmosphere are highly contradictory. W. Fitzgerald [1996] considers that this flux is insignificant in terms of the global cycle - (20-90 t/yr) At the same time there are estimates [Siegel and Siegel, 1984] that only one volcano Kilauea on Hawaii throws out 260 tonnes of mercury vapour per year. Mercury vapour concentrations in the air above fumarole fields of this volcano are within 2700-40600  $\text{ng/m}^3$  [Davies and Nottcut, 1996]. When it is assumed that only 10 of 700 active volcanoes of the world can be compared with Kilauea then total volcanic flux should amount to several thousands tonnes of mercury per year.



On the way of juvenile mercury to the atmosphere there is a geochemical barrier - soil. Mercury content in soil can be higher than in the underlying rock. Soil mercury in its turn can be volatile to the atmosphere but this process is not very intensive. O.Lindqvist et al. [1991] consider that mercury emission from the land surface outside planetary mercury belts is about  $1 \text{ g/km}^2/\text{yr}$  and within planetary mercury belts - to  $10 \text{ g/km}^2/\text{yr}$ . Soil emission of coniferous forests does not exceed  $1 \text{ g/km}^2/\text{yr}$  [Lindqvist et al., 1991]. Emission intensity of forest soils in the USA is less than  $2 \text{ g/km}^2/\text{yr}$  [Munthe, 1993]. V. Fursov [1983] carried out measurements of mercury flux from the soil to the atmosphere in arid zones of the USSR using "box" and gradient methods. In the first case the mean flux was  $50 \text{ g/km}^2/\text{yr}$  and in the second one (gradient method) -  $23 \text{ g/km}^2/\text{yr}$ . One should bear in mind that at present soil emission is not purely natural because of global anthropogenic pollution by mercury. According to data of W.Fitzgerald and R.Mason [1996] the natural flux from the continents (excluding the Antarctic) is  $9.7 \text{ g/km}^2/\text{yr}$  and the total natural flux to the continental atmosphere is estimated to be 1000 tonnes/yr.

Specific (per area unit) mercury emission from fresh waters is essentially higher than from soils. On the whole lake waters (especially in the summer period) are supersaturated by elemental mercury compared with the atmosphere. It is found that about 10% of mercury coming from the atmosphere to a lake is re-emitted [Vandal et al., 1991]. The intensity estimates of this process available in literature are extremely contradictory. On the average it may be accepted that the emission from the water surface is within the range of  $2\text{-}20 \text{ g/km}^2/\text{yr}$  [Lindqvist et al., 1991]. J.Munthe [1993] provides data for Sweden lakes ( $18\text{-}180 \text{ g/km}^2/\text{yr}$ ) which are by 1-2 orders of magnitudes higher than for lakes of the USA ( $0.7\text{-}1.5 \text{ g/km}^2/\text{yr}$ ). As in the case with soil it is impossible to single out purely natural constituent of lake emissions due to global pollution by mercury.

Appreciable role in the mercury natural cycle plays the world ocean because of  $\text{Hg}^{2+}$  reduction by biological processes occurring in the marine environment [Kim and Fitzgerald, 1986]. The intensity of mercury input from the ocean to the atmosphere in many respects is specified the surface state as a function of wind speed [Baeyens et al., 1991]. The most high emission from the oceanic surface is observed in upwelling zones where the surface layer is supersaturated by elemental mercury due biological reduction of  $\text{Hg}^{2+}$  (elemental form fully dominates) and air mercury concentration is 1.5-2 times higher than over other regions of the ocean. W.Fitzgerald et al. [1984] estimated that in the latitudinal band from  $4^\circ\text{N}$  to  $10^\circ\text{S}$  of the Pacific ocean the annual input to the atmosphere is 30 tonnes (about  $3 \text{ g/km}^2/\text{yr}$ ) The total flux from the world ocean is assessed as  $2900 \pm 1800$  tonnes/yr [Kim and Fitzgerald, 1986] Later this estimate was reduced to 600 tonnes/yr [Fitzgerald and Mason, 1996].

I.Trakhtenberg and M.Korshun [1990] are of the opinion that within the global scale volatilization of mercury of the natural origin is 30000-150000 tonnes per year. According to R.Garrels et al. [1975] data on the total natural emission is 25000 tonnes per year. O.Lindqvist et al. estimated natural emission as 3000 with possible scattering from 2000 to 9000 tonnes per year. R.Mason et al. [1994] believes that total natural emission is of the order of 1000 tonnes/yr. Detailed assessment of individual fluxes of natural emissions was made by J.Nriagu [1989]. The obtained values are presented in table 2.1.

**Table 2.1** Natural fluxes of mercury to the atmosphere, t/yr

Flux	Range	Mean
Dust particles elevated by wind	0-100	50
Marine salt particles	0-40	20

Volcanoes	30-2000	1000
Spontaneous forest fires	0-50	20
Biogenic processes on continents(aerosol)	0-40	20
Biogenic processes on continents (gas)	20-1200	610
Biogenic processes in ocean	40-1500	770
<b>Total</b>	<b>100-4900</b>	<b>2500</b>

Later J.Nriagu data were revised. P.Rasmussen [1994] considered that the extent of uncertainty is even higher than it was found by J.Nriagu and it exceeds an order of magnitude. The maximum integral value is about 35000 tonnes per year [Rasmussen, 1994].

At present it is estimated sufficiently reliably that at past natural emission was not constant. Investigations of Antarctic glaciers demonstrated that during recent tens of thousand years the maximum input from the atmosphere (hence maximum content in the atmosphere) was 15-30 thousands years ago [Fitzgerald and Mason, 1996].

Natural emission is mainly represented by gaseous fraction. Actually only two gaseous compounds  $Hg^0$  and DMHg can be considered. In spite to all the efforts DMHg emission was not found experimentally [Munthe, 1993] though there are indirect indication of the fact that part of the emission from lakes and the World ocean is represented just by is compound. For example, N.Bloom et al., [1996] consider that the basic source of atmospheric MMHg over the USA is a degradation of DMHg which in its turn enters the atmosphere from the ocean in zones of upwelling. Direct natural emission of MMHg has not been found [Fitzgerald and Mason, 1996]. They believe that in the ocean  $Hg(II)$  is reduced to  $Hg^0$  and mainly elemental mercury enters the atmosphere. MMHg emission from unpolluted soils was not revealed and DMHg input is of a tracer character [Carpi et al., 1996]. F.Axenfeld et al [1991] consider that 10% of natural emission in Europe is represented by gaseous compounds of oxidized mercury but it was not proved experimentally.

It is important to mention in the context of transport modelling that in the middle latitudes there is a seasonal variation of the emission from lakes and soil [Lindberg et al., 1992] Emission from forest soils is reduced practically to zero during winter time [Lindqvist et al., 1991, 1992]. Data on Swedish lakes show that emission is practically stopped at the temperature below  $+2^{\circ}C$ . In addition diurnal variation of the emission intensity from lakes is also found - at night the emission is 2-3 times lower than in the daytime [Xiao et al., 1991].

Spatial distribution of natural mercury emission in Europe is not uniform. First of all it is connected with the mercury geochemical belt in the southern part of the continent. At the same time natural emission is impacted by soil types and temperature regime. B.Moisseev [1997] made an attempt to evaluate the natural constituent on mercury emission in Europe with spatial resolution  $150 \times 150 \text{ km}^2$ .

### 3. Anthropogenic sources

Mercury is known to people during more than 2000 years. Beginning with medieval centuries mercury has been widely spread in Europe and its production is placed on the industrial level. Earlier almost all mercury was mined in Italy and Spain and up till now about 50% of global extraction of mercury takes place in the region of the Mediterranean Sea [Trakhtenberg and Korshun, 1990]. Table 3.1 displays dynamics of mercury production in the world [Melnikov,

1971]. According to data of I.Trakhtenberg and V.Lukovenko [1990] during XIX century 126500 tonnes was mined. This estimate differs appreciably from that of S.Melnikov [1971].

**Table 3.1** Mercury world production dynamics, t

Year	Production for the whole period	Mean annual production	Years	Production for the period	Mean annual production
1500 - 1600	8000	80	1901-1946	193000	4200
1601 - 1700	58200	582	1947-1967	143000	6700
1701 - 1800	81900	820	1968	8000	8000
1801 - 1900	308000	3080			

An appreciable part of mercury was used for gilding. Therefore it can be supposed that about half of mercury produced before XX century entered the atmosphere. At present the bulk of anthropogenic sources are identified, however, their quantitative characteristics are known with insufficient accuracy.

One of the main anthropogenic sources is combustion of fossil fuels which mercury content as a rule is significantly higher than in the lithosphere on the whole. Coal is mostly enriched in mercury which concentrations reach hundred grams per tonnes. In oils mercury content is 5-100 times higher than mean contain in the lithosphere, and in gases - in 5-1000 higher than in soil air [Fursov, 1983]. Relatively high content of mercury in fuels results in the fact that its concentrations in flue gases can reach tens of  $\mu\text{g}/\text{m}^3$  [Porcella et al., 1996]. At the global level the contribution to the total anthropogenic emission from coal combustion is about 65% [Slemr, 1996].

Mercury content in coals is different from one deposit to another within the limits of several orders of magnitude (for example, in coals of the USA - from 0.012 to 33 mg/kg [Trakhtenberg and Korshun, 1990] therefore it is difficult to evaluate emissions. Mean content of mercury in coals of the USA is 0.085 mg/kg [Chu and Porcella, 1995] In coals of the Netherlands mercury content is about 0.2 mg/kg [Meij, 1991]. Coal mined in the domain of the mercury belts are most rich in mercury [Karasik et al, 1962; Slemr et al., 1995].

In the process of fuel combustion the bulk of mercury (not less than 85-90% for coal [Lindberg, 1980; Fahlke and Bursik, 1995]) comes to flue gases. Large power plants as a rule are equipped with treating facilities for dust, sulphur and nitrogen oxides, some of them treat a certain amount of mercury compounds. For example, some installations for desulphurization with application of lime can remove 50-70% of mercury [Meij, 1991]. The total treatment efficiency estimates are rather contradictory. According to data of P.Chu and D.Porcella [1995] at the dry trapping of dust from flue gasses of coal combustion the efficiency of mercury trapping is 30% but in combination with "wet" absorbers of sulphur dioxide it grows up to 45%.

Metallurgy is also referred to the main source of mercury [Fitzgerald and Mason, 1996]. Ores of many non-ferrous metals (especially lead, zinc, copper, nickel) are abundant in mercury as a by-product. Natural gold contains up to 10% of mercury. At thermal treatment of ores and metal melting mercury is emitted to the atmosphere mainly in elemental form.

An important anthropogenic source is dumps their input is 25% of total anthropogenic emission [Slemr, 1996]. According to V.Fursov data [1983] in the vicinity of dumps mercury air concentration is by an order of magnitude higher than the background. In flue gases of waste incineration mercury concentrations can reach  $1000 \mu\text{g}/\text{m}^3$  [Porcella et al., 1996].

Since organic mercury compounds are very toxic fungicides containing mercury they very widely used in agriculture. Air concentrations of mercury near agricultural regions where such fungicides were applied was to 10000-20000 ng/m<sup>3</sup> [Trakhtenberg and Lukovenko, 1990]. Quantitative assessments of this source are not available but this value can be appreciable. For example in the past in the USA about 400 tonnes of mercury was used as pesticides (18% of US total consumption). An essential fraction of this mercury after the decay of fungicides most probably entered the atmosphere [Trakhtenberg and Korshun, 1990].

A certain contribution to the anthropogenic emission makes non-industrial activity. For example, as a result of breaking thermometers up to 60 tonnes per year of mercury can emanate to the environment [Trakhtenberg and Korshun, 1990], but it is not clear what part of this mercury enters the atmosphere. In a number of countries a considerable input makes crematoriums since in the process of incineration mercury of tooth fillings is removed with gases to the air.

Physical and chemical forms of mercury emitted by anthropogenic sources play an important role. Parameters of airborne transport and scavenging depend on chemical forms [Fitzgerald and Mason, 1996]. At fuel combustion, especially coal, partially mercury can be oxidized and emitted with flue gases as oxidized compounds [Horvat, 1996]. In the flame zone mercury is present in elemental form but with flue gas cooling it can be oxidized by oxygen and chloride-hydrogen on particle surfaces [Munthe, 1993]. Immediately after the combustion chamber mercury is present in the oxidized form (77%), however, the efficiency of oxidized substance trapping is appreciably higher than of elemental mercury. Therefore at the output to the atmosphere treated gas contains 24% of oxidized mercury and 76% of elemental one [Fahlke and Bursik, 1995]. A certain fraction of mercury may be present as aerosol [Lindberg, 1980]. V. Ionov et al. [1976] showed that at the first stage of transport after the emission from a stack the redistribution between gaseous and aerosol phases is very intensive in the plume. The concentration of gaseous mercury is rapidly cut down in the plume and its life-time in plumes of metallurgical plants is about 30 min. and for other plants it varies from 10 to 40 min.

According to R.Meij [1991] there is a direct dependence between HCl content in flue gases and the fraction of oxidized mercury. An analysis of flue gases from coal-fired power plants demonstrated that about 40% of emission is accounted for metallic mercury, about 15% - for compounds of HgCl<sub>2</sub> type - and the rest - for MMHg [Brosset, 1987]. E.Prestbo and N.Blum [1995] analysed flue gases from coal, oil combustion and waste incineration and found that the share of oxidized fraction is dominated for coal (67%) and waste (71%) whereas for oils it is only 23%. At waste incineration the share of oxidized mercury may be great but this process cannot be a serious source of methylated mercury [Petersen et al., 1996].

For Sweden on the whole the relationship of elemental and oxidized mercury emission is 3:1 [Munthe and Oslund, 1994]. P.Chu and D. Porcella [1995] assessed the input of oxidized mercury to be 50%. E.Constantinou et al. [1995] in model calculations assume that 80% of mercury in the emission of a hypothetical power station is represented by elemental form and 20% - by oxidized one (like HgCl<sub>2</sub>). J.Munthe and A.Iverfeldt [1995] consider that the fraction of oxidized mercury at coal combustion can reach 94%. In treatment facilities for nitrogen oxide removal almost complete oxidation (96%) can take place [Fahlke and Bursik, 1995]. Table 3.5 summarizes generalized data on contributions of different forms of mercury in emissions from various sources [Lindqvist et al., 1991]. It is necessary to mention that these data are of an approximate character. J.Munthe and A.Iverfeldt [1995] note that at

present reliable information on the question is not available. Nevertheless an attempt is made to evaluate the input of different forms of mercury to the total emission at the level of individual countries of Europe [Axenfeld et al, 1991; Pacyna and Munch, 1991]. The authors point out that the uncertainty of these estimates is at least within a factor of 2. According to their data on the average all European countries are characteristic of the following relationship for anthropogenic emission:  $\text{Hg}^0$ -57%,  $\text{Hg}^{2+}_{(\text{gas})}$ -30%,  $\text{Hg}^{2+}_{(\text{particles})}$ -13%.

**Table 3.2** Percentage contribution of different forms of mercury in emissions of various sources.

Source	$\text{Hg}^0(\text{gas})$	$\text{Hg}(\text{II})(\text{gas})$	$\text{Hg}(\text{particles})$
Coal combustion	50	30	20
Production of chlorine and alkali	50-90	10-50	0
Roasting of metal sulfide ores	80-90	0	10-20
Pyrite burning	100	0	0
Waste incineration	20	60	20

Estimates of global anthropogenic emission of mercury are extremely contradictory. In the 70-ies it was considered that emission resulted from human activity is 15-20 thousand tonnes per year [Seiler et al., 1980; Trakhtenberg and Lukovenko, 1990]. Participants of the international conference of 1991 [Lindqvist et al., 1991] arrived at the conclusion that global anthropogenic emission of mercury amounts to about 4500 ( $\pm 1500$ ) t/yr. R. Mason et al [1994], W. Fitzgerald and R. Mason [1996] give a bit lower value, however, they indicate that mercury coming from the ocean can be partially of the anthropogenic origin. Table 3.3 gives assessments of anthropogenic emission at the global level from different sources as it was in 1983 [Nriagu and Pacyna, 1988].

**Table 3.3** Anthropogenic sources of mercury input to the atmosphere [Nriagu and Pacyna, 1988]

Source category	Source subcategory	Emission ,t/yr
Coal combustion	Combustion at power plants	155-542
	Industrial combustion and individual heating	495-2970
Non-ferrous metal production	Lead production	7.8-16
	Copper and nickel production	37-207
Waste destruction	Domestic wastes	140-2100
	Aeration fields	15-60
Wood burning		60-300
<b>Total emission</b>		<b>3560 (910-6200)</b>

As industry developed anthropogenic emission varied with time, however, trends in various regions of the globe demonstrated different trends. N.Pirrone et al. [1996] provide data on the variation of the global anthropogenic emission during the decade from 1983 to 1992 (tonnes/year):

1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
1861	1905	1989	2042	2104	2224	2288	2217	2201	2199

The authors indicated that before 1989 emission in developed countries was growing by 4.5 - 5.5% per year and then it was stabilized. In the developing countries emission continues to grow by 2.7 - 4.5 % per year.

Spatial distribution of mercury anthropogenic emission first of all reflects the level of coal consumption in various regions. However, some sources connected with chlorine and alkali production with old technologies as well as sources connected with mining and production of mercury itself are put down on this relatively uniform field. Table 3.4 presents data on anthropogenic emission of mercury by different sources in European countries in 1990 [Pacyna, 1996].

Presumably these data are of an approximate character. It is safe to say that in the USSR a considerable amount of mercury was emitted to the atmosphere with waste destruction. The table data shows that almost half of all emissions comes from the eastern part of Germany (former GDR) where a great amount of chlorine and alkaline were produced with application of mercury electrodes. However, in the USSR the production of these products was even greater with application of a technology similar to that of GDR.

In addition to anthropogenic pollution it is necessary to single out the input to the atmosphere of previously accumulated mercury from various environmental compartments. (soil, lakes, seas). This process is usually called re-emission. According to R.Hadson's and his co-authors opinion [Hadson et al., 1995] re-emission of "old mercury" amounts to about a half of modern direct emission at the global level. At present ideas on re-emission are of an exclusively qualitative character. The impossibility to separate purely natural flux from the anthropogenic one, since almost all ecosystems of the globe were exposed to anthropogenic impact, always presented unpenetrable barrier for a quantitative description. It is possible to assert that the re-emission field should be similar to that of total deposition for recent 100 years. Mercury life-time in some reservoirs (soil, lakes, seas) is as long as decades the re-emission effect will be observed during a long period of time after anthropogenic impact on the atmosphere. According to data of J.Pacyna [1996] re-emission and natural emission

together amount to 250 t/yr within the EMEP grid. B.Moisseev [1997] made an attempt to evaluate re-emission fields for Europe with spatial resolution 150×150 km<sup>2</sup>. In his approach in the first approximation it was assumed that the bulk of mercury emitted falls out on the underlying surface of a source-cell. Hence the re-emission value is proportional to that of direct anthropogenic emission in a given cell. This approach does not consider the atmospheric transport to neighboring cells as well as it ignores the variation of direct anthropogenic emission with time. Obviously the longer a source of anthropogenic emission is acting the higher is re-emission of mercury accumulated in underlying surface elements. In spite of all disadvantages of B.Moisseev's approach his data will be used in the first tentative model calculations. Estimates of B.Moisseev show that natural emission and anthropogenic re-emission amount to about 290 t/yr on the EMEP domain.

**Table 3.4** Mercury anthropogenic emission in Europe in 1990 [Pacyna, 1996], t/yr

Country	Fuel combustion	Waste destruction	Industry	Other sources	SUM
Austria	1.0	0.7	2.0	0.6	4.3
Albania	0.6	-	-	0.2	0.8
Belgium	2.6	0.2	5.2	-	8.0
Bulgaria	6.0	0.2	4.7	-	10.9
Great Britain	19.2	9.4	22.2	0.4	51.2
Hungary	2.1	-	-	0.1	2.2
Germany (former Western)	10.0	11.0	14.0	11.0	46.0
Germany (former Eastern)	17.2	0.3	278.5	-	296.0
Greece	1.4	-	-	-	1.4
Denmark	0.4	2.0	0.1	1.0	3.5
Iceland	0.6	-	-	-	0.6
Spain	5.5	-	4.4	-	9.9
Italy	4.0	1.0	5.4	-	10.4
Netherlands	0.9	0.1	3.2	-	4.2
Norway	0.3	0.3	0.1	0.1	0.8
Poland	25.1	-	8.2	-	33.3
Portugal	2.9	-	2.3	-	5.2
Romania	12.5	-	2.4	-	14.9
USSR (European part)	61.5	-	13.9	-	75.4
Finland	1.0	0.2	0.4	-	1.6
France	12.5	1.9	8.9	-	23.3
Switzerland	0.2	-	-	-	0.2
Sweden	0.3	0.3	0.6	0.3	1.5
Czechoslovakia	1.9	-	12.4	0.6	14.9
Yugoslavia	5.4	-	1.3	-	6.7
<b>Total</b>	<b>195.1</b>	<b>27.6</b>	<b>390.2</b>	<b>14.3</b>	<b>627.2</b>

While re-emission evaluation one should bear in mind a very important fact that independent of chemical form of deposited mercury the re-emission is represented by elemental (90-95%) and methylated forms. Re-emission in aerosol form due to soil weathering makes very small contribution (2%) at the local level during not long period of time.

#### 4. Content of different chemical forms of mercury in the atmosphere and other media

In spite of apparent simplicity of the method for measuring of gaseous mercury compounds in the atmosphere sufficiently accurate determination of concentrations of individual forms of mercury is a very difficult problem. NATO expert meeting [Pacyna et al., 1996] stated that the method of sampling and analysis of total gaseous mercury has been accurately developed (standard deviation 10-15%). At the same time measurements of aerosol component is not standardized and standard deviation can reach 100%. At present it is impossible to measure individual mercury compounds with sufficient accuracy. Another group of experts [Schroeder et al., 1995] is more pessimistic and notes that while intercalibration of methods for sampling and analysis of total gaseous mercury, only 8 of 13 synchronized sampling made by most advanced laboratories in the USA, Canada and Germany provided an acceptable agreement of results. No agreement was obtained for the aerosol fraction. D.Porcella et al. [1996] believed that almost all data obtained before 1990 may cast doubt upon unsolved methodological problems. Therefore it is necessary to be careful while interpreting data on concentrations of mercury and its compounds in the environment.

Mercury concentration measurements at the level of the global background in the continental atmosphere have been made mainly in central Eurasia and North America. In the 70-80-ies numerous measurements of total gaseous mercury were made by V.Fursov [1983, 1988] in Central Asia and Kazakhstan. Comparatively recently measurements have been made in Siberia [Leermakers et al., 1996]. F.Slemr [1996] showed that in clean continental atmosphere about 83% of mercury is in the form of vapours elemental mercury. Concentration data on various forms of mercury in the continental background atmosphere are presented in table 4.1.

**Table 4.1** Mercury concentrations in the background continental atmosphere

Region	Media & Hg form	Concentration	Reference
Central Asia & Kazakhstan (1160 measurements)	Total gaseous	2.01 (1.55-2.99) ng/m <sup>3</sup>	Fursov [1983,1988]
Siberia, Baikal	Total gaseous Hg	0.73-2.31 ng/m <sup>3</sup> (summer) 1.2-6.15 ng/m <sup>3</sup> (winter)	Leermakers et al, 1996
	Particulate Hg	0.005-0.02 ng/m <sup>3</sup> (summer) 0.022-0.09 ng/m <sup>3</sup> (winter)	
	Rain, total Hg	2.92-20.1 ng/l (summer)	
	Rain, methylated	0.1 - 0.25 ng/l (summer)	
	Snow, total Hg	8.6 - 60 ng/l (winter)	
	Snow, methylated	0.09 - 0.29 ng/l (winter)	
USA, Western coast	DMHg	0.005 - 0.03 ng/m <sup>3</sup>	Bloom et al, 1996
USA, Internal regions	DMHg	0 - 0.002 ng/m <sup>3</sup>	
USA, Internal regions	Particulate Hg	0.05 - 1.3 pg/m <sup>3</sup>	Schroeder et al., 1987

Investigations of mercury content in the oceanic atmosphere were carried out in the Pacific ocean [Fitzgerald et al., 1991] and in the Atlantic [Seiler et al., 1990; Slemr, 1996]. It was demonstrated that the content of gaseous mercury in the oceanic atmosphere is sufficiently uniform: in the northern Atlantic - 2.25 ng/m<sup>3</sup>, in the southern Atlantic -1.5 ng/m<sup>3</sup>. in the northern Pacific - 1.77±0.15 ng/m<sup>3</sup>. At station "Mace Head" (Ireland) in Atlantic air masses



gaseous mercury concentration was  $1.5 \text{ ng/m}^3$  whereas in the air mass transported from Europe concentrations were about  $2.5 \text{ ng/m}^3$  [Ebinghaus et al., 1996].

About 92% of mercury in clean oceanic atmosphere is represented by  $\text{Hg}^0$  [Slemr, 1996]. The fact of sharply pronounced diurnal variations of gaseous mercury in the near-water layer - maximum in the daytime, minimum - at night [Seiler et al., 1980; Ebinghaus and Kruger, 1996] attracts a particular attention. F.Slemr [1996], however, does not confirm the diurnal variations at least in the limits of the method error ( $\pm 5.8\%$ ). If variations do occur probably it is connected with the diurnal cycle of emission from the marine environment (may be from the surface microlayer).

In the equatorial Pacific total concentrations of all the mercury forms in precipitation varied within the range of  $1.8\text{-}4.5 \text{ ng/l}$  [Mason et al, 1992], i.e. they were of the same order of magnitude as in industrial countries of Europe and America. The input of methylated mercury did not exceed  $0.1 \text{ ng/l}$ .

A limited number of measurements of mercury content in the Arctic atmosphere were made only during recent years. The total amount of gaseous mercury at Alert station in Canadian Arctic ( $82.5 \text{ N}$ ,  $62.3 \text{ W}$ ) was  $1.47 \pm 0.35 \text{ ng/m}^3$  (minimum -  $0.67$ , maximum -  $2.82$ ) [Schroeder et al, 1995]. This value is comparable with concentration levels observed in the clean atmosphere of middle latitudes. The authors found a certain decrease of gaseous mercury concentrations (TGM) to the north which can be described by expression:

$$\text{TGM} (\text{ng/m}^3) = -0.028 \times \text{LATITUDE}(\text{degree}) + 3.06$$

Most likely it is explained by the distance from anthropogenic sources confirmed by positive correlation between TGM and soot concentration:

$$\text{TGM} (\text{ng/m}^3) = 0.0075 \times [\text{soot}] (\text{ng/m}^3) - 0.25$$

Investigations at Alert station and during a marine expeditions revealed a reverse dependence of gaseous mercury concentrations (TGM) on air temperature. W.Schroeder et al. [1995] set forth four possible reasons for this: (1) temperature partitioning in the "gas-particle" system, (2) differences in the atmospheric transport during warm and cold seasons, (3) temperature dependence of re-emission, (4) intensification of dry uptake at the temperature drop. Possibly just temperature effect of redistribution between gaseous and solid phases may be the reason for record-breaking low concentrations of gaseous mercury at Alert station ( $0.03 \text{ ng/m}^3$ ) with simultaneous sharp increase of aerosol mercury concentrations up to  $0.5 \text{ ng/m}^3$  [Lu et al., 1997].

Mercury content in precipitation of high latitude which produced glaciers of Greenland and the Antarctica is an indicator of global changes in the mercury atmospheric cycle. In the 70-ies the growth of concentrations during recent decades was revealed in the Antarctica, however, later on it was shown that these data are not reliable [Wolff and Peel, 1985]. In Greenland no changes in mercury concentrations were found which could be interpreted as the effect of global anthropogenic alterations [Appleqvist et al., 1978]. During recent 150 years concentrations varied within  $2\text{-}19 \text{ ng/l}$ . Later R.Semkin et al. [1996] found in ice of Greenland concentrations even lower than  $1.3\text{-}4.2 \text{ ng/l}$ . In the Antarctic in glacier depth  $4.6 \text{ m}$  mercury concentrations varied from  $0.1$  to  $1 \text{ ng/l}$  revealing no temporal tendencies [Sheppard et al., 1991]. At present it can be considered to be determined that mercury concentrations in atmospheric precipitation of the Antarctic do not exceed  $1 \text{ ng/m}^3$  [Dick et al., 1990].

At the regional level the most numerous data were obtained in Europe (Sweden, Norway and Germany) and North America (USA and Canada). In southern Norway concentrations of

gaseous mercury are within 2.4÷5.7 ng/m<sup>3</sup> [Thrane, 1978]. During the 80-ies extensive investigations were carried out in Sweden. It was shown than elevated concentrations of mercury and its compounds are characteristic of winds from the south. In addition it was pointed out that mercury concentrations correlate with soot content. These data allowed to assert that major sources are located in central Europe and they are of an industrial character. Table 4.2 gives monitoring data of three Swedish stations located at different distances from major sources of atmospheric mercury.

**Table 4.2** Mercury concentrations in air and precipitation in Sweden [Brosset, 1987]

Stations	Latitude, degree	Concentration in gas phase, ng/m <sup>3</sup>		Concentration in precipitation, ng/l	
		Hg <sub>tot</sub>	Hg <sup>II</sup>	Hg <sup>IIa</sup>	Hg <sup>IIb</sup>
Ekerod	55.9	2.84	0.19	3.0	10.0
Onsala	57.4	2.66	0.14	3.4	7.8
Vindeln	64.2	2.22	0.09	2.2	3.4

Note: Hg<sub>tot</sub> - sum of all gaseous components;  
 Hg<sup>II</sup> - oxidized gaseous mercury;  
 Hg<sup>IIa</sup> - completely inorganic (for example, Cl-Hg-Cl);  
 Hg<sup>IIb</sup> - partially organic (for example, Cl-Hg-CH<sub>3</sub>).

It follows from the table that there is an obvious gradient of concentrations in air and precipitation from the south to the north. However, concentration variation of elemental mercury from the south to the north are relatively small, but concentrations of oxidized mercury in air and precipitation are rapidly decreased in the northern direction. It is possible that Hg<sup>IIb</sup> concentrations in the Arctic atmosphere are close to zero. G.Petersen et al. [1995] point out that concentration gradient of elemental mercury is more pronounced in winter. For elemental mercury weak dependence on the transport direction was found - in southern Sweden the exceedance at the transport from central Europe was only 0.2-0.4 ng/m<sup>3</sup> [Lindqvist et al., 1991]. During 1985-89 total mean concentration of oxidized mercury in precipitation revealed an obvious trend of decreasing from 25 to 30 ng/l in southern regions of Sweden dropping to 5 ng/l in northern ones [Lindqvist et al., 1991].

It was established [Brosset, 1987] that Hg<sup>IIa</sup> concentrations in precipitations depend on concentrations of ozone, Hg<sup>0</sup> water pH and on concentrations of complex producer like Cl<sup>-</sup> type. Since concentrations of Hg<sup>0</sup>, O<sub>3</sub>, [H<sup>+</sup>] and [Cl<sup>-</sup>] are rather spatially uniform, Hg<sup>IIa</sup> concentrations depend only slightly on the sampling location. At the same time Hg<sup>IIb</sup> most probably is scavenged in the vicinity of a source (coal-fired power stations) and therefore Hg<sup>IIb</sup> concentrations are strongly dependent on mutual location of region-source and sampling site. Nevertheless it should be mentioned that the input of methylated mercury to the total concentration of precipitation is highly variable (from 0.1 to 3% [Lee and Iverfeldt, 1991]) therefore it is impossible to make any conclusions.

Typical concentrations of aerosol mercury at the regional level in Europe are 0.05-0.1 ng/m<sup>3</sup> or 2% of total mercury. Under the conditions of Sweden the meridional gradient of aerosol mercury concentrations has not been found.

Summarized literature data on concentration levels of various forms of mercury in the atmosphere and its precipitations at the regional scale are presented in table 4.3.

**Table 4.3** Mercury concentrations in the atmosphere and precipitations at the regional level.

Region	Mercury form	Concentration	Dimension	References
Sweden, south	ΣHg <sub>(gas)</sub>	3.2	ng/m <sup>3</sup>	Iverfeldt, 1991 a

Sweden, north	$\Sigma\text{Hg}_{(\text{gas})}$	2.8	$\text{ng}/\text{m}^3$	Iverfeldt, 1991 a
Sweden, summer	$\Sigma\text{Hg}_{(\text{gas})}$	2.8	$\text{ng}/\text{m}^3$	Iverfeldt, 1991 a
Sweden, winter	$\Sigma\text{Hg}_{(\text{gas})}$	3.7	$\text{ng}/\text{m}^3$	Iverfeldt, 1991 a
Ontario, USA	$\Sigma\text{Hg}_{(\text{gas})}$	2.5 (2.2-3.7)	$\text{ng}/\text{m}^3$	Schroeder et al., 1996
Florida, USA	$\Sigma\text{Hg}_{(\text{gas})}$	1.64±0.76	$\text{ng}/\text{m}^3$	Gill et al., 1995
Florida, USA	$\Sigma\text{Hg}_{(\text{gas})}$ Precipit. $\Sigma\text{Hg}^{2+}$ $\text{Hg}^{\text{II}}_{(\text{particle})}$	2 (1.5-3) 44 (14-130) 0.04 (0.01-0.12)	$\text{ng}/\text{m}^3$ $\text{ng}/\text{l}$ $\text{ng}/\text{m}^3$	Dvonch et al., 1995
Wisconsin, USA	$\Sigma\text{Hg}_{(\text{gas})}$ $\text{CH}_3\text{HgX}_{(\text{gas})}$ $\text{Hg}^{\text{II}}_{(\text{particle})}$ Rain, $\Sigma\text{Hg}^{2+}$ Snow, $\Sigma\text{Hg}^{2+}$ Rain, $\text{CH}_3\text{HgX}$	1.57±0.40 0.012±0.013 0.022±0.019 10.5±4.8 6.9±0.9 0.156±0.068	$\text{ng}/\text{m}^3$ $\text{ng}/\text{m}^3$ $\text{ng}/\text{m}^3$ $\text{ng}/\text{l}$ $\text{ng}/\text{l}$ $\text{ng}/\text{l}$	Fitzgerald et al., 1991
USA north-east	$\text{Hg}^{\text{II}}_{(\text{gas})}$	0.00005-0.00015	$\text{ng}/\text{m}^3$	Stratton & Lindberg, 1995
Europe, industrial regions	$\text{Hg}^{\text{II}}_{(\text{particle})}$ $\text{Hg}^{\text{II}}_{(\text{gas})}$ $\text{CH}_3\text{HgZ}_{(\text{gas})}$	0.001-0.086 0.05-0.15 <0.001-0.008	$\text{ng}/\text{m}^3$ $\text{ng}/\text{m}^3$ $\text{ng}/\text{m}^3$	Petersen et al., 1996
Ontario, USA	$\text{Hg}^{\text{II}}_{(\text{particle})}$	0.08	$\text{ng}/\text{m}^3$	Schroeder et al., 1996
USA	$\text{Hg}^{\text{II}}_{(\text{particle})}$	0.00005-0.16	$\text{ng}/\text{m}^3$	Schroeder et al., 1987
Norway, south	$\text{Hg}^{\text{II}}_{(\text{particle} < 2.5 \mu\text{m})}$ $\text{Hg}^{\text{II}}_{(\text{particle} > 2.5 \mu\text{m})}$	0.04 0.06	$\text{ng}/\text{m}^3$ $\text{ng}/\text{m}^3$	Foltescu et al., 1996
Sweden	$\text{Hg}^{\text{II}}_{(\text{particle})}$ Precipit. $\Sigma\text{Hg}^{2+}$	0.05-0.06 20-40	$\text{ng}/\text{m}^3$ $\text{ng}/\text{l}$	Petersen et al., 1995
American Samoa, Pacific ocean	$\text{Hg}^{\text{II}}_{(\text{particle})}$ Rain, $\Sigma\text{Hg}^{2+}$	0.0004-0.002 9±5	$\text{ng}/\text{m}^3$ $\text{ng}/\text{l}$	Fitzgerald et al., 1991
USA and Canada	Precipit. $\Sigma\text{Hg}^{2+}$	14	$\text{ng}/\text{l}$	Vandal et al., 1991
Europe, industrial regions	Precipit. $\Sigma\text{Hg}^{2+}$ Precipit. $\text{CH}_3\text{HgX}$	5-50 0.05-0.5	$\text{ng}/\text{l}$ $\text{ng}/\text{l}$	Pleijel, 1993 and Munthe, 1995
Sweden, south	Precipit. $\Sigma\text{Hg}^{2+}$	0.3	$\text{ng}/\text{l}$	Munthe, 1993
Sweden, north	Precipit. $\Sigma\text{Hg}^{2+}$	0.15	$\text{ng}/\text{l}$	
Sweden	Precipit. $\Sigma\text{Hg}^{2+}$	13±4	$\text{ng}/\text{l}$	Iverfeldt, 1991b

According to data of North American monitoring network [Vandal et al., 1991] maximum concentrations in precipitation (about 5 ng/l above the mean) are observed in summer. A detailed investigation of the content of various forms of mercury in air and precipitation of Wisconsin, the USA was carried out by R.Mason et al. [1992] and Lamborg et al. [1995]. Their data are presented in table 4.4.

**Table 4.4** Mercury concentrations in air and precipitation in Wisconsin, USA

Observation period	Total gas. Hg, $\text{ng}/\text{m}^3$	Aerosol Hg, $\text{ng}/\text{m}^3$	Total Hg in precip., $\text{ng}/\text{l}$	Methyl.Hg in precip., $\text{ng}/\text{l}$
1989			10.05 ± 4.8 (*)	0.16 ± 0.07
1990			9.9 ± 4.2 (*)	0.07 ± 0.03
1988/89			6.0 ± 0.9 (**)	0.05 ± 0.02
1989/90			3.0 ± 0.8 (**)	0.10 ± 0.04

August 1992	1.21 ± 0.49	0.063 ± 0.032	2.58 ± 2.23 (*)	
January 1993	1.79 ± 0.43	0.006 ± 0.004	1.63 ± 0.91 (**)	
Summer 1993	1.8 ± 0.4	0.014 ± 0.023	6.70 ± 5.55 (*)	0.112 ± 0.432
May 1994	1.68 ± 0.26		8.74 ± 2.59 (*)	

Note: (\*) - rain; (\*\*) - snow.

Contrary to data obtained in Sweden [Lidqvist et al., 1991], appreciable spatial variability of aerosol mercury concentrations (to 60%) were recorded within Wisconsin, USA [Lamborg et al., 1995].

It is important to mention that mercury in precipitations can be in insoluble form and incorporated in insoluble particles. In industrial regions the undissolved form (most likely soot particles) dominate over dissolved one [Pleijel and Munthe, 1995]. In Wisconsin, USA, the dissolved fraction was 23% in rain and 51% - in snow [Lamborg et al., 1995]. According to data of G.Petersen et al., [1996] the fraction of mercury absorbed on particles in water phase is varied from less than 10% in clean regions to >90% in polluted ones.

For modelling purposes it is important to possess data on seasonal concentration variations in air and precipitations. For Sweden conditions it was found that in the late 80-ies gaseous mercury concentrations were 3-4 ng/m<sup>3</sup> in winter and they dropped down to 1.5-3 ng/m<sup>3</sup> in summer [Lidqvist et al., 1991]. Later on it was revealed that winter concentrations are by 10-15% higher than mean annual ones [Iverfeldt et al., 1995]. In Wisconsin aerosol mercury concentration varied from season to season as much as 3-5 times. Fine fraction (<2.5 µm) dominated in winter. In summer coarse fraction (>2.5 µm) appeared with concentrations about 0.001 ng/m<sup>3</sup>, which the authors [Lamborg et al., 1995] connected with re-suspension of soil particles. This process gives only 2% to the total deposition of mercury in a given region. J. Burke et al., [1995] found in Vermont, USA, that maximum concentrations of aerosol mercury are characteristic of winter months at mean value 11 pg/m<sup>3</sup>. Sharply pronounced seasonal variations were observed in Michigan, USA: from 1-2 ng/l in winter to 40 more than ng/l in summer [Hoyer et al., 1995].

Near sources at the local level mercury concentrations can be very high and a relative contribution of different forms of mercury can appreciably vary depending on a source type. For example, in flue gases of coal-fired power station observed concentrations were within 1-20 µg/m<sup>3</sup>, at waste incineration - 50-1000 µg/m<sup>3</sup> [Porcella et al., 1996].

Aerosol mercury content is represented on local level by both fine particle (diameter is about 1 µm) and coarse particles (>2.5 µm). According to N.Pirrone et al. [1995] in Detroit the bulk (86%) of particulate mercury is fixed with fine particles at mean concentration about 0.3 ng/m<sup>3</sup>. It is contradictory to data that in US industrial regions mercury content in coarse aerosol fraction (>2.5 µm) is comparable with that of gaseous fraction and mercury concentration on particles reach 1.2 ng/m<sup>3</sup> whereas at the regional level it is by 1-2 orders lower [Keeler et al., 1995]. In the region of a relatively clean city of Goteborg (Sweden) mercury content of particles is 3-17% (or 0.11-0.57 ng/m<sup>3</sup>) of the total mercury content [Xiao et al., 1991]. W.Schroeder et al. [1987] give similar values for USA cities. According to data of N.Bloom et al. [1996] Hg(II) gasphase concentration under city conditions is varied within limits 9-150 pg/m<sup>3</sup> (maximum in dry summer period).

In order to understand mercury behaviour in the atmosphere it is important to have an idea on its vertical distribution. Unfortunately there are very few works dealing with the determination of mercury vertical profiles. One of the first aircraft field experiments were

carried out by V.Ionov et al. [1976] in Central Asia. They found a sharp decrease of gaseous mercury concentration with height in the layer of 3 km, however, in term of quantity their data are unreliable and indicate only a trend. According to data of C.Brosset [1987] in the coastal atmosphere of south-western Sweden concentrations of elemental mercury vapours decreased with height by 30-40% in the layer to 3 km. At the same time the concentration of oxidized gaseous mercury compounds is noticeably increased with height. Similar results were obtained by K.Kastkus et al. [1985]. Their data show that the content of total gaseous mercury is decreased with height in 2 times from 0 to 5 km. In Fergana valley (Uzbekistan) at the level of the boundary layer inversion (about 1 km) a drastic decrease of concentrations was observed from  $10 \text{ ng/m}^3$  to  $4 \text{ ng/m}^3$  followed by gradual decline to  $2 \text{ ng/m}^3$  at 5 km. In clean oceanic air parcels at the western USA coast  $\text{Hg}^0$  concentration dropped with height from 2.1 near the ground surface to  $1.6 \text{ ng/m}^3$  (in normal condition) at height 4 km. The input of methylated mercury on the contrary increased with height from 2-5% near the ground to 12% at 3.7 km [Lindqvist et al., 1991].

V.Fursov [1983] made measurements at various heights above the sea level up to 4655 m in mountains and found no height dependence. Helicopter studies in southern Russia (Krasnodar territory) confirmed that within layer 50-400 m the concentration practically did not changed. According to F. Slerm [1996] concentrations at the border of the boundary layer and in the free troposphere (Wank summit, 1780 m above the sea level, southern Germany) mean concentration of gaseous mercury was  $2.54 \text{ ng/m}^3$  which does not differ from normal surface concentrations. In summer when an intensive vertical exchange is observed no diurnal variation was detected. It shows lack of vertical gradients exceeding the accuracy of the method (4.8%). Measurements at high flights (at the level of the tropopause) from Germany to Chili as well as at flights over Europe (6-12 km layer) showed no considerable vertical trend [Seiler et al., 1980; Slemr et al., 1985]. A noticeable difference between the North and South Hemispheres were highlighted: mean concentration at the flight height was  $1.45 \pm 0.22 \text{ ng/m}^3$  in the North Hemisphere, and in the South -  $1.08 \pm 0.36$ .

Mercury content in soils of the world is within the limit of one order of magnitude:  $(3 \div 7) \times 10^{-8}$  is an average value for cultural world soils [Vinogradov, 1957];  $(2 \div 8) \times 10^{-8}$  for Kazakhstan [Prokofiev, 1981];  $(2-4) \times 10^{-8}$  for Nevada and Texas [Williston, 1968]. E.Nater and D.Grigal [1992] found a regularity of mercury concentration on clay and silt content in unpolluted soil expressed by equation:

$$[\text{Hg}] \text{ ng/g} = 5.12 + 0.523 \times (\text{clay} + \text{silt})\%$$

Upon the impact of anthropogenic mercury deposition its natural content can be exceeded.

In Kazakhstan mercury concentration in soil decreases with depth (i.e. with humus content decrease) from  $6 \times 10^{-8}$  in the upper horizon to  $3 \times 10^{-8}$  in the lower one [Fursov, 1983]. The same regularity is found for soils of the north-eastern USA - in the lower horizon mercury concentration decreases to  $(1.4 \pm 0.2) \times 10^{-8}$  [Nater and Grigal, 1992].

## 5. Wet removal from the atmosphere

Scavenging from the atmosphere is a process of a substance removal from the atmosphere by condensed atmospheric water. It is possible to distinguish reversible and irreversible wet removal. The reversible removal results in substance scavenging to liquid phase of fog or cloud drops. Absorbed by a drop the substance remained in the atmosphere. For example, mercury atom by this or that way enter a cloud drop. Most likely the drop will evaporate and produce aerosol particle with the mercury atom in its composition. The particle can again be

captured by a drop. H.Rodhe [1992] estimated that each particle during its existence in the atmosphere passes a similar cycle 5 times. During this time the mercury atom in question is present in the atmosphere being reversibly removed many times. At irreversible wet removal the mercury atom in a rain drop or flake comes from the atmosphere onto the underlying surface.

All mercury forms can be wet removed out. As it was mentioned above vapours of elemental mercury though weakly but are dissolved in water according to Henry's law. In a drop elemental mercury can be oxidized breaking the equilibrium in the "air-drop" system and leading to the solution of new portions of elemental mercury vapours. Thus the process of elemental mercury wet removal is determined not by the rate of physical dissolution but by the rate of chemical interaction in liquid phase. Gaseous compounds like  $\text{HgCl}_2$  or  $\text{CH}_3\text{HgCl}$  as a rule are easily dissolved in water, and their wet removal rate is determined by the rate of physical dissolution according to Henry's law. Wet removal of mercury incorporated in particles is determined by processes of interactions of a particle and a drop. Mercury concentration in a particle (in reasonable limits) in no way affect the process rate. One should be aware that at the reversible wet removal originally gaseous mercury after evaporation of the drop is converted to aerosol [Expert Panel on Mercury Atmospheric Processes, 1994].

Irreversible wet removal can go on both in cloud with subsequent formation of large rain drops and in the subcloud layer by falling rain drops or flakes. In the latter case the effect of inertial collision of a falling drop or flake with a particle containing mercury becomes to be important. When there are elevated concentrations of mercury in the subcloud layer the first portions of rain or snow have higher concentrations than subsequent ones.

Due to high solubility of gaseous compounds in comparison with vapours of elemental mercury the wash-out coefficient of compounds which is expressed by the ratio of concentration in water phase to concentration in gaseous phase should be by several orders higher [Schroeder et al., 1991]. O.Lindqvist and H. Rodhe [1985] estimated the wash-out coefficient of different forms of mercury by the following way:

$$(\Sigma\text{Hg, precipitation})/(\Sigma\text{Hg,air})=1,000 \text{ (urban)} \div 10,000 \text{ (rural)}$$

$$(\Sigma\text{Hg,precip.})/(\text{Hg,air,soluble})=100,000 \text{ (rural, Sweden)}$$

$$(\Sigma\text{Hg,precip.})/(\text{Hg,air,particles})=1,000,000 \text{ (tropical Pacific)}$$

The authors indicate that aerosol and water soluble fractions can be washed out in the vicinity (tens of km) from the emission source.

On the basis of prolonged measurements C.Brosset [1987] calculated wash out coefficients ( $K_w$ ) for three Swedish stations located at various distances from central Europe:

Ekerod station (southern Sweden)  $K_w=71,000$

Onsala station (central Sweden)  $K_w=77,000$

Vindeln station (northern Sweden)  $K_w=38,000$

C.Brosset considers that cloud water captures mainly inorganic gaseous mercury.

For modelling M.Galperin et al. [1994] assumed the following values of wash-out coefficients for different forms of mercury:

$\text{Hg}^0$ , $(\text{CH}_3)_2\text{Hg}$	2-3
$\text{CH}_3\text{HgCl}$	100,000
$\text{HgCl}_2$	20,000,000

Hg(particles) 10,000

It should be mentioned that it is rather expert estimates and not the data proved by experiments.

C.Lamborg et al [1995] making use of the fact of high correlation between mercury and sulphate in precipitation [Iverfeldt, 1990] supposed that wet removal mechanisms of these substances are similar. Hence it follows that at the regional level the bulk of mercury should be removed due to nucleation and dissolution inside a cloud. However experiments show that in initial portions of rain mercury concentration (30-70 ng/l) can be several times higher than in subsequent ones (2-18 ng/l) [Ferrara et al., 1982; Ferrara et al., 1986; Lamborg et al., 1995]. It may imply that the basic contribution to wet removal makes the subcloud wash out. J. Sorensen et al., [1994] do not confirm the correlation of mercury and sulphate concentration in precipitation therefore the question of similarity of wet removal out mechanism is remained open.

## 6. "Dry" uptake by underlying surface

"Dry" uptake of a substance by elements of the underlying surface is determined by the intensity of turbulent flux of a substance from the atmosphere to the surface, flux intensity through a thin laminar air layer adjacent to the surface and physical-chemical properties of the surface itself. As a rule "dry" uptake process is described in terms of turbulent, laminar and surface resistances. The opposition of "dry" uptake to "wet" removal out has no sense since "dry" uptake is a continuous process taking place independent of precipitation event occurrence. In the process of atmospheric precipitation only characteristics of the underlying surface are being changed (as a rule wet surface can better capture molecules and particles especially when these substances are water soluble).

If water is the underlying surface and substance being sorbed is soluble in water, it is possible to describe dry uptake process in terms of Henry's law [Schroeder, 1996]. At the border air-water the flux is equal to:

$$F_{\text{Hg}_0} = K_{w,a} \times [C_{w,g} - C_{a,g} \times (R \times T/H)]$$

where:  $F_{\text{Hg}_0}$  - resulting flux of gaseous elemental mercury, (mol/m<sup>2</sup>/yr);

$K_{w,a}$  - resulting mass coefficient of transport (m/yr);

$C_{w,g}$  - concentration of soluble elemental mercury in water, mol/m<sup>3</sup>;

$C_{a,g}$  - concentration of gaseous elemental mercury in air, mol/m<sup>3</sup>;

R - universal gas constant,  $R = 8.314 \text{ Pa} \times \text{m}^3/\text{mol} \times \text{K}$ ;

T - temperature, °K;

H - Henry's constant ( $\text{Pa} \times \text{m}^3/\text{mol}$ ).

For the system "air-water" mass coefficient of the transport can be accepted to be equal to 0.32 m/day (possible range - from 0.2 to 3.0 m/day). Concentration in water of dissolved Hg<sup>0</sup> ( $C_{w,g}$ ) is accepted as 0.06 ng/l (possible range - from 0.02 to 0.15 ng/l). A similar approach can be applied to gaseous Hg(II), but for the description of the process there is no quantitative information so far.

For model parametrization the notion "dry deposition" is often used though this term is conventional for gases and fine particles since they are not subjected to gravitational settling. It is more logical to use the term "dry uptake rate" with formal dimension of linear velocity.

If the flux is directed from the underlying surface to the atmosphere the linear velocity can be negative. In reality as a rule we deal simultaneously with both absorption and emission fluxes. In this case the value and sign of linear velocity describe a resulting flux [Meyers et al., 1996].

Elemental mercury vapours especially near sources where concentration levels are elevated, dry uptake of  $\text{Hg}^0$  by plants through stomata is possible. In the process of absorption and emission mercury displays the availability of "compensation point" - if air concentrations are high a plant absorbs and vice versa. For some forest compensation point is considerably higher than typical regional concentration levels of elemental mercury [Expert Panel on Mercury Atmospheric Processes, 1994].

The literature is abundant in data on linear velocities of dry uptake. These data are obtained as on the basis of experiments (through-fall observations, micrometeorological gradient method), so by expert estimates on the basis of a comparison of mercury properties and those of its compounds with adequately studied species (sulphur and nitrogen compounds). Table 6.1 give experimental and expert estimates of the dry deposition velocities for different forms of mercury and various types of the underlying surface.



**Table 6.1** Estimates of dry deposition linear velocities of different mercury forms

Hg form	Surface type	Linear absorption rate, cm/s	Reference
Hg <sup>0</sup>	Summer forest	0.03	Petersen et al., 1996
Hg <sup>0</sup>	Winter forest	<< 0.03	
Hg <sup>0</sup>	Other surfaces	0	
HgCl <sub>2</sub>	Middle latitudes	like for HNO <sub>3</sub>	
ΣHg <sub>(particle)</sub>	Middle latitudes	like for SO <sub>4</sub> <sup>=</sup>	
Hg <sup>0</sup>	Deciduous forest : summer	0.1	Lindsberg et al, 1992
Hg <sup>0</sup>	: winter	<0.01	
Hg <sup>0</sup>	Deciduous forest : summer	0.12	Lindsberg et al, 1992
Hg <sup>0</sup>	: summer, night	0.04	
Hg <sup>0</sup>	: summer day, 10°C	0.06	
Hg <sup>0</sup>	: summer day, 15°C	0.09	
Hg <sup>0</sup>	: summer day, 20°C	0.11	
Hg <sup>0</sup>	: summer day, 25°C	0.16	
Hg <sup>0</sup>	: summer day, 30°C	0.20	
Hg <sup>0</sup>	: winter	0.006	
Hg <sup>0</sup> Hg <sup>II</sup> <sub>(gas)</sub>	Typical landscape of middle latitudes	0.05 - 0.1 as for HNO <sub>3</sub>	Expert Panel, 1994
Hg <sup>0</sup>	Typical landscape of middle latitudes	0.03	Bloxan et al, 1996
Hg <sup>0</sup>	Dry surface	0.01	Galperin et al, 1994
Hg <sup>0</sup>	Wet surface	0.03	
HgO & HgCl <sub>2</sub>	Dry surface	0.5	
HgO & HgCl <sub>2</sub>	Wet surface	1 - 2	
ΣHg <sub>(particle)</sub>	Typical landscape of middle latitudes	0.1	
ΣHg <sub>(gas)</sub>	Sweden, winter	~0	Iverfeldt, 1991b
ΣHg <sub>(particle)</sub> <0.5 μm	Typical landscape of middle latitudes	0.1	Lamborg et al, 1995
ΣHg <sub>(particle)</sub> 2 μm		0.5	
ΣHg <sub>(particle)</sub>	Great Lakes region	0.5	Fitzerald et al, 1991
ΣHg <sub>(particle)</sub>	Water	0.2	Shroeder, 1996
ΣHg <sub>(particle)</sub>	Typical landscape of middle latitudes	0.1 - 0.5	Lindqvist and Rodhe, 1985
Small particles (as for Cd)	Coniferous forest	5.5	Müller, 1990
	Deciduous forest	1.8	
	Grass	0.1	
	Water	0.03	

Dry uptake can provide an appreciable fraction of the total scavenging of mercury from the atmosphere. It was estimated that at the global level this process provides about 30% of total deposition (2500 tonnes of 7500), however, the accuracy of this value is within the range of an order of magnitude [Lindqvist et al., 1991]. At local and regional levels this input can vary within sufficiently wide limits depending on the underlying surface type, climatic peculiarities, relationship of mercury forms in emission. For example, for boreal forests of Sweden the input of dry deposition is relatively small and amounts to 16% [Xiao et al., 1991]. In the region of the Great Lakes according to data of W.Fitzgerald et al. [1991] dry deposition amounts to 35%. For Ontario, the USA, W.Schroeder [1996] estimated the contribution of dry deposit to be 25%. For the same region in through-fall observations in a deciduous forest the contribution of dry deposition was estimated to be 80% [Rea et al., 1996].

## **7. Deposition from the atmosphere: modern data and historical trends**

Mercury deposition intensity from the atmosphere can substantially differ in different regions of the world depending on the anthropogenic load. To re-establish the pattern of depositions in the pre-industrial period is very difficult. As it was said in chapter 4 glaciers of Greenland and the Antarctic do not reflect any changes during this historical period. The more so it was shown that during recent tens of thousand years considerable (to several times) variations of deposition took place due to mere natural changes in the environment. The only sufficiently reliable confirmation of the anthropogenic impact is the mercury concentration increase in upper layers of peat bogs and bottom sediments of lakes.

In order to evaluate the extent of anthropogenic impact H.Rodhe [1996] introduced the notion of "amplification factor". Numerically it is equal to the ratio of mercury concentration in deep (free of anthropogenic influence) layers of peat bogs or bottom sediments to concentrations in modern layers. According to his data at the global level this factor is within the limits of (2.4-4.4) in the USA - (2.5-3.4) and about 5 - in southern Sweden. We believe that on the global scale this factor should be noticeably lower than at the regional level, where oxidized mercury is efficiently scavenged and produces apparent gradients near sources [Expert Panel...,1994]. Investigations concerned with historical monitoring is carried out mainly in industrial regions (Sweden, Denmark, USA) therefore an the issue on the spatial scale of the environment pollution is remained open. In order to answer the question on the extent of the phenomenon in the global scale it is necessary to have data on peat bogs and bottom sediment located far from sources.

W.Fitzgerald and R.Mason [1995, 1996] believe that during recent years atmospheric mercury concentrations are increasing at the global level by 0.6-0.7% per year ( $0.01 \text{ ng/m}^3$  per year). German scientists [Slemr, 1996] revealed the growth of mercury vapour concentrations at the global level during 1977-90 by 17% in the North hemisphere and by 14% in the South one explaining this fact by the increase of anthropogenic emission. However during 1990-94 they mentioned an essential reduction of the global concentration in both hemispheres (North - by 20.4%, South - by 21.2%). The reason for this reaction the author connects with the decrease of anthropogenic emission in countries of Eastern Europe. However, this fact cannot explain a simultaneous cut down of concentrations in the South Hemisphere where in many countries intensive industrial development took place with minimum investments to the environment protection. Probably we are dealing with large-scale natural variations reasons for which have not yet been understood. At the regional level

during historical period is very significant and it is directly connected with the anthropogenic activity. At the regional level air concentrations increased as much as 3-4 times during the historical period, in precipitations - by an order of magnitude. Clearly mercury deposition is also increased.

Elevated concentrations of mercury in the upper layer of peat bogs for the first time were detected in Denmark [Pheiffer-Madson, 1981]. It was found the deposition during recent 150 years increased in 3-5 times from 10-20 g/km<sup>2</sup>/yr to 50-100 g/km<sup>2</sup>/yr. In Sweden [Meily, 1995] pre-industrial deposition levels were about 2 g/km<sup>2</sup>/yr hence it follows that by now the growth of depositions is as much as 8-10 times. A.Jensen and A.Jensen [1991] for south - western Sweden give more moderate growth during the current century - from 10 to 30 g/km<sup>2</sup>/yr. As it was shown by data on mercury content in lake sediment in the central part of North American continent since 1850 deposition has been increased from 3.7 to 12.5 g/km<sup>2</sup>/yr [Swain et al., 1992].

At present considerable changes take place in European regional cycle of mercury. In this region during recent 5-10 years the intensity of anthropogenic emission drastically decreased due to both environmental protection action and a deep industrial crisis in countries of Eastern Europe. It resulted in the reduction of deposition. According to A.Iverfeldt et al. [1995] data wet deposition in Sweden decreased from 27 g/km<sup>2</sup>/yr in 1987-89 - to 10 g/km<sup>2</sup>/yr in 1990-92. Similar variations are characteristic of the USA where since the beginning of the century till 1987-89 depositions has been increased from 10 to 38 g/km<sup>2</sup>/yr and then has dropped to 25 g/km<sup>2</sup>/yr by 1991.

During recent years deposition level in the south-east USA and south-western Sweden are varied within limits 10-20 g/km<sup>2</sup>/yr [Fitzgerald et al., 1991; Iverfeldt, 1991b]. At the background in the Pacific ocean deposition is 3-4 g/km<sup>2</sup>/yr [Fitzgerald, 1989].

For modelling purposes it is important to have an idea on seasonal variations. According to data of M.Hoyer [1995] the bulk (about 90%) of deposition in the north-east USA is conditioned by rains during a warm period of the year. It is confirmed by data of J.Sorensen et al. [1994] who showed that in the summer period deposition reaches 1 g/km<sup>2</sup>/week whereas in winter they drop practically to zero. Data of J.Sorensen et al. are plotted in fig.7.1.

## **8. Physical-chemical process in gaseous, liquid and solid phases**

It was shown above that mercury atom in many ways is similar to the atom of inert radon. To some extent this fact determines a relative chemical stability and low dissolubility of elemental mercury in the atmosphere. Beside high volatility elemental mercury and a number of its compounds make it possible for them to occur both in the gaseous phase and on aerosol particles. Thus physical-chemical properties can change both chemical and aggregate state of mercury.

Under natural conditions processes of redistribution of mercury and its gaseous compounds between gaseous and aerosol phases due to absorption - desorption take place practically permanently. M.Galperin et al. [1994] assumed that at temperature  $\leq 39^{\circ}\text{C}$  elemental mercury is present only in the form of particles. Vapour pressure, however, over solid mercury is sufficiently high to speak on possibility of mercury vapour at temperatures below the melting point.

**Fig.7.1** Seasonal variations of mercury deposition in north-eastern part of the USA [Sorensen et al., 1994]

Simultaneous measurements of both gaseous and aerosol mercury are very few. It is worth mentioning of data of W.Schroeder et al. [1995] describing a reverse link relation between vaporous mercury concentrations and temperature:

$$\text{TGM (ng/m}^3\text{)} = -0.89 \times 1000/\text{K} + 4.95 \quad (\text{Alert station})$$

$$\text{TGM (ng/m}^3\text{)} = -1.59 \times 1000/\text{K} + 7.21 \quad (\text{Expedition of scientific research vessel "POLARSTERN"}).$$

The authors suggested several explanations for this connection and interphase redistribution included. Unfortunately aerosol component has not been measured by the authors. J. Lu et al. [1997] making investigations in the Arctic found in one of samples abrupt redistribution of mercury between phases but they made no indication of temperature while sampling.

On the basis of general ideas on properties of gaseous mercury temperature effect of their redistribution between gaseous and solid phases can be admitted. For more wide spread inorganic compound  $\text{HgCl}_2$  the vapour pressure is considerably lower and the pressure drop with temperature is considerably steeper than for elemental mercury [Lindqvist et al., 1991]. In addition,  $\text{HgCl}_2$  is easily dissolved in water and therefore at relatively high humidity it should be well scavenged from gaseous phase by aerosol particles. Mercury oxide,  $\text{HgO}$ , most likely is predominantly occurs in aerosol phase. Partially methylated mercury (for example,  $\text{CH}_3\text{HgCl}$ ) by its behaviour should be similar to mercury chloride, and DMHg - to elemental mercury.

In gaseous phase elemental mercury can be oxidized by ozone. An indirect confirmation in favour of mercury oxidation by ozone in atmospheric conditions may serve the fact that elemental mercury concentration is in a good correlation with ratio  $\text{NO}_2/\text{NO}$  ( $r=-0.64$ ) [Foltescu et al, 1996]. In its turn this ratio is proportional to ozone concentration. In laboratory conditions this reaction was realized for the first time by V. P'yankov [1949] but the conditions of the reaction were not accurately described hampering the assessment of reaction rate. Due to the uncertainty of initial conditions estimates of rate constants are varied from  $4.2\text{E-}19$  [Slern et al., 1985] to  $4.9\text{E-}18 \text{ cm}^3/\text{molec/s}$  [Schroeder et al., 1991]. K. Pleijel and J. Munthe [1995a] consider the latter value to be highly overestimated.

Later on laboratory experiments with mercury oxidation by ozone were repeated [Hall et al., 1995]. The obtained rates ( $(3\pm 2)\text{E-}20 \text{ cm}^3/\text{molec/s}$  at  $20^\circ\text{C}$ ) are several times lower than those estimated on the basis of P'yankov's experiments. B.Hall [1995] supposed that the reaction of oxidation by ozone has the order of 0.8. In this case the life-time of elemental mercury vapours in the atmosphere can be about 3 months.

In addition to ozone there are many other potential oxidants of mercury. W.Schroeder et al. [1991] on the basis of data on reactions enthalpy showed that besides ozone hydrogen peroxide, atomic oxygen and radical  $\text{NO}_3^\bullet$  can be potential oxidants. C.Seigneur et al. [1994] consider that most likely in addition to ozone the oxidation reaction can take place with gaseous hydrogen peroxide ( $K \leq 4.1\text{E-}16 \text{ cm}^3/\text{molec/s}$  at  $25^\circ\text{C}$ ) and chlorine atoms ( $K \leq 4.1\text{E-}16 \text{ cm}^3/\text{molec/s}$  at  $25^\circ\text{C}$ ). The authors believe that in certain conditions the latter reaction can be very significant and the half-life of gaseous metallic mercury can be several hours. B. Halls et al. [1991] indicate that mercury can be oxidized at room temperature by molecular chlorine, hydrogen chloride, oxygen if catalysts are present and nitrogen dioxide. It should be mentioned that at present quantitative information on reactions of elemental mercury oxidation in gaseous phase with any oxidants but ozone if not available.

In the upper layers of the atmosphere where radiation with wavelength of 253.6 nm penetrates in considerable quantities, mercury atom can be activated and enter into reactions of oxidation [Schroeder et al., 1991].

It was assumed that in the atmosphere the reaction of mercury methylation can take place.  $\text{CH}_3\text{I}$  and  $(\text{CH}_3)_2\text{S}$  were considered as potential donors of the methyl group [Munthe, 1993; Hall et al., 1995]. It is shown that these species act (if at all) very slowly and cannot explain essential concentrations of methylated mercury in precipitation.

Products of gas phase oxidation of elemental mercury should be relatively quickly scavenged from the atmosphere by precipitation. At the global level this process provides an explanation for the concentration of oxidized mercury (1 ng/l) in precipitation [Hall, 1995]. It is a minor fraction of actually observed concentrations in the atmosphere of industrial regions.

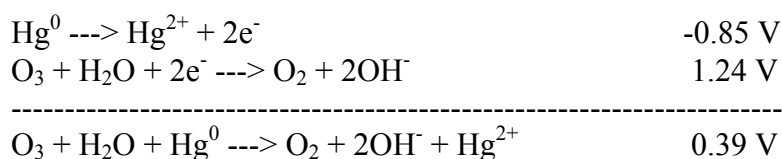
In the gaseous phase photolysis of oxidized mercury compounds ( $\text{HgCl}_2$ ,  $\text{Hg}(\text{OH})_2$ ) with the formation of elemental mercury can take place, however quantitative data on these reactions are absent [Seigneur et al., 1994].

In molecules like  $\text{R}^{\cdot}\text{-Hg-R}^{\cdot}$  the bond  $\text{Hg-C}$  is rather weak (the binding energy is from 13 to 52 kcal/mol depending on R) [Prokofiev, 1981] therefore DMHg can easily react with  $\text{OH}^{\cdot}$  radical with constant rate equal to  $1.97\text{E-}11 \text{ cm}^3/\text{molec/s}$  [Niki et al., 1983]. G.Petersen [1992] points out to a possibility of reaction with atomic chlorine with constant rate  $2.75\text{E-}10 \text{ cm}^3/\text{molec/s}$ . At such oxidation rates life-time of  $(\text{CH}_3)_2\text{Hg}$  is several hours in middle latitudes. M.Horvat [1996] is of the same opinion taking the life-time of  $(\text{CH}_3)_2\text{Hg}$  in the atmosphere to be short due to intensive photochemical and chemical degradation.

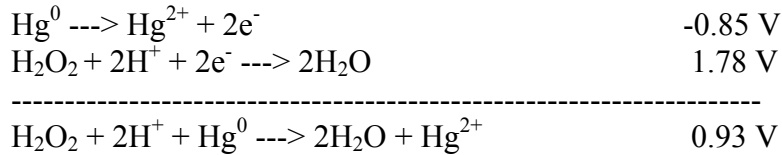
In the liquid-drop phase the reaction of dissolved elemental mercury by dissolved ozone [Iverfeldt and Lindqvist, 1986] is most important. Ozone solubility in water is sufficiently high (Henry's coefficient is 0.013 mol/l/atm at  $10^\circ\text{C}$  [Kelly et al., 1985]) to provide the availability of high levels of an oxidant in a drop. J.Munthe [1992] found that this reaction is of the second order and its rate  $K = (4.7 \pm 2.2)\text{E}7 \text{ M}^{-1} \text{ s}^{-1}$  is independent of pH and temperature. According to his provisional estimates at water-droplet phase content  $0.5 \text{ g/m}^3$ , mercury concentration  $3 \text{ ng/m}^3$ , ozone 30 ppb the oxidation rate can be 2-3% per day. Later J.Munthe [1997], however, came to the conclusion that this value was seriously overestimated.

It a radically new viewpoint on oxidation process of atmospheric elemental mercury should be mentioned. E.Constantinou et al. [1995] believe that oxidation by ozone in the liquid phase runs rapidly and the rate of the whole oxidation process is limited by the rate of physical dissolution of mercury in a drop.

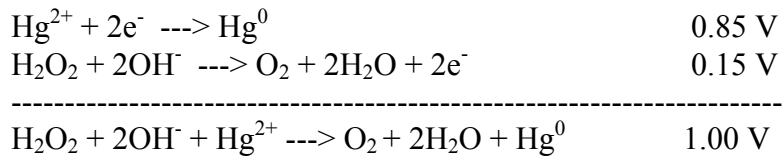
Allowing for electrochemical potentials the oxidation reaction can be described by the following equations [Schroeder et al., 1991]:



In the liquid phase in addition to ozone elemental mercury can be oxidized by hydrogen peroxide at  $\text{pH} < 5.5$  [Schroeder et al., 1991] following the scheme:



However, in parallel with oxidation a reverse process of reduction can take place which is dominating at  $\text{pH} > 5.5$ .



J.Munthe and W.J.McElroy [1992] doubt a possibility of mercury oxidation by hydrogen peroxide in the liquid phase.

Mercury oxide produced in the liquid phase reacts with ions available in the solution. Theoretically a great number of reactions are possible but actually for understanding of atmospheric mercury chemistry only some of them are important. These most important reactions with their constants are presented in table 8.1.

**Table 8.1** The most important reactions of mercury in the liquid phase

No.	Reactions	Reaction constants		
		*1	*2	*3
R01	$\text{Hg}^0 + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2$	$4.5\text{E}7 \text{ M}^{-1}\text{s}^{-1}$	$4.7\text{E}7 \text{ M}^{-1}\text{s}^{-1}$	$4.7\text{E}7 \text{ M}^{-1}\text{s}^{-1}$
R02	$\text{HgO} + \text{H}^+ \rightarrow \text{Hg}^{2+} + \text{OH}^-$	$1\text{E}10 \text{ M}^{-1} \text{ s}^{-1}$		
R03	$\text{Hg}^{2+} + \text{SO}_3^{2-} \rightleftharpoons \text{HgSO}_3$	$4\text{E}-12 \text{ M}$		$2\text{E}-13 \text{ M}$
R04	$\text{HgSO}_3 + \text{SO}_3^{2-} \rightleftharpoons \text{Hg}(\text{SO}_3)_2^{2-}$			$4\text{E}-12 \text{ M}$
R05	$\text{HgSO}_3 \rightarrow \text{Hg}^0 + \text{SO}_3^{2-}$	$0.6 \text{ s}^{-1}$		$0.6 \text{ s}^{-1}$
R06	$\text{Hg}(\text{SO}_3)_2^{2-} \rightarrow \text{Hg}^0 + 2 \text{SO}_3^{2-}$		$4\text{E}-4 \text{ c}^{-1}$	$1\text{E}-4 \text{ s}^{-1}$
R07	$\text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+$	$1.82\text{E}-7 \text{ M}$		
R08	$\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2$	$3.31\text{E}-7 \text{ M}$		
R09	$\text{Hg}(\text{OH})_2 \rightleftharpoons \text{Hg}^{2+} + 2\text{OH}^-$			$1\text{E}-22 \text{ M}^2$
R10	$\text{HgCl}_2 \rightleftharpoons \text{Hg}^{2+} + 2\text{Cl}^-$			$1\text{E}-14 \text{ M}^2$

\*1 - [Pleijer and Munthe, 1995a]

\*2 - [Petersen et al., 1996]

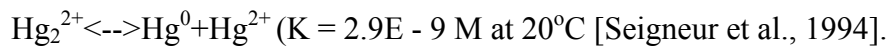
\*3 - [Constantiou et al., 1995]

Under real conditions for mercury ion formed due to reaction (R02) is most accessible is chlorine ion, however, reactions with ions of other halogens are possible. Reaction (R03) with sulphite ion with the formation of unstable intermediate mercuric sulphite is important for understanding mercury chemistry in the liquid phase. Mercuric sulphite is rapidly distracted with mercury reduction to elemental form. However, the addition of one more sulphite ion to mercuric sulphite is possible (R04) with the formation of more stable complex  $\text{Hg}(\text{SO}_3)_2^{2-}$ . Thus the sum of reactions conditions provides the establishment of dynamic equilibrium between elemental and oxidized mercury in the liquid phase of a cloud drop. J.Munthe et al., [1991] suggested a scheme in which generalized rate of the reduction

reaction is in an inverse dependence on sulphite ion concentrations. At low air concentrations of SO<sub>2</sub> and at pH<5.5 the rate of Hg(SO<sub>3</sub>)<sub>2</sub><sup>2-</sup> reduction to Hg<sup>0</sup> can exceed 1% per hour.

The process of oxidized mercury reduction to elemental mercury can be realized with the participation of CO, SO<sub>2</sub>, NO but quantitative characteristics of the reactions are unknown [Schroeder et al., 1991].

A.Prokofiev [1981] indicates one more mechanism of oxidized mercury reduction. In water solution mercury can be present in univalent state as Hg<sub>2</sub><sup>2+</sup>. This ion is distracted in the disproportionation reaction:



At the presence of complex producers forming strong covalent bonds, at the abundance of oxidants the reaction is irreversibly shifted to the right. At the presence of ammonium ion Hg(I) is immediately converted to Hg(II) and Hg<sup>0</sup> [Prokofiev, 1981].

In the liquid phase photo-dissociation of oxidized compounds with the formation of elemental mercury can take place. The irradiation of Hg(OH)<sub>2</sub> solution of by visible light ( $\lambda > 290 \text{ nm}$ ) leads to photo-dissociation with quantum yield 0.14. The rate constant is such that Hg(OH)<sub>2</sub> life-time relative to this reaction is 2 months in middle latitudes [Xiao et al., 1994]. Photo-reduction of HgS<sub>2</sub><sup>2-</sup> leads to the formation of elemental mercury and its sulphide but quantitative characteristics of the reaction are unknown. Mercury chloride is not distracted at light [Munthe and McElroy, 1992].

The formed complex HgCl<sub>2</sub> can volatile from a drop to air. Model experiments demonstrated [Pleijel and Munthe, 1995a] that this process practically does not affect oxidized mercury concentration in the liquid phase. Mercury compounds formed due to liquid phase reactions can be absorbed by soot particles from the water solution thereby shifting the equilibrium between Hg<sup>0</sup> and Hg<sup>2+</sup> to the direction of oxidized mercury. It is considered that oxidized mercury absorbed on a soot particle is not reduced to elemental one [Munthe, 1997]. The process is limited by the diffusion rate in the liquid. G.Petersen et al. [1995] consider that the reverse transport process is described by equation:

$$\text{Hg(II)}_{(\text{solid})} = \text{Hg(II)}_{(\text{liquid})} \times C_{\text{soot}} \times k/r$$

where C<sub>soot</sub> - soot concentration in the liquid phase, g/m<sup>3</sup>; k = 5E-6 m<sup>4</sup>/g; r- soot particle radius, m.

According to data of K.Pleijel and J.Munthe [1995a] soot particles with diameter of order 0.5 μm play a key role in mercury chemistry in the liquid phase. Model calculations showed that at air soot concentration 1 μg/m<sup>3</sup> the relationship of dissolved and absorbed mercury from Hg(II) is 1:1. However, there arises a question - is the amount of soot particles in the atmosphere sufficient to provide the absorption in each drop? If cloud water content is 1 g/m<sup>3</sup>, mean diameter of cloud drops is 10 μg then 1 m<sup>3</sup> contains 2×10<sup>9</sup> drops. If it is assumed that at the regional level soot particle concentration is 1 μg/m<sup>3</sup>, specific density of a soot particles is 1g/cm<sup>3</sup>, mean diameter of soot particle is equal to 0.5 μm, all (!) soot particles within the cloud volume are captured by drops, the soot particle number in droplet phase does not exceed 2×10<sup>7</sup>. Thus only 1% of water drops contains soot particles. The assumed here diameter of soot particles was used in calculations of K.Pleijel and J.Munthe [1995a]. J.Müller [1995] considers that mean mass diameter of soot particles is 0.5-0.8 μm and H.Rodhe [1997] recommends to use values 0.1-0.2 μm. Even in the last case a deficiency of soot particles will occur.



Note that when large rain drops are formed each of them will contain tens - hundreds of soot particles. On the other hand the life-time of rain drops is tent of minutes whereas according to data of K.Pleijel and J.Munthe [1995a] in order to reach the equilibrium the process of mercury accumulation by a drop takes about 2 days. Thus simple estimates show that the role of soot particles in the atmospheric chemistry is not yet completely clear.

In the first evaluations of a generalized rate of mercury oxidation by ozone in the liquid phase A.Iverfeldt and O.Lindqvist [1986] assumed that since ozone relative to mercury is in a considerable excess, the oxidation reaction can be considered as a reaction of the quasi-first order. The obtained values of the generalized rate of oxidation were in the limits of  $0.01 \text{ h}^{-1}$  in the clean atmosphere to  $0.04 \text{ h}^{-1}$  in the atmosphere of industrial regions. Later on the basis of model calculations K.Pleijel and J.Munthe [1995a] showed that the oxidation process is considerably slower and the generalized rate for the conditions of southern Sweden is of an order of  $0.0001 \text{ h}^{-1}$ .

On the whole the scheme mercury chemistry in the liquid phase is complex enough, rate constants of many reactions are determined with insufficient accuracy but general regularities are sufficiently well known. According to J.Munthe and A.Iverfeldt [1995] the increase of air ozone concentration in 2 times (from 20 to 40 ppb) results in the increase of mercury oxidation rate in the liquid phase and is followed removal from the atmosphere by 10%. The same effect should be observed when air soot concentration is doubled (from 1 to  $2 \text{ ng/m}^3$ ) and at the increase of chlorine ion concentration from 70 to  $100 \text{ }\mu\text{g/l}$ . On the contrary doubling of  $\text{SO}_2$  concentration leads to 10% reduction of the oxidation rate.

In the surface waters of rivers and lakes the reduction of oxidized mercury in the liquid phase at the interaction with humic acids [Prokofiev, 1981] is possible. Humic acids being free organic radicals reduce  $\text{Hg(II)}$  to  $\text{Hg}^0$  in water solutions at  $\text{pH} = 6.5 - 8.2$  by the first order reaction ( $K=0.009 \text{ h}^{-1}$ ).

Actually nothing is known about atmospheric reactions of mercury and its compounds in the solid state. Theoretically heterogeneous reactions of mercury oxide and mercury sulphide with  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{NO}$  on aerosol particles can take place but constant rates are unknown [Seigneur et al, 1994]. O.Lindqvist et al. [1991] considered that oxidized mercury in aerosol particle after evaporation of a cloud drop is rapidly reduced to the elemental form by photo-dissociation. At present there are no experimental data to prove this phenomenon.

## 9. Model description

The simulation of mercury atmospheric transport is a comparatively new direction of investigations. The state of the art in the field of modelling the airborne transport of mercury within the scale of Europe, a number of unsolved problems, requirements for the accuracy of model estimates were characterized by G.Petersen [1996] on Moscow workshop on the evaluation of EMEP activity concerned with heavy metals, Moscow 1996. The workshop formulated requirements to models describing atmospheric mercury transport - to obtain realistic values of mean monthly and annual values of concentrations and deposition at the regional level within the accuracy of factor 2. To develop a prototype of an operational model we used approaches to atmospheric mercury modelling elaborated in works [Petersen et al., 1990; Petersen et al., 1995; Pleijel and Munthe, 1995a; Pleijel and Munthe, 1995b; Petersen et al., 1996].

While development of basic principles behind the model we took into consideration two things. First, the model should operate with sufficiently long time intervals (months, seasons,

years). Second, some key-parameters describing mercury behaviour in the atmosphere are known with a low accuracy (up to an order of magnitude). Thus at this stage there is no sense to complicate the model with the consideration of many secondary mechanisms. Operational model should give values of fluxes and concentrations within a factor of 3 at the mean monthly level and within a factor of 2 at the level of a season-year. The model should reflect the presence of gradients of concentration and deposition fields.

Eulerian three-dimensional model ASIMD was used as a basis of a mathematical model for numerical calculations. This model has been developed by M.Pekar [1996] and it was used for modelling of heavy metals (Pb, Cd). The calculated fields are represented by three independent components: elemental gaseous mercury, aerosol mercury and gaseous mercury compounds. All three components participate in transport processes in horizontal and vertical directions with appropriate diffusion parameters. The following two processes are most crucial for the accuracy of model calculations: dry deposition and wash out by precipitation. The parametrization of these processes for various components is described below. For mathematical description of these processes with allowance for sources and sinks the method of operator splitting is applied to diffusion equation. Dry deposition is described by relevant boundary conditions. For the description of elemental gaseous mercury wet removal a scheme of chemical transformation described below is used.

The calculation area covers the EMEP grid with gridsize  $150 \times 150 \text{ km}^2$ . The division along the vertical is unequal and contains 4 layers.: 0-100, 100-400, 400-1100, 1100-2100 m.

Relative contribution of various mercury forms to emission is taken to be constant for all countries of the region.

The integration step of equations was taken to be 1 hour. The calculation period is 1 year. Averaging of deposition, surface concentrations and concentrations in precipitation was made for each calculated month.

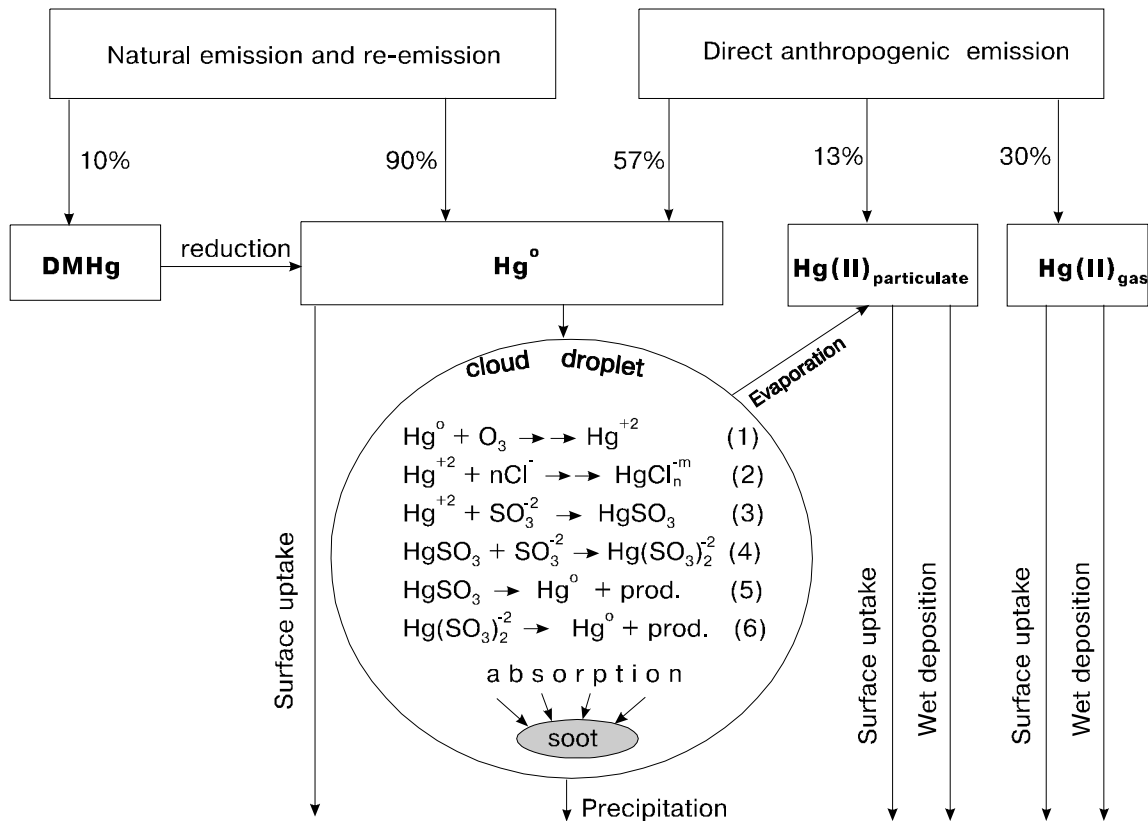
Mercury and its compounds removal from the atmosphere is due to rain-out, "dry" uptake by the underlying surface, and chemical reactions in gaseous and liquid phases. A general scheme of the module of mercury scavenging from the atmosphere is presented in fig. 9.1. Emission is prescribed by two fields:

- (1) total natural emission and re-emission represented by DMHg and  $\text{Hg}^0$ ;
- (2) direct anthropogenic emission represented by  $\text{Hg}^0$ , particulate mercury and oxidized inorganic gaseous compounds.

The oxidation process of gaseous elemental mercury by ozone in gaseous phase is extremely slow therefore it is ignored in model calculations. For DMHg it is considered that the uptake by the underlying surface is absent since its emission is a "net" flux, i.e. the difference between the release and uptake. In view of low DMHg solubility in water wet scavenging of this substance was not considered (washout ratio is about 1). Thus DMHg is scavenged from the atmosphere only due to reaction of chemical redaction to elemental mercury. Particulate mercury and oxidized inorganic gaseous compounds are scavenged from the atmosphere by dry and wet depositions. Possible reactions of the reduction of oxidized inorganic gaseous compounds to elemental mercury were not considered. Processes of the redistribution between gaseous and aerosol fractions according to temperature were is not taken into account at the first stage of the model development.

It is assumed that gaseous elemental mercury is dissolved in water drops according to Henry's law. In the liquid phase elemental mercury is oxidized by ozone with the formation of divalent ion (reaction 1 in fig. 9.1). The most probable irreversible reaction (2) with the

formation of a set of complex compounds with chlorine and apparently with other halogens. Dissolved in water complex compounds are irreversibly absorbed by soot particles inside drops. In the solution a reaction of divalent mercury ion with sulphite ion (reaction 3) is possible with subsequent addition of one more sulphite ion (reaction 4). Both  $\text{HgSO}_3$  and  $\text{Hg}(\text{SO}_3)_2^{2-}$  are decayed with the formation of elemental mercury (reactions 5 and 6). Its formation leads to a decline of the rate of the input of new portions of elemental mercury to a drop from the gaseous phase. The distribution of dissolved oxidized mercury between drop liquid phase and solid phase of a soot particle is described by Langmuir isotherm [Petersen et al., 1995].



**Fig.9.1** Modelling scheme of chemical transformations and removal of mercury from the atmosphere

The process of elemental mercury oxidation in the liquid phase takes place exclusively in clouds which occupy only a part of the atmosphere in the model blocks. It is assumed that clouds are present only in the third and fourth layers (from 400 m and above). The bulk of cloud water does not precipitate but it is evaporated. While cloud drops evaporation, aerosol particles are formed thereby replenishing aerosol reservoir in the atmosphere. It is assumed that the evaporation process takes place only when precipitation is absent. The model does not consider a reverse volatilization of elemental mercury from the liquid phase to the air since at least during two days [Pleijel and Munthe, 1995a] there is a deficiency of mercury in the liquid phase and the life-time of real clouds is as a rule less than 2 days.

## 10. Selection of model parameters and the assessment of their uncertainties

For program debugging and demonstration serviceability of the general scheme of modelling at the first stage approximate values for a number of parameters were chosen. Data on emissions, meteorological parameters and measurement data were taken not for one specific year, but for those years which data seemed to be most reliable. Below numerical values of individual model parameters are presented.

### Ozone concentration

In the first version of the model ozone concentration field was not calculated. It was assumed that ozone concentration spatially is constant (along the vertical and horizontal). Mean monthly concentration is varied with time like elevated sinusoid from 20 ppb in January to 40 ppb in July (at mean annual value 30 ppb).

### Soot particle concentrations

It was assumed that soot particle concentration is proportional to that of sulphur dioxide in the relation of 1 : 10 [Cook and Wilson 1996; Feichter et al., 1996]. The calculated field of mean monthly concentrations of sulphur dioxide with spatial resolution 150×150 km<sup>2</sup> for 1987 [Sofiev et al., 1994] was used. It was accepted that sulphur dioxide concentration and consequently concentration of soot particles is constant along the vertical.

### Dissolubility in the liquid phase of clouds and rain

It was assumed that dissolubility of elemental gaseous mercury and ozone follows Henry's law. The dimensionless Henry's constant (the ratio of concentration in liquid to concentration in gas) for gaseous elemental mercury versus temperature was calculated by the relationship:

$$K_H^{\text{Hg}}(t) = 0.00984 \times T \times \exp[2800 \times (1/T - 1/298)], \text{ where } T - \text{temperature, } ^\circ\text{K.}$$

The temperature dependence was estimated on the basis of data given in table 1.2

Henry's constant for ozone and temperature dependence were taken as a mean value of all figures published by R.Sander [1997]. The constant versus temperature was calculated using relationship:

$$K_H^{\text{O}_3}(t) = 0.000951 \times T \times \exp[2325 \times (1/T - 1/298)]$$

where T - temperature, °K.

For the temperature below 273°K it was assumed that cloud water is in a supercooled liquid state. Corresponding Henry's constants for both mercury and ozone were calculated with the allowance for extrapolation of known temperature dependencies to the range of low temperatures.

### Washout of individual forms of mercury

Washout of inorganic gaseous oxidized mercury in the cloud liquid phase is prescribed by a washout coefficient characteristic of nitric acid:  $1.4 \times 10^6$  [Jonsen and Berge, 1995]. On the other hand, the washout of organic mercury (DMHg) by the liquid phase of clouds does not

take place (washout coefficient is about 1) and this mechanism is not considered in calculations.

It is assumed that particles containing mercury behave like sulphate particles and the washout ratio is taken to be  $7 \times 10^5$  [Iversen et al., 1989].

### **Dry uptake by the underlying surface**

Linear velocity of dry deposition of elemental mercury depends on the type of underlying surface. In its turn the character of the underlying surface is varied from season to season. It is assumed that for land during the period from May to October the value of linear velocity of elemental mercury dry deposition is 0.03 cm/s, during the rest of the year months - 0.01 cm/s in case the surface air temperature is positive otherwise dry deposition does not occur. For the marine surface this rate is always zero.

For oxidized gaseous inorganic mercury it was considered that dry deposition velocity is 0.5 cm/s independently of a season and a type of underlying surface.

Dry deposition velocity of aerosol particles containing mercury was calculated using the approach suggested by M.Pekar [1996] depending on wind speed, underlying surface roughness, solar radiation intensity. The velocity values are varied within the range from 0.02 to 0.2 cm/s.

### **Elemental mercury oxidation in the liquid phase**

Dissolved elemental mercury is oxidized by ozone with the rate  $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [Munthe, 1992]. The constant of chemical equilibrium for reaction (2) is taken to be  $2.5 \text{ E}^{-7} \text{ M}$ . It is assumed that in the liquid phase sulphite ion quantity is abundant compared with mercury ions. Consequently rapid formation of mercury sulphite ( $\text{HgSO}_3$ ) and sulphite complex [ $\text{Hg}(\text{SO}_3)_2^{2-}$ ] of mercury takes place (reactions 3 and 4). Mercury sulphite and sulphite complex are destroyed with rates 0.6 and  $0.0004 \text{ s}^{-1}$  with the reduction to elemental mercury (reactions 5 and 6). Process of absorption by soot particles is considered using the scheme suggested by Petersen et al. [1995] with the assumption that mean radius of soot particles is  $0.5 \text{ }\mu\text{m}$ .

### **Evaporation process of cloud drops**

It was assumed that the life-time of clouds relative to the evaporation process in summer is 5 hours, in the autumn-spring period - 10 hours and in winter - 20 hours. Corresponding rate constants of mercury transfer from the liquid reservoir to aerosol one is 0.2, 0.1 and  $0.05 \text{ h}^{-1}$ .

### **Reduction of gaseous organic mercury to elemental one**

The life-time of organic mercury compounds in the atmosphere is relatively short due to destruction reactions of organic molecules followed by the reduction of mercury to elemental form. It is assumed that these are reactions of the first order and a generalized rate constant of elemental mercury reduction is  $2.3 \times 10^{-5} \text{ s}^{-1}$ .

## 11. Emission

Total anthropogenic emission of all mercury forms for the EMEP region with spatial resolution  $150 \times 150 \text{ km}^2$  for 1987 was taken from the work by G.Petersen et al. [1995], and for 1990 - from the work by J.Berdovsky et al. [1997]. In the first case the total emission for 1987 was 726 tonnes, and in the second one - 440 tonnes. The basic difference of the two emission fields lies in the fact that in 1987 there are powerful sources in GDR which in the EMEP square ( $x=22$ ;  $y=17$ ) emitted 215 tonnes of mercury making up 30% of the total emission in Europe. After the unification of Germany the emission in this region was reduced practically by an order of magnitude. Total national emissions of countries are given in table 11.1. The emission field for 1987 is shown in fig. 11.1 with spatial resolution  $150 \times 150 \text{ km}^2$  and for 1990 - in fig 11.2 with spatial resolution  $50 \times 50 \text{ km}^2$ .

For the evaluation of the emission of individual forms of mercury (elemental gaseous, oxidized gaseous inorganic, aerosol) mean relationship of mercury forms for European emissions 57:30:13 [Axenfeld et al., 1991; Pacyna and Munch, 1991) was used in each EMEP grid cell. In calculations it was assumed that 65% of anthropogenic mercury is emitted in the surface layer below 100 m, and the rest - in layer 100-400 m. Individual point sources were not considered.

The total field of natural emission and re-emission with spatial resolution  $150 \times 150 \text{ km}^2$  was taken from the paper by B.Moisseev [1997]. It is accepted that that the relationship of elemental gaseous and oxidized gaseous organic (methylated) mercury in natural emission and re-emission is 90 : 10 [Axenfeld et al., 1991]. Total natural emission and re-emission in individual countries are presented in table 11.1. The natural emission and re-emission with spatial resolution  $150 \times 150 \text{ km}^2$  is shown in fig. 11.3.

In calculations it was assumed that both anthropogenic and natural sources operate uniformly during the year.

The uncertainty of estimates of direct anthropogenic emission for individual countries is at least within a factor of 2. The uncertainty of natural emission and re-emission without accounting seasonal variation is higher and it is in the range of factor 5. The relationship of mercury forms in emissions is known within the accuracy up to factor 3.

**Fig.11.1** Total anthropogenic emission of mercury for 1987/88 in EMEP grid cells  
(150×150 km<sup>2</sup>), 10 kg Hg/yr

**Fig.11.2** Total anthropogenic emission of mercury for 1990 in EMEP grid cells (50×50 km<sup>2</sup>), kg Hg/yr



**Fig.11.3** Natural emission and re-emission of mercury in EMEP grid cells (150×150 km<sup>2</sup>), kg Hg/yr

**Table 11.1** Mercury emission by individual European countries, t/yr [Petersen et al., 1995; Berdovski et al., 1997; Moisseev, 1997]

Country	Anthropogenic emission		Natural emission and re-emission
	1987	1990	
Albania	0.834	0.51	1.3
Austria	1.083	4.27	1.9
Belgium	8.895	8.86	2.0
Bulgaria	8.665	6.90	7.1
Czechoslovakia	14.977	-	-
Czech Republic	-	9.31	3.9
Slovakia	-	12.40	1.7
Denmark	4.780	6.92	1.0
Finland	4.142	3.04	2.1
France	29.876	32.50	24.1
Germany		113.00	28.9
former Eastern	330.506	-	-
former Western	64.977	-	-
Great Britain	40.568	25.6	10.5
Greece	2.106	7.12	7.6
Hungary	2.749	4.20	3.3
Iceland	0.001	0.05	0.4
Ireland	8.789	1.62	3.4
Italy	13.113	11.8	14.2
Yugoslavia	7.180	-	-
Bosnia & Herzegovina	-	0.22	1.8
Croatia	-	1.8	2.4
The FYR Macedonia	-	1.49	1.3
Slovenia	-	0.87	0.7
Yugoslavia	-	3.86	5.2
Luxembourg	0.066	0.77	0.1
Netherlands	8.265	2.64	2.5
Norway	2.060	2.34	1.9
Poland	44.746	33.30	15.1
Portugal	5.494	5.48	6.6
Romania	15.986	7.50	10.7
Spain	10.755	20.20	28.1
Sweden	7.501	1.45	3.9
Switzerland	0.228	6.82	0.8
USSR *	87.675	-	-
Belarus	-	0.09	4.1
Estonia	-	2.2	0.4
Latvia	-	0.34	0.6
Lithuania	-	0.003	0.8
Republic of Moldova	-	1.52	1.0
Russian Federation*	-	64	58.0
Ukraine	-	36	19.2
Kazakhstan*	-	-	6.6
Transcaucasian Republics	-	-	8.8
<b>Total in Europe</b>	<b>726</b>	<b>440</b>	<b>294</b>

\*) - within the EMEP grid

## 12. Model validation base

As it was demonstrated in chapter 4 measurement data on concentrations and deposition in Europe are rather contradictory. The most reliable data seem to be obtained in Germany and

Sweden. Such values for 1988 were used by G.Petersen et al. [1995] and M.Galperin et al., [1996] in testing the operation of their mercury transport models. According to measurements atmospheric elemental mercury concentrations over central Europe are within 3-5 ng/m<sup>3</sup> and mercury in aerosol form - from 0.05 to 0.1 ng/m<sup>3</sup>. Over the periphery regions of the EMEP grid the concentration field of elemental mercury is rather uniform and values are varied within the limits of 1.5 to 3.0 ng/m<sup>3</sup>. Aerosol concentrations are less than 1% of total gaseous mercury concentration.

Mercury concentrations in precipitation and deposition are characterized by higher gradients from the center of the region to its periphery. In the northern part of Germany in 1988 monitored concentrations were at the level of 50 ng/l. Further to the north concentrations decreased to 10 ng/l (northern Sweden). Total (dry and wet) deposition in southern Sweden were 30 g/km<sup>2</sup>/yr and in the southern part - 5 g/km<sup>2</sup>/yr.

### **13. Meteorological parameters**

Meteorological information for 1994 was used for assessment calculations. The information with spatial resolution 6 hours was provided by Hydrometeorological Centre of Russia. Temperature variations with height was prescribed with a factor of 6 degree °C/km. It was assumed that on the average in Europe clouds in the modelling layer occupy 35% of the atmosphere volume in winter (December-February), 13% - in spring and autumn and 8% - in summer (June-August) [Rodhe and Forsstrom, 1989]. Mean water content in a cloud was assumed to be 0.5 g/m<sup>3</sup>.

Meteorological parameters averaged over time can vary from year to year within about 30%. It implies that the selection of meteorological parameters for 1994 instead of any other can lead to errors in concentrations and deposition at the level of 30%.

### **14. Preliminary Model Estimates of Mercury Deposition in the EMEP Region**

The operational model prototype developed was used to calculate mean annual mercury concentration and deposition for two full years: 1987 and 1990. The objective was to obtain a likely pattern of mercury concentration and deposition in the EMEP region and compare the estimates with observations. The years 1987 and 1990 were selected because the anthropogenic emission field had changed significantly over the time interval that separates them, primarily due to the closure of intensive mercury emission sources in East Germany after the unification of the country. Besides, the selection of 1987 allows to compare our estimated data with those estimated by G. Petersen et al. [1995].

Figs 14.1 and 14.2 show the total concentration distribution of all mercury species in the surface atmosphere in 1987 and 1990. Mercury concentration outside industrial regions is determined by mean hemispheric concentrations of the elemental form (of course, European sources make their own contribution to the formation of background hemispheric levels, however, the model does not take it into account). In general, mercury concentrations typical of Europe range from 2 to 5 ng/m<sup>3</sup>. The highest concentrations are characteristic of industrial

**Fig.14.1**      Calculated total mercury concentrations in air for 1987, ng/m<sup>3</sup>

**Fig.14.2**      Calculated total mercury concentrations in air for 1990, ng/m<sup>3</sup>

regions in Central Europe where they reach a few dozen  $\text{ng}/\text{m}^3$ . Emission reduction in Germany between 1987 and 1990 resulted in a significant concentration reduction over Central Europe, but it did not cause a noticeable change in the general pattern of mercury concentration distribution over the EMEP region as a whole. Elemental form make a major contribution to the total mercury concentrations in the atmosphere. Near emission sources, their share is 60-80%, but with distance this form becomes dominant.

Table 14.1 compares observed and estimated atmospheric concentrations of various mercury species. The comparison shows that the model presented provides a good correlation with the observed concentrations of elemental mercury far from major European sources (over Scandinavia). The difference between the observed and estimated concentrations over Germany reaches the factor of 2 which can be considered a rather good result. As to comparisons with the estimated data obtained by G. Petersen et al. [1995] the correlation is good for elemental mercury in the periphery of the region, but near major emission sources there is a significant difference (up to 4 times). However, it should be noted that G. Petersen et al. give figures for a specific point in space while this work calculates a concentration averaged over the entire EMEP cell. Under conditions of extremely high concentration gradients near an intensive source, such appears to be not quite correct.

**Table 14.1** Comparison of modelled (Petersen et al. [1995] and this work) and measured concentrations of mercury in air,  $\text{ng}/\text{m}^3$ .

EMEP cell (X-Y)	Monitoring stations	Observed in 1987 -1988		Modelled by Petersen et al. [1995]		Modelled in this work		
		Hg <sup>0</sup>	Particulate	Hg <sup>0</sup>	Particulate	Hg <sup>0</sup>	Particulate	Oxidized gaseous
22-17	-	-	-	10.1	0.28	40	4.4	2.6
22-18	-	-	-	4.9	0.21	16	0.5	0.4
21-17	Landenbrügge*	4.2	-	4.1	0.11	8	0.5	0.2
21-19	-	-	-	3.6	0.11	6	0.1	0.05
19-20	Rurvik	2.8	0.06	2.5	0.025	3.8	0.1	0.05
20-22	-	-	-	2.5	0.019	2.6	0.01	0.05
17-26	Vindeln	2.5	0.05	2.1	0.005	2.4	<0.01	<0.01
14-28	Overbygd	2.6	-	2.1	0.002	2.6	<0.01	<0.01

\* observations of 1992

For particulate mercury, the difference between estimated and measured concentrations is within an order of magnitude which can be considered an acceptable result, taking into account significant measurement errors and our limited knowledge of particulate mercury removal factors. Comparison of data obtained by G. Petersen et al. with measurements also shows a difference within an order of magnitude.

Model calculations of the concentrations of gaseous oxidized mercury (such as  $\text{HgCl}_2$ ) indicate that its contribution to the total concentration near major emission sources in Central Europe can be quite noticeable (about 5%). With distance from sources, the concentration of these mercury species decreases rapidly, primarily due to efficient precipitation washout. In southern Sweden, its contribution most probably does not exceed 2%.

It is natural that the pattern of atmospheric mercury deposition to the underlying surface is similar to the pattern of total mercury concentrations in air: areas with high concentrations are characterised by intensive deposition. Fig. 14.3 and 14.4 show estimated total deposition fields for 1987 and 1990, respectively. In both cases, the highest deposition is typical of

industrial regions in Central Europe where the deposition level exceeds  $100 \text{ g/km}^2/\text{yr}$ . Let us note that the deposition intensity in the most polluted part of Germany (EMEP cell 22-17) has reduced 15 times after the closure of the most intensive industrial sources of mercury emissions. The closure of these sources had a less pronounced effect on deposition in remote regions: deposition level in south-west Sweden reduced 3 times while there was practically no reduction in the eastern periphery of the EMEP region. On the whole, the deposition field had the same configuration in 1990.

Relatively low total deposition over seas is engaged the attention. It is explained by the fact that far from sources elemental mercury is a dominant form and its velocity of dry deposition on the marine surface is assumed to be zero. On the other hand, wet removal takes place independent of the underlying surface. Thus total deposition over the sea surface is estimated to be somewhat lower than over land.

Increased mercury concentration in precipitation is related to the washout of all three forms of mercury considered. Fig. 14.5 and 14.6 show mean annual mercury concentrations in precipitation for 1987 and 1990, respectively. It follows from the Figures that mercury concentrations in precipitation decrease rapidly with distance from Central Europe. Comparison of mercury deposition with precipitation observed in Germany and Sweden and estimated data obtained by G. Petersen et al. (1995) with our model calculations (Table 14.2) indicates that the data generally correlate within the factor of 3. Near powerful sources the discrepancies between model results are most significant. For Scandinavia the correlation can be considered quite satisfactory.

**Table 14.2** Comparison of measured and modelled (Petersen et al. [1995] and this work) total concentrations in precipitation (ng/l) and wet deposition ( $\text{g/km}^2/\text{yr}$ ) of mercury

EMEP cell (X-Y)	Monitoring stations	Observed in 1987 -1988		Modelled by Petersen et al. [1995] for 1988		Modelled in this work	
		Concentration	Deposition	Concentration	Deposition	Concentration	Deposition
22-17	-	-	-	331	114	1380	772
22-18	-	-	-	234	95	409	255
21-17	Landenbrügge*	52	-	66	39	93	117
21-19	-	-	-	62	46	47	60
19-20	Rurvik	35	27	17	15	16	18
20-22	-	18	10	17	10	18	11
17-26	Vindeln	11	7.3	7.0	4.9	7	4
14-28	Overbygd	9	5.0	3.9	2.1	2	3

\* observations of 1992

The mercury deposition field is formed by wet and dry removal of three different forms of mercury whose atmospheric emissions is taken into account in our model. Table 14.3 shows the contribution (percent) of individual forms to wet and dry deposition. Near emission sources, both wet and dry deposition is dominated by relatively short-lived “regional” forms:

**Fig.14.3**      Calculated total deposition of mercury for 1987, g/km<sup>2</sup>/yr



**Fig.14.4**      Calculated total deposition of mercury for 1990, g/km<sup>2</sup>/yr

**Fig.14.5** Calculated annual average concentrations of mercury  
in precipitation for 1987, ng/l

**Fig.14.6** Calculated annual average concentrations of mercury  
in precipitation for 1990, ng/l

particulate mercury and oxidized gaseous species. There is an increase in the share of elemental mercury with distance from major sources; this species can be considered a “global” pollutant. Model calculations indicated that dry deposition made a major contribution to mercury removal from the atmosphere to land both at small and large distances from sources. That fact contradicts to the majority of experimental data and can be indicative of a possible overestimation of dry deposition velocities.

**Table 14.3** Relative contributions of different forms of mercury into wet and dry deposition, %.

EMEP cell (X-Y)	Wet deposition			Dry deposition			Ratio "wet to dry"
	Hg <sup>0</sup>	Aerosol	Oxidized gaseous compounds	Hg <sup>0</sup>	Aerosol	Oxidized gaseous compounds	
22-17	8	32	60	15	13	72	0.4
22-18	7	37	56	31	12	57	0.7
21-17	9	38	53	29	15	56	0.6
21-19	10	40	50	29	12	59	0.8
19-20	22	39	39	57	10	33	0.9
20-22	28	36	36	63	11	26	0.6
17-26	50	25	25	86	7	7	0.3
14-28	≈100	≈0	≈0	≈100	≈0	≈0	0.5

The regional nature of oxidized mercury deposition was confirmed earlier by model calculations performed by O.R. Bullock Jr. [1996] and R. Bloxam et al. [1996]. Data for 48 states obtained by O.R. Bullock Jr. using the Lagrangian model indicate that the bulk of oxidized mercury settles down within 500 km from major anthropogenic sources while deposition of elemental mercury is only 3% of the initial emission. Calculations made by R. Bloxam et al. show that the pattern of wet deposition in Europe is largely dependent on the removal of easily soluble Hg<sup>2+</sup>. The bulk of this species is removed from the atmosphere with wet and dry deposition within a few hundred kilometres from its sources.

The investigations made demonstrated that the developed prototype of the operational model adequately described the pattern of mercury concentration and deposition fields within European scale. The calculated values correlate with observational results within the factor of 3. Provisional calculation results showed that the major part (about 60%) of anthropogenic mercury emitted by European sources is removed from the atmosphere within the scope of the EMEP grid. This part is represented mainly by oxidized mercury species and makes a regional mercury problem in Europe. The remained part (40%) contributes to the global atmospheric pollution.

## 15. Approaches to Further Model Improvement

This work formulates basic principles of the operational model construction and gives the first rough estimates. Some model parameters were evaluated in the first approximation. Further model improvement would require specifying both input parameters and model constants adopted. Some of these changes seem self-evident and they have not been taken into account only due to the lack of time. Others need to be seriously thought over. Provisions to be specified in the near future are listed below:

### Input data

- Input of individual mercury forms to the total anthropogenic emission to each EMEP grid cell.
- Consideration of individual powerful point sources of anthropogenic emission.
- Contribution of various mercury species to natural emission.
- Refinement of re-emission fields.
- Input of high (>100 m) and low sources.
- Seasonal variations of anthropogenic and natural emissions.
- Mercury emission from the sea surface.
- Application of mean-monthly concentrations of ozone and sulphur dioxide to each EMEP grid cell obtained in operational calculation in MSC-W.

#### Model parameters

- Refinement of the constant rate of elemental mercury oxidation by ozone in the liquid phase and consideration of this process in the model.
- Refinement of the role of soot particles in the liquid phase chemistry of mercury and model sensitivity to soot particle sizes in the liquid phase.
- Possibility of desorption of mercury compounds to the liquid phase.
- Refinement of the relationship between soot particle concentrations and sulphur dioxide and the assessment of these values for each country.
- The role of reduction reaction in the atmosphere.
- Seasonal variations of dry deposition velocities of all forms of mercury on various types of the underlying surface.
- Redistribution of mercury between gaseous and aerosol phases in accordance with meteorological parameters.
- Mechanisms of the input to the liquid phase from the gaseous one or mechanisms of dimethyl mercury formation directly in the liquid phase.

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