

**MERCURY IN THE ATMOSPHERE OF EUROPE:
CONCENTRATIONS, DEPOSITION PATTERNS,
TRANSBOUNDARY FLUXES**

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EMEP/MSC-E Report 7/98

June 1998

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Glossary

Advective transport - species transport in the atmosphere with horizontal wind air mass transfer.

Atmospheric boundary layer - lower layer of the troposphere, where turbulent friction forces can play a significant role comparable with Coriolis and pressure gradient forces; usually its height ranges within 1-2 km.

Atmospheric surface layer - atmospheric layer nearest to the ground which physical-chemical properties to a considerable extent are determined by the interaction of air with elements of the underlying surface; the atmospheric surface layer is characterized by sharp vertical gradients of meteorological parameters; the height of 100 m very conventionally can be accepted as the upper boundary of the surface layer.

Balance (=budget) - totality of quantitative estimates of input and output substance fluxes for a given geophysical reservoir (as a rule being in dynamic equilibrium).

Direct anthropogenic emission - mercury input to the atmosphere as a result of current human activity.

DMM - dimethyl mercury ($\text{CH}_3\text{-Hg-CH}_3$)

Dry deposition - process of species transport from the atmosphere to the underlying surface at their direct (without precipitation) physical-chemical interaction with elements of the underlying surface; dry deposition is of a continuous character independent of the occurrence or absence of atmospheric precipitation.

Dry uptake velocity - a characteristic of species uptake intensity from the atmosphere by the underlying surface at dry deposition which formally has the dimension of linear velocity.

EMEP reservoir - atmospheric volume over the EMEP region bounded along the height by the layer for which model calculations are carried out; in this work the calculation region height is 2100 m.

Eulerian type model - a model which uses a fixed co-ordinate system; calculations of all mechanisms are carried out in each grid cell.

Free troposphere - the atmospheric layer from the boundary atmospheric layer to the tropopause; it is assumed that the troposphere composition is practically homogenous and the influence of the underlying surface is negligible.

Irreversible washout - the process of species transfer from air to liquid (solid) phase of cloud or rain drops (ice crystals) with subsequent deposition from the atmosphere to the underlying surface.

Lagrangian type model - a model which operates with moving co-ordinate system; calculations of all mechanisms are carried out along an air parcel trajectory.

Life-time - time during which the first order processes (or totality of the first order processes) of scavenging results in species mass reduction in e times in a geophysical reservoir; for a reservoir with homogeneous species distribution the life-time is equal to the ratio of the mass contained in the reservoir to scavenging rate.

Load - the intensity of input of (polluting) species to a given ecosystem from the environment; atmospheric load - the intensity of input from the atmosphere.

Model validation - confirmation the model efficiency based on an independent experimental data.

Model verification - selection of model parameter values in order to obtain model results as close as possible to available experimental data.

Natural emission - mercury input to the atmosphere which is not connected with current or previous human activity.

Natural globally averaged concentration - average species concentration in the Earth atmosphere as whole caused by natural sources only; the term can be applied to a period preceding the beginning of human activity.

Pre-industrial state - a conventional term implying the state of mercury natural cycle before the beginning of human industrial activity; in Europe the beginning of a noticeable production and consumption of mercury is related to medieval centuries.

Re-emission - secondary input of mercury to the atmosphere from geochemical reservoirs (soil, sea water, fresh water bodies) where mercury has been accumulating as a result of previous and current human activity.

Reversible washout - the process of species transfer from air to liquid (solid) cloud phase not leading to the removal of the species from the atmosphere.

Underlying surface - the surface of contact between gas phase of the atmosphere and solid/liquid phase of the Earth.

Wet deposition - flux of substance from the atmosphere on the underlying surface with atmospheric precipitation.

Introduction

One of the responsibilities of Meteorological Synthesizing Centre-East (MSC-E) is to provide operational model calculations of heavy metals airborne transport and deposition. Among other toxic heavy metals mercury takes a special place. Mercury has a number of distinguishing peculiarities. First of all it is one of most toxic elements. Some of its chemical compounds can be even more toxic than metallic mercury itself. The life-time of mercury and its compounds is long enough to provide their long (many thousands km) atmospheric transport. Mercury is emitted by anthropogenic and natural sources in various chemical forms with peculiar features and different efficiencies as to removal from the atmosphere. Finally, mercury is the only metal which undergoes substantial physical-chemical transformations in the atmosphere drastically changing its basic properties relative to processes of scavenging from the atmosphere.

During a historical period the natural geochemical cycle of mercury in the atmosphere underwent essential alterations. According to modern ideas anthropogenic emission of mercury to the atmosphere is several times higher than natural one. On the global level elemental mercury content in the atmosphere increases probably by 1.5-3 times. On the regional level mercury concentrations in pit bogs and bottom sediments raised in 3-5 times (Rodhe, 1996). These facts condition an enhanced interest of scientists and public to the mercury problem. In June 1998 within the framework of Convention on Long-Range Transboundary Air Pollution, UN ECE, countries signed the protocol on restrictions of heavy metal (mercury in particular) emissions into the atmosphere.

It is possible to distinguish several key-processes determining regional environmental pollution by mercury: (1) mercury emission to the atmosphere; (2) physical-chemical transformation of mercury and mercury-containing compounds in the atmosphere; (3) dispersion in the atmosphere and airborne transport to long distances; (4) mercury scavenging from the atmosphere; (5) physical-chemical cycle of mercury in soils/waters and re-emission to the atmosphere. This very complicated combination of processes occurring within the continental scale can be studied only with the help of mathematical modeling. Model calculations of airborne transport and deposition of mercury in Europe should provide Parties signed the Convention with information on the transboundary mercury transport including "country-by-country" matrices and to identify trends of pollution levels in Europe.

MSC-E began to develop the operational model of mercury transboundary transport in 1997. The model prototype was based on a simplified scheme of mercury physical-chemical transformations in the atmosphere. The objectives of the further work discussed here are as follows:

- to improve the available prototype of the operational mercury model of the atmospheric transport and deposition;
- to evaluate natural (pre-industrial) levels of the concentration and deposition of various mercury forms in Europe;
- to estimate tentatively mercury transport and deposition within the EMEP region following the "country-by-country" scheme.

1. Mercury behavior in the atmosphere

Basic properties of mercury and its compounds determining the intensity of processes of its transformation in the atmosphere were considered earlier (Ryaboshapko and Korolev, 1997) when the model prototype was under development. One should bear in mind, however, that current scientific publications improve model parameters. In this section the attention will be focused on those mercury properties which were not either considered by A.Ryaboshapko and V.Korolev (1997) or were refined during last year.

As before in this report mercury is considered in two chemical forms: elemental mercury (Hg^0) and oxidized divalent mercury (Hg^{+2}). Elemental mercury can occur in the gas-phase as vapors and in the liquid phase of cloud and rain drops as a solution of metallic mercury in water. Potentially elemental mercury can take place in the atmosphere in particulate form being absorbed by aerosol particles. The spectrum of divalent mercury compounds occurring in the atmosphere is very wide. Within the normal temperature range part of these compounds, for example, dimethylated mercury (DMM) is in the gaseous state. Other compounds can be very volatile and occur in the atmosphere both as gases and as particles. The notion "total gaseous mercury - TGM" which is often used implies metallic mercury vapors, gaseous organic and inorganic compounds. Finally mercury compounds can be incorporated to a drop composition in the liquid phase. In this case they are represented either by a solution or by the solid phase of insoluble particles.

Physical-chemical properties of individual forms differ drastically from each other. As a result they differently behave in the atmosphere and have different mechanisms of the exchange between environmental compartments. Therefore it is necessary to model different forms separately with allowance for possible redistribution between forms in the course of the atmospheric transport. Below four different physical-chemical forms of mercury will be considered separately: elemental gaseous mercury (Hg^0), oxidized inorganic gaseous mercury ($\text{Hg}^{+2}_{\text{gas}}$) and organic gaseous mercury (DMM) and aerosol mercury ($\text{Hg}^{+2}_{\text{particle}}$).

It is assumed that in the atmosphere mercury and its compounds can be firmly absorbed by aerosol particles especially by soot particles. It is conceivable that absorption-desorption processes should be of a dynamic character, the ratio of gas- and solid phases must depend on the temperature (as temperature decreases absorption should increase and the bulk of the matter is transferred to the solid state). However, simultaneous measurements of gaseous and aerosol mercury at different temperatures are rather few and experimental data available are very contradictory.

W.Schroeder et al. (1995) described an inverse dependence of vaporous mercury concentration (TGM) on temperature (T):

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

$$\text{TGM (ng/m}^3\text{)} = - 1.59 * 1000/T + 7.21 \text{ (expedition of scientific research vessel "Polarstern")}$$

The authors suggested several explanations for this connection including interphase redistribution. Unfortunately the authors have not measured the aerosol component. While investigations in the Arctic G.Lu et al. (1997) found in a sample a pronounced redistribution of mercury between phases, but no information about ambient temperature during sampling was reported.

On the other hand, prolonged observations in the Arctic showed that within a wide temperature range (from 0⁰ to -40⁰C) TGM concentration remains almost unchangeable (Schroeder et al., 1998). W.Schroeder believes (1998) that most probably a noticeable redistribution of elemental mercury between phases is absent. There is no theoretical explanation for this phenomenon as yet. In the Arctic atmosphere TGM is actually represented mainly by elemental mercury. It is difficult to say to what extent this phenomenon is characteristic of other gaseous (DMM) and volatile (HgCl₂) mercury compounds. Nevertheless at this stage of the model development we neglect temperature dependence of "gas-aerosol" ratio in our computational scheme.

The question about the phase in which mercury compounds are present in the atmosphere is important while interpretation of gas-phase oxidation of metallic mercury. On the one hand, the reaction products can be in the gaseous phase, on the other - they can be readily absorbed by atmospheric aerosol. The phase state of reaction products determines their removal rate from the atmosphere.

G.Petersen et al. (1995; 1998) believes that products of mercury gas-phase oxidation are gaseous. Most probably mercury oxide (HgO) and mercury chloride (HgCl₂) can be such products. The most volatile inorganic mercury compounds (HgCl₂) are tens-hundreds times less volatile than elemental mercury (Lindqvist et al., 1991; Schroeder et al., 1991). Besides HgCl₂ is easily dissolved in water and at high relative humidity it should be intensively removed from the gas-phase by aerosol particles. Mercury oxide (HgO) is much less volatile than HgCl₂ and most likely it should occur in aerosol form. On the basis of these assumptions in our scheme we suppose that products of gas-phase oxidation of elemental mercury occur in the atmosphere in aerosol phase and they are removed from the atmosphere with rates typical of submicron aerosol particles. The same interpretation of the physical-chemical form of products of gas-phase oxidation of elemental mercury is suggested in the report of the US Environmental Protection Agency (EPA, 1997) to the USA Congress.

It is known that metallic mercury is slightly soluble in water. The solution process from gas-phase follows Henry law. On the basis of literature data on Henry constant value (K_H^{Hg}) at different temperatures (Lindqvist et al., 1984; Clever et al., 1985; Schroeder et al, 1991; Petersen, 1992; Seigneur et al., 1994; Schroeder, 1996) A.Ryaboshapko and V.Korolev derived the following temperature dependence:

$$K_H^{Hg}(t) = 0.00984 * T * \exp[2800 * (1/T-1/298)] \quad \text{where } T - \text{temperature, } ^0K.$$

Here Henry constant is interpreted as an equilibrium ratio of mercury mass in a unit volume of water to mercury mass in the same volume of air.

Under the conditions of the real atmosphere the question on a possibility of extrapolation of this dependence to the region of negative temperature becomes important. It is known that cloud drop water can remain in the liquid state up to very low temperatures. At temperature -15°C about half of cloud water is in the liquid state (Matveev, 1984). There is no ground to suppose that supercooled liquid water will change its properties relative to the process of gaseous mercury dissolution. However, the question about a possibility of mercury dissolution in ice crystals remains open.

2. Estimation of background (pre-industrial) levels of individual forms of mercury in the atmosphere

In order to evaluate effects in the biosphere caused by elevated concentrations and deposition of an anthropogenic pollutant first of all one should have an idea on the atmospheric content of this pollutant before the beginning of human activity. If anthropogenic pollution became of a global character (as in case of mercury) direct measurements of background levels are impossible. Under these circumstances only indirect assessments can be made which are based as a rule on ideas on pollutant life-time in this or that geochemical reservoir.

Literature data on atmospheric TGM concentrations were summarized by A.Ryaboshapko and V.Korolev (1997). Reasoning from available data (Fursov, 1983, 1988; Leermakers et al., 1996; Slemr, 1996; Fitzgerald et al., 1991, Ebinhaus et al., 1996; Slemr and Scheel, 1998; Lee et al., 1998) it is possible to accept that at present mean global TGM concentration is within the range of 1.5-2 ng/m³. With allowance for that fact that a part of TGM is represented by not elemental mercury form, the value of 1.5 ng/m³ can be accepted as mean global concentration of elemental mercury at the end of XX century.

An attempt to consider the evolution of atmospheric mercury cycle for recent 100 years was made by W.Fitzgerald and R. Mason (1996). On the basis of this work one can estimate the value of global mean natural concentration of elemental mercury before the beginning of human activity. At the same time one should take into account that in the scheme of W.Fitzgerald and R Mason (1996) the input of juvenile mercury from the mantle was not considered and it is most likely that they underestimated natural emission.

In this report we discuss three possible approaches for the assessment of the global mean natural concentration.

First, according to data of W.Fitzgerald and R.Mason (1996) specific mean natural mercury emissions on land (without the Antarctic) is 10 g/km²/yr and total natural emission on land is 1500 t/yr. Global natural emission of the World ocean is accepted to be 600 t/yr. Estimates of the life-time of elemental mercury vary from 0.5 to 2 years (Lindqvist and Rodhe, 1985; Pacyna et al., 1996; Rodhe, 1996; Slemr, 1996). A substantial value of the life time suggests a relatively uniform distribution of mercury concentrations over the whole atmosphere. Taking into account all said above natural mean global concentration should be assessed within the range from 0.25 to 1 ng/m³. However, it is well to bear in mind that due to only gas-phase oxidation of mercury by ozone and other oxidants (Hall, 1995; Petersen et al.,

1998) mercury life-time should be about a year long. Hence, for further considerations it is reasonable to take the maximum value of the estimate range.

Second, W.Fitzgerald and R. Mason (1996) estimated that at present the atmosphere contains 3400 tons of anthropogenic mercury in all its forms. Hence the anthropogenic component of the modern mean global concentration of mercury is 0.8 ng/m^3 . As mentioned above modern mean global concentration was estimated in the range of $1.5\text{-}2.0 \text{ ng/m}^3$. Thus mean global natural concentration should be in the range of $0.7\text{-}1.2 \text{ ng/m}^3$.

Third, W.Fitzgerald and R.Mason (1996) suggested that during recent 100 years atmospheric mercury concentration was growing linearly with rate $0.01 \text{ ng/m}^3/\text{yr}$. Therefore if we ignore the anthropogenic factor which took place 100 years ago then it is possible to accept that mean global natural concentration should be in the range of $0.5\text{-}1.0 \text{ ng/m}^3$.

On the basis of these estimates we assume that before human activity mean natural concentration of elemental mercury in the Earth atmosphere was 1 ng/m^3 . It implies that due to human activity mercury concentration in the Earth atmosphere increased in 1.5 times. It is self-evident that the accuracy of such estimates is very arbitrary. Our estimate complies with data of the report of the US Environmental Protection Agency (EPA, 1997) to the USA Congress according to which from 40% to 75% of mercury total content in the atmosphere is conditioned by the anthropogenic activity.

Some mechanisms of elemental mercury removal from the atmosphere lead to the formation of its aerosol form. Consequently on the global scale a certain quantity of elemental mercury concentration is bound to correspond to some equilibrium concentration of aerosol mercury. The latter can be assessed on the basis of relationships of the rates of known mechanisms of mercury removal from the atmosphere.

According to the scheme taken in this work the gas-phase reaction of oxidation by ozone produces mercury aerosol form. At mean global ozone concentration of 30 ppb the rate constant of the quasi-first order process is $2.22\text{E-}8 \text{ s}^{-1}$ (Petersen et al., 1998). Using the approach of G.Petersen et al. (1995) the washout ratio for elemental mercury can be estimated in average as 1800. Hence at mean precipitation intensity 660 mm/yr in the EMEP region the washout rate constant is $1.8\text{E-}8 \text{ s}^{-1}$. A.Ryaboshapko and V.Korolev (1997) assumed that 80% of cloud drops are evaporated with the formation of aerosol particles. Therefore the rate constant of aerosol formation in the process of incloud washout is $1.8\text{E-}8 * 0.8 = 1.44\text{E-}8 \text{ s}^{-1}$. The resulted constant of both processes of aerosol formation is equal to $3.66\text{E-}8 \text{ s}^{-1}$. The life-time of submicron aerosol particles in the atmospheric planetary boundary layer can be within the range from 3 days to a week and corresponding scavenging rate constant - within $1.6\text{E-}6 - 3.8\text{E-}6 \text{ s}^{-1}$. Reasoning from the ideas of dynamic equilibrium between both mercury forms the accepted elemental mercury concentration should correspond to the mean global concentration of aerosol mercury being in the range from 0.004 to 0.009 ng/m^3 . For further calculation we take the mean value 0.007 ng/m^3 .

3. Sources of mercury input to the atmosphere of the EMEP region

Sources of mercury input to the atmosphere can be divided into three categories: natural emission, direct anthropogenic emission and re-emission of anthropogenic mercury. Natural emission implies mercury input to the atmosphere from soils, mountain rocks, water bodies which has no connection with human activity. This flux remains constant during a given geological epoch. The direct anthropogenic emission is related to immediate discharge of mercury as a result of current human activity. Direct emissions can be from point sources (for example, stack of coal-fired power station) and area sources (for example, application of insecticides containing mercury). Finally, re-emission is an additional input to the natural fraction of mercury from natural objects contaminated by previous anthropogenic activity.

3.1 Natural emissions

Evidently a certain mercury atmospheric cycle existed before human activity. Mercury inflow and outflow were balanced in this cycle. Any element of the Earth surface was and remained to be natural sources: mountain rocks, vegetation, soil, water bodies. The highest natural emissions are observed in regions of mercury deposits and geochemical anomalies.

As a rule mercury deposits coincide with deep fractures and form so-called the Earth mercury geochemical belts. One of these belts goes along southern Europe from the Caucasus mountains to Pyrenees. From data of I.Trakhtenberg and M.Korshun (1990) typical mercury geochemical anomaly is characterized by the mercury content in the surface air at the level of 10 ng/m^3 exceeding that of the background as much as 5-10 times. In the air surface layer above mercury deposits mercury concentrations increase in thousands-tens of thousands times.

It is known that volcanic activity is an important natural source of mercury emission to the atmosphere. In Europe Etna, an acting volcano in the mercury belt, is a possible source of mercury input to the atmosphere. P.Buat-Menard and A.Arnold (1978) have found that only particulate mercury concentrations in Etna plume can amount to 500 ng/m^3 . Nothing is known about emissions from fumaroles of Icelandic volcanic system.

Natural mercury content in soils and associated emissions from them to the atmosphere depend on properties of the underlying bed-rocks. O.Lindqvist et al. (1991) are of the opinion that outside the mercury belts soil emission is about $1 \text{ g/km}^2/\text{yr}$, inside the belts - up to $10 \text{ g/km}^2/\text{yr}$. According to W.Fitzgerald and R Mason (1996) mean intensity of natural mercury flux from land to the continental atmosphere (without the Antarctic) is $9.7 \text{ g/km}^2/\text{yr}$.

Specific (per area unit) mercury emission from fresh waters can be appreciably higher than from soil. On the whole lake waters (especially during summer) are oversaturated by elemental mercury relative to the atmosphere. Estimates of the process intensity available in literature are very contradictory. It may be thought that mean emissions from lake surfaces are within the range of $2\text{-}20 \text{ g/km}^2/\text{yr}$ (Lindqvist et al., 1991). J.Munthe (1993) presents data for Swedish lakes ($18\text{-}180 \text{ g/km}^2/\text{yr}$) but one should be aware that the current mercury flux from Swedish water bodies is not purely natural.

It is an essential for Europe that the snow cover does not prevent from mercury inflow to the atmosphere (Fursov, 1983). V. Fursov (1983) found that in the snow cover above an ore bodies gaseous mercury haloes are formed. Snow practically does not accumulate mercury and easily gives it up to the atmosphere. On the other hand, as temperature drops mercury emission from soil and water basins decreases (Lindberg et al., 1991; 1992). However, at present there is no scientific basis for the evaluation of the natural emission seasonal cycle.

The World Ocean plays an essential role in the natural cycle of mercury due to Hg^{2+} reduction most likely in biological processes taking place in marine water (Kim and Fitzgerald, 1986). Total natural flux of mercury from the World ocean is estimated as 600 t/yr (Fitzgerald and Mason, 1996). Taking into account the World ocean area the intensity of mean natural emission from the ocean surface is estimated as 1.7 g/km²/yr.

In Europe spatial distribution of natural emission is non-uniform. First of all, it is connected with the geochemical mercury belt in the southern part of the continent. Besides natural emissions are affected by soil types and temperature regime. Attempts to assess the natural component of mercury emissions in Europe were made by F.Axenfeld et al. (1991) and B.Moisseev, 1997). Both studies were based on a spatial distribution of soil properties and underlying bed-rocks. Besides an important factor is mean annual temperature.

In both studies natural emissions from countries of the EMEP region which do not participate in EMEP (countries of Africa and Asia) have not been estimated. In this work we assume that in these countries the emission intensity is equal to the mean value for all the continents - 10 g/km²/yr (Fitzgerald and Mason, 1996).

According to F.Axenfeld et al. (1991) total natural emission of mercury from land in the EMEP domain (without Turkey and African countries) is 265 t/yr or on the average - 21 g/km²/yr. Natural emission estimated by B.Moisseev (1997) is 70 t/yr or on the average 5.6 g/km²/yr. In comparison with the mean continental estimate made by W.Fitzgerald and R.Mason (1996) value 21 g/km²/yr seems to be overestimated and value 5.6 g/km²/yr - underestimated.

In spite of the difference in absolute values, emission field configurations in works by F.Axenfeld et al. (1991) and B.Moisseev (1997) are almost the same. It may be assumed that before the epoch of anthropogenic activity mean concentrations of atmospheric mercury in this region corresponded to the global level with allowance made that the ratio "land : sea" is higher in the EMEP region than on the Earth on the whole, therefore the contribution of more intensive emissions from land is more essential here. Thus mean natural concentration of atmospheric elemental mercury in the EMEP region should somewhat exceed global value 1 ng/m³.

The evaluation of the total natural emission in the EMEP region can be made on the basis of some assumptions. To provide comparability EMEP region was taken of the same size (39x37 cells) as in the works by B.Moisseev (1997) and F.Axenfeld et al. (1991). An essential part (39% or 12.7E6 km²) of EMEP the region of this size is covered by a sea surface. Besides 15% of the EMEP grid cells covers both land and sea surfaces. On the average it is

conceivable that the relation "land : sea" is 1:1 in such cells. Hence the total natural emission of mercury from the sea surface is 26 t/yr in the EMEP region (39x37 cells).

Greenland and an essential part of the Arctic ocean are permanently covered by ice (about 9% of the EMEP region). It may be assumed that there is no mercury emission from ice surface.

In view of geochemistry of mercury European continent does not differ much from the land of the globe on the whole. The mercury belts are also characteristic of other continents. Therefore it may be accepted that natural emission intensity on the land within the EMEP is equal to mean global value 10 g/km²/yr (Fitzgerald and Mason, 1996). Consequently total natural emission from the land in the EMEP region (containing 39x37 cells) is 145 t/yr.

F.Axenfeld et al. (1991) did not make assessments of natural emissions from Turkey and African countries of the EMEP region (containing 39x37 cells). If we presume that the emission intensity at these territories is equal to mean value 10 g/km²/yr (Fitzgerald and Mason, 1996) of all continents, then their total emission will amount to 27 tons. Thus natural emission to the atmosphere from the Contracting Parties to EMEP is 145-27=118 tons of mercury annually.

In further calculations the obtained value of natural emissions (118 t/yr) was spatially distributed keeping the configuration of the natural emission field presented in the work of F.Axenfeld et al. (1991). The intensity of natural emission from sea surface is taken to be spatially uniform. It is also assumed that natural emission intensity is uniform in countries which were not considered by F.Axenfeld et al. (1991). Spatial distribution of natural emissions with 150 x 150 km resolution is shown in fig. 3.1. As it is seen from the figure maximum emission values (up to 25 g/km²/yr) are characteristic of the zone of the mercury geochemical belt. The emission intensity decreases to the north and reaches zero in the Arctic region.

Natural emissions are presented mainly by the gas-phase. Actually only two gaseous species - Hg⁰ and DMM can be considered. In spite of all efforts DMM emissions have not been found experimentally (Munthe, 1993), though there are indirect indications that part of emissions from lakes and the World ocean is represented by this compound. F.Axenfeld et al. (1991) consider that 10 % of mercury natural emissions in Europe is represented by gaseous organic compounds, however, it is not proved experimentally. Nevertheless in our computational scheme we presume that in natural emissions the ratio between Hg⁰ and DMM is 9:1.

It was mentioned above that natural emission intensity depends on temperature. At this stage it was assumed that natural sources in Europe operate uniformly around the year.

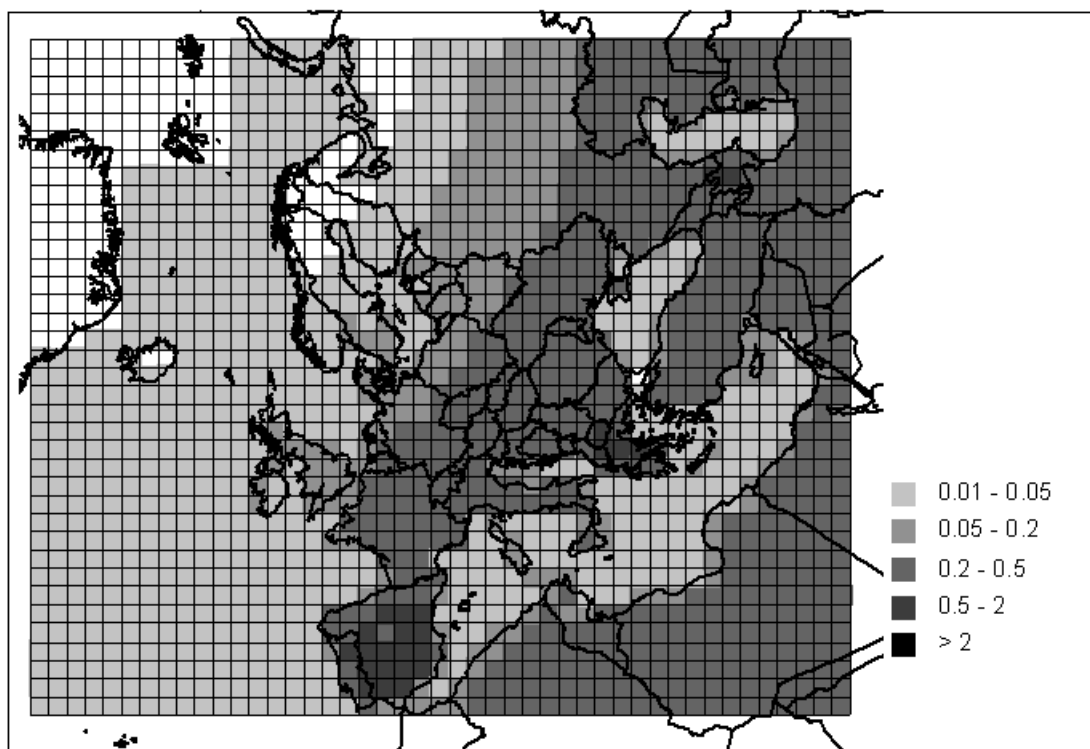


Figure 3.1 Natural emission distribution with the EMEP region, spatial resolution 150x150 km, t/yr

3.2 Direct anthropogenic emissions of mercury to the atmosphere in the EMEP region

One of the main anthropogenic sources is combustion of fossil fuels which mercury content as a rule is appreciably higher than in the lithosphere on the whole. Coal is mostly enriched in mercury. In some deposits (for example, Donbass) mercury concentration reaches hundred grams per ton. Mercury content in oils is 5-100 times higher than mean content in the lithosphere, in natural gas - 5-1000 times higher than in soil air (Fursov, 1983). On the global level the contribution of coal combustion to total anthropogenic emission is about 65% (Slemr, 1996).

Metal smelting (Fitzgerald and Mason, 1996) also belong to main sources of mercury emission to the atmosphere. Ores of many non-ferrous metals contain appreciable quantities of mercury as accompanying admixture. Thermal treatment of ores and metal smelting result in the emissions of mercury mainly in the elemental form.

Landfills are another significant anthropogenic source - to 25% of the total anthropogenic emission (Slemr, 1996). According to data of V.Fursov (1983) in the vicinity of landfills atmospheric mercury concentrations are by an order of magnitude higher than the background. At waste incineration mercury concentrations in flue gases can reach 1000 $\mu\text{g}/\text{m}^3$ (Porcella et al., 1996).

Due to high toxicity of mercury compounds fungicides containing mercury were widely applied to agriculture. The contribution of this source to atmospheric anthropogenic mercury has not been estimated, however, its magnitude can be significant. For example, previously in the USA 400 tons of mercury was applied to the content of pesticides (18% of the total consumption of mercury in the USA). An appreciable fraction of this mercury after decomposition of pesticides most likely enters the atmosphere (Trakhtenberg and Korshun, 1990).

A certain contribution to the anthropogenic emissions make non-industrial human activities. For example, breaking of thermometers releases up to 60 tons a year of mercury (Trakhtenberg and Korshun, 1990) to the environment, on the global level, however, how much of it enters the air is not estimated. In a number of countries a considerable input makes crematoria since mercury of tooth fillings is removed with gases to the atmosphere.

Due to peculiarities of economic development of different EMEP countries the contribution of individual source categories can vary considerably from country to country. Table 3.1 gives data taken from J.Berdowski et al. (1997) on emission estimates of different source categories in the EMEP countries for 1990. Question marks in the table means that emissions in a given category can exist but they have not yet been assessed quantitatively. It follows from the table that almost in all countries the basic contribution to emissions makes the combustion of fossil fuels and some industrial sources. Hence a significant conclusion can be drawn that a considerable part of mercury is likely to be emitted from high sources (>100 m). Therefore in calculations it was assumed that 35% of anthropogenic mercury is emitted in the near-surface layer below 100 m, and the rest of it in the layer above 100 m. Individual point sources are not considered. Since the input to emissions makes fuel combustion it is natural to assume that there should be a tangible seasonal variation of the emission intensity. However, at this stage it is assumed in calculations that anthropogenic sources operate uniformly in Europe around the year.

According to J.Berdowski et al. (1997) the accuracy of the data presented in table 3.1 is not high. For north-western countries actual values can differ from the given ones by 20-50% and for the countries of central and eastern Europe the uncertainty can be within factors of 2.5-3.5.

Physical and chemical forms of mercury emitted by anthropogenic sources are of a paramount importance. These forms determine parameters of the transport and removal of mercury from the atmosphere. Table 3.2 present summarized data on inputs of various mercury forms in emissions of different sources (Lindqvist et al., 1991). However, it is well to bear in mind that data of table 3.2 are of a preliminary character.

Table 3.1 Anthropogenic mercury emissions from different source categories in European countries in 1990, t/yr (Berdowski et al., 1997)

Country	Stationary combustion	Iron & steel industry	Non-ferrous metal industry	Chloro-alkali industry	Cement industry	Waste treatment & disposal	Others
Albania	0.230	-	0.001	-	0.188	0.093	-
Austria	1.75	0.200	0.010	0.270	1.38	0.630	0.03
Belarus	0.084	-	-	?	?	0.002	0.005
Belgium	1.79	0.806	0.047	1.02	1.59	2.77	0.828
Bosnia&Herzegovina	0.013	0.056	-	-	-	0.152	-
Bulgaria	3.12	0.230	0.162	0.248	0.988	2.12	0.034
Croatia	0.376	0.005	-	-	0	0.001	0.695
Cyprus	0.021	-	-	-	0.283	-	-
Czech Republic	6.69	0.754	?	?	1.54	0.355	-
Denmark	2.48	-	-	0.025	0.414	4.00	-
Estonia	1.76	-	-	-	0.226	0.029	0.002
Finland	2.17	0.189	0.007	0.100	0.417	0.152	-
France	11.9	0.000	0.001	2.58	?	17.9	-
Germany	40.8	1.59	36.0	10.4	24.2	0.200	0.081
Greece	3.53	0.150	-	-	3.39	0.050	-
Hungary	1.59	0.157	?	?	1.20	1.25	0.001
Iceland	0.018	-	-	-	0.029	0.001	-
Ireland	1.14	0.049	0.019	-	0.406	0.010	-
Italy	1.46	1.09	0.600	1.63	3.80	3.22	-
Latvia	0.336	-	-	-	?	?	-
Lithuania	0.000	?	-	-	?	?	0.003
Luxembourg	0.045	0.156	-	-	0.159	0.407	-
The FYR Macedonia	0.424	-	0.843	-	0.152	0.072	-
Republic of Moldova	0.992	-	-	-	0.452	0.080	-
Netherlands	1.03	1.60				?	-
Norway	0.524	0.060	-	0.050	0.315	1.39	-
Poland	31.5	0.799	0.000	0.996	-	?	-
Portugal	1.23	0.083	-	2.30	1.82	0.050	-
Romania	4.42	0.415	0.267	-	0.391	0.597	0.102
Russian Federation*	56.1	5.67	2.35	?	19.4	2.68	0.095
Slovakia	0.896	3.83	5.28	0.297	1.36	0.760	0.012
Slovenia	0.300	0.041	0.013	-	0.450	0.066	-
Spain	14.7	1.65	-	1.97	-	1.82	-
Sweden	0.220	0.270	0.250	0.200	-	0.470	-
Switzerland	0.498	1.11	-	0.385	0.156	4.83	-
Ukraine	25.8	3.67	0.051	?	5.44	0.942	0.031
United Kingdom	6.26	1.14	2.37	7.90	0.157	7.62	0.16
Yugoslavia	2.06	0.182	0.119	-	0.509	0.340	-
Total	229	24.3	48.4	30.4	70.8	55.0	2.078

* European territory and the Urals

Table 3.2 Percentage of various mercury forms in emissions of different sources (Lindqvist et al., 1991).

Source	Hg ⁰ (gas)	Hg ⁺² (gas)	Hg ⁺² (particle)
Coal combustion	50	30	20
Chlorine and alkali production	50-90	10-50	0
Roasting of metal sulfide ores	80-90	0	10-20
Pyrite combustion	100	0	0
Waste incineration	20	60	20

Attempts were made (Axenfeld et al., 1991; Pacyna and Münch, 1991) to evaluate total emissions of various mercury forms on the level of individual countries of Europe. The evaluation results are given in table 3.3. Previously A.Ryaboshapko and Korolev used (1997) in calculations mean the relationship of anthropogenic emissions for all European countries: Hg⁰ - 57%, Hg²⁺_(gas) - 30%, Hg²⁺_(particles) - 13%. In this work data on relationships of mercury forms characteristic of each country are used (table 3.3).

Table 3.3 The relationship of various mercury forms in direct anthropogenic emissions in different European countries (Axenfeld et al., 1991)

Country	Fraction of emission, %			Country	Fraction of emission, %		
	Hg ⁰	Hg ^{II} _{gas}	Hg ^{II} _{part}		Hg ⁰	Hg ^{II} _{gas}	Hg ^{II} _{part}
Albania	50	30	20	Latvia *	51	29	20
Austria	58	25	17	Lithuania *	51	29	20
Belarus *	51	29	20	Luxembourg	51	29	20
Belgium	60	25	15	The FYR Macedonia *	56	27	17
Bosnia&Herzegovina*	56	27	17	Republic of Moldova *	51	29	20
Bulgaria	55	27	18	Netherlands	36	47	17
Croatia *	56	27	17	Norway	69	23	8
Cyprus **	51	29	20	Poland	52	29	19
Czech Republic *	52	30	18	Portugal	63	30	7
Denmark	44	40	16	Romania	50	30	20
Estonia *	51	29	20	Russian Federation *	51	29	20
Finland	74	18	8	Slovakia *	52	30	18
France	51	30	19	Slovenia *	56	27	17
Germany	60	31	9	Spain	64	26	10
Greece	51	29	20	Sweden	74	19	7
Hungary	52	29	19	Switzerland	55	27	18
Iceland	100	0	0	Ukraine *	51	29	20
Ireland	50	30	20	United Kingdom	52	34	14
Italy	62	29	9	Yugoslavia *	56	27	17

* The relationship is based on data for the former USSR, Yugoslavia and Czechoslovakia

** The relationship is accepted equal to that of Greece.

National estimates of mercury emissions to the atmosphere are not available for many countries. A general idea on the completeness of official data on mercury emissions gives table 3.4. In this work we used expert estimates made by J.Berdowski et al. (1997) also given in table 3.4. The comparison of these estimates with available official data show that the discrepancy can reach several times.

Table 3.4 Expert estimates and official data of mercury emissions to the atmosphere in different European countries, (t/yr)

Country	Expert estimates	Official data for 1990-95 ²⁾					
	for 1990 ¹⁾	1990	1991	1992	1993	1994	1995
Albania	0.511						
Austria	4.27					2.2	
Belarus	0.091	0.092					0.052
Belgium	8.86						3.3 ³⁾
Bosnia&Herzegovina	0.222						
Bulgaria	6.90	13.2					6.9
Croatia	1.08	1.075					0.246
Cyprus	0.305						
Czech Republic	9.31						
Denmark	6.92					8.2	8.5
Estonia	2.02						
Finland	3.04	1.8	1.7	1.3	1.3	1.6	1.6
France	32.5	32.0					
Germany	113	112.4					31.0 ⁴⁾
Greece	7.12						
Hungary	4.20	4.2	4.2	3.2	3.2	3.1	3.1
Iceland	0.048						
Ireland	1.62						
Italy	11.8	20.0				13.2	
Latvia	0.336	0.37	0.32	0.27	0.22	0.37	0.17
Lithuania	0.003	0.018	0.016	0.011	0.14	0.013	0.012
Luxembourg	0.767					0.244	0.198
The FYR Macedonia	1.49						
Republic of Moldova	1.52						
Netherlands	2.64	3.0		2.7		1.6	1.3
Norway	2.34	1.3					
Poland	33.3	33.3	32.7	31.9	32.5	32.4	32.3
Portugal	5.48						
Romania	7.50						
Russian Federation ⁵⁾	66.5						
Slovakia	12.4						
Slovenia	0.869						
Spain	20.2	20.2					
Sweden	1.45	1.5		1.2		0.9	
Switzerland	6.82	6.8	6.1	5.4	4.7	4.0	3.3
Ukraine	36.0						
United Kingdom	25.6	30.0	26.4	25.2	20.4	19.5	19.7
Yugoslavia	3.86						
Total	443						

¹⁾ Berdowski et al., 1997;

²⁾ UN/ECE, EB.AIR/GE.1/1997/3; EB.AIR/GE.1/1997/3/Add.1;

³⁾ Only for the Wallonie and Flanders; ⁴⁾ Preliminary data; ⁵⁾ European part

Spatial distribution of the anthropogenic mercury emissions first of all reflects the mean level of coal consumption in different regions. However, this relatively uniform field is superimposed by individual point sources, for example of chlorine and alkali productions with old technology or sources connected mining and production of mercury itself. The field

of direct anthropogenic emissions is taken from the paper by J.Berdowski et al. (1997). Fig. 3.2, 3.3 and 3.4 demonstrate fields of direct anthropogenic emissions of three forms of mercury (elemental, oxidized gaseous and aerosol). Spatial resolution is 150x150 km.

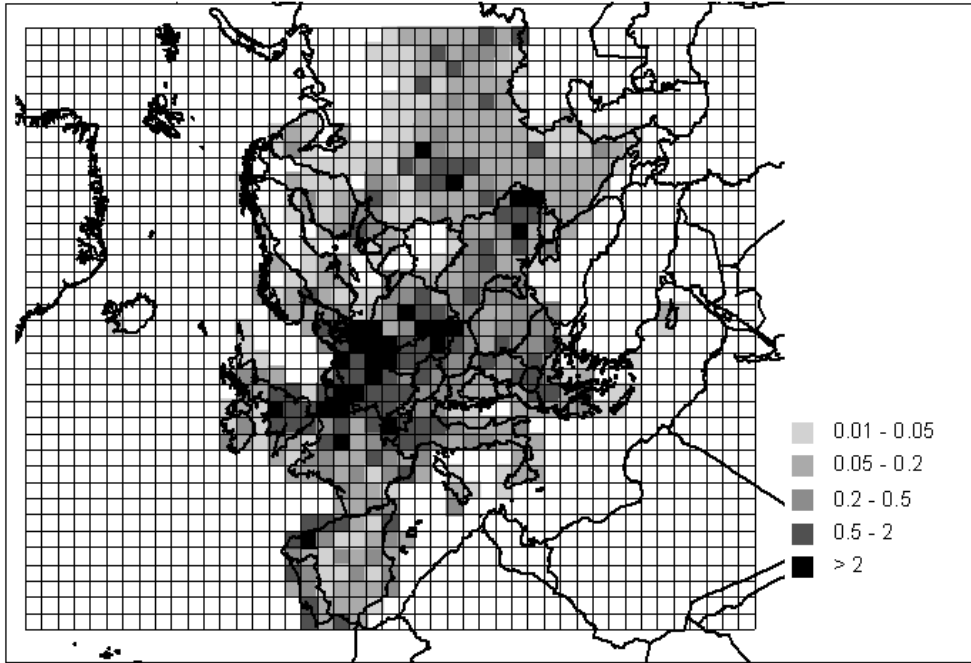


Figure 3.2 Direct anthropogenic emission field of elemental mercury with spatial resolution 150x150 km, t/yr

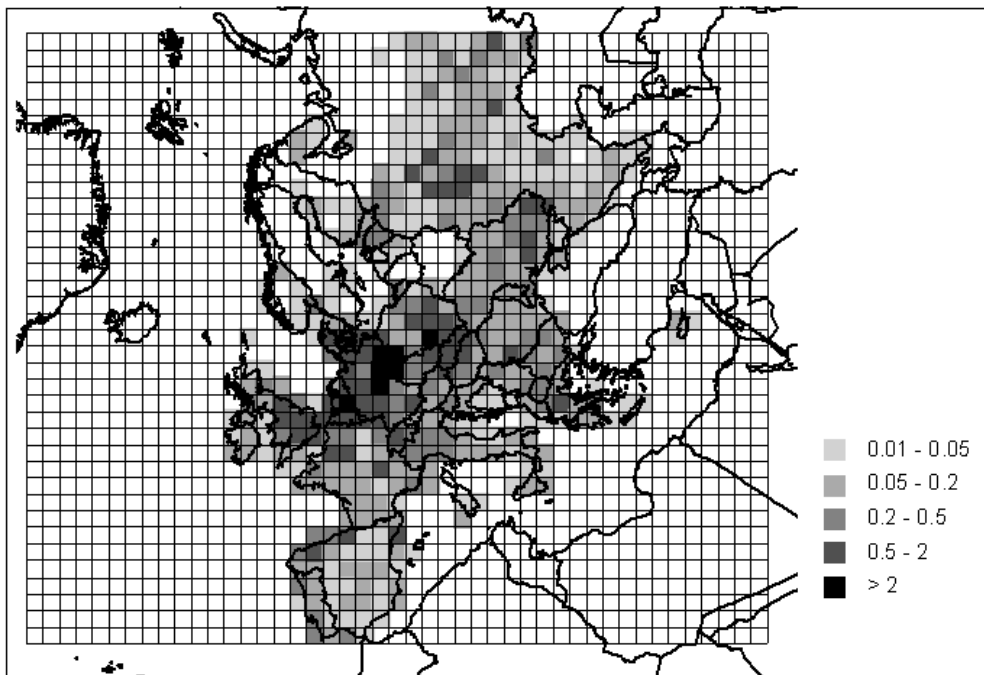


Figure 3.3 Direct anthropogenic emission field of gaseous oxidized mercury with spatial resolution 150x150 km, t/yr

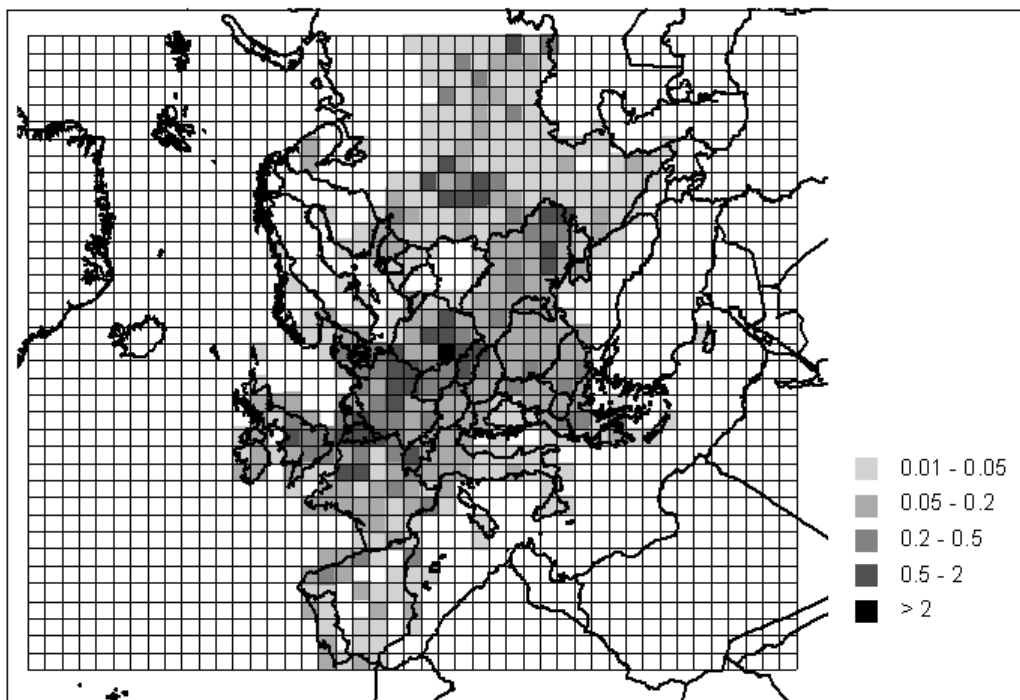


Figure 3.4 Direct anthropogenic emission field of particulate mercury with spatial resolution 150x150 km, t/yr

3.3 Anthropogenic mercury re-emission to the atmosphere in the EMEP region

The question to what extent re-emission can affect the regional mercury cycle in the atmosphere of Europe is still open. Argumentation in this field is of exclusively speculative character. Significance of re-emission process is determined first of all by the capacity of soils to accumulate mercury and by mercury life-time in soils relative to different removal mechanisms. Among such mechanisms it is reasonable to consider hydrological run-off into water bodies, washout from upper soil layers to deep ones and at last evasion to the atmosphere.

There are no literature data on mercury accumulation in soils of regions where high levels of mercury atmospheric pollution have been observed. It is known that minimum content of mercury in soils is about $3 \cdot 10^{-6} \%$ (Vinogradov, 1957). Let us assume that only upper 20 cm layer of soil can interact with the atmosphere. Specific density of soils is roughly 2 t/m^3 . Intensity of mercury fluxes from soils to the atmosphere can reach $100 \text{ g/km}^2/\text{yr}$ (Schroeder and Munthe, 1998). Hence the minimum estimate of mercury life-time in soils (relative to evasion to the atmosphere) can be about 100 years. It is impossible to estimate the upper limit of this value because under some conditions the evasion intensity can drop practically to zero. Keeping this in mind it is possible to believe that the value of mercury life-time in soils relative to the flux into the atmosphere (400 yr) published by I.Trakhtenberg and M.Korshun (1990) is rather reasonable.

W.Fitzgerald and R.Mason (1996) estimated that the bulk (190000 t or 95%) of anthropogenic mercury emitted to the atmosphere during recent 100 years, at present is being accumulated by soils. According to estimates of I.Trakhtenberg and M.Korshun (1990) the

life-time of mercury in soils relative to volatilization processes is 400 years (process rate constant - 0.0025 yr^{-1}) and relative to the runoff to water basins - 900 years (process rate constant - 0.0011 yr^{-1}). Based on these values it is possible to evaluate the range of conceivable values of re-emission to the atmosphere of Europe.

On the assumption that anthropogenic mercury is uniformly distributed with soils of all continents, then for Europe re-emission value could be only 32 t/yr. This is minimum estimate, since the bulk of emissions during recent 100 years took place in Europe and European soils accumulated much more mercury per unit soil mass than soils of other continents. In addition part of anthropogenic mercury entered soils (or in-land water bodies) directly from industrial plants. This share of mercury can also volatile to the atmosphere as re-emission.

Mercury life-time in soils (400 years) exceeds considerably the period of really noticeable anthropogenic impact (100-150 years). It means that there was no significant redistribution of previously deposited mercury. Hence the re-emission field should be similar to the field of total deposition for the last 100-150 years. About 75% of deposited mercury during the last 100 years on a given region is still remained in the soils of this region.

According to data of J.Pacyna (1996) within the EMEP grid (containing 39×37 cells) re-emission and natural emission in sum amount to about 250 t/yr. Allowing for above estimates of natural emissions, in this case re-emission should be only about 70 t/yr. B.Moisseev (1997) made an attempt to evaluate roughly the re-emission field for Europe with spatial resolution $150 \times 150 \text{ km}$. According to his estimates the total value of re-emission on the EMEP area is 222 t/yr. B.Moisseev (1997) presumed that mercury emitted to the atmosphere falls out on the underlying surface only within a cell-source. Consequently the re-emission value is proportional to the value of direct anthropogenic emission in a given cell. This approach does not take into account the atmospheric transport of mercury outside the cell-source and its deposition in neighboring and remote cells.

In this work the total re-emission in Europe was estimated on the basis of a number of assumptions. The total direct anthropogenic emission in Europe for the end of the 80-s was assessed as 726 t/yr (Petersen et al., 1995). According to A.Ryaboshapko and V.Korolev (1997) about half of this amount (let it be 350 t/yr) deposited on the territory of Europe. Let us admit like W.Fitzgerald and R.Mason (1996) that during recent hundred years a linear growth of emissions is observed (and deposition respectively) and one hundred years ago the deposition from direct anthropogenic sources was negligible. Reasoning from these assumptions and rates of mercury removal from the soil (Trakhtenberg and Korshun, 1990) we find that in Europe nowadays anthropogenic mercury re-emission in the EMEP region caused by direct anthropogenic emissions in Europe makes up 36 t/yr. Besides, a part of mercury deposition in the EMEP region was resulted from globally distributed sources outside Europe. If we assume that the total emission in Europe during XIX and XX centuries amounted to 1/3 of the global one and that mercury of non-European origin was evenly distributed in soils of all continents the value of re-emission in Europe from these sources should be about 11 t/yr. Thus the total re-emission from soils of the EMEP region at the beginning of the 90-s should not exceed 47 t/yr or 10% of the modern value of direct anthropogenic emission.

It was mentioned above that mercury is firmly fixed with soil and the bulk of mercury deposited in previous years is still contained in soil. Then it is possible to assume that during last 50-100 years the configuration of direct anthropogenic emission field did not undergo considerable changes. The resulting re-emission field should comply with mean climatic deposition field. Two factors, however, can distort the re-emission field configuration: on the one hand, the temperature decrease is accompanied by re-emission intensity reduction, on the other, the same is happened at the increase of organic carbon content in soil. Under European conditions to a certain extent these effects compensate each other - from the north to the south both mean temperature and organic carbon content are increased. Here we presume in the first approximation that the re-emission field configuration complies with the deposition field produced by direct anthropogenic emissions for 1995.

The violation of global atmospheric mercury cycle by human activity inevitably should lead to the increase of mercury content in the oceanic surface layer and consequently to the growth of emission intensity from the sea surface. Earlier we assumed that at the global level due to anthropogenic factor mercury content in the atmosphere increased in 1.5 times. On this basis we assume that current emission from the sea surface is in 1.5 times higher than natural one and amounts to $2.5 \text{ g/km}^2/\text{yr}$. A combined re-emission field over both land and ocean used further in calculations is shown in fig. 3.5.

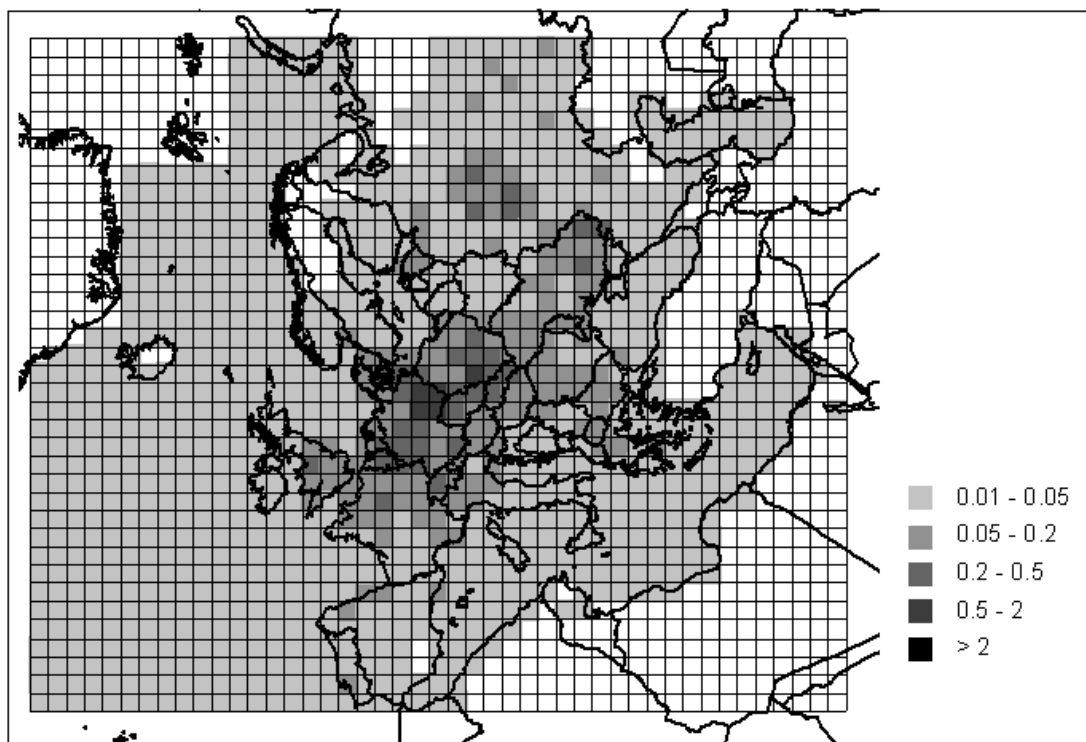


Figure 3.5 Field of mercury re-emission in the EMEP region, t/yr

When considering re-emission one should bear in mind an important thing that irrespective of chemical mercury form in deposition, re-emission is mainly represented by the elemental (90-95%) and methylated forms. Re-emission in aerosol form caused by aeolian soil weathering can give but a small contribution (to 2%) on the local scale and in the course of short periods.

Like natural emission re-emission depends on temperature. However, at this stage of calculations the re-emission intensity was considered to be constant during a year.

4. Model description

The state of the art in the field of modeling of the airborne mercury transport within European scale, indication of unsolved problems, requirements to the accuracy of model estimates were characterized by G.Petersen (1996) at the workshop on the evaluation of the activity under EMEP on heavy metals (Moscow, 1996). At the workshop requirements to models for atmospheric mercury transport were formulated: they are to obtain realistic values of mean monthly and mean annual values of concentrations and deposition on the regional level within the accuracy to factor 2. For the development of an operational model we used approaches to modeling of atmospheric mercury developed by G.Petersen et al., (1990; 1995; 1996; 1998), K.Pleijel and J.Munthe (1995a, 1995b).

When working on principles underlying the model two circumstances were considered. First, the model should operate with sufficiently long periods of time (months, seasons and years). Second, many key-parameters are still known with low accuracy (up to an order of magnitude). Hence at this stage it is unreasonable to complicate the model with the consideration of many secondary mechanisms. The operational model should yield 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 year. The model should adequately reflect gradients of concentration and deposition fields.

Three-dimensional Eulerian model ASIMD was used as a basis for numerical calculations of atmospheric mercury transport. This model has been developed by M.Pekar (1996) and used for the simulation of heavy metal transport in aerosol form. For the mathematical description of dry uptake and washout by precipitation allowing for sources and sinks the splitting method is applied to the operator of diffusion equation. Dry deposition is described by appropriate boundary conditions (Pekar, 1996).

The time step for the integration of equations was taken to be 1 hour. The calculations are made for the period of one year. Monthly averaging of deposition, surface concentrations and concentrations in precipitation was made.

Calculations of concentration and deposition fields of various forms of mercury were performed over the expanded EMEP grid (45x37 cells) with spatial resolution 150x150 km. Model has four unequal layers along the vertical: 0-100, 100-400, 400-1100, 1100-2100. Thus model calculations cover the atmospheric boundary layer only. This fact is a serious disadvantage when modeling long-lived pollutants which mercury belongs to.

Mercury emissions to the atmosphere are given by fields of the natural emission, direct anthropogenic emission and anthropogenic re-emission with spatial resolution 150x150 km. Natural emissions and re-emission are represented by elemental mercury (90%) and DMM (10%). Direct anthropogenic emissions are represented by gaseous elemental form, particulate and oxidized inorganic gaseous compounds. Natural emission and re-emission enter the lowest atmospheric layer. Direct anthropogenic emissions are distributed between the first (35%) and the second (65%) model layers indicating predominance of high industrial sources. Scavenging of mercury and its compounds takes place due to washout by clouds and precipitation, "dry" uptake by the underlying surface and chemical reactions both in gaseous and liquid phases. A general scheme of mercury transport and removal is presented in fig. 4.1. A detailed description of individual processes are given below.

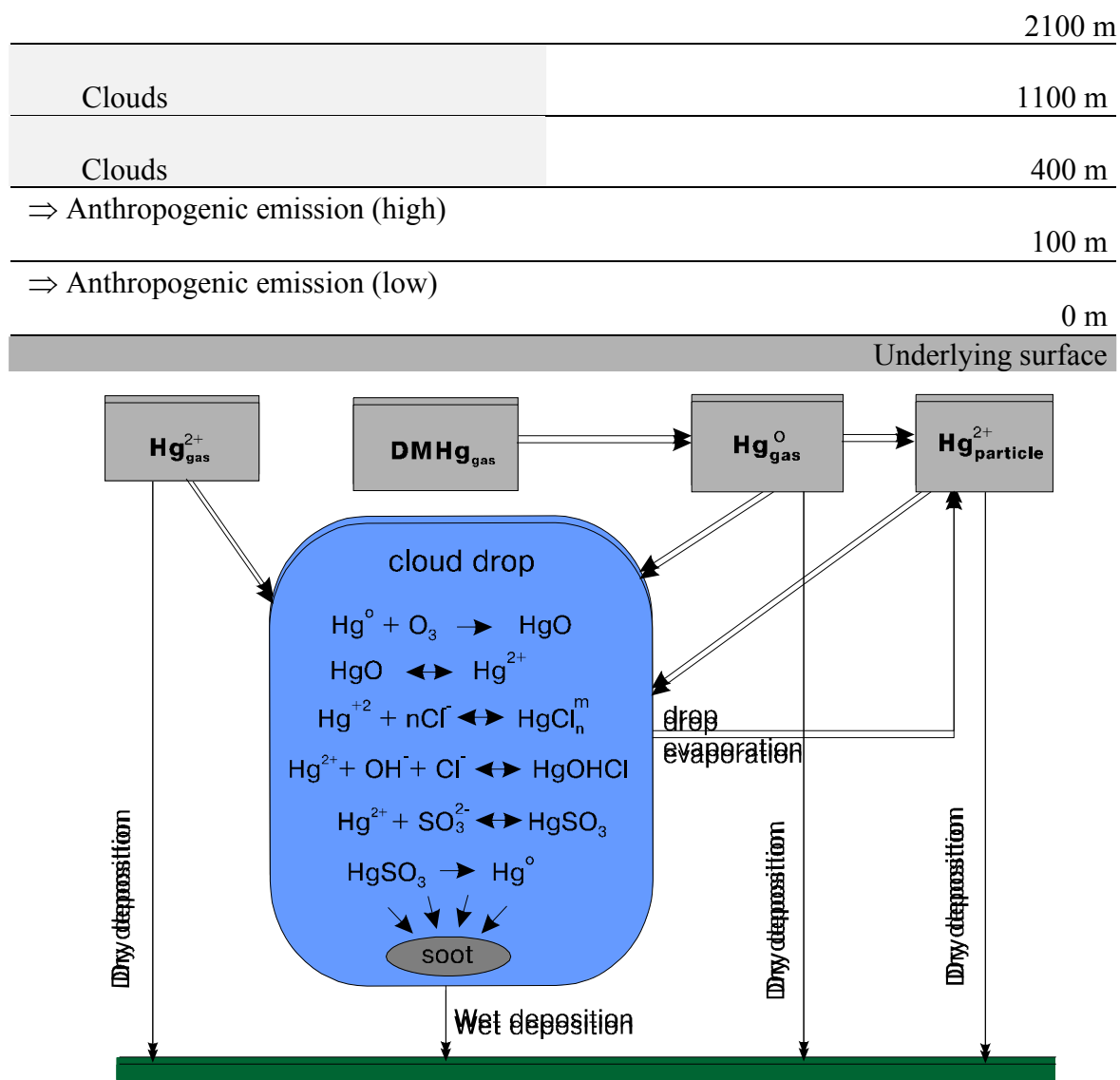


Figure 4.1 General model scheme of mercury transport and removal from the atmosphere.

4.1 Advection, vertical transport, diffusion, meteorological parameters and boundary conditions

Advection determining the pollution transport in horizontal direction is described in the model by approaches developed according to M.Pekar (1996). The transport can take place into two leeward neighboring cells and to a leeward cell along the diagonal.

Pollution diffusion in the horizontal direction is described on the basis of the approach presented in the paper by Yu.Izrael et al. (1980). The description of vertical diffusion is based on the classical idea that the flux of a substance mass through a surface unit is proportional to the concentration gradient of this substance. The coefficient of turbulent diffusion in the vertical direction is taken for the coefficient of proportionality which is calculated at each time step. (Pekar, 1996).

The convergence of air fluxes in cyclones and troughs and the divergence in anticyclones and ridges produce ordered air motions along the vertical. The vertical transport velocity is calculated at each step proceeding from air balance conservation in each grid cell with allowance for its non-compressibility. The highest layer of the model reservoir is open for the exchange with upper atmosphere which have constant background characteristics of the content of mercury and its compounds. The same background characteristics were used for the air coming to the model reservoir through lateral limits due to advection.

In calculations of the pre-industrial mercury balance for the elemental mercury concentration value 1 ng/m^3 and for aerosol mercury - 0.007 ng/m^3 were taken. In calculations of the modern state background concentrations were - 1.5 и 0.01 ng/m^3 .

Meteorological data for 1995 were used in calculations. The choice of this very year was conditioned by a number of circumstances. First of all it is supposed that in future this year 1995 will be the basic year for the evaluation of the emission intensity in all countries of the region, i.e. emission data will be most detailed and accurate. In addition accompanying information on concentration fields of ozone and sulfur dioxide for 1995 was available. These fields were calculated by Meteorological Synthesizing Centre-West. The set of meteorological parameters prepared by Hydrometcentre of Russia included wind fields on the baric levels of 1000, 925 and 850 hPa, temperatures on the same levels and precipitation amount. Data on wind fields and temperature are presented as instantaneous values for basic meteorological periods (0, 6, 12, 18 o'clock UTC) and precipitation - as the amount for 6 hours.

In model calculations for the fourth layer wind speed on 850 hPa level was used for the third and second layers - on 925 hPa and 1000 hPa respectively. The wind speed in the first model layer was calculated using the boundary layer parametrization (Pekar, 1996).

4.2 Physical-chemical processes in gaseous, liquid and solid phases

Mercury atom in many respects is similar to inert radon atom and this fact to a considerable extent determines relative chemical stability and low solubility of elemental mercury in water. Besides, high volatility of mercury and of a number of its compounds make it possible for it to occur both in gas-phase and on aerosol particles. Thus physical-chemical processes can change both chemical and aggregate states of mercury.

In the gas-phase elemental mercury can be oxidized by ozone and possibly by other oxidants (Pyankov, 1949; Hall, 1995, Schroeder et al., 1991; Seigneur et al., 1994). Rate constant values available in literature vary from $4.2\text{E-}19$ (Slemr et al., 1985) to $4.9\text{E-}18 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Schroeder et al., 1991). K.Pleijel and J.Munthe (1995a) consider the latter estimate to be highly overestimated. Laboratory experiments concerned with mercury oxidation by ozone in the gas-phase have been recently carried out by B.Hall (1995). The obtained rates ($(3\pm 2)\text{E-}20 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 20°C) were several times lower than those obtained earlier by V.Pyankov.

In addition to ozone there are a lot of potential oxidants of mercury in the atmosphere. On the basis of data on reaction enthalpy V.Schroeder et al., (1991) showed that hydrogen peroxide, atomic oxygen and radical NO_3 can be also potential oxidants. K.Seigneur et al., (1994) believe that most likely in addition to ozone the oxidation reaction can take place with gaseous hydrogen peroxide ($K \leq 4.1\text{E-}16 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 25°C) and with atoms of chlorine ($K \leq 4.1\text{E-}16 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 25°C).

Similar to G.Petersen et al. (1998) here it is assumed that elemental mercury in the gas-phase is oxidized by ozone with the rate constant of the second order reaction $0.74\text{E-}9 \text{ ppb}^{-1} \text{ s}^{-1}$. Since ozone relative to mercury is present in appreciable excess, the reaction may be considered as a process of the quasi-first order. If on the global level we take that in the troposphere the ozone concentration is 30 ppb, the life-time of mercury relative to gas-phase oxidation reaction is 1.4 yr.

It was taken that in the atmosphere the reaction of gas-phase mercury methylation can take place. CH_3I and $(\text{CH}_3)_2\text{S}$ were considered as potential donors of the methyl group (Munthe, 1993; Hall et al., 1995). It was shown that these agents act (if at all) very slowly and they cannot explain significant concentrations of methylated mercury in precipitation. Therefore the process of gas-phase methylation is neglected in this work.

In molecules of $\text{R}'\text{-Hg-R}''$ type bond Hg-C is rather weak (bond energy is from 13 to 52 kcal/mol depending on R) (Prokofiev, 1981), therefore DMM can easily react with radical OH^\bullet with rate constant $1.97\text{E-}11 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Niki et al., 1983). G.Petersen (1992) points out to a possibility of the reaction with atomic chlorine with rate constant $2.75\text{E-}10 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. At these oxidation rates $(\text{CH}_3)_2\text{Hg}$ life-time will be several hours under the conditions of middle latitudes. M.Horvat (1996) shares this opinion and considers that $(\text{CH}_3)_2\text{Hg}$ life-time in the atmosphere is short because of intensive photochemical and chemical degradation. Here we presume that DMM destruction reaction followed by the formation of elemental mercury is of the first order with rate constant $2.3\text{E-}5 \text{ s}^{-1}$. Hence DMM atmospheric life-time will be 12 hours.

In the liquid-drop phase the reaction of dissolved elemental mercury with dissolved ozone (Iverfeldt and Lindqvist, 1986) is most important. Ozone solubility in water is sufficiently high (Henry coefficient is $0.013 \text{ mol l}^{-1} \text{ atm}^{-1}$ at 10°C (Kelly et al., 1985)) to provide an appreciable quantity of the oxidant in a drop. J.Munthe (1992) found that this reaction is of the second order and its rate ($K = (4.7 \pm 2.2)\text{E}7 \text{ M}^{-1} \text{ s}^{-1}$) does not depend on pH and temperature.

Mercury oxide produced as a result of liquid-phase oxidation reacts with ions available in the solution. Theoretically plenty of reactions can take place but only several of them are of practical importance for atmospheric mercury chemistry. The most important reactions and their rate constants are given in table 4.1.

Table 4.1 The most important reactions of the liquid-phase mercury chemistry

№	Reaction	Rate 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 s^{-1}		0.6 s^{-1}
R06	$\text{Hg}(\text{SO}_3)_2^{2-} \rightarrow \text{Hg}^0 + 2 \text{SO}_3^{2-}$		$4\text{E}-4 \text{ s}^{-1}$	$1\text{E}-4 \text{ s}^{-1}$
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- (Pleijel and Munthe, 1995a) *2 - (Petersen et al., 1996) *3 - (Constantinou et al., 1995)

In real conditions chlorine ion is most easily accessible for mercury ion formed in reaction (RO2) however, reactions with ions other halogens are possible. Reaction (RO3) with the formation of intermediate unstable mercury sulfite is important for understanding of the liquid phase mercury chemistry. Mercury sulfite is rapidly destroyed with the reduction of mercury to elemental form. However, mercury sulfite can attract one more sulfite ion (RO4) and more stable sulfite complex $\text{Hg}(\text{SO}_3)_2^{2-}$ is produced. Thus the totality of reactions leads to the dynamic equilibrium between elemental and oxidized mercury in the liquid phase of a cloud drop. J Munthe et al. (1991) suggested a scheme according to which the summarized rate of reduction reactions inversely dependent on sulfite ion concentration. At low SO_2 air concentrations and at $\text{pH} < 5.5$, $\text{Hg}(\text{SO}_3)_2^{2-}$ the reduction rate to Hg^0 can exceed 1% per hour.

In this work it is accepted that dissolved elemental mercury is oxidized by ozone with rate $4.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (Munthe, 1992). Mercury sulfite and sulfite complex are destroyed with rates 0.6 and 0.0004 s^{-1} with the reduction of elemental mercury.

Mercury compounds formed in liquid phase reactions can be sorbed from the water solution by soot particles shifting the chemical equilibrium between Hg^0 and Hg^{2+} to oxidized state. It is believed that oxidized mercury sorbed on a soot particle is not reduced to elemental form (Munthe, 1997). The process is limited by the diffusion velocity in liquid. According to G.Petersen et al. (1995) the process of reversible transport is described by equation:

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

where C_{soot} - soot concentration in the liquid phase, g/m^3 ; $k=5\text{E}-6$, m^4/g ; r - soot particle radius, m.

Here processes of adsorption by soot particles are considered according to the scheme suggested by G.Petersen et al. (1995) with the assumption that mean radius of soot particles is equal to 0.5 μm .

In the liquid phase photodissociation of oxidized compounds with the formation of elemental mercury can take place. However, rates of these reactions are small (Xiao et al., 1994) and here this process is neglected.

Obviously the process of mercury oxidation in the liquid phase takes place in only clouds which occupy atmospheric volumes within certain model layers. It is assumed that clouds occur only in the third and fourth layers (from 400 m and higher). The bulk of cloud water does not precipitate but it is evaporated. When the cloud drop is evaporated aerosol particles are formed thereby replenishing the aerosol mercury reservoir in the atmosphere. It is also assumed the evaporation process takes place in the absence of precipitation. The model does not take into account volatilization of elemental mercury from the liquid phase back to air, since there is a deficiency of mercury in the liquid phase at least during 2 days (Pleijel and Munthe, 1995a) and as a rule the life-time of real clouds is less than 2 days.

Ozone concentration fields (150x150 km) presented as mean monthly values for the lower atmospheric layer in 1995 were provided by Meteorological Synthesizing Center - West (MSC-W). These fields were calculated using a special model of Lagrangian type (Simpson et al, 1997). For the calculation of the natural mercury it was taken that in space natural ozone concentrations linearly decreased in 3 times with the latitude from 30°N to the pole. In time mean monthly concentration of natural ozone varies for 60°N following elevated sinusoid from 20 ppb in January to 40 ppb in July (at mean annual value 30 ppb)

It was assumed that soot particle concentration is proportional to sulfur dioxide concentration as 1:10 (Feichter et al., 1996). Estimates of spatial distribution of soot concentration were made on the basis of mean monthly sulfur dioxide fields for 1995 with spatial resolution 150x150 km prepared by MSC-W. Sulfur dioxide fields were computed but Eulerian model for acidifying compounds (Jakobsen et al., 1996). It was assumed that concentration of sulfur dioxide and, therefore, soot particles vertically uniform. In calculations of the natural mercury cycle it was assumed that sulfur dioxide concentration was constant in time and space and it was 0.1 $\mu\text{gS}/\text{m}^3$.

It was assumed that the dissolution of gaseous elemental mercury and ozone follows Henry law. The dimensionless Henry constant (the ratio of concentration in liquid to concentration in gas) for gaseous elemental mercury in dependence on temperature was calculated according to the following relation (Ryaboshapko and Korolev, 1997):

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

Henry constant for ozone and temperature dependence were taken as an average value of all values published by R.Sander (1997). Depending on temperature the constant was calculated from ratio:

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

For temperatures below 273⁰K it was supposed that cloud water is partially in the supercooled liquid state. For the liquid phase both for mercury and ozone appropriate Henry constants were calculated with the allowance for extrapolation of known temperature dependencies to the range of negative temperatures. However it is necessary to take into account that the probability of the liquid phase availability in a cloud rapidly decreases with temperature decrease. An appreciable part of the ice crystal mass can be produced due to sublimation avoiding liquid phase. Based on said above here it is taken that the share of the liquid phase linearly decreases from 1 at 0⁰C to 0 at - 15⁰C. It was accepted that mercury dissolution in solid phase (ice crystal) did not take place. Thus it was assumed that the quantity of dissolved mercury increased with temperature decrease to 0⁰C and then it linearly dropped to zero in the range from 0⁰C to -15⁰C.

4.3 Washout

Washout is a process of substance removal from air with condensed atmosphere moisture. Irreversible and reversible washout can be distinguished. Reversible washout leads to the removal of a substance from the air to the liquid phase of clouds or fog. Being absorbed by a drop nevertheless the substance remains in the atmosphere. For example, by this or that way mercury atom enters a cloud drop. Most likely the drop will be evaporated producing an aerosol particle with a given atom in its composition. This particle can again enter a drop. H.Rodhe (1992) estimated that on the average each particle being in the atmosphere 5 times goes through this cycle. During this time the mercury atom considered will remain in the atmosphere being repeatedly reversibly washed out. At the irreversible washout mercury atom in a rain drop or snow flake comes from the atmosphere on the underlying surface.

All forms of mercury can be subject to the washout process. As it was said above elemental mercury vapors though weakly but dissolve in water following Henry law. In a drop elemental mercury can be oxidized breaking the equilibrium the "air-drop" system and dissolving new portions of elemental mercury vapors. Thus the process of elemental mercury washout is not determined by the rate of physical dissolution but by the rate of the chemical interaction in the liquid phase. As a rule, gaseous mercury compounds like HgCl₂ or CH₃HgCl are easily dissolve in water and their washout rate is determined by physical dissolution rate according to Henry law. Washout of particulate mercury is determined by interaction processes between particle and drop. Mercury concentration in a particle (within reasonable limits) in no way affects the process rate. It should be kept in mind that at the reversible washout of originally gaseous mercury after the evaporation is converted to aerosol mercury (Expert Panel on Mercury Atmospheric Processes, 1994).

The irreversible washout can take place both in cloud with the consequent formation of large rain particles and in the subcloud layer by falling rain drops or snow flakes. In the latter case the effect of inertial collision of the falling drop or flake with a particle containing mercury becomes important. With the availability of elevated concentrations of mercury in the subcloud layer the first portions of rain or snow will have higher concentrations than the following ones (Ferrara et al., 1982).

In this work washout of elemental mercury vapors is interpreted as a process of dissolution and chemical oxidation in the liquid phase of clouds described in the previous section. It is assumed that the subcloud washout is negligible compared to the incloud one, since chemical oxidation processes are slow and the existence time of a rain drop is short.

Due to high solubility of gaseous inorganic mercury compounds in comparison with elemental mercury vapors the washout coefficient of these compounds expressed by the ratio of concentrations in the water phase versus concentrations in the gas-phase, should be by several orders of magnitude higher (Schroeder et al., 1991). K.Brosset (1987) believes that cloud water captures mainly inorganic gaseous mercury. Here washout of inorganic gaseous oxidized mercury by the liquid phase of clouds is prescribed by the washout ratio characteristic of nitric acid: 1.4×10^6 (Petersen et al., 1995; Jonsen and Berge, 1995). On the other hand washout of organic gaseous mercury (DMM) by the liquid phase of clouds does not occur (washout ratio is about 1). In calculations this process is neglected.

It is supposed that mercury containing particles behave like sulfate particles and the washout ratio is taken to be 7×10^5 (Petersen et al., 1995; Iversen et al., 1989).

4.4 Dry uptake of pollution by the surface

"Dry" uptake of a substance by elements of the underlying surface is determined by the intensity of turbulent transport of the substance from the atmosphere to the surface, by the transport intensity through a thin laminar layer adjacent to the surface and by physical-chemical properties of the surface itself. Usually "dry uptake" process is described in terms of resistance: turbulent, laminar and surface. To contrast "dry uptake" and wet absorption is of no sense, since "dry" absorption is a process taking place continuously independent of atmospheric precipitation occurrence. During a precipitation event only characteristics of the underlying surface are changed (as a rule wet surface more easily traps molecules or particles from the atmosphere particularly if substances are water soluble).

At the model parametrization the notion "dry deposition velocity" is often used though this term is conventional for gases and fine particles not subjected to own gravitational sedimentation. More logical to use the term "dry uptake velocity" which formally has the dimension of linear velocity. If a flux is directed from the underlying surface to the atmosphere the linear velocity can be negative. Actually we deal as a rule simultaneously with both deposition and emission fluxes. In this case the value and sign of the linear velocity are described by the resulting flux (Meyers et al., 1996).

For elemental mercury vapors especially in the vicinity of sources, where concentration levels are elevated, dry uptake of Hg^0 by plants through stomata is possible. In literature there is a great number of values for linear velocities of elemental mercury dry uptake. These data are obtained both in experiments (observations carried out under crowns of trees, micrometeorological gradient method) and by expert estimates on the basis of the comparison of mercury properties and its compounds with species fairly well studied (sulfur and nitrogen

compounds). Experimental data and expert estimates of dry uptake velocities of various forms of mercury and underlying surface types are presented in table 4.2.

Table 4.2 Estimates of dry uptake linear velocities of different mercury forms

Mercury form	Surface type	Uptake linear velocity, cm/s	Reference
Hg ⁰	Summer forest	0.03	Petersen et al., 1996
Hg ⁰	Winter forest	<<0.03	
Hg ⁰	Other surfaces	0	
HgCl ₂	Middle latitudes	as for HNO ₃	
ΣHg _(particles)	Middle latitudes	as for SO ₄ ⁼	
Hg ⁰	Deciduous forest: summer	0.1	Lindberg et al., 1991
Hg ⁰	: winter	<0.01	
Hg ⁰	Deciduous forest: summer	0.12	Lindberg et al., 1992
Hg ⁰	: summer, night	0.04	
Hg ⁰	: summer daytime 10°C	0.06	
Hg ⁰	: summer, day, 15°C	0.09	
Hg ⁰	: summer, day, 20°C	0.11	
Hg ⁰	: summer, day, 25°C	0.16	
Hg ⁰	: summer, day, 30°C	0.20	
Hg ⁰	: winter	0.006	
Hg ⁰	Typical landscape of middle latitudes	0.05-0.1	Expert Panel..., 1994
Hg ^{II} _(gas)		as for HNO ₃	
Hg ⁰	Typical landscape of middle latitudes	0.03	Bloxam et al., 1996
ΣHg _(gas)	Sweden, winter	~0	Iverfeldt, 1991
ΣHg _{(particles), <0.5 μm}	Typical landscape of middle latitudes	0.1	Lamborg et al., 1995
ΣHg _{(particles), 2 μm}		0.5	
ΣHg _(particles)	Region of the Great Lakes	0.5	Fitzgerald et al., 1991
ΣHg _(particles)	Water	0.2	Schroeder, 1996.
ΣHg _(particles)	Typical landscape of middle latitudes	0.1-0.5	Lindqvist and Rodhe, 1985
Fine particles (like for cadmium)	Coniferous forest	5.5	Müller, 1990
	Deciduous forest	1.8	
	Grass	0.1	
	Water	0.03	

Dry uptake can condition a substantial part of mercury scavenging from the atmosphere. On the regional and local levels its contribution varies in sufficiently wide ranges depending on the underlying surface type, climatic peculiarities of a region and the ratio of mercury forms in emissions.

On the basis of data presented in table 4.2 it is supposed that for land during May - October included linear velocity of elemental mercury dry uptake is equal to 0.03 cm/s, during other months - 0.01 cm/s if near the surface temperature is positive. Otherwise there is no dry uptake. For the sea surface this velocity is always accepted to be zero.

For oxidized gaseous inorganic mercury dry absorption velocity is assumed to be 0.5 cm/s irrespective of season and the underlying surface type. For DMM absence of dry uptake is assumed.

Dry uptake velocity of aerosol particles containing mercury is calculated using the approach suggested by M.Pekar (1996) depending on wind speed and underlying surface roughness. The velocity values vary in the range from 0.02 to 0.2 cm/s.

5. Model verification base

A.Ryaboshapko and V.Korolev (1997) showed that measurement data on mercury concentrations and deposition available for Europe are very contradictory. Experimental data obtained in Germany and Sweden seem to be most reliable. These data for 1988 were used by G.Petersen et al. (1995) for testing of their airborne transport mercury model. According to this data set elemental mercury concentrations measured in the atmosphere over Central Europe were within the range of 3-5 ng/m³, aerosol mercury - from 0.05 to 0.1 ng/m³. Over the EMEP region periphery the observed elemental mercury concentration field was rather uniform and its values varied from 1.5 to 3 ng/m³. Concentrations of the aerosol form were less than 1% of the total gaseous mercury.

Mercury concentrations in atmospheric precipitation and mercury deposition were characterized by higher gradients from the center to periphery. In the northern part of Germany in 1988 typical concentrations recorded were at the level of 50 ng/l. Further to the north concentrations in precipitation decreased to about 10 ng/l (northern Sweden). Total deposition (dry and wet) in southern Sweden observed were on the level of 30 g/km²/yr and in the northern part - 5 g/km²/yr.

It is necessary to keep in mind that the data used by G.Petersen et al. (1995) and by A.Ryaboshapko and V.Korolev (1997) for validation of their models were obtained in the end of the 80-s. By the middle of the 90-s anthropogenic mercury emissions in many countries were considerably reduced. Especially sharp and quick reduction took place in Germany just after the unification in 1989. The changes in anthropogenic emissions were reflected in dropping of atmospheric concentration levels (Slemr and Scheel, 1998). Since the calculations of this work were made with the emission base of the 90-s therefor the concentration and deposition values obtained can be 1.5-2 times lower than observed ones during the 80-s.

During the 90-s observations of mercury content in air and precipitation remain to be very sparse. The accuracy and reliability of experimental data in many cases provoke serious doubts. Below observational values are gathered which in our opinion can be used as the base for model verification.

Since the beginning of the 80-s regular observations of mercury concentrations in the atmosphere over the south-western coast of Sweden were carried out (Iverfeldt et al., 1995). At the beginning of the 90-s the concentrations noticeably decreased. The mean value of TGM concentration amounted to 2.7 ng/m³.

In the framework of EMEP only two stations provided monitoring of TGM concentrations during the 90-s: Norwegian stations Spitzbergen in the Arctic and Lista in the southern part of the country (Berg et al., 1996). The mean value for the period of 1994-1995 at Spitzbergen was 1.7 ng/m^3 and at Lista during 1992-1993 - 1.95 ng/m^3 .

Regular observations of TGM were made in southern Germany at the height of 1780 m above the sea level (Slemr and Scheel, 1998). The authors demonstrated obvious practically linear decreasing of TGM concentrations from 3 to 2 ng/m^3 during the period of 1990-1996. The mean value for 1990-1995 period was 2.5 ng/m^3 (Slemr, 1996). However, one should remember that the data obtained at about 2 km height reflect rather global trends than the processes in Europe.

In near-surface layer of the atmosphere TGM concentrations were measured over Germany at three stations located in regions of different mercury pollution levels: Bitterfeld, Langenbrügge and Zingst. Mean concentration values for 1992-1994 period were 8.2, 4.2 and 2.5 ng/m^3 respectively (Petersen et al., 1996).

Monitoring of TGM in the central part of southern England during a year (1995-1996) revealed a considerable temporal variability of concentrations around average value of 1.68 ng/m^3 (Lee et al., 1998). The background TGM concentration in unpolluted air masses was estimated as 1.5 ng/m^3 . Observations in western Ireland at Mace Head at the beginning of the 90-s showed that in Atlantic air masses the concentration was about 1.5 ng/m^3 while in air masses coming from the continent concentrations were obviously higher (about 2.5 ng/m^3) (Ebinghaus et al., 1996). Taking into account the fact that probabilities of wind from the ocean and from the continent were roughly equal it is possible to suggest that the mean TGM concentration in western Ireland at the beginning of the 90-s was about 2 ng/m^3 .

Relatively short campaign of TGM observations (two summer months in 1995) was carried out by S. Schmolke (1995) at 4 stations located in the meridian direction. The maximum concentration of 2.1 ng/m^3 was recorded at the most southern station Neuglobsow in Germany. Northward concentrations dropped: 1.83 ng/m^3 on southern Baltic coast (Zingst station), 1.54 ng/m^3 on south-western coast of Sweden (Rörvik station), 1.51 ng/m^3 at Aspöret station (the eastern part of central Sweden). It should be noted that the observed values could be somewhat lower than mean annual ones because the observations were performed during summer time.

Routine measurements of particulate mercury in the 90-s were provided by only one station in southern Norway. According to V.L. Foltescu et al. (1996) average concentration of mercury bound up with fine particles was about 0.04 ng/m^3 .

Monitoring of mercury in atmospheric precipitation is carried out only by few European stations. The data from three of them operated under HELCOM seem to be rather reliable (HELCOM, 1997). In 1993 on German coast of Baltic (Zingst station) average mercury concentration in precipitation was about 20 ng/l . In 1994 in southern Sweden (Vavihill station) the value was lower - 14 ng/l and in the central part of Sweden it was practically the same - 18 ng/l .

In the period of 1992-1994 monitoring of mercury in precipitation was carried out in Germany by GKSS Research Center (Petersen et al., 1996) at three stations (Bitterfeld, Langenbrügge and Zingst) located in different distances from major mercury anthropogenic

sources (Halle-Leipzig region). Mean concentration values for the period of 1992-1994 were 462, 52 and 49 ng/l correspondingly. Note that for Zingst station this value is 2 times higher than the data obtained within HELCOM (1997).

6. Model calculation results of mercury concentrations and deposition in the EMEP region

The developed version of the operational model was used for calculations of mean annual concentrations of mercury in air and precipitation as well as its deposition. The calculations were aimed at the acquisition of mercury concentration and deposition patterns in the EMEP region and at the comparison of them with observations. Separate calculations were performed both for natural sources and for a combination of natural and anthropogenic (including re-emission) sources. It allows us to assess spatial distribution of the anthropogenic impact on natural atmospheric mercury cycle.

6.1 Natural levels of mercury concentrations and deposition in the EMEP region

It was estimated earlier that before the beginning of human activity mean concentration of natural elemental mercury in the atmosphere was 1 ng/m^3 . Relevant equilibrium concentration of mercury in aerosol form was 0.007 ng/m^3 . Obviously under the impact of local geophysical factors concentration values of these mercury forms could differ from mean values.

Fig. 6.1 shows the calculated field of natural concentrations of mercury in the surface layer of the atmosphere in the EMEP region. As evident from the figure the zone of elevated concentrations is located along the southern boundary of Europe indicating the effect of the mercury geochemical belt (see fig. 3.1). In the north direction concentrations decrease to 0.9 ng/m^3 since in northern Europe there are no natural sources and due to removal processes the concentration becomes even lower than the accepted global level. Calculations show that the mean natural concentration of elemental mercury is 1.07 ng/m^3 for the region on the whole. It means that before the beginning of human activity the EMEP region relative to elemental mercury was practically in a full geochemical equilibrium with the Earth atmosphere.

The most important sink of aerosol mercury is washout by precipitation. Aerosol mercury natural concentrations vary within a factor of 3 over the region. Minimum values (0.003 ng/m^3) are characteristic of the western coast of Norway and maximum ones (0.01 ng/m^3) - of southern part of EMEP region where precipitation amount is minimum.

The concentration field of natural mercury in precipitation (fig. 6.2) is rather uniform in Europe. For the majority of the region values are within the range of 3 to 5 ng/l. In fig. 6.2 a zone of elevated concentrations is distinguished in northern Africa. These elevated concentrations are conditioned by the fact that aerosol substance is removed from the atmosphere by relatively small amount of precipitation.

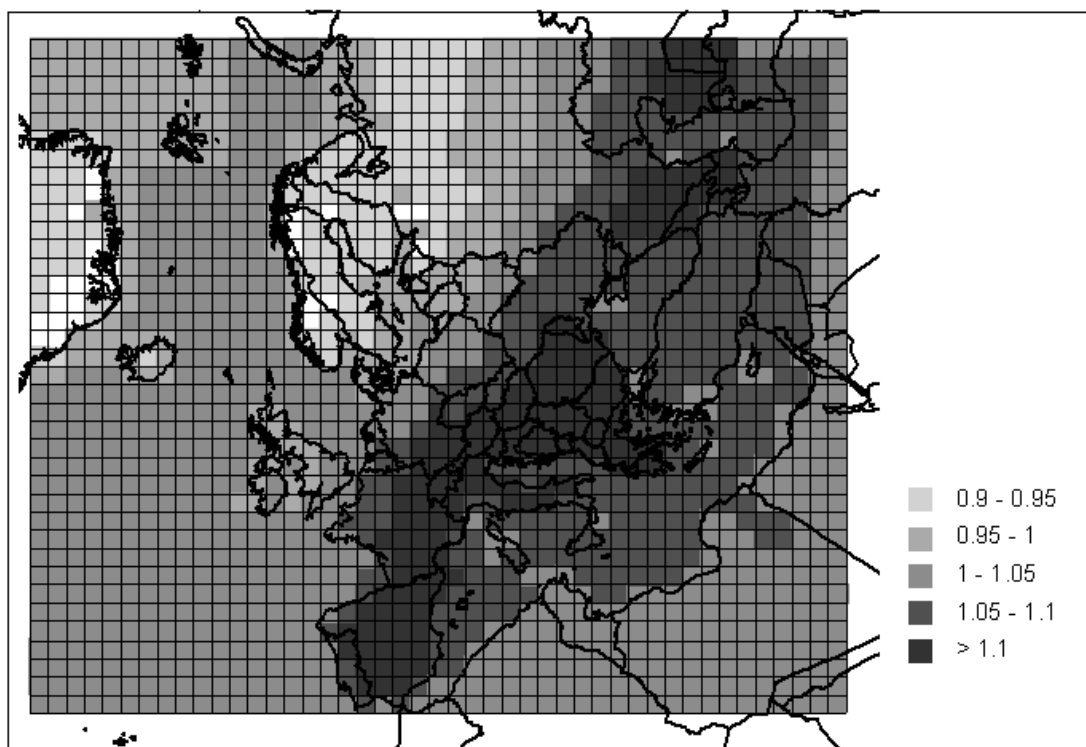


Figure 6.1 Calculated natural mercury concentration field in surface layer in the EMEP region, ng/m^3

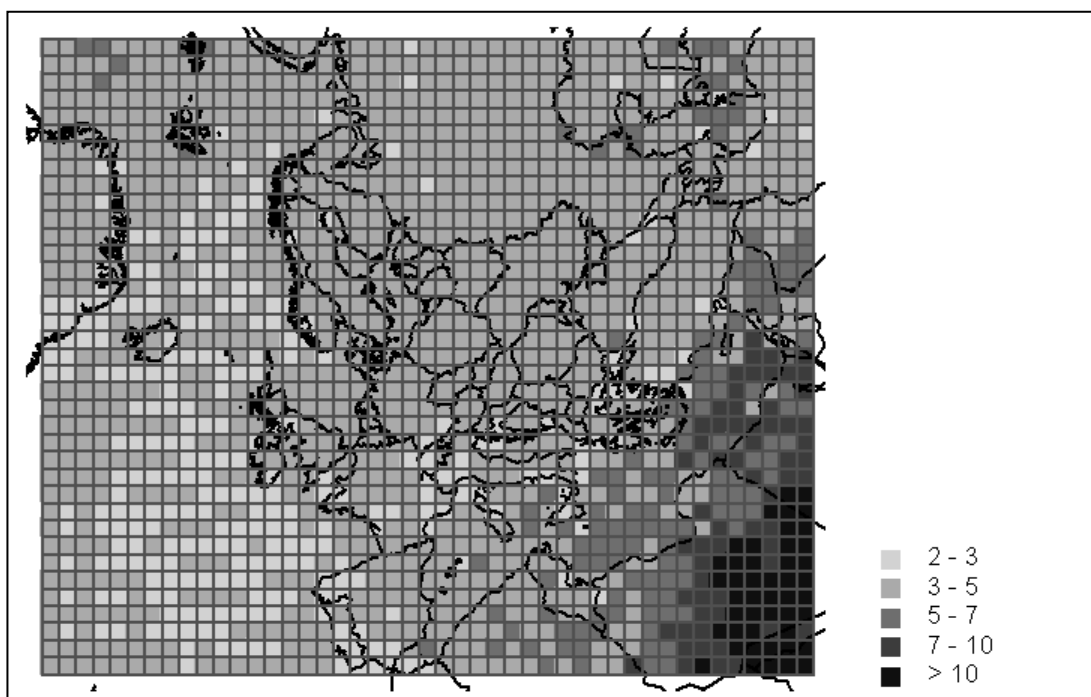


Figure 6.2 Calculated field of natural mercury concentration in atmospheric precipitation in the EMEP region, ng/l

The pattern of natural mercury deposition from the atmosphere is determined by several factors: airborne concentration fields of both mercury forms, dependence of dry uptake velocity on seasonal variations of meteorological elements and seasonal peculiarities of the underlying surface, precipitation field configuration. The total (dry and wet) deposition field of both mercury forms is presented in fig. 6.3. In accordance with the model computational scheme between two mechanisms of natural mercury scavenging from the atmosphere dry uptake is most efficient. Since it is assumed that dry absorption by the marine surface is absent the field of total deposition actually repeats the continent contours: over seas the deposition intensity is 1-2 g/km²/yr, whereas over land - 6-10 g/km²/yr. Maximum deposition complies with the zone of the geochemical mercury belt in southern Europe. In addition enhanced deposition zone is found on the western coast of Norway. It is connected with a considerable precipitation intensity.

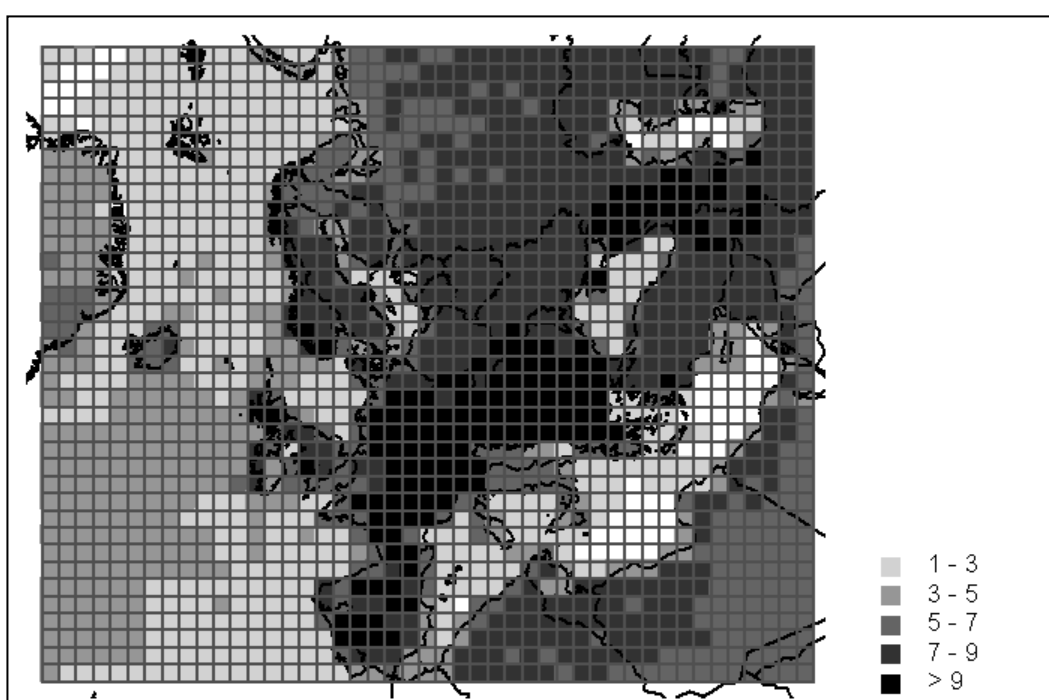


Figure 6.3 Field of natural total deposition (dry and wet) of elemental and aerosol mercury forms, g/km²/yr

For southern Europe the contribution of dry uptake of natural mercury from the atmosphere by the land surface to total deposition is about 75%. For the central and eastern parts of Europe this value is 60-70%. For most rainy regions of Norway the contribution of wet deposition of natural mercury can reach 50%.

The vertical distribution of the two forms of mercury in the atmosphere is practically uniform. Clearly in regions with high natural emissions surface concentrations are somewhat higher than at the height of the boundary layer. For the aerosol component maximum concentration correspond to the third and fourth layers of the model. It is conditioned by the fact that according to the computational scheme the most important mechanism of aerosol mercury formation is the evaporation of cloud drops.

On assumptions used for emissions and the degradation rate of methylated mercury values of its calculated concentrations are within the limits of 0.005-0.01 ng/m³ in the lowest model layer. The concentration of the methylated form sharply decreases with height due to its relatively short life-time. Very low concentrations obtained and weak solubility in water cannot explain actual concentrations of methylated mercury observed in atmospheric precipitation.

6.2 Mercury concentrations and deposition in the EMEP region conditioned by the operation of all sources

The evaluation of mercury concentration and deposition levels in the EMEP region was made on the basis of total emission field represented by all the sources considered above. Direct anthropogenic emission values were estimated for 1990 and meteorological fields were taken for 1995. With allowance made for high uncertainty of input parameters it may be considered that calculated concentration and deposition values characterize the situation in the EMEP region for the first half of the 90-s.

It should be repeated that calculations deal with four mercury forms: gaseous elementary, aerosol, gaseous inorganic oxidized and gaseous methylated mercury. Each form is characterized by considerably different removal parameters; this fact determines a complicated configuration of concentration and deposition fields.

Verification of the model was performed by comparison of the observational data obtained for the 90-s (see Section 5) and the calculation results. Besides, these calculation results are compared with the model results obtained by G.Petersen et al. (1995) and by A.Ryaboshapko and V.Korolev (1997).

Comparison of the observational data with the calculation results for TGM, particulate mercury and mercury in precipitation is shown in Table 6.1. The table also presents a «discrepancy factor - DF» which is the ratio of greater value to lower one. As follows from the table that for TGM the calculation values nearly coincide with the observational ones. Only in one case the discrepancy factor exceeds the value of 2. For regions remote from the main mercury sources the difference between the calculation and observation results is on the level of 30%. For particulate mercury the discrepancy is rather high - the observations exceed the calculations by a factor of 4. Most probably, it is caused by underestimation of the rate of atmospheric particulate mercury formation in the model. As for precipitation mercury, the discrepancy factor equals on the average to 2.

Table 6.2 shows the comparison of observed and calculated concentrations of mercury various forms in the atmosphere. It should be reminded that the modelling estimates obtained by G.Petersen et al. (1995) and by A.Ryaboshapko and V.Korolev (1997) are referred to the end of the 80-s when anthropogenic emission in Europe was 1.5-2 times higher than at the beginning of the 90-s. The comparison demonstrates that the model results (with regard to emission reduction) are in a good agreement with observed elemental mercury concentrations and with calculation results obtained by G.Petersen et al. (1995). The current model describes the meridian gradient of elemental mercury concentrations much better than the previous version (Ryaboshapko and Korolev, 1997).

Table 6.1 Comparison of calculated and observed values of mercury concentrations

Country	Station	EMEP cell coordinates		Concentrations		DF
		X	Y	Observation	Calculation	
<i>Concentrations of gaseous mercury in air, ng/m³</i>						
Germany	Bitterfeld	23	17	8.2	7.9	1.0
	Langenbrügge	21	17	4.2	2.37	1.8
	Wank Mt.	23	14	2.5	1.56	1.6
	Neuglobsow	22	18	2.1	5.55	2.6
	Zingst	21	19	2.5	2.65	1.1
	Zingst	21	19	1.83	2.65	1.4
Sweden	Rörvik	19	21	2.7	1.60	1.7
	Rörvik	19	21	1.54	1.60	1.0
	Aspvreten	20	23	1.51	1.63	1.1
Norway	Lista	17	20	1.95	1.55	1.3
	Spitzbergen	9	31	1.7	1.44	1.2
Great Britain	Harwell	17	13	1.7	2.04	1.2
Ireland	Mace Head	13	13	2	1.56	1.3
<i>Concentrations of particulate mercury, ng/m³</i>						
Norway	Lista	17	20	0.04	0.01	4
<i>Concentrations of mercury in atmospheric precipitation, ng/l</i>						
Germany	Bitterfeld	23	17	462	178	2.6
	Langenbrügge	21	17	52	34	1.5
	Zingst	21	19	49	53	1.1
	Zingst	21	19	20	53	2.7
Sweden	Vavihill	20	20	14	31	2.2
	Aspvreten	20	23	18	13	1.4

The comparison of mercury concentrations in precipitation observed in Germany and Sweden, of calculated values obtained by G.Petersen et al. (1995) as well as by A.Ryaboshapko and V.Korolev (1997) with our modelling results is shown in Table 6.3. When comparing the data one should not forget about 1.5-2 times reduction of anthropogenic emissions. Analysis of table 6.3 data shows that the current version of the model describes spatial features of the fields of concentrations in precipitation much better than the previous one (Ryaboshapko and Korolev, 1997) and complies better with the data of G.Petersen et al., (1995).

Table 6.2 Comparison of modeling and observational (before 1990) mercury concentration values in air, ng/m³

EMEP cell (X-Y)	Monitoring station	Observations [Petersen et al., 1996]		Model calculations for 1988 [Petersen et al., 1995]		Model calculations for 1988-1989 [Ryaboshapko and Korolev, 1997]			Model calculations for the 90-s, this work		
		Hg ⁰	Particulate	Hg ⁰	Particulate	Hg ⁰	Particulate	Oxidized gaseous	Hg ⁰	Particulate	Oxidized gaseous
23-17	Bitterfeld	8.2	-	10.1	0.28	40	4.4	2.6	5.5	0.21	0.39
22-18	Neuglobsow	-	-	4.9	0.21	16	0.5	0.4	5.2	0.22	0.37
21-17	Langenbrüge	4.2	-	4.1	0.11	-	-	-	2.3	0.06	0.07
21-19	Zingst	3.6	-	3.6	0.11	6	0.1	0.2	2.5	0.073	0.092
19-20	Rörvik	2.8	0.06	2.5	0.025	3.8	0.1	0.05	1.7	0.029	0.017
20-22	Aspvreten	-	-	2.5	0.019	2.6	0.01	0.05	1.7	0.012	0.005
17-26	Vindeln	2.5	0.05	2.1	0.005	2.4	<0.01	<0.01	1.4	0.006	<0.001
14-28	Overbygd	2.6	-	2.1	0.002	2.6	<0.01	<0.01	1.4	0.004	<0.001

Table 6.3 Comparison of modeling and observational (before 1990) values of concentrations in precipitation (ng/l) and of wet deposition (g/km²/yr)

EMEP cell (X-Y)	Monitoring station	Observations [Petersen et al., 1996]		Model calculations for 1988 [Petersen et al., 1995]		Model calculations for 1988-1989 [Ryaboshapko and Korolev, 1997]		Model calculations for the 90-s, this work	
		Concentration	Wet deposition	Concentration	Wet deposition	Concentration	Wet deposition	Concentration	Wet deposition
23-17	Bitterfeld	462	-	331	114	1380	772	155	129
22-18	Neuglobsow	-	-	234	95	409	255	176	103
21-17	Langenbrüge	52	-	66	-	-	-	34	25
21-19	Zingst	49	-	62	46	47	60	50	29
19-20	Rörvik	35	27	17	15	16	18	21	12
20-22	Aspvreten	18	10	17	10	18	11	13	8
17-26	Vindeln	11	7.3	7.0	4.9	7	4	7	5
14-28	Overbygd	9	5.0	3.9	2.1	2	3	5	5

Fig. 6.4 presents total concentration distribution of all mercury forms in the surface atmospheric layer. The figure demonstrates that the highest airborne concentrations ($>6 \text{ ng/m}^3$) are characteristic of Central Europe where maximum emission intensity is observed. In these region the total concentration is mainly determined by elemental mercury, however, in the vicinity of anthropogenic sources the contribution of particulate and oxidized gaseous forms can be noticeable (0.3 and 0.4 ng/m^3 respectively). As we move away from main anthropogenic sources the total air concentration of mercury decreases and a relative contribution of the elemental form increases. On the whole mercury concentrations within the range from 2 to 4 ng/m^3 are characteristic of European countries.

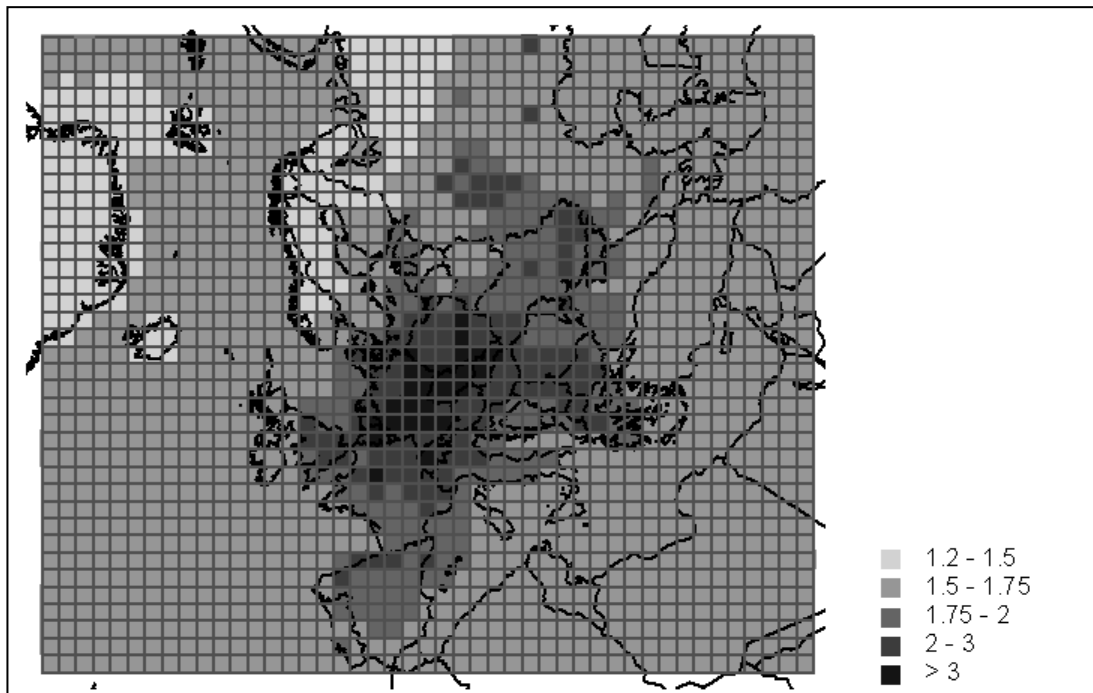


Figure 6.4 Current spatial distribution of total concentrations of all mercury forms in surface layer in the EMEP region, ng/m^3 .

Mercury concentration in precipitation is determined by scavenging of three forms of considered ones. Fig. 6.5 demonstrates mean annual mercury concentrations in precipitation. It is evident from the figure that concentrations in precipitation decrease sharply with distance from Central Europe.

Mercury deposition field is formed by wet and dry deposition of three different forms of mercury (DMM is removed only by photochemical decomposition) which emissions are considered in this model. Aerosol and oxidized gaseous forms are most efficiently removed from the atmosphere. Reasoning from this it can be expected that deposition field on the underlying surface should be similar to the concentration field of these forms in air. In other words deposition should be maximum near anthropogenic sources. Fig. 6.6 shows the calculated field of total deposition in the EMEP region. The figure demonstrates that in industrial regions of Central Europe deposition values can be as much as $300 \text{ g/km}^2/\text{yr}$. When moving far away from sources deposition intensity sharply decreases and in remote regions of Europe it is from 5 to $20 \text{ g/km}^2/\text{yr}$.

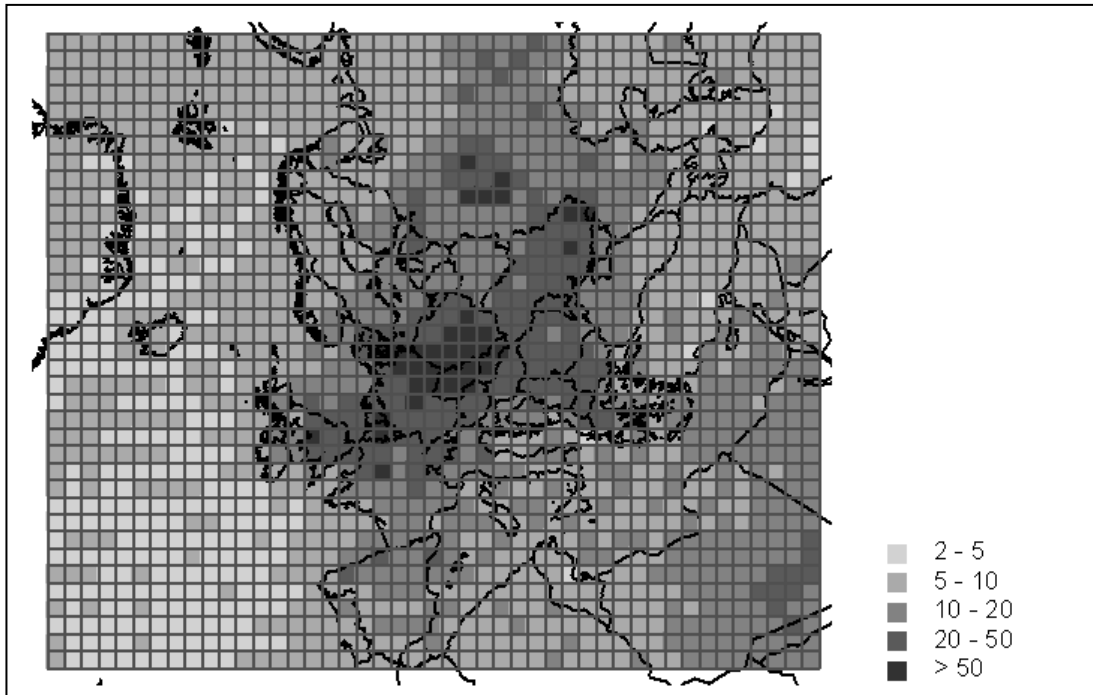


Figure 6.5 Current mean annual mercury concentration in atmospheric precipitation of the EMEP region, ng/l

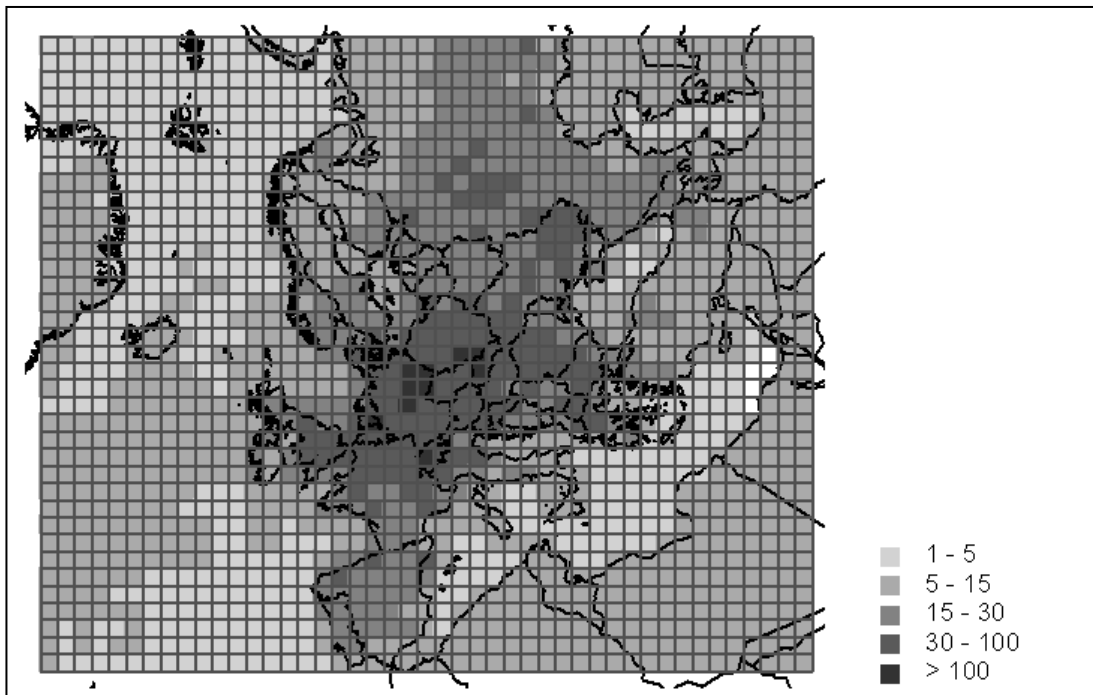


Figure 6.6 Calculated field of current mercury total deposition in the EMEP region, g/km²/yr

Table 6.4 shows percentage contribution of individual forms to wet and dry deposition. In the vicinity of emission sources relatively short-lived "regional" forms - aerosol and oxidized gaseous - predominate in both wet and dry deposition. The input of elemental mercury, which can be considered as "global" pollutant, is growing with the distance from major sources.

Table 6.4 Relative contribution of various mercury forms to wet and dry deposition, %.

EMEP cells (X-Y)	Wet deposition			Dry deposition			Contribution of dry deposition to total one
	Hg ⁰	Particulate	Oxidized gaseous	Hg ⁰	Particulate	Oxidized gaseous	
22-17	6	72	22	30	11	59	46
22-18	4	73	23	30	9	61	50
21-17	17	54	29	47	11	42	54
21-19	8	64	28	30	8	62	46
19-20	14	36	50	58	8	35	40
20-22	25	42	33	78	8	14	42
17-26	35	52	13	92	6	2	63
14-28	38	59	3	95	4	1	42

It follows from the table that both at short distances from sources and in the periphery of the EMEP region contributions of dry and wet depositions are of the same importance. At present it is difficult to evaluate the competence of this statement since measurements of dry deposition are practically absent. Probably estimates of dry deposition velocities used in the presented scheme are somewhat overestimated.

H.Rodhe (1996) for the evaluation of the extent of the anthropogenic impact introduced the notion "amplification factor". Numerically it is equal to the ratio of mercury concentration in deep (free from anthropogenic impact) layers of peat bogs or bottom sediments to concentrations in modern layers. A similar approach is used in this work with the correction for the fact that we take the "amplification factor" as the ratio of modern levels of total mercury deposition to purely natural ones. The spatial distribution of the "amplification factor" with the EMEP region is presented in fig. 6.7. It follows from the figure that mercury input from the atmosphere has essentially changed as a result of human activity. Obviously, the anthropogenic load increased most of all in regions of major industrial sources - in Germany, Poland and the Eastern Ukraine. Here the "amplification factor" can exceed 10. In Sweden where mercury accumulation in peat bogs was measured this value varies from 2 to 6. These data are in a good agreement with data obtained in the analysis of mercury concentration profiles in peat bogs. At the periphery of the region (for example, in the north-eastern part of European Russia) the anthropogenic load of mercury increased in about 1.5-2 times.

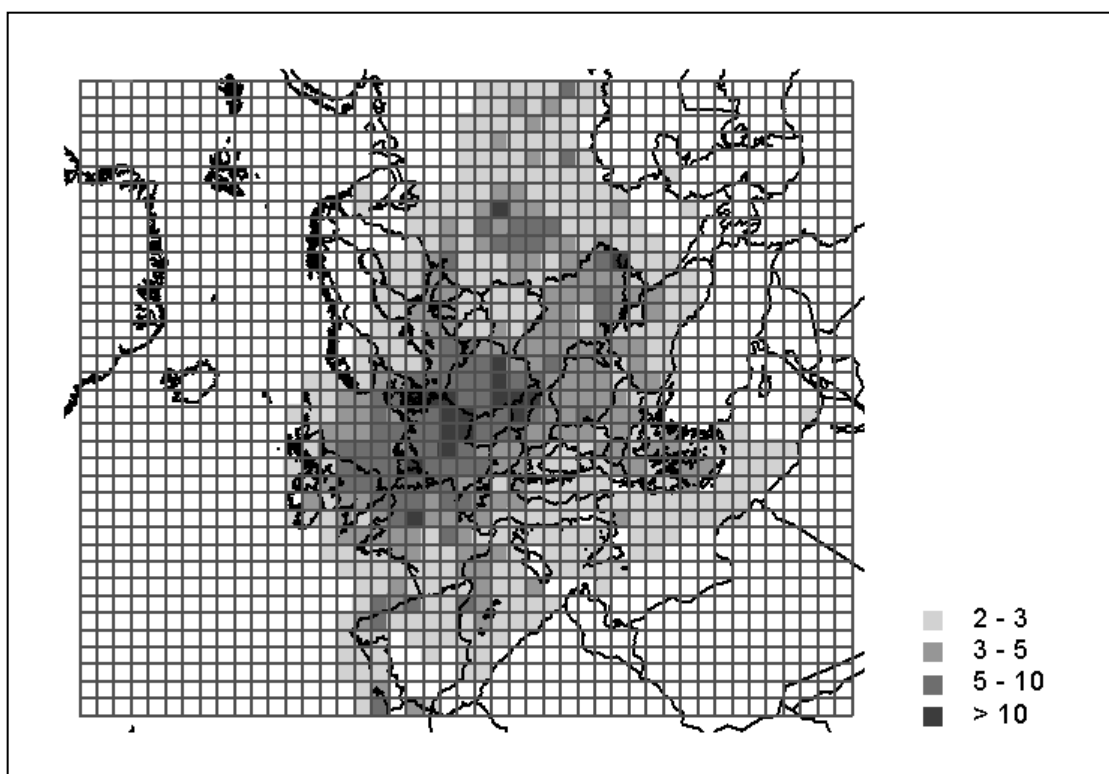


Figure 6.7 Spatial distribution of «amplification factor» with the EMEP region

6.3 Atmospheric mercury budget in the EMEP region

A general idea on the impact of the anthropogenic activity on the mercury atmospheric cycle and on the seriousness of the problem at European scale can be visualized from the totality of income and outcome items of the mercury atmospheric budget. The calculations made allowed us to evaluate each component of the budget and to compile the mercury budget for the EMEP region on the whole. The budget was calculated for the «EMEP reservoir» of area $6750 \times 5550 \text{ km}^2$ and height 2100 m. Individual budget items are summarized in table 6.5.

Table 6.5 Atmospheric budget of mercury in the EMEP region, t/yr

Budget item	Mercury form				
	Hg^0	$\text{Hg}^{+2}_{\text{gas}}$	$\text{Hg}^{+2}_{\text{part}}$	DMM	ΣHg
Total emissions	483	132	67	27	709
Natural emissions	194	0	0	22	216
Direct anthropogenic emissions	244	132	67	0	443
Anthropogenic re-emission	45	0	0	5	50
Advection transport in the region	4621	0	32	0	4653
Vertical transport from the free troposphere	7570	0	50	0	7620
Total deposition	214	104	204	0	522
Dry deposition	197	45	23	0	265
Wet deposition	17	59	181	0	257
Advective transport outside the region	4718	2	48	1	4769
Vertical transport to the free troposphere	7605	3	80	<0.5	7688

The consideration of the budget components shows that anthropogenic emission of elemental gaseous mercury only to small extent determines its occurrence in the EMEP reservoir and in deposition on the underlying surface. The bulk of elemental mercury deposition is conditioned by the global background level in the Earth atmosphere. Out of 244 tons of elemental mercury emitted in the EMEP domain during a year only 12% is deposited in this region, the bulk is exported outside the region and enters the global mercury cycle. Emissions of mercury compounds in the forms of gaseous compounds and aerosol particles are more significant in view of the environment of the region. Just these forms determine high levels of deposition in Central Europe. Only 8% of gaseous mercury compounds and 13% of aerosol mercury are transported outside the region.

Similar estimates were obtained by mathematical simulation in the USA: only a small part of deposition was determined by national emissions of elemental mercury (EPA, 1997). Its main part is transported outside the country. The bulk of deposition in the USA resulted from emissions of gaseous oxidized compounds (70% is deposited within the country) and aerosol particles containing mercury (38% is deposited within the country). A regional character of environmental problem of oxidized mercury compounds was confirmed earlier by model calculations of Ir.Bullock (1996) and R.Bloxam et al. (1996).

Essential anthropogenic emissions in some countries and sufficiently long life-time of all mercury forms in the atmosphere create prerequisites to give a rise to the problem of transboundary pollution. In the framework of EMEP for short it is accepted to code the names of the countries, regions, seas as it is shown in Table 6.6. Seas and the Arctic (within the EMEP grid) are given as conventional «countries». Traditionally an assessment of «country-by-country» impact is based on deposition values on the *i*-th country resulted from anthropogenic emissions in the *j*-th country. Table 6.7 presents «country-by-country» deposition matrix of mercury for the EMEP region. In the matrix the countries-emitters are placed in rows and the countries/regions/seas-receivers are placed in columns. In addition to countries-emitters natural sources within EMEP region (code NAT) and unidentified anthropogenic sources (code AAC) which include re-emission within the region and anthropogenic part of global mean mercury concentration are also considered. Table data give a possibility to determine the deposition budget for each country. Clearly, contributions of various countries to deposition to a given country can be considerably different.

To facilitate the comprehension of the situation in each country-receiver Table 6.8 shows data on three most important country-emitters. Besides, the table presents per-cent contribution of these country-emitters to total deposition on the territory of each country-receiver as well as contribution from own emission sources. As seen from the table that Germany is the main transboundary mercury source for many European countries. At the same time the contributions from own sources exceed as a rule the contributions from neighboring countries.

Table 6.6 Codes of countries, regions and seas

Countries, regions, seas	Code	Countries, regions, seas	Code
Albania	AL	Russian Federation	RU
Austria	AT	Slovakia	SK
Belarus	BY	Slovenia	SI
Belgium	BE	Spain	ES
Bosnia & Herzegovina	BA	Sweden	SE
Bulgaria	BG	Switzerland	CH
Croatia	HR	Ukraine	UA
Cyprus	CY	United Kingdom	GB
Czech Republic	CS	Yugoslavia	YU
Denmark	DK		
Estonia	EE	Armenia	AR
Finland	FI	Azerbaijan	AZ
France	FR	Georgia	GG
Germany	DE	Kazakhstan	KZ
Greece	GR	Malta	ML
Hungary	HU	Turkey	TR
Iceland	IS		
Ireland	IE	Asia	AS
Italy	IT	Africa	AF
Latvia	LV		
Lithuania	LT	Atlantic Ocean	ATL
Luxembourg	LU	English Channel	ECH
The FYR Macedonia	FYM	North Sea	NOS
Republic of Moldova	MD	Baltic Sea	BAS
Netherlands	NL	Mediterranean Sea	MED
Norway	NO	Black Sea	BLS
Poland	PL	Caspian Sea	CAS
Portugal	PT		
Romania	RO	The Arctic	ARC

Table 6.7 «Contry-by-country» matrix, kg

	al	at	by	be	ba	bg	hr	cy	cs	dk	ee	fi	fr	de	gr	hu	is	ie	it	lv	lt
al	83.0	1.9	0.0	0.7	1.3	11.1	2.3	0.0	1.8	0.4	0.1	0.1	6.1	12.2	155.9	3.0	0.0	0.1	27.3	0.0	0.0
at	0.3	908.6	0.0	23.3	0.6	1.1	10.9	0.0	203.2	8.7	0.6	0.8	82.6	648.3	1.5	57.0	0.0	1.1	109.3	0.1	0.0
by	0.2	11.2	27.1	10.8	0.2	4.9	1.1	0.0	44.3	27.9	17.6	8.7	24.8	343.5	2.3	20.0	0.0	1.1	4.9	11.1	0.2
be	0.0	0.5	0.0	927.8	0.0	0.0	0.1	0.0	2.8	5.8	0.1	0.1	583.5	568.0	0.0	0.3	0.0	2.2	1.4	0.0	0.0
ba	4.6	13.2	0.0	2.7	44.4	3.9	76.6	0.0	9.6	1.6	0.2	0.3	19.4	53.9	8.6	27.7	0.0	0.2	44.0	0.0	0.0
bg	5.1	9.8	0.1	3.3	1.0	1378.8	3.9	0.0	14.2	3.2	0.6	0.9	12.2	85.5	80.9	29.2	0.0	0.3	18.9	0.1	0.0
hr	2.0	29.0	0.0	4.0	17.0	2.7	166.9	0.0	13.3	2.0	0.2	0.3	29.2	74.8	5.9	75.3	0.0	0.3	80.5	0.0	0.0
cy	0.0	0.0	0.0	0.0	0.0	0.6	0.0	11.1	0.1	0.0	0.0	0.0	0.2	0.6	1.3	0.1	0.0	0.0	0.3	0.0	0.0
cs	0.1	256.2	0.1	22.8	0.2	0.7	2.2	0.0	1939.6	19.3	1.0	1.4	59.7	3664.3	0.6	33.8	0.0	1.2	13.9	0.2	0.0
dk	0.0	0.6	0.0	17.8	0.0	0.0	0.0	0.0	4.1	945.8	0.4	0.5	28.2	357.0	0.0	0.4	0.0	1.5	0.6	0.1	0.0
ee	0.0	0.7	0.3	3.5	0.0	0.3	0.1	0.0	4.1	12.6	298.2	55.0	6.7	100.5	0.2	0.9	0.0	0.4	0.5	11.0	0.0
fi	0.0	1.9	0.3	13.9	0.0	0.7	0.2	0.0	9.7	58.3	74.3	338.1	26.2	264.8	0.4	2.2	0.0	2.0	1.8	3.6	0.0
fr	0.2	8.8	0.0	897.0	0.2	0.9	1.8	0.0	23.9	29.0	0.9	1.3	9473.0	1366.6	0.7	3.7	0.1	19.5	196.5	0.2	0.0
de	0.1	141.6	0.1	568.3	0.2	0.7	2.0	0.0	835.2	264.2	2.7	3.3	1272.5	28208.0	0.7	14.2	0.1	11.8	61.8	0.6	0.0
gr	25.6	4.5	0.0	2.0	1.1	262.6	2.9	0.0	6.2	1.4	0.3	0.4	13.7	41.2	1055.3	9.1	0.0	0.2	28.0	0.1	0.0
hu	1.2	155.7	0.0	8.7	3.2	7.1	52.8	0.0	64.3	7.6	0.5	0.8	30.5	250.8	6.1	883.9	0.0	0.5	31.1	0.1	0.0
is	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.2	1.4	0.1	0.1	3.8	8.4	0.0	0.0	0.5	0.9	0.1	0.0	0.0
ie	0.0	0.2	0.0	6.4	0.0	0.0	0.0	0.0	0.7	2.3	0.1	0.1	20.3	23.7	0.0	0.2	0.0	239.0	0.3	0.0	0.0
it	2.5	83.2	0.0	20.4	2.2	4.7	23.5	0.0	22.9	3.9	0.3	0.6	318.8	231.9	8.4	15.3	0.0	1.4	2355.1	0.1	0.0
lv	0.0	1.5	1.6	5.1	0.0	0.6	0.1	0.0	9.0	16.6	81.9	9.2	10.5	166.9	0.5	2.0	0.0	0.5	0.9	59.3	0.2
lt	0.0	2.6	1.6	5.9	0.0	0.6	0.3	0.0	16.2	19.1	7.5	3.7	13.0	216.9	0.5	3.7	0.0	0.6	1.3	21.4	0.6
lu	0.0	0.1	0.0	15.3	0.0	0.0	0.0	0.0	0.3	0.3	0.0	0.0	83.7	30.1	0.0	0.0	0.0	0.1	0.2	0.0	0.0
fym	19.7	2.1	0.0	0.7	0.6	110.7	1.7	0.0	2.6	0.6	0.1	0.1	4.2	15.7	104.4	4.4	0.0	0.1	10.5	0.0	0.0
md	0.2	1.5	0.1	1.2	0.1	7.4	0.6	0.0	3.8	1.6	0.4	0.4	2.8	30.4	1.4	4.9	0.0	0.1	2.1	0.1	0.0
nl	0.0	0.4	0.0	306.5	0.0	0.0	0.0	0.0	3.6	11.6	0.1	0.1	138.1	813.4	0.0	0.2	0.0	2.5	0.8	0.0	0.0
no	0.0	1.1	0.1	24.9	0.0	0.2	0.1	0.0	6.9	90.5	2.1	5.7	62.1	272.8	0.1	1.2	0.1	6.0	1.6	0.3	0.0
pl	0.4	62.6	1.7	46.5	0.5	3.4	4.1	0.0	1264.5	153.4	6.0	6.9	107.2	4800.6	2.3	91.0	0.0	3.7	17.6	2.2	0.1
pt	0.0	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.1	0.6	0.0	0.0	14.3	7.0	0.0	0.0	0.0	0.9	0.2	0.0	0.0
ro	4.0	32.9	0.2	12.5	3.3	181.0	12.5	0.0	58.2	12.8	1.8	2.4	36.9	325.2	21.7	222.8	0.0	1.0	37.3	0.5	0.0
ru	2.2	27.8	8.6	59.6	1.1	80.5	5.5	0.4	98.8	126.8	323.3	191.1	134.9	1383.1	31.9	52.1	0.2	7.1	29.7	34.4	0.2
sk	0.3	118.9	0.0	6.6	0.4	1.7	4.5	0.0	127.0	7.4	0.4	0.7	19.3	219.9	1.6	251.3	0.0	0.4	9.6	0.1	0.0
si	0.2	62.7	0.0	2.2	0.7	0.3	18.3	0.0	6.2	0.8	0.1	0.1	12.0	36.2	0.8	10.5	0.0	0.1	37.6	0.0	0.0
es	0.1	0.6	0.0	29.9	0.1	0.2	0.3	0.0	1.2	3.5	0.2	0.3	355.9	74.9	0.2	0.2	0.0	4.7	11.1	0.0	0.0
se	0.0	3.1	0.2	33.5	0.0	0.5	0.3	0.0	19.6	479.3	14.4	38.4	61.0	716.7	0.3	4.4	0.1	5.0	2.7	2.3	0.0
ch	0.0	27.6	0.0	18.3	0.0	0.1	0.5	0.0	10.4	2.0	0.1	0.1	251.9	221.7	0.1	1.3	0.0	0.9	192.8	0.0	0.0
ua	2.4	31.8	4.7	23.7	1.6	85.7	8.7	0.1	84.4	37.7	10.1	9.2	55.6	636.8	23.6	125.1	0.0	2.4	28.7	2.9	0.0
gb	0.0	0.9	0.0	104.2	0.0	0.1	0.2	0.0	4.7	22.4	0.5	0.5	221.3	218.6	0.1	0.9	0.1	76.9	2.1	0.1	0.0
yu	19.1	23.6	0.0	4.2	10.3	88.2	21.9	0.0	19.6	3.1	0.4	0.6	21.5	105.1	30.6	89.5	0.0	0.3	41.8	0.1	0.0
ar	0.0	0.1	0.0	0.1	0.0	0.3	0.0	0.0	0.2	0.1	0.0	0.1	0.2	1.9	0.2	0.1	0.0	0.0	0.1	0.0	0.0
az	0.0	0.2	0.0	0.2	0.0	0.7	0.0	0.1	0.4	0.2	0.1	0.2	0.6	4.5	0.4	0.3	0.0	0.0	0.3	0.0	0.0
gg	0.1	0.4	0.0	0.5	0.0	2.3	0.1	0.2	0.9	0.4	0.2	0.2	1.2	8.9	1.2	0.8	0.0	0.0	0.6	0.0	0.0
kz	0.1	1.3	0.1	2.2	0.1	5.5	0.3	0.0	3.7	3.1	2.6	3.0	5.4	41.9	2.3	2.9	0.0	0.2	1.6	0.4	0.0
ml	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0
tr	3.5	8.6	0.2	6.2	0.8	182.0	3.2	18.3	15.9	5.1	1.8	2.6	24.9	130.5	151.4	16.9	0.0	0.6	26.5	0.4	0.0
as	0.9	2.6	0.1	2.6	0.2	21.3	0.8	17.2	4.6	1.9	0.9	1.3	11.3	45.3	31.7	3.8	0.0	0.2	10.0	0.2	0.0
af	8.6	13.9	0.1	19.5	2.3	75.3	8.3	1.7	15.8	4.9	0.7	1.2	164.4	171.3	184.2	16.9	0.0	1.7	149.0	0.2	0.0
atl	0.1	2.7	0.1	125.7	0.1	0.3	0.5	0.0	11.6	62.5	1.9	3.0	842.2	428.2	0.3	3.1	0.7	321.2	5.6	0.4	0.0
ech	0.0	0.3	0.0	41.2	0.0	0.0	0.1	0.0	1.2	4.1	0.1	0.1	318.9	61.3	0.0	0.2	0.0	7.8	0.8	0.0	0.0
nos	0.0	2.5	0.0	405.7	0.0	0.1	0.3	0.0	19.5	465.8	1.6	1.9	570.7	1402.3	0.1	1.9	0.0	34.1	4.7	0.3	0.0
bas	0.1	5.7	0.5	43.3	0.1	0.8	0.5	0.0	43.2	924.7	162.2	196.8	72.7	2219.1	0.7	6.8	0.0	4.3	3.7	17.9	0.1
med	60.8	35.3	0.1	33.5	10.9	232.9	69.0	60.4	27.5	9.1	0.9	1.4	1028.2	271.2	989.9	38.7	0.0	3.2	1341.7	0.2	0.0
bls	2.4	7.1	0.3	5.1	0.7	330.5	3.0	0.9	12.6	4.7	1.6	1.5	13.8	101.8	62.9	18.9	0.0	0.5	13.8	0.4	0.0
cas	0.0	0.3	0.0	0.5	0.0	1.2	0.1	0.1	0.8	0.6	0.4	0.4	1.2	8.6	0.7	0.7	0.0	0.0	0.4	0.1	0.0
arc	0.0	1.6	0.1	17.7	0.0	0.3	0.2	0.0	8.2	36.2	8.3	17.3	43.5	207.7	0.2	1.7	0.2	8.1	1.4	1.0	0.0
sum	250	2112	49	3943	106	3096	513	111	5103	3909	1031	913	16717	51701	2976	2156	2	779	4965	173	2

Table 6.7 continue

	lu	fym	md	nl	no	pl	pt	ro	ru	sk	si	es	se	ch	ua	gb	yu	aac	nat	sum
al	0.1	52.9	0.4	0.1	0.1	5.2	0.4	8.4	0.6	5.1	0.8	3.4	0.1	1.0	3.1	1.4	35.6	191	430	1047
at	3.4	0.5	0.2	6.3	1.2	152.6	0.7	4.8	3.4	173.4	89.6	5.3	0.9	80.8	4.9	28.6	6.9	615	1257	4493
by	1.0	0.6	8.8	4.0	5.2	520.4	0.4	18.9	209.4	84.0	1.1	2.7	4.9	4.3	421.5	24.2	4.3	957	1978	4812
be	43.1	0.0	0.0	95.1	0.5	5.2	0.7	0.1	0.6	1.2	0.1	5.3	0.3	5.0	0.6	128.1	0.1	195	353	2926
ba	0.3	3.8	0.3	0.6	0.3	19.9	0.5	10.8	1.2	25.8	10.9	5.1	0.2	4.4	3.9	4.3	58.8	358	807	1627
bg	0.3	37.2	15.5	0.9	0.7	44.8	0.5	406.8	12.4	52.3	2.1	4.1	0.6	3.0	96.9	6.2	89.0	761	1711	4893
hr	0.5	2.3	0.3	0.9	0.4	25.9	0.7	8.0	1.4	35.9	45.3	5.8	0.3	8.0	4.2	5.8	27.2	385	854	1915
cy	0.0	0.1	0.1	0.0	0.0	0.2	0.0	0.3	0.2	0.2	0.0	0.1	0.0	0.0	0.9	0.1	0.1	25	54	96
cs	2.8	0.3	0.3	8.6	2.2	762.4	0.5	4.9	5.7	376.7	3.5	3.6	1.7	19.3	10.0	32.3	4.5	693	1159	9109
dk	0.8	0.0	0.0	16.8	4.6	27.0	0.3	0.2	1.4	2.6	0.0	1.9	21.6	1.7	0.9	54.0	0.1	178	323	1993
ee	0.3	0.1	0.3	1.6	2.5	30.6	0.1	1.0	54.4	3.6	0.1	0.6	3.3	0.7	13.9	8.8	0.3	167	322	1105
fi	0.9	0.1	0.7	7.0	18.5	59.1	0.6	2.4	199.2	9.3	0.2	3.5	24.8	2.7	34.4	43.9	0.9	1142	2271	4620
fr	145.6	0.3	0.2	97.1	3.4	47.2	23.2	2.0	6.4	13.9	1.9	377.2	2.2	603.5	3.9	669.9	1.8	3069	6526	23619
de	118.3	0.3	0.3	275.8	10.6	536.1	3.3	3.8	14.2	72.6	5.2	24.8	10.4	474.7	13.1	375.5	3.2	2673	4504	40507
gr	0.2	140.4	4.4	0.4	0.4	20.3	0.8	37.0	4.6	17.6	1.3	6.9	0.3	2.3	30.5	4.0	35.1	629	1426	3816
hu	1.1	2.8	1.2	2.5	1.0	157.4	0.5	107.9	3.4	940.1	16.4	4.1	0.8	9.2	30.5	12.2	82.0	587	1230	4695
is	0.1	0.0	0.0	0.4	0.6	1.1	0.1	0.0	0.7	0.2	0.0	0.7	0.2	0.1	0.2	8.6	0.0	334	677	1041
ie	0.3	0.0	0.0	2.5	0.4	3.3	1.1	0.0	0.5	0.7	0.0	4.8	0.1	0.3	0.3	148.4	0.0	237	485	1178
it	2.7	2.5	0.3	3.6	0.9	36.8	3.9	7.3	2.5	29.9	42.5	42.5	0.6	346.8	4.3	31.8	11.4	1422	3101	8189
lv	0.4	0.1	0.7	2.1	3.4	79.8	0.1	2.2	48.2	8.3	0.1	0.9	4.5	1.1	29.7	11.7	0.7	247	494	1301
lt	0.5	0.1	1.1	2.3	3.3	182.6	0.2	3.5	99.5	15.9	0.2	1.1	4.0	1.7	35.7	13.2	1.0	298	593	1573
lu	21.7	0.0	0.0	0.8	0.0	0.5	0.0	0.0	0.0	0.1	0.0	0.4	0.0	1.1	0.0	4.0	0.0	16	30	206
fym	0.1	236.4	1.4	0.1	0.1	8.0	0.2	16.7	1.5	7.5	0.6	2.2	0.1	0.8	9.9	1.3	87.9	188	431	1272
md	0.1	0.5	145.2	0.4	0.3	21.3	0.1	74.0	9.7	13.8	0.3	0.6	0.2	0.6	213.7	2.4	4.7	171	377	1095
nl	3.0	0.0	0.0	375.6	1.1	6.9	0.5	0.1	0.7	1.2	0.0	3.6	0.5	2.5	0.5	132.0	0.1	189	343	2338
no	1.6	0.0	0.1	12.0	274.9	38.8	1.4	0.8	21.4	5.9	0.1	7.7	12.7	3.4	6.8	144.1	0.4	1205	2423	4636
pl	4.8	0.9	3.1	18.7	10.7	11605.5	1.2	32.7	91.6	753.3	4.4	7.6	11.4	19.8	203.6	87.5	11.8	1960	3393	24796
pt	0.1	0.0	0.0	0.9	0.2	0.4	592.2	0.0	0.2	0.1	0.0	146.9	0.1	0.2	0.1	10.8	0.0	431	956	2166
ro	1.3	10.2	92.8	3.8	2.2	230.6	1.0	2090.5	26.9	360.6	6.4	7.7	1.8	10.1	407.8	21.4	185.9	1465	3225	9117
ru	4.9	7.0	44.9	21.5	38.0	650.4	3.5	122.2	27534.1	173.3	4.3	21.4	33.7	19.5	3399.0	146.3	27.9	14643	30356	79850
sk	0.8	0.7	0.5	2.1	0.9	799.4	0.2	18.4	2.7	2368.4	5.0	1.8	0.8	5.0	37.4	10.1	11.3	361	666	5064
si	0.3	0.2	0.0	0.5	0.1	12.5	0.2	1.1	0.5	18.0	126.7	1.6	0.1	4.8	0.9	2.8	1.9	127	277	765
es	2.4	0.1	0.0	7.3	0.9	3.3	285.0	0.3	1.3	0.8	0.2	3386.8	0.5	8.2	0.6	66.8	0.3	2465	5724	12437
se	1.9	0.1	0.6	21.4	160.2	142.7	1.1	2.8	49.2	20.3	0.3	6.9	169.5	4.8	28.2	122.8	1.0	1615	3200	6930
ch	3.8	0.0	0.0	2.7	0.4	9.9	0.7	0.4	0.7	4.5	0.8	6.9	0.2	1847.9	0.6	24.4	0.3	337	656	3625
ua	2.2	7.0	310.7	8.5	6.1	685.0	1.3	325.8	980.6	436.5	5.7	8.7	5.5	11.8	10892.2	49.6	48.1	3209	6768	24937
gb	2.9	0.0	0.0	42.9	3.0	18.1	4.1	0.3	3.3	3.7	0.2	22.8	1.2	3.1	1.6	5006.6	0.2	1121	2186	9075
yu	0.5	48.9	2.7	1.0	0.6	44.1	0.7	148.4	3.2	57.7	5.5	6.7	0.5	5.4	21.8	7.0	901.9	644	1464	3844
ar	0.0	0.0	0.1	0.0	0.0	0.8	0.0	0.4	8.9	0.4	0.0	0.1	0.0	0.0	5.4	0.2	0.1	168	411	599
az	0.0	0.1	0.3	0.1	0.1	2.0	0.0	0.9	37.3	1.0	0.0	0.2	0.1	0.1	13.9	0.4	0.2	400	965	1430
gg	0.0	0.2	0.9	0.1	0.1	3.6	0.0	2.7	113.8	2.3	0.1	0.3	0.1	0.2	33.3	0.8	0.6	372	894	1443
kz	0.2	0.4	3.0	0.7	1.0	19.4	0.3	7.7	592.1	8.5	0.2	1.4	0.8	0.8	182.2	4.6	1.6	2220	5081	8203
ml	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	1	2
tr	0.5	12.4	20.5	1.5	1.5	58.0	1.3	80.1	131.3	42.2	1.9	11.7	1.4	4.8	319.4	12.1	22.9	3859	8884	14066
as	0.2	3.0	4.0	0.5	0.7	18.1	0.7	13.2	84.5	9.9	0.5	5.3	0.6	2.1	96.1	4.9	5.1	6934	16064	23404
af	1.7	22.2	5.2	3.4	1.2	46.5	29.8	39.6	9.7	33.2	4.1	218.2	1.0	21.7	40.1	32.7	33.6	13441	29846	44670
atl	5.6	0.1	0.2	53.9	61.3	56.8	496.7	1.0	18.1	12.4	0.5	1387.6	4.7	7.0	6.6	1721.9	0.8	11956	25084	42686
ech	1.1	0.0	0.0	14.3	0.4	4.2	2.2	0.1	0.7	0.9	0.0	17.1	0.2	1.3	0.4	726.7	0.1	243	482	1931
nos	9.4	0.0	0.1	529.3	101.7	76.9	4.9	0.6	9.1	10.1	0.3	29.9	12.0	11.0	4.3	2450.2	0.4	1260	2529	9951
bas	2.9	0.2	1.1	26.3	31.0	536.4	0.8	4.9	214.3	32.9	0.5	5.1	101.8	6.4	46.0	114.4	1.7	958	1843	7632
med	3.8	59.6	13.2	7.5	1.9	65.4	48.9	87.6	20.8	64.4	23.9	1061.6	1.3	75.2	108.2	63.0	85.2	4396	9449	19851
bls	0.5	9.3	86.6	1.7	0.9	49.8	0.5	170.6	406.2	47.2	1.9	3.5	0.8	2.6	1134.4	10.0	24.3	1072	2299	5905
cas	0.0	0.1	0.8	0.1	0.1	3.9	0.1	1.8	115.2	2.1	0.1	0.3	0.1	0.2	45.0	0.9	0.4	589	1305	2081
arc	1.0	0.1	0.4	8.1	35.8	41.7	1.1	1.3	205.1	7.5	0.2	5.8	6.7	2.3	17.8	113.2	0.4	6638	13878	21318
sum	402	664	774	1696	797	17979	1519	3877	31365	6370	416	6893	452	3655	18021	12709	1824	99817	212042	521880

Table 6.8 The most important countries-emitters and their contribution (%) on the deposition in countries-receivers

Country-receiver	Most important countries-emitters (input in %)			Contribution of own sources, %	Contribution of natural sources, %
Albania	Greece – 15	The FYR Macedonia - 5	Yugoslavia - 3	8	41
Austria	Germany –14	Czech Rep. - 5	Slovakia - 4	20	28
Belarus	Poland – 11	Ukraine -9	Germany - 7	1	41
Belgium	France – 20	Germany - 19	UK - 4	32	12
Bosnia & Herzegovina	Croatia – 5	Yugoslavia - 4	Germany - 3	3	50
Bulgaria	Romania - 8	Ukraine - 2	Yugoslavia - 2	28	35
Croatia	Italy - 4	Hungary - 4	Germany - 4	9	45
Cyprus	Greece - 1	Ukraine - 1	Germany -1	12	57
Czech Rep.	Germany - 40	Poland - 8	Slovakia - 4	21	13
Denmark	Germany - 18	UK - 3	France - 1	47	16
Estonia	Germany - 9	Finland - 5	Russia - 5	27	29
Finland	Germany - 6	Russia - 4	Estonia - 2	7	49
France	Germany - 6	Belgium - 4	UK - 3	40	28
Germany	France - 3	Czech Rep. - 2	Belgium - 1	70	11
Greece	Bulgaria - 7	The FYR Macedonia - 4	Germany - 1	28	37
Hungary	Slovakia - 20	Germany -5	Poland - 3	19	26
Iceland	UK - 1	Germany - 1	France - 0	0	65
Ireland	UK -13	Germany - 2	France - 2	20	41
Italy	Switzerland - 4	France - 4	Germany - 3	29	38
Latvia	Germany - 13	Estonia - 6	Poland - 6	5	38
Lithuania	Germany - 14	Poland - 12	Russia - 6	0	38
Luxembourg	France - 41	Germany - 15	Belgium - 7	11	15
The FYR Macedonia	Bulgaria - 9	Greece - 8	Yugoslavia - 7	19	34
Rep. of Moldova	Ukraine - 20	Romania - 7	Germany - 3	13	34
Netherlands	Germany - 35	Belgium - 13	France - 6	16	15
Norway	Germany - 6	UK - 3	Denmark - 2	6	52
Poland	Germany - 19	Czech Rep. - 5	Slovakia - 3	47	14
Portugal	Spain - 7	France - 1	UK - 1	27	44
Romania	Ukraine - 5	Slovakia - 4	Germany - 4	23	35
Russia *)	Ukraine - 4	Germany - 2	Poland - 1	34	38
Slovakia	Poland - 16	Hungary - 5	Germany - 4	47	13
Slovenia	Austria - 8	Italy - 5	Germany - 5	17	36
Spain	France - 3	Portugal - 2	Germany - 1	27	46
Sweden	Germany -10	Denmark - 7	Norway - 2	2	46
Switzerland	France - 7	Germany - 6	Italy - 5	51	18
Ukraine	Russia - 4	Poland - 3	Germany - 3	44	27
UK	France - 2	Germany - 2	Belgium -1	55	24
Yugoslavia	Romania - 4	Germany - 3	Hungary - 2	23	38
Baltic Sea	Germany - 29	Denmark - 12	Poland - 7	-	24
North Sea	UK-25	Germany - 14	France - 6	-	25
Mediterranean Sea	Italy - 7	Spain - 5	France - 5	-	48

*) within EMEP region

In the computational scheme used it is assumed that dry uptake by the underlying sea surface does not take place (the sea remained to be a net-source of elemental mercury). Nevertheless values of atmospheric mercury deposition on seas adjacent to Europe are rather essential. The most intensive deposition is on the Baltic (on the average 18 g/km²/yr) and North Seas (on the average 20 g/km²/yr). The most important country-emitters for these seas are Germany, Great Britain, Denmark, and France (see table 6.8). The intensity of mercury deposition on seas located far away from Central Europe is appreciably lower. It is conditioned by the fact that far from sources the main contribution to the content of mercury in the atmosphere makes elemental mercury poorly removed from the atmosphere. In the Arctic the deposition intensity is minimum and accounts for about 3 g/km²/yr.

7. Unsolved problems and ways to further improvement of the model

In this work an attempt is made to summarize modern knowledge on mercury behavior in the atmosphere and to incarnate them in a regional model of the airborne transport of mercury in Europe. It is quite evident that inaccuracy of many key-parameter estimates is very high and understanding of some mechanisms of mercury transport and transformation in the atmosphere are not sufficient for relatively accurate calculations. Further progress in modeling will require the refinement of both input parameters and assumed model constants. Below a list of problems, which solution will allow us to improve essentially the operational model of mercury transport and deposition in Europe is presented. The activity under MEPOP/EUROTRAC of EUREKA shows a promise of the progress in the field.

In this report natural emission of mercury in Europe is evaluated on the basis of ideas on the pre-industrial state of the global mercury cycle in the atmosphere. Here key-problems are:

What is the relationship of the intensity of natural and anthropogenic sources on the global level at present?

What was the mean global concentration of mercury in the atmosphere before the beginning of human activity?

What is seasonal cyclicity of natural emission intensity?

Estimates of mercury re-emission from soil in Europe are based on the notion of mercury fate in soils and assessments of its life-times in soil relative to different removal mechanisms. Here the following questions arise:

What is the dynamics of mercury accumulation in soils in different regions of Europe for recent 100-200 years?

What is the uncertainty of the life-times of mercury in soil relative to volatilization to the atmosphere (400 years) and relative to hydrological weathering (900 years)?

How do these values depend on soil type, temperature, precipitation intensity and other parameters?

What is current intensity of mercury emission from seas surrounding Europe?

In what chemical forms does mercury re-emit to the atmosphere?

What is seasonal cyclicity of re-emission intensity?

Uncertainty of available estimates of direct mercury anthropogenic emissions in European countries is very high. It refers both to total emission values and to contributions of various physical-chemical forms of mercury. The relationship of mercury forms in emissions is of a crucial importance for modeling. It is necessary to give answers to the following questions:

What are total mercury emissions in European countries as of 1995?
What is the relationship of various physical-chemical forms both in individual powerful sources and in individual countries on the whole?
What is the size spectrum of particles-carriers in the primary emissions ?
What is seasonal variability of direct anthropogenic emissions in different countries?
What is height distribution of sources in different countries?
How did direct anthropogenic emissions change in different countries during recent 100-200 years?

Atmospheric content of mercury is monitored by few stations in Europe. These sites are mainly concentrated in Germany, Sweden and other countries adjacent to the North and Baltic Seas. As a rule, observation programmes are limited by measurements of total gaseous mercury in air or by mercury concentration in atmospheric precipitation. The aerosol component, organic compounds and gaseous inorganic compounds are not measured on a routine basis. The following questions need to be answered:

What is spatial and temporal variability of concentrations in air and precipitation separately for various mercury forms in different European regions ?
What is mercury concentration in cloud water?

We have every reason to believe that the process of gas-phase oxidation of elemental mercury is relatively important in its atmospheric cycle. Probably in addition to ozone other species can be oxidants. To make quantitative account of this mechanism effect it is necessary to answer the following questions:

How much accurate is our knowledge on the reaction constant of mercury oxidation by ozone and does it depend on temperature?
What are reaction constants of mercury oxidation by other oxidants, what are characteristic concentrations of these oxidants in the atmosphere, do oxidation rates depend on temperature?
By what compounds are oxidation products represented and in what form (gaseous or aerosol) do they occur?

Recently a considerable progress is made in understanding of the mechanism of incloud elemental mercury vapour washout (Petersen et al., 1998). However, many parameters of this mechanism remained to be rather uncertain. In particular the following questions can be put:

What is temperature dependence of Henry constant for elemental mercury vapours and ozone in the range from supercooled water (-40°C) to $+25^{\circ}\text{C}$?
What is the uncertainty of reaction constants of liquid-phase oxidation of mercury by ozone, of the reaction of mercury sulfite complex formation, of the reaction of sulfite complex decomposition followed by elemental mercury reduction?
What are actual concentrations of sulfite ion in a wide range of pH, air concentrations of sulfur dioxide, oxidant concentrations and S^{+4} to S^{+6} oxidation catalyser concentrations?
What is the importance of competing reactions of the formation of persistent haloid complexes in a wide range of chloride, bromide, iodide concentrations? What are their actual concentrations in cloud water of different regions of Europe?
What is soot particle concentration distribution with European territory?
What is the vertical profile of soot particle concentration?

Gaseous inorganic mercury compounds play a crucial role in mercury deposition on local and subregional levels. Their contributions to direct anthropogenic emissions are sufficiently high. At the same time the information on coefficients of dry and wet deposition of these compounds is absolutely absent. It is conventionally assumed that by their properties they are similar to nitric acid. The following questions arise:

- To what extent gaseous inorganic mercury compounds are similar to nitric acid when interacting with cloud/rain drops and with the underlying surface?
- How does the washout rate depend on temperature?
- How does dry uptake velocities depend on the underlying surface type?
- Do redistribution processes of these substances between gaseous and aerosol phase take place in the real atmosphere and how do these processes depend on temperature and relative humidity?

Aerosol fraction plays a significant role in mercury removal from the atmosphere. However, the question is remained open:

- What is particles-carriers size distribution in the boundary layer and in the free troposphere?

Practically nothing is known about atmospheric chemistry of organic mercury compounds. It is necessary to answer the following questions:

- How long is the life-time of organic compounds in the atmosphere relative to chemical (photochemical) degradation processes?
- By what form is mercury represented in products of these reactions?
- What is the formation mechanism of mercury organic compounds in the liquid phase of atmospheric precipitation?

According to the computational scheme used the intensity of mercury deposition from the atmosphere to a considerable degree is determined by dry uptake of elemental mercury vapours. However, the process rates are determined with insufficient accuracy. The accuracy of deposition estimates depends on answers to the following questions.

- What are values of uptake velocities of elemental mercury vapours by different elements of the underlying surface?
- Is there a «compensation point» at the mercury transfer between vegetation and the atmosphere and how does it change versus vegetation type and season?

8. Conclusions

1. A simplified version of the operational model of Eulerian type has been developed for calculations of the regional airborne mercury transport and for the evaluation of the atmospheric transboundary pollution in the EMEP region. The model considers advective and vertical transports of a pollutant in the atmosphere, processes of physical-chemical transformations of mercury and its compounds in the atmosphere, processes of removal from the atmosphere. Meteorological information with temporal resolution 6 hours, data on emissions of various physical-chemical forms of mercury to the atmosphere, calculated concentrations of sulphur dioxide and ozone are used as initial information. Model results reproduce fields of deposition and concentrations of mercury in various forms within the EMEP domain with spatial resolution similar to that of input parameters.
2. Model estimates of concentrations of mercury various forms in the atmosphere and precipitation as well as mercury deposition intensities in the EMEP region with spatial

resolution 150×150 km have been obtain. Calculation results are in a satisfactory agreement with measurement data available: for polluted regions of central Europe the differences are within a factor of 2 and for remote regions they do not exceed 40%. Elemental mercury makes the main input (up to 99%) to the air mercury concentration. Total concentrations of all mercury forms over the most polluted regions reach 8 ng/m³. Mercury concentration field far away from sources is rather uniform: the values lie within 1.3 - 1.7 ng/m³. In regions with intensive emissions the deposition is conditioned first of all by washout and dry uptake of gaseous inorganic mercury compounds and by aerosol particles containing mercury. Here the deposition intensity can exceed 300 g/km²/yr. With the distance from major emission sources the role of in-cloud washout of elemental mercury with subsequent liquid-phase oxidation increases. Values of mercury deposition in the EMEP periphery lie within 3 - 10 g/km²/yr.

3. ‘Country-by-country’ matrices for Parties to the Convention are calculated. Countries-sources making the main contribution to the transboundary pollution by mercury and its compounds are determined for each individual country. Inland seas (the Mediterranean, Black, Baltic, North Seas) and the Arctic are singled out as conventional ‘countries-receivers’.
4. The current balance of mercury in the atmosphere of the EMEP region is calculated. It is demonstrated that out of 709 tons of mercury annual input to the atmosphere about 462 tons are exported outside the region, 108 tons are removed by dry deposition, and 130 tons are washed out from the atmosphere by precipitation. Vaporous elemental mercury is mainly transported outside the EMEP domain, the deposition within the region is conditioned to a considerable extent by emissions of gaseous inorganic mercury compounds and aerosol particles containing mercury.
5. The natural atmospheric mercury cycle in the EMEP region before a tangible impact of human activity is estimated. The comparison of current and purely natural fields of mercury deposition allowed us to evaluate the contribution of anthropogenic factor to the atmospheric pollution by mercury and associated atmospheric loads. Spatial distribution of the amplification factor within the EMEP domain has been calculated. The obtained values are compared with measurement data on mercury accumulation in bottom sediments and peat bogs. It is demonstrated that due to human activity (mainly directly in Europe) for the historical period the atmospheric load increased in 2 - 8 times.
6. The re-emission value of anthropogenic mercury in the EMEP domain is estimated. It is shown that at present the input of mercury to the atmosphere of this region does not exceed 10%. The re-emission field configuration compiles with the field of multi-annual anthropogenic mercury deposition in this region.
7. Uncertainties of key-parameters determining mercury behaviour in the atmosphere are analysed. The ways of improvements in the model are outlined.

ACKNOWLEDGEMENTS

The authors express their sincere gratitude to Dr. Leonid Erdman and Mr. Sergey Dutchak valuable recommendations and editorial comments. Data on spatial distribution of ozone and sulphur dioxide concentrations prepared and kindly provided by specialists of Meteorological Synthesizing Centre-West Dr. Leonor Tarasson and Dr. David Sympton and Svetlana Tsyenko. An inestimable role is of Mrs. Larissa Zayavlina, Ms. Irene Strizhkina and Ms. Olga Rosovskaya who made the translation of the text and technical preparation of the report materials.

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