



**MEDITERRANEAN ACTION PLAN  
MED POL**

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**UNITED NATIONS ENVIRONMENT PROGRAMME**



**WORLD METEOROLOGICAL ORGANIZATION**

**ATMOSPHERIC INPUT OF MERCURY  
TO THE MEDITERRANEAN SEA**

**Prepared by  
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## CONTENTS

|  |   |    |
|--|---|----|
| Chapter 1  | Introduction  | 1  |
| 1.1  | General properties of mercury   | 1  |
| 1.2  | Mercury in natural compartments   | 1  |
| 1.3  | Bioaccumulation   | 3  |
| 1.4  | Inertness of processes  | 4  |
| 1.5  | Global mercury cycle  | 4  |
| 1.6  | Regional seas   | 6  |
| Chapter 2  | Sources of mercury input to the marine environment  | 9  |
| 2.1  | Mercury sources   | 9  |
| 2.2  | Evaluation of the direct mercury inputs to the marine environment through rivers and from the sea bed | 12 |
| 2.3  | Mercury input to the atmosphere   | 12 |
| Chapter 3  | Atmospheric mercury   | 16 |
| 3.1  | Behaviour in the atmosphere   | 16 |
| 3.2  | Removal from the atmosphere   | 18 |
| 3.3  | Mercury concentration in the atmosphere and precipitation   | 19 |
| Chapter 4  | Modelling of mercury atmospheric transport and its deposition   | 24 |
| 4.1  | Modelling approaches  | 24 |
| 4.2  | MSC-E Model   | 26 |
| Chapter 5  | Evaluation of mercury deposition on the seas  | 30 |
| 5.1  | Results of mercury deposition calculation (MSC-E model test runs)                                     | 30 |
| 5.2  | Synoptic analysis   | 42 |
| 5.3  | Comparison with measurements and other estimates  | 43 |
| Chapter 6  | Potential measures for reduction of mercury load on the seas  | 48 |
| 6.1  | Assimilative capacity   | 48 |
| 6.2  | Measures undertaken by some countries   | 51 |
| Chapter 7  | General remarks   | 54 |
| Conclusions                                      |   | 55 |
| References                                       |   | 57 |
| Publications of the MAP Technical Reports Series |   | 65 |

## Chapter 1 INTRODUCTION

Mercury belongs to a category of heavy metals, which includes such toxic substances as lead and cadmium. Mercury is also toxic and occurs in the environment as both a component of different compounds and in the elemental form.

### 1.1 General properties of mercury

Under natural conditions elemental mercury ( $\text{Hg}^0$ ) is a liquid metal of silvery colour from which its Latin name Hydrargirum, i.e. “liquid silver” is derived. Physical and physical-chemical properties of mercury are unique. The melting temperature of mercury is  $-38.8^\circ\text{C}$  (the lowest melting temperature for the metals) [Schröder *et al.*, 1991]. Within temperature ranges typical of the environment, mercury is present in liquid and gaseous states and as particles. An important characteristic for understanding the behaviour of mercury in the environment, particularly in the atmosphere, is the pressure of saturated vapour which is equal to 0.160 Pa at  $20^\circ\text{C}$ , corresponding to air concentrations of  $13.2\text{ mg/m}^3$  [Schröder *et al.*, 1991]. In real atmospheric conditions concentrations of mercury, even in heavily polluted areas, are lower by several orders of magnitude than the above-mentioned value and, as such mercury cannot exist in the atmosphere in the liquid phase [Matheson, 1979].

Under normal conditions mercury is chemically inert. The availability of elemental mercury in various environmental compartments and in the atmosphere is explained by its high ionization potential. The degree of mercury oxidation is “+1” and “+2”. At room temperature mercury is oxidized by ozone to mercury oxide  $\text{HgO}$  [Great Chemical Encyclopedia, 1995].

In addition to its elemental form mercury can be present as a number of chemical compounds, some of them are more toxic than  $\text{Hg}^0$ . These compounds as well as elemental mercury can exist in gaseous form, on aerosols and in water, in particular in cloud and rain drops [Horvat, 1996; Lamborg *et al.*, 1995; Schröder *et al.*, 1991]. Brosset (1987) suggested classification of mercury compounds in accordance with their chemical forms:

- elemental  $\text{Hg}^{\text{Ia}}=\text{Hg}^0$ ;
- fully organic  $\text{Hg}^{\text{Ib}}=\text{DMHg}$ ;
- fully inorganic  $\text{Hg}^{\text{IIa}}=\text{XHgX}'$  where  $\text{X}=\text{OH}, \text{Cl}, \text{Br}, \text{I}$  (e.g.  $\text{HgCl}_2$ );
- partially organic  $\text{Hg}^{\text{IIb}}=\text{MMHgX}$  (e.g.  $\text{MMHgCl}, \text{MMHgOH}$ ).

Iverfeldt and Rodhe (1988) introduced into consideration an additional fraction  $\text{Hg}^{\text{Ib}}$  - very strongly bound mercury, probably in particulate phase. Physical-chemical properties of all the forms are very different, therefore their behaviour in the environment as well as mechanisms of their inter-media transport are different. In particular, solubility of various species usually decreases from inorganic divalent mercury halides via methylmercury (II) halides to  $\text{DMHg}$  and  $\text{Hg}^0$  [Iverfeldt, 1992] as shown in Table 1.1, adapted from [Ryaboshapko and Korolev, 1997] where data on the solubility of various compounds in water are presented as Henry's coefficients.

### 1.2 Mercury in natural compartments

Different forms and phases of mercury compounds dominate in different media.

#### 1.2.1 Atmosphere

In the atmosphere mercury is present mainly as elemental mercury. A considerably smaller part of gaseous mercury accounts for methylmercury playing an important role in natural cycles [Petersen et al., 1995]. Near anthropogenic sources inorganic compounds of divalent

**Table 1.1:** Solubility of mercury compounds in water\*\*

| Source                         | Henry's coefficients (in brackets - temperature, °C) |                       |                                     |                          |                           |                          |
|--------------------------------|--|-----------------------|-------------------------------------|--------------------------|---------------------------|--------------------------|
|                                | Nomenclature [Brosset, 1987]                         |                       |                                     |                          |                           |                          |
|                                | I <sup>a</sup>                                       | I <sup>b</sup>        | II <sup>a</sup>                     |                          | II <sup>b</sup>           |                          |
|                                | Hg <sup>0</sup>                                      | DMHg                  | MHgCl                               | MHgOH                    | HgCl <sub>2</sub>         | Hg(OH) <sub>2</sub>      |
| <i>Lindqvist et al., 1984</i>  | 0.14 (20)  | 0.13 (25)<br>0.30 (0) | 2200 (25)<br>2650 (15)<br>4800 (10) |                          | 1.4E6* (25)<br>3.6E6 (10) | 1.3E4 (25)<br>2.7E4 (10) |
| <i>Clever et al., 1985</i>     | 0.112  |                       |                                     |                          |                           |                          |
| <i>Schröder et al., 1991</i>   | 0.13 (25)<br>0.24 (5)                                |                       |                                     |                          |                           |                          |
| <i>Fitzgerald et al., 1991</i> |  |                       |                                     | 2.5E5 (15)               |                           |                          |
| <i>Petersen, 1992</i>          | 0.14 (20)<br>0.12 (25)                               | 0.13 (25)             | 2200 (25)<br>2200 (15)              | 1.5E5 (25)<br>2.5E5 (15) | 1.4E6 (25)<br>3.6E6 (10)  |                          |
| <i>Seigneur et al., 1994</i>   | 0.11 (20)  | 0.13 (25)             | 2200 (25)                           |                          | 1.4E6 (25)                | 1.2E4 (25)               |
| <i>Schröder, 1996</i>          | 0.21 (10)  |                       |                                     |                          |                           |                          |

\* - here and below 1.4E6 = 1.4·10<sup>6</sup>

\*\* - adapted from [Ryaboshapko and Korolev, 1997]

mercury can occur in gaseous and solid phases [Lindqvist and Schager, 1990] but in remote areas their content in total mercury is negligible [Petersen et al., 1995]. The contribution of the aerosol component to total mercury at the regional level is from fractions to units of per cent [Horvat, 1996; Lamborg et al., 1996; Petersen et al., 1995; Schröder et al., 1991].

In precipitation mercury can either be dissolved or on particles. The particulate matter/soluble matter ratio is highly variable in precipitation. The fraction of particulate matter varies from 90 % in polluted regions to 10% in remote ones [Iverfeldt, 1991b; Ferrara et al., 1986a].

### 1.2.2 Rivers

In rivers mercury is present both in the dissolved form and bound to particulate matter. According to data given in [TDA MED, 1997] the fractions of particulate matter amount to 88% in the Po River [Pettine and Camusso, 1991] and 99% in the River Rhone [Pout et al., 1996]. For the Schelde river this fraction is 98% in the upper estuary and 90% near the mouth [Baeyens and Leermakers, 1996]. For the Katun river (Siberia) in the upper course the ratio of particulate matter/soluble fraction is 3-6 [Vasiliev et al., 1996]. Apparently the bulk of mercury in rivers is present on particulate matter.

### 1.2.3 Marine environment

Due to the relatively high content of suspended particles particulate mercury often makes the major contribution to the pollution of coastal waters [Cossa et al., 1996]. The ratio of particulate mercury to total mercury varies considerably. For example the contribution of particulate mercury in the English Channel and Narragganset Bay varies from 20 to 97% [Cossa et al., 1994; Vandal and Fitzgerald, 1995; Mason et al., 1993]. According to Ferrara et al. (1986b); and Fujita and Iwashima, (1981) the contribution of particulate mercury to

total mercury content in coastal waters of the Tyrrhenian Sea and Suruga Bay (Japan) is less than 50%. As in river water, mercury enrichment of particulate matter is proportional to the content of organic carbon in it.

In the open sea and oceans the bulk of mercury is present in dissolved form. It may be exemplified by data on the Tyrrhenian Sea [Seritti *et al.*, 1982]: near the coast (mouths of rivers, beaches, harbors, lagoons etc.) concentrations of Hg(P) (mercury on particles) varies within the range of 1.0-80 ng l<sup>-1</sup> (arithmetic mean =19 ng l<sup>-1</sup>), in the open sea from 0.3 to 1.2 ng l<sup>-1</sup> (arithmetic mean =0.7 ng l<sup>-1</sup>), the concentrations of the soluble fraction for coastal waters and open sea almost coincide. In [Lindqvist and Rodhe, 1985] the proportion of dissolved inorganic mercury components is the following: HgCl<sub>4</sub><sup>2-</sup> - 66%, HgCl<sub>3</sub>Br<sup>2-</sup> - 12%, HgCl<sub>3</sub><sup>-</sup> - 12%. According to Mason *et al.* (1995) the content of dissolved elemental mercury in marine water is 10-30% of total dissolved mercury. Investigations in the open ocean show that Hg<sup>0</sup>, DMHg and, to a lesser extent MMHg are present in dissolved form in deep ocean layers [Mason and Fitzgerald, 1996]. According to data from these authors, DMHg content in the northern Atlantic is several per cent of total dissolved mercury, and its fraction increases with depth.

In a large-scale experiment with marine water (1300 m<sup>3</sup>) it was shown that over 72 days more than 90% of mercury was fixed in bottom sediments [Prokofiev, 1981]. It is presumed [Horvat, 1996] that oceanic bottom sediments are the basic sink of mercury in its practically insoluble sulphide form.

### 1.3 Bioaccumulation

Bioaccumulation is an ability of living organisms to accumulate mercury compounds in their tissues, and biomagnification increase the concentration of these compounds in the tissues as one ascends the food chain. Although the fraction of MMHg in total mercury content is not high (up to 1% in soils, up to 5% in air, up to 30%(!) in precipitation and fresh water [Horvat, 1996]), organisms have an ability to accumulate it in a greater amount than other mercury compounds.

If mercury enters the lower links of the trophic chain (mainly autotrophs) from water due to passive diffusion [UNEP/FAO/WHO, 1987], subsequent links accumulate it mainly with food as it was shown, for example, in the experiments with mussels and shrimps [Fowler *et al.*, 1978] and plaices [Pentreath, 1976a,b,c].

The main factors determining the level of methylmercury in fish are diet, level in the trophic chain, age of fish, microbiological activity and mercury concentration in the upper layers of bottom sediments, content of dissolved organic substances, salinity, pH and redox potential [Horvat, 1996]. Pastor *et al.* (1994) noted tunnies and some crustaceans in the Mediterranean Sea are good indicators of mercury.

It is known that even high mercury concentration in fish (at least up to 5-10 mg/kg) does not inflict harmful impact on them [Lithner, 1989]. For people a steady diet of fish containing mercury can be dangerous. For this reason "the mercury problem" has changed from a situation which could be described as "local and acute", resulting from point source emissions, to a situation, which is "regional and chronic" [Mercury in the Environment, 1991]. Mercury compounds are especially dangerous for pregnant women and babies receiving methylmercury through mother's milk.

In Sweden more than 300 lakes were included in the "black list" because of high mercury content (>1mg/kg) in pike. It was estimated that if the investigations had been carried out all



over the country, the number of such lakes so afflicted would have been about 10000. In 1992 the “black list” was abolished and new standards were introduced the mercury content in fish was set at: 0.05 mg Hg/kg - for children, 0.5-1.0 mg Hg/kg - for adults.

#### 1.4 Inertness of processes

Processes connected with the occurrence of mercury in the natural environment can be characterized as inert. Mercury that has accumulated in fish is only removed from it quite slowly.

As it was noted in *Mercury in the Environment* (1991), some lakes where direct input of mercury was discontinued, the mercury level in fish fairly rapidly decreased and returned to “normal” in about 10 years. However, in a number of other lakes with no known direct mercury input in, the observed increased level of mercury in fish is connected with atmospheric deposition. Although mercury emissions in Sweden have been highly reduced since the end of the sixties no reduction in the level of mercury in fish has been detected; the level even increased during the 70s and 80s [*Mercury in the Environment*, 1991]. One possible reason for this could be acidification of lakes and streams which may affect biological and biochemical mercury cycles and forming new food chains.

Data on mercury accumulation in bottom sediments of lakes show that the level of pollution in sediments of Swedish lakes increased appreciably over the last 200-300 years [*Johansson*, 1985]. At present the mercury content in the Baltic Sea surrounding Sweden exceeds background concentrations 10 fold. Maximum mercury concentrations in the Baltic herring occurs in the Gulf of Bothnia. Thus pollution of various media by mercury is the reason for lasting and large-scale effects in marine organisms [*Mercury in the Environment*, 1991].

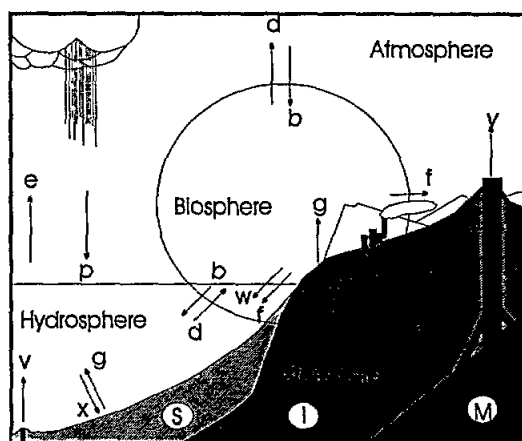
#### 1.5 Global mercury cycle

Mercury simultaneously takes part in cycles on different scales - from local and regional to global. On the one hand these cycles are caused by general geophysical processes (formation of precipitation and aerosols in the atmosphere and their removal, transport of air and oceanic masses, transport of suspended particles by rivers and sea current and their sedimentation etc.), biological processes on land and in water, and, on the other hand, by the variety of different physical and chemical mercury forms with a wide spectrum of properties determining their behaviour in various media (see Figure 1.1 taken from *Mitra* (1986)). Conversion from one form into another is a basic feature of mercury dispersion, its local and global cycles, biological enrichment and effects.

It was noted by *Lindqvist and Rodhe* (1985) that two most significant mercury cycles are the atmospheric cycle and water-biological cycle. The atmospheric cycle results from the transformation of divalent mercury in soil and water and its subsequent conversion to elemental form  $Hg^0$  and/or dimethylmercury (DMHg) and their input to the atmosphere. In the atmosphere,  $Hg^0$  is again oxidized to water-soluble forms which fall out onto the underlying surface. The atmospheric cycle is characterized by a considerable residence time of elemental mercury in the atmosphere and the resulting by long-range transport of mercury compounds.

The basic feature of the water-biological cycle is the formation of methylmercury, its biomagnification in water organisms and food chains, and its eventual destruction (demethylation). As stated above MMHg, being a dominant mercury form in higher

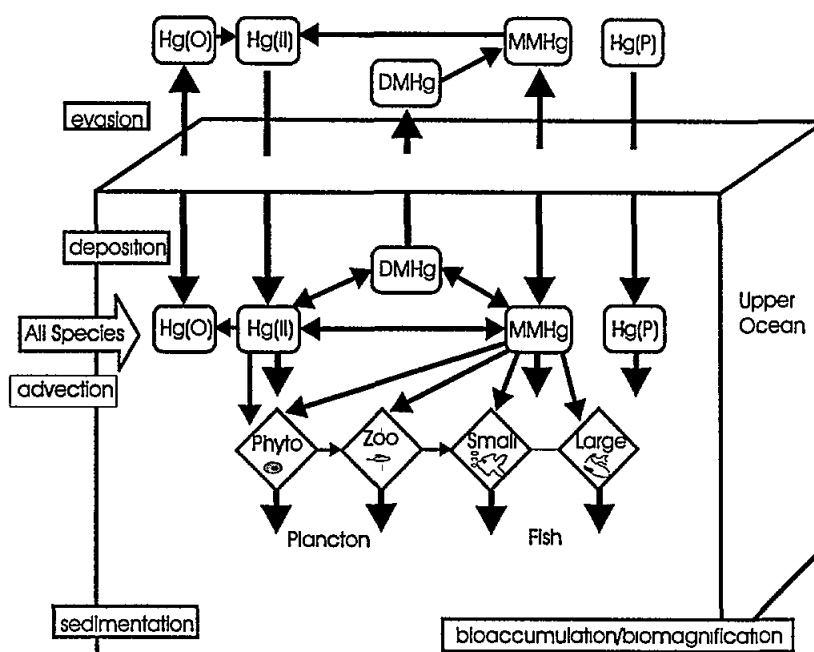
organisms is present in water and in the atmosphere in minor quantities. Therefore the input/removal of mercury from sea organisms is mainly determined by rates of methylation/demethylation [Lindqvist and Rodhe, 1985].



- |                      |                            |                       |               |
|----------------------|----------------------------|-----------------------|---------------|
| b - uptake by biota  | f - anthropogenic emission | v - volcanic activity | I - rocks     |
| d - release by biota | g - degassing              | w - weathering        | M - mantle    |
| e - evasion          | p - precipitation          | x - sedimentation     | S - sediments |

**Figure 1.1** Biogeochemical cycle of mercury (adapted from Mitra, 1986)

The biogeochemical cycle of mercury in sea water is presented in Figure 1.2 adapted from Hudson *et al.* (1994). In marine water mercury is present as elemental mercury ( $Hg^0$ ), divalent mercury compounds ( $Hg(II)$ ), methylmercury (MMHg), dimethylmercury (DMHg) and mercury on particles ( $Hg(P)$ ). The input of these compounds is connected with advection from other areas of the ocean, seas, coastal regions, rivers etc. and from the atmosphere (apparently, DMHg from the atmosphere does not enter the ocean). Redox processes take place with participation of elemental mercury  $Hg^0$  and divalent mercury  $Hg(II)$ , as well as processes of methylation/demethylation with the participation of  $Hg(II)$ , MMHg and DMHg. Then  $Hg(II)$  and MMHg enter phytoplankton and process of mercury uptake along the ascending food chain through zooplankton and small fish to large ones, and the phenomenon of bioaccumulation/biomagnification begins. All the links in the food chain beginning with zooplankton intake only MMHg as compared with phytoplankton taking up MMHg and  $Hg(II)$ .



**Figure 1.2** Mercury cycling in seawater (adapted from Hudson, 1994)

The major sinks of mercury compounds in the marine environment are the lower oceanic layers, bottom sediments, advection to other oceanic areas and the atmosphere where the evasion (re-emission) of elemental and methylated mercury in the forms of  $DMHg$  and  $MMHg$  takes place.

The intensity of processes discussed varies with ambient conditions. In any case cycles of  $Hg^0$  and  $MMHg$  are closely connected. Therefore,  $MMHg$  input to fish to a large extent depends on atmospheric mercury transport (first of all of  $Hg^0$ ) to the ocean. The recycling between the upper oceanic layer and the atmosphere prolongs time of natural and anthropogenic mercury impact on sea organisms. *Fitzgerald and Mason (1996)* suggested the principal scheme of atmospheric  $Hg(II)$  input to the equatorial zone of the Pacific Ocean which is extremely biologically productive. In the middle latitudes of both hemispheres mercury deposits as  $Hg(II)$ . Sea currents transport these compounds to the equatorial region where active methylation and formation of elemental mercury takes place. In elemental form mercury enters the atmosphere, then is transported to middle latitudes where it deposits as  $Hg(II)$  closing the cycle.

The mercury global cycle, including three main compartments (land, water and atmosphere), is given in the scheme taken from *Mason et al. (1994)* and adapted in [*Expert panel ..., 1994*] (Fig. 1.3). Both “modern” (Fig.1.3a) and “pre-industrial” (Fig.1.3b) cycles are presented. From the figures it follows that at present the mercury flows between the atmosphere and the ocean have increased three times as the well as the mercury “pool” in the ocean surface layer.

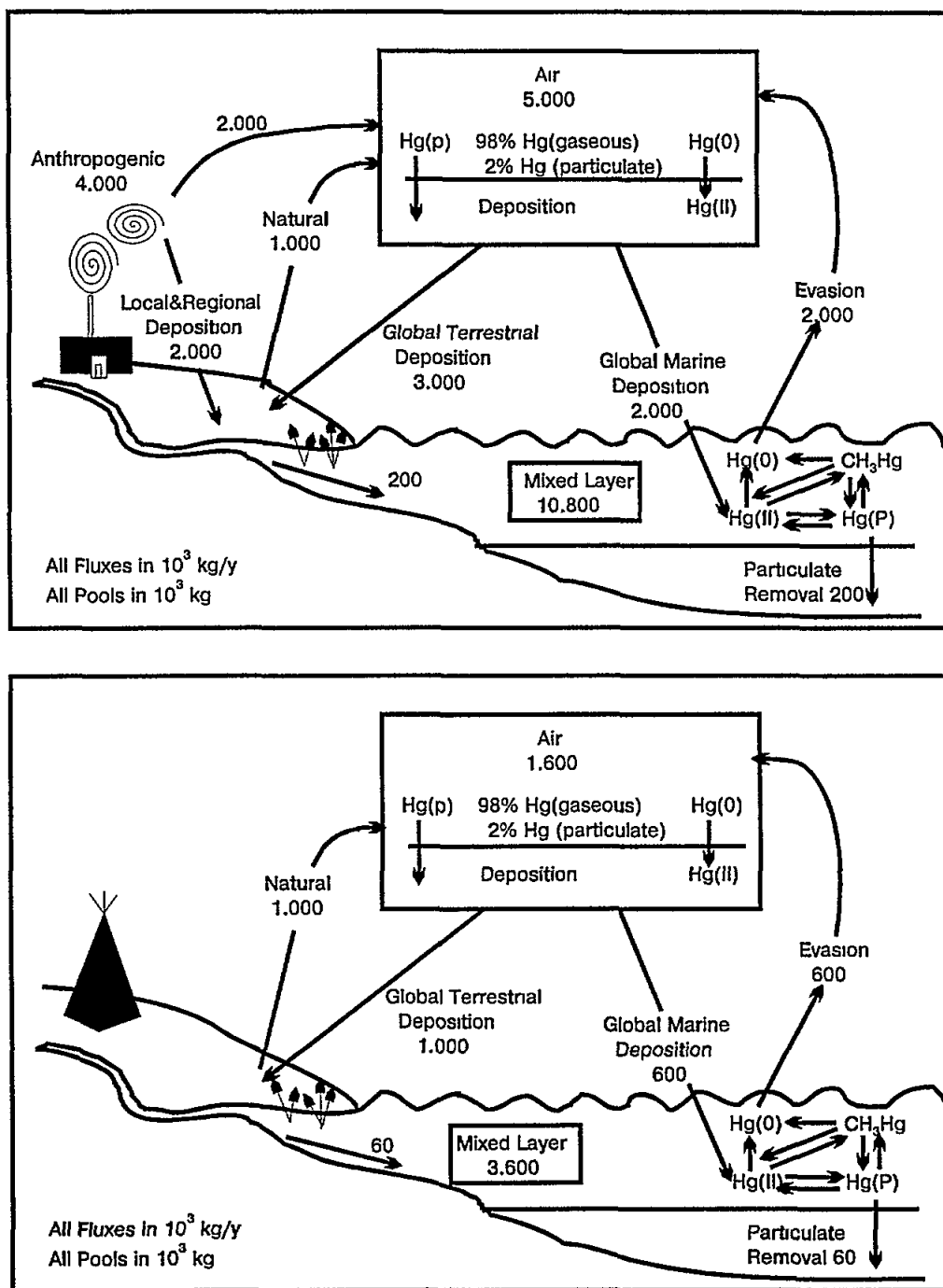
### 1.6 Regional seas

For regional seas mercury pollution is of particular importance. As it was noted in *GESAMP (1990)* pollution of fish and birds in coastal zones can be several orders higher than in the same oceanic species. The seas and particularly their coastal zones are exposed to the effect of river runoff and coastal discharges. Mercury on particles (especially large ones) is deposited by sedimentation processes in estuaries resulting in additional source of mercury pollution. Atmospheric particulate mercury deposition from land-based sources in the

regional seas is higher than in the open ocean. It should be noted that coastal zones are biologically more productive and play an essential role in biological cycles of fish.

International conventions on protection of regional seas (PARCOM, OSPARCOM, HELCOM, Barcelona Convention and its MED POL programme) include mercury as a priority pollutant.

For the Mediterranean Sea the mercury problem could be especially important since Mediterranean countries occupying about 0.5% of the Earth's surface undertake more than half of the world mercury mining (from 60% to 85% according to estimates for different years) and contain no less than a half of the world supply.



**Figure 1.3** Mercury budgets and fluxes (adapted from [Mason *et al.*, 1994])  
Current (upper)  
Pre-industrial (lower)

## Chapter 2 SOURCES OF MERCURY INPUT TO THE MARINE ENVIRONMENT

### 2.1 Mercury sources

Mercury enters the sea from the top (from the atmosphere through gas exchange and particle deposition processes and with precipitation), from rivers and coastal wastes and runoff, from the bottom thermal processes and from sediments.

Neither the atmosphere nor rivers directly generate mercury. However, mercury entering these media is subject to considerable transformation. Each flux is formed from natural and anthropogenic constituents, and in a number of cases it is difficult to separate one from the other. Primary sources of mercury input to the sea either directly or via other media are considered below.

#### 2.1.1 Primary mercury sources

Mercury is dispersed in the Earth's mantle. According to various estimates the Clark content of mercury in the Earth's mantle amounts to  $8 \cdot 10^{-8}$ , in the granite layer -  $3.3 \cdot 10^{-8}$  [Dobrovolsky, 1983], with allowance for basaltoids -  $4.5 \cdot 10^{-8}$  [Ozerova, 1986]. In its concentrated form mercury is present in three natural objects [Obolensky et al., 1995]

- a) mercury deposits;
- b) other deposits containing mercury;
- c) rocks with elevated mercury content.

In deposits mercury is mainly present as cinnabar (HgS). According to estimates [Obolensky et al., 1995] the mercury content in these deposits is about 0.02% of its total content in the earth crust. Estimated mercury content in the granite layer within the land domain down to a depth of 1 km is 13 billion tonnes and in deposits - 0.44 million tonnes for 1976 (without countries of eastern Europe and the former USSR), i.e. about 0.003% of its content in the 1-km layer [Dobrovolsky, 1983]. Mercury deposits are observed near volcanic and ore-forming planetary belts coinciding with deep-laid fractures of mantle deposits [Obolensky, 1996]. Main mercury deposits are concentrated in the Mediterranean belt, along the western coast of North and South America, along the Pacific volcanic arc and in Central Asia.

The greatest industrial deposits of mercury reside in the Mediterranean region (see Figure 2.1 adapted from UNEP/FAO/WHO (1987)): Almaden in Spain and Mt Amiata in Italy as well as large deposits in Idrija, Yugoslavia and Izmir in Turkey. It should be noted that the mercury content in rocks insufficient for industrial exploitation, but considerably exceeding the background level, is observed in many regions of the Mediterranean [UNEP/FAO/WHO, 1987, p.7] (Figure 2.1).

In addition to cinnabar there are several tens of mercury minerals including secondary ones. Ore deposits such as pyrite, semi-metallic antimony, molybdenum-tungsten also contain mercury with concentrations 10-100 times their Clark content. Substantial quantities of mercury are contained in gas, oil and coal. Since the mercury content in gas can reach 1-3 mg/m<sup>3</sup>, and in oil -  $2 \cdot 10^{-3}$ % of volume, the large quantities of these fossil fuels means the total stock of mercury is correspondingly high [Skotnikova et al., 1997].

The formation of mercury and mercury containing deposits is accompanied by evolution of haloes whose genesis, structure and scales depend on many factors. In a primary halo the mercury concentration dispersion can exceed the background by 2-3 orders of magnitude and its concentration in air at 1 m reaches tens and hundreds of nanograms per m<sup>3</sup> [Obolensky et al., 1995].

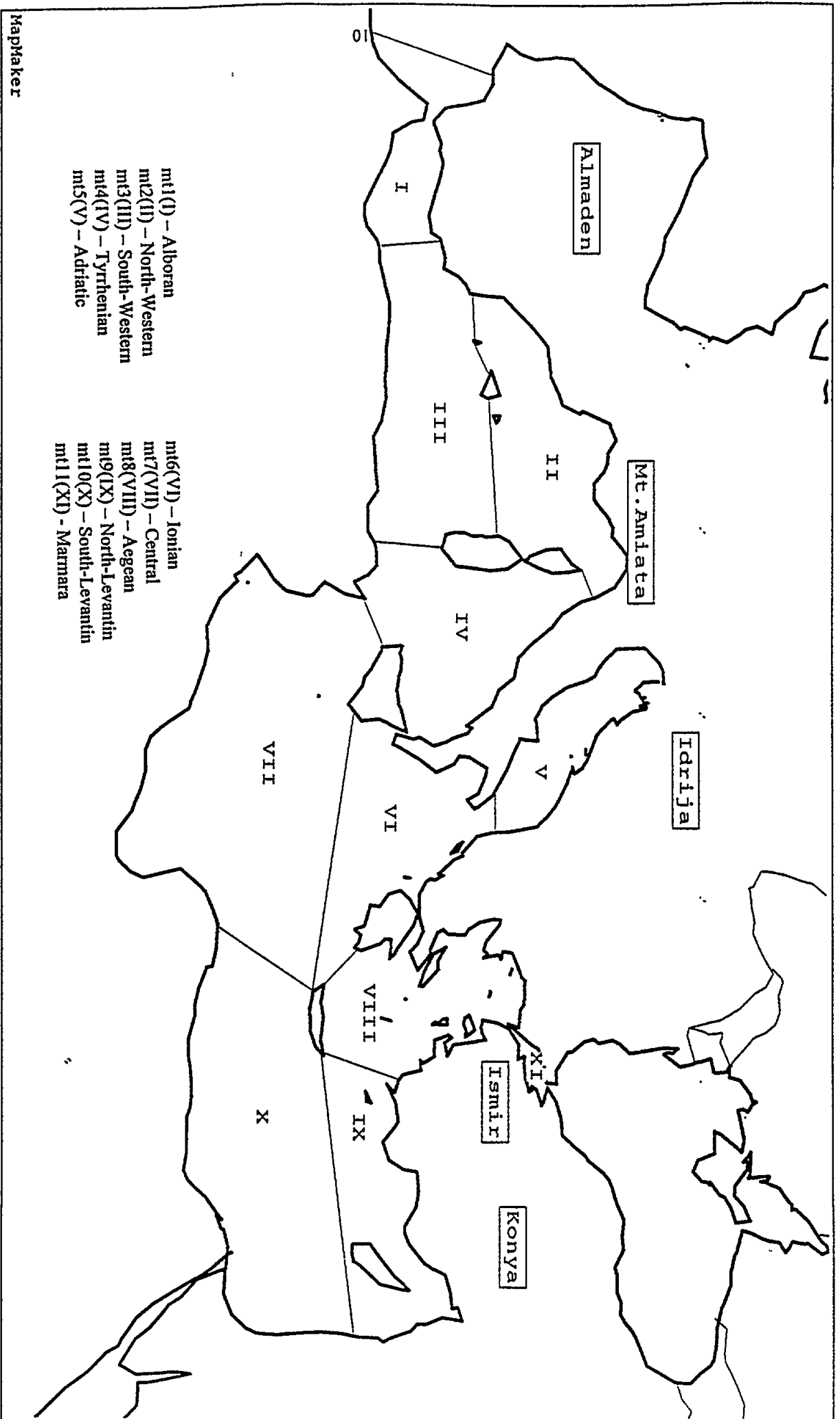


Figure 2.1 MED-POL areas and mercury mining areas (data from UNEP, 1980).

### 2.1.2 Natural input of mercury to "mobile" media: fresh water, sea water, atmosphere

From the lithosphere mercury enters "mobile" environmental compartments either directly or via biota (Figure 1.1). From the upper mantle mercury enters the air and water through deep-laid fractures and volcanoes. From the core due to outgassing processes via soil mercury enters the air and via bottom sediments enters water. Bottom sediments and the soil layer although acting as a geochemical barrier, through these processes become sources of mercury input to mobile media especially as the mercury input to them takes place from both the "top" and "bottom".

Major sources of the natural mercury input to the atmosphere are deep-laid fractures, volcanoes, weathering of mountain rocks and soil particles, plant transpiration, evaporation from the soil and water surface and forest fires.

The natural input of mercury to rivers takes place from the atmosphere due to water erosion of soils and mountain/sediment rocks and runoff.

### 2.1.3 Anthropogenic sources

Mercury was originally present in the environment. Over long periods of time in the pre-industrial age the dynamic equilibrium between different compartments was established when mercury input was balanced by its removal. The industrial epoch resulted in additional quantities of mercury entering the atmosphere, terrestrial systems and sea water thus influencing the main global cycle of mercury.

Dynamics of world mercury production is given in Table 2.1 taken from [Melnikov, 1971]. According to *Trakhtenberg and Lukovenko* (1990) mercury mined during the 19th century amounted to 126500 tonnes. This value is considerably lower than shown in the table.

**Table 2.1** Dynamics of world mercury production, tonnes

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

The basic anthropogenic input of mercury to water comes from the chemical industry (especially chloralcaline and acetaldehyde), mining of mercury and gold, diffuse sources and runoff from contaminated soil. The life-time of mercury compounds in soil is estimated at 250 years [Bandman et al, 1988]. Therefore soil contamination by mercury is a long-term problem inflicting pollution of water, air and biota.

Estimates presented in *Progress report* (1995) show that inputs of mercury to water in industrial countries (Belgium, Denmark, Germany, the Netherlands, Sweden, Great Britain) is several times (from 3 to 10) lower than its emissions to the atmosphere.

According to modern perceptions [Berdowski et al., 1997] the combustion of various kinds of fossil fuel (primarily coal), mining and industrial processes (ferrous and non-ferrous metallurgy, cement production, chloalkali industry) and waste incineration are basic sources of mercury emissions to the atmosphere.



The total global anthropogenic input of mercury estimated by *Nriagu and Pacyna* (1988) and *Pacyna* (1996) amounts to 2.2 - 23.8 kt/y. Emissions to the atmosphere is from 1.0 to 6.1 kt/y, discharges in water - from 0.2 to 7.0 kt/y, and to the soil - from 1.0 to 10.7 kt/y (only direct input is considered, neglecting "secondary" transport from one compartment to another).

Assessments made for 1975 [*Watson, 1979*] showed that total anthropogenic emission of mercury to the environment amounts to 7500 t/y, 2400 t/y going to the atmosphere, 300 t/y to water and 4800 t/y to the soil.

## **2.2 Evaluation of the direct mercury inputs to the marine environment through rivers and from the sea bed**

### **River runoff**

Due to human economic activity, industrial, municipal and domestic wastes containing mercury enter rivers directly. In addition, further mercury contributions to the rivers arrive indirectly from their watersheds. The total discharge from all the world rivers to coastal zones is estimated at 26 t/y of dissolved mercury and 940 t/y of mercury absorbed on particles [*Cossa et al., 1996*]. In the Mediterranean region which contains a majority of the world's known mercury deposits, soil erosion caused by the action of water/precipitation increases the mercury loading of both rivers and the Sea.

The obtained total value of mercury discharged to the seas from rivers (about 1000 t/y) should be properly interpreted with allowance for the fact that particulate matter (95% according to [*Martin and Windom, 1991*]) deposited in the coastal zone. The authors [*Cossa et al., 1996*] estimated the quantity of mobile mercury discharged from rivers to all the seas as 160 t/y with 1-5% in the form of methylated mercury [*Leermakers et al., 1995; Coquery and Cossa, 1995*]. A value 200 t/y for net input of mercury was obtained by *Mason et al.* (1994).

It is worth noting that previous estimates [*UNEP, 1984*] of total mercury discharge from rivers to the Mediterranean Sea, without allowance for sedimentation in the coastal zone, amounted to 130 tonnes per year (range 50-200 t/y), i.e. 5-20% of the estimate obtained by *Cossa et al.* (1996) (1000 t/y) for all the rivers of the world. At the same time, the total river runoff into the Mediterranean ( $4.3 \cdot 10^{11}$  m<sup>3</sup>/year) represents only 1% of the global total.

### **Sediments and thermal sources**

According to the general opinion of the authors of the report [*Mason et al., 1996*] the bulk of inorganic mercury from hydrothermal veins is captured by sediments. The subsequent fate of mercury in sediments remains unknown, i.e. the rate of its demobilization and its input to the marine environment. Further research is required in this area.

Oil and gas deposits may also be important sources of mercury input to coastal and shelf domains of the ocean affecting regional and/or global mercury cycles.

## **2.3 Mercury input to the atmosphere**

Mercury enters the atmosphere from natural and anthropogenic sources. Here anthropogenic emissions implies direct input of mercury to the atmosphere as a result of human activity, and natural emission - any other mercury input from other compartments including indirect anthropogenic one (for example, evasion to the atmosphere from lakes where it was directly discharged).

Volcanoes are considered to be the main direct source of mercury entering the atmosphere. Volcanic activity in Europe is not of a particular importance for either global or regional cycles, but globally the volcanoes make a noticeable contribution to the mercury global cycle via the atmosphere. Volcanic contributions to atmospheric mercury is estimated to be from 30 to 2000 t/y [Nriagu, 1989]. Fitzgerald (1996) states that volcanoes are not very important in the mercury global cycle and discharge to the atmosphere only 20-80 tonnes per year. However, there is an evidence [Zoller, 1983] that the output of each the following volcanoes: El Chicon (Mexico), St.Helens (USA) and Poas (Costa Rica) is about 30 tonnes per year. Volcano Kulaueua (Hawaii) discharges every year about 260 tonnes of mercury vapours [Siegel and Siegel, 1984]. Hence, if only a few of the 700 active volcanoes in the world have comparable outputs then the lower limit of volcanic emissions should be hundreds of tonnes. Note that according to *Buat-Menard and Arnold* (1978) the main flux of the Etna volcano has concentrations of mercury of 250 ng/m<sup>3</sup>, and in samples taken from hot veins (>300°C) - 500 ng/m<sup>3</sup>.

Soil being a geochemical barrier for juvenile mercury can contain greater concentrations of mercury than underlying mountain rocks. Outgassing processes in soil and from underlying rocks via soil may be an important source of mercury input to the atmosphere. At the same time outgassing from soil proper takes place due to biotic activity, especially vegetation and microorganisms. Estimates of outgassing rates in different regions, depending on soil composition, temperatures, underlying surface type, soil pollution and obviously methods applied, varied by several orders of magnitude (from 1 g/km<sup>2</sup> per year for Swedish soils [Schröder et al., 1989]) to 3·10<sup>5</sup> g/km<sup>2</sup> per year for soils near mercury mining or heavy industrial pollution [Lindberg and Turner, 1977].

According to *Lidqvist et al.* (1991) emissions from land outside the planetary mercury belts is 1 g/km<sup>2</sup>/year and within the domain of mercury belts - 10 g/km<sup>2</sup>/year. It was estimated [Munthe, 1993] that emission intensity from USA forest soils is less than 2 g/km<sup>2</sup>/year. According to *Fitzgerald and Mason* (1996) natural continental mercury flux to the atmosphere (excluding Antarctica) is about 1000 t/y, corresponding to a mean outgassing rate of approximately 10 g/km<sup>2</sup>/year.

Mercury evasion rates from fresh-water lakes exceeds outgassing rates from soils in background regions [Axenfeld et al., 1991]. On average [Lindqvist et al., 1991] the evasion rate is within 2-20 g/km<sup>2</sup>/year, and for Swedish lakes this value is within the limits of 18-180 g/km<sup>2</sup>/year, and for American lakes - 0.7-1.5 g/km<sup>2</sup>/year [Munthe, 1993].

A number of scientists consider that the ocean is one of the main sources of mercury to the atmosphere. Elevated emissions from the ocean is observed in the upwelling zone where, in the top layer, high biological productivity takes place. The predominant form of mercury is Hg<sup>0</sup> reduced from Hg(II) and mercury air concentrations are in 1.5-2 times higher than in other ocean regions. Here the evasion rate reaches 3 g/km<sup>2</sup>/year [Kim and Fitzgerald, 1986]. Estimates of the total mercury input from the ocean to the atmosphere are: 2900±1800 t/y [Kim and Fitzgerald, 1986], 800 t/y [Nriagu, 1989] and 2000 t/y [Mason et al., 1994].

Global natural emission is assessed by different authors over rather wide ranges. Estimate summaries of contemporary global natural mercury emissions to the atmosphere are given in Table 2.2.

**Table 2.2** Estimates of contemporary natural global input of mercury to the atmosphere  
(in 10<sup>3</sup> tonnes, in brackets - mean values)

| Volcanoes | Continents | Ocean     | Total   | Reference                               |
|-----------|------------|-----------|---------|---|
|           |            |           | 30-150  | <i>Trakhtenberg and Korshun, 1990</i>   |
|           |            |           | 25      | <i>Garrels et al., 1975</i>             |
|           |            |           | 2-9     | <i>Lindqvist et al., 1991</i>           |
|           |            |           | (3)     |   |
|           | 17.8       |           |         | <i>Weiss et al., 1971</i>               |
|           |            | 21        |         | <i>Lantzy and Mackenzie, 1979</i>       |
|           |            |           | <15     | <i>Lindqvist, 1986</i>                  |
|           |            |           | (6.0)   | <i>Nriagu &amp; Pacyna, 1988</i>        |
| 0.03-2    | 0.02-1.4   | 0.04-1.54 | 0.1-4.9 | <i>Nriagu, 1989</i>                     |
| (1.0)     | (0.7)      | (0.8)     | (2.5)   |   |
| 0.1-2     | 0.3        | 2         | 2.4-4.3 | <i>Fitzgerald, 1990; Petersen, 1992</i> |
|           | 1          | 2         | 3       | <i>Mason et al., 1994</i>               |

It has been assessed [*Lindqvist, 1986*] that, currently natural inputs of mercury from Europe were less than 150 t/y. In work by *Axenfeld et al.* (1991) the European total "natural" emission was estimated to be 265 t/y. *Moisseev* (1997) obtained a similar value (294 t/y).

Contemporary natural emissions in Mediterranean countries (only of the European region including Portugal, Bulgaria and Romania) according to *Axenfeld et al.*, (1991) are approximately 115 t/y, i.e. more than 40% of the European emission (see also Table 2.3 presented below). It is necessary to emphasize once more that natural emission implies any mercury input to the atmosphere from other compartments which is not directly anthropogenic. Therefore natural emission involves secondary anthropogenic pollution which is difficult to isolate from "pre-industrial" natural emission.

Global anthropogenic emission is also evaluated within wide ranges. According to *Lindqvist* (1986) it is 2-17 thousand tonnes per year, while *Nriagu and Pacyna* (1988) and *Pacyna* (1996) from 1.0 to 6.1 (mean 3.6) thousand tonnes per year. The main contribution is made by fuel combustion, waste destruction and industrial processes. The input from combustion of coal enriched with mercury (mercury concentrations in coal reach 100 g per tonnes [*Ryaboshapko and Korolev, 1997*]) is nearly 65% of the global anthropogenic emission [*Slemr, 1996*]. Another considerable source is metal production since ores used contain considerable quantities of mercury as by-product pollution. For example, natural gold can contain 10% (!) mercury [*Ryaboshapko and Korolev, 1997*].

Assessments of mercury anthropogenic emission in Europe have been made for several years. Table 2.3 shows mercury emission from European countries for 1982, 1987 and 1990 reference years. Data for 1982 and 1987 are taken from *Axenfeld et al.* (1991), and for 1990 from *Berdowski et al.* (1997). The last work is an inventory of emission in Europe made on the basis of emission data provided by Parties to OSPARCOM, HELCOM and the Convention on LRTAP. Data on natural emission were taken from *Axenfeld et al.* (1991) and *Moisseev* (1997).

The contribution of the European Mediterranean countries to the European emission (Portugal, Bulgaria and Romania included) is 73 tonnes for 1982 (or more than 15%), 94

tonnes for 1987 (about 12%) and 95 tonnes for 1990 (more than 20%). If natural emission is taken into account the contribution of the Mediterranean countries to the total European emission is about 25% for 1982, about 20% for 1987 and approximately 30% for 1990. Interannual variability of estimates is most probably due to methods of evaluation.

**Table 2.3** Mercury emission from European countries, t/y [Axenfeld *et al.*, 1991; Berdowski *et al.*, 1997; Moisseev, 1997]

| Country                  | Anthropogenic emission |            |            | Natural emission and re-emission             |                |
|--------------------------|------------------------|------------|------------|--|----------------|
|                          | 1982                   | 1987       | 1990       | <i>Axenfeld et al., 1991; Moisseev, 1997</i> |                |
| Albania                  | 0.60                   | 0.834      | 0.51       | 1.3  | 1.859          |
| Austria                  | 0.20                   | 1.083      | 4.27       | 1.9  | 3.293          |
| Belgium                  | 12.60                  | 8.895      | 8.86       | 2.0  | 0.814          |
| Bulgaria                 | 8.60                   | 8.665      | 6.90       | 7.1  | 6.178          |
| Czechoslovakia (former)  | 14.90                  | 14.977     | -          | -  | 3.975          |
| Czech Republic           |                        | -          | 9.31       | 3.9  |                |
| Slovakia                 |                        | -          | 12.40      | 1.7  |                |
| Denmark                  | 2.00                   | 4.780      | 6.92       | 1.0  | 0.382          |
| Finland                  | 3.00                   | 4.142      | 3.04       | 2.1  | 0.472          |
| France                   | 16.72                  | 29.876     | 32.50      | 24.1   | 22.753         |
| Germany                  | 1.50                   |            | 113.00     | 28.9   |                |
| former Eastern           | 23.75                  | 330.506    | -          | -  | 2.153          |
| former Western           | 64.23                  | 64.977     | -          | -  | 6.741          |
| Great Britain            | 37.71                  | 40.568     | 25.6       | 10.5   | 3.356          |
| Greece                   | 1.50                   | 2.106      | 7.12       | 7.6  | 8.976          |
| Hungary                  | 2.90                   | 2.749      | 4.20       | 3.3  | 3.777          |
| Iceland                  |                        | 0.001      | 0.05       | 0.4  | 0.025          |
| Ireland                  | 0.20                   | 8.789      | 1.62       | 3.4  | 1.002          |
| Italy                    | 10.80                  | 13.113     | 11.8       | 14.2   | 14.665         |
| Yugoslavia (former)      | 6.45                   | 7.180      | -          | -  | 13.375         |
| Bosnia & Herzegovina     |                        | -          | 0.22       | 1.8  |                |
| Croatia                  |                        | -          | 1.8        | 2.4  |                |
| The FYR Macedonia        |                        | -          | 1.49       | 1.3  |                |
| Slovenia                 |                        | -          | 0.87       | 0.7  |                |
| Yugoslavia               |                        | -          | 3.86       | 5.2  |                |
| Luxembourg               |                        | 0.066      | 0.77       | 0.1  | 0.078          |
| Netherlands              | 6.68                   | 8.265      | 2.64       | 2.5  | 0.712          |
| Norway                   | 1.30                   | 2.060      | 2.34       | 1.9  | 0.693          |
| Poland                   | 40.00                  | 44.746     | 33.30      | 15.1   | 6.495          |
| Portugal                 | 2.60                   | 5.494      | 5.48       | 6.6  | 5.411          |
| Romania                  | 16.06                  | 15.986     | 7.50       | 10.7   | 10.836         |
| Spain                    | 9.30                   | 10.755     | 20.20      | 28.1   | 31.566         |
| Sweden                   | 7.30                   | 7.501      | 1.45       | 3.9  | 1.123          |
| Switzerland              | 0.10                   | 0.228      | 6.82       | 0.8  | 1.877          |
| USSR* (former)           | 99.40                  | 87.675     | -          | -  | 113.182        |
| Belarus                  |                        | -          | 0.09       | 4.1  |                |
| Estonia                  |                        | -          | 2.2        | 0.4  |                |
| Latvia                   |                        | -          | 0.34       | 0.6  |                |
| Lithuania                |                        | -          | 0.003      | 0.8  |                |
| Republic of Moldova      |                        | -          | 1.52       | 1.0  |                |
| Russian Federation*      |                        | -          | 64         | 58.0   |                |
| Ukraine                  |                        | -          | 36         | 19.2   |                |
| Kazakhstan*              |                        | -          | -          | 6.6  |                |
| Transcaucasian Republics |                        | -          | -          | 8.8  |                |
| <b>Total in Europe</b>   | <b>763</b>             | <b>726</b> | <b>440</b> | <b>294</b>                                   | <b>265.081</b> |

\* - within the EMEP grid

## Chapter 3 ATMOSPHERIC MERCURY

### 3.1 Behaviour in the atmosphere

#### 3.1.1 Forms, reactions, removal constants

The bulk of atmospheric mercury is elemental mercury ( $\text{Hg}^0$ ). Only a minor fraction is present as gaseous divalent mercury ( $\text{Hg}(\text{II})$ ) which is subdivided into organic and inorganic forms and mercury on particles. Due to anthropogenic emissions new portions of mercury continuously enter the atmosphere. Atmospheric mercury is subject to chemical and physical-chemical transformations. Mercury is removed from the atmosphere by both wet and dry deposition processes. These processes continuously change total concentrations of atmospheric mercury compounds and the relationships of its various forms.

#### 3.1.2 Phase transition.

Elemental and other gaseous forms of mercury can be taken up on aerosols or dissolved in water drops. Processes of redistribution between gaseous and aerosol phases due to absorption/desorption steadily take place in the atmosphere. However, it may be assumed that the equilibrium state in absorption/desorption processes is shifted to the left at low temperatures [Ryaboshapko and Korolev, 1997]. These effects are possible for  $\text{HgCl}_2$  whose saturated vapour pressure is much higher than for  $\text{Hg}^0$  especially at low temperatures. In addition, due to its good solubility in water,  $\text{HgCl}_2$  should be readily taken up by aerosols at high relative humidity.  $\text{HgO}$  is mainly present in the aerosol phase. DMHg behaves like  $\text{Hg}^0$  and MMHg - like  $\text{HgCl}_2$  [Ryaboshapko and Korolev, 1997].

#### 3.1.3 Atmospheric reactions

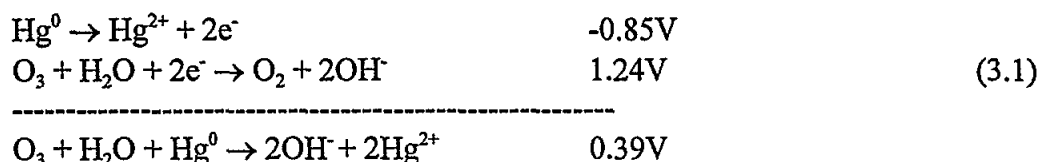
Under normal conditions an oxidation reaction of elemental mercury by ozone can take place [P'yankov, 1949]. Indirectly this reaction has been confirmed with a good correlation ( $r=0.64$ ) of  $\text{Hg}^0$  concentrations with the ratio of  $\text{NO}_2/\text{NO}$  which in its turn is proportional to the ozone content [Foltescu et al., 1996].

Estimates of reaction constants vary within a wide range: from  $5 \cdot 10^{-16} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$  [Stevens et al., 1982] to  $(3 \pm 2) \cdot 10^{-20} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ . Hall (1995) assumed that the reaction is of the order of 0.8. In this case  $\text{Hg}^0$  life-time in the atmosphere should be about 3 months. As to other possible atmospheric reactions no qualitative information is available.

#### 3.1.4 Liquid-phase reactions

In the liquid-droplet phase oxidation of elemental mercury and the establishment of dynamic equilibrium between elemental and oxidized forms is a basic process.

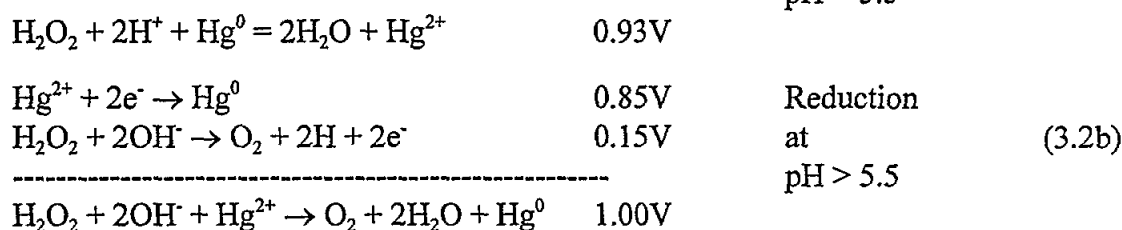
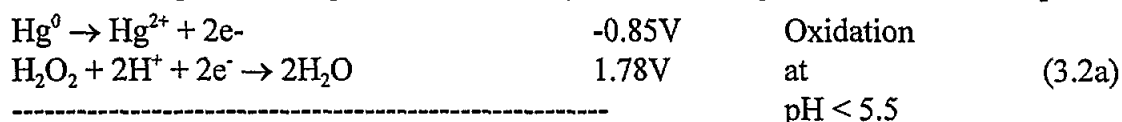
$\text{Hg}^0$  is mainly oxidized by ozone following the reactions [Schröder et al., 1991]:



According to Munthe (1992) this reaction is of the second order and its rate ( $K=(4.7 \pm 2.2) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) does not depend on pH and temperature. Ozone should be present in a drop because of its good solubility (the Henry's coefficient is 0.013 M/atm. at 10°C [Kelly et al., 1985]). According to estimates of Iverfeldt and Lindqvist (1986) the mercury oxidation rate by ozone is 1% h<sup>-1</sup> (at cloud water content 1 g/m<sup>3</sup>, 26 µg/m<sup>3</sup> of gaseous ozone and 1

ng/m<sup>3</sup> of elemental mercury). Provisional assessments by *Munthe* (1993) show the oxidation rate can be 2-3% per day (at mercury and ozone concentrations 3 ng/m<sup>3</sup> and 30 ppb). Later, *Munthe* (1997) came to the conclusion that it is an overestimated value. The authors [*Constantinou et al.*, 1995] believe that the oxidation rate is limited by the rate of dissolution of gaseous mercury in a drop, since oxidation by ozone occurs quickly.

In addition to this reaction when interacting with hydrogen peroxide mercury can be oxidized/reduced depending on pH value following the reactions [*Schröder et al.*, 1991].



*Munthe and McElroy* (1992) dispute the possibility of reaction (3.2a).

Dynamic equilibrium between elemental and oxidized mercury is achieved by redox reactions the most important of which are presented in Table 3.1 [*Ryaboshapko and Korolev*, 1997].

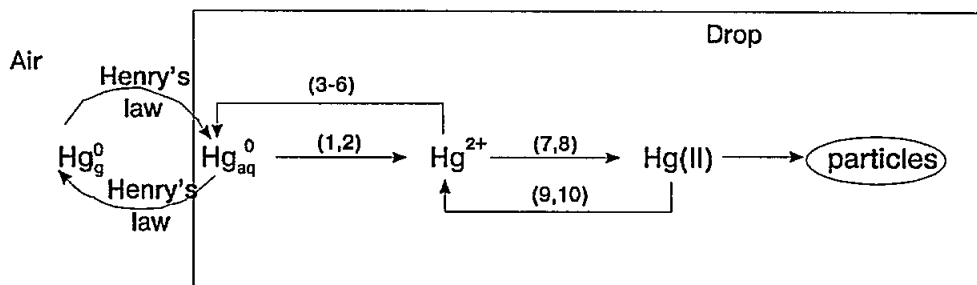
Under real conditions for ion Hg<sup>2+</sup> produced in reaction RO2, the most suitable partner is chlorine ion (reactions RO7 and RO8) (reactions with other halogens are also possible). A set of reactions with sulphite-ion (SO<sub>3</sub>)<sup>2-</sup> (reactions RO3-RO6) is also important providing reduction processes in a drop.

**Table 3.1** Most important reactions of mercury liquid-phase chemistry\*

| No  | Reaction   | Reaction constants **                 | ***  | ****                                  |
|-----|--|---------------------------------------|--|---------------------------------------|
| RO1 | Hg <sup>0</sup> +O <sub>3</sub> -->HgO+O <sub>2</sub>  | 4.5E7 M <sup>-1</sup> s <sup>-1</sup> | 4.7E7 M <sup>-1</sup> s <sup>-1</sup><br>1 | 4.7E7 M <sup>-1</sup> s <sup>-1</sup> |
| RO2 | HgO+H <sup>+</sup> -->Hg <sup>2+</sup> +OH <sup>-</sup>  | 1E10 M <sup>-1</sup> s <sup>-1</sup>  |  |                                       |
| RO3 | Hg <sup>2+</sup> +SO <sub>3</sub> <sup>2-</sup> -->HgSO <sub>3</sub>                                     | 4E-12 M                               |  | 2E-13M                                |
| RO4 | HgSO <sub>3</sub> +SO <sub>3</sub> <sup>2-</sup> --><br>>Hg(SO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> |                                       |  | 4E-12 M                               |
| RO5 | HgSO <sub>3</sub> -->Hg <sup>0</sup> +SO <sub>3</sub> <sup>2-</sup>                                      | 0.6 s <sup>-1</sup>                   |  | 0.6 s <sup>-1</sup>                   |
| RO6 | Hg(SO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> -->Hg <sup>0</sup> +2SO <sub>3</sub> <sup>2-</sup>       |                                       | 4E-4s <sup>-1</sup>                        | 1E-4 s <sup>-1</sup>                  |
| RO7 | Hg <sup>2+</sup> +Cl <sup>-</sup> -->HgCl <sup>+</sup>   | 1.82E-7 M                             |  |                                       |
| RO8 | HgCl <sup>+</sup> +Cl <sup>-</sup> -->HgCl <sub>2</sub>  | 3.31E-7M                              |  |                                       |
| RO9 | Hg(OH) <sub>2</sub> -->Hg <sup>2+</sup> +2OH <sup>-</sup>  |                                       |  | 1E-22M <sup>2</sup>                   |
| R10 | HgCl <sub>2</sub> -->Hg <sup>2+</sup> +2Cl <sup>-</sup>  |                                       |  | 1E-14M <sup>2</sup>                   |

\* - [*Ryaboshapko and Korolev*, 1997] \*\* - [*Pleijel and Munthe*, 1995a] \*\*\* - [*Petersen et al.*, 1996]  
\*\*\*\* - [*Constantinou et al.*, 1995]

When drops contain soot particles divalent mercury can be absorbed on them. Since absorbed divalent mercury obviously cannot be reduced to elemental one [*Munthe*, 1997] the particles become a sink of divalent mercury, providing additional "pumping" of elemental mercury to a drop. The scheme of this process with regard to elemental mercury is shown in Fig.3.1.



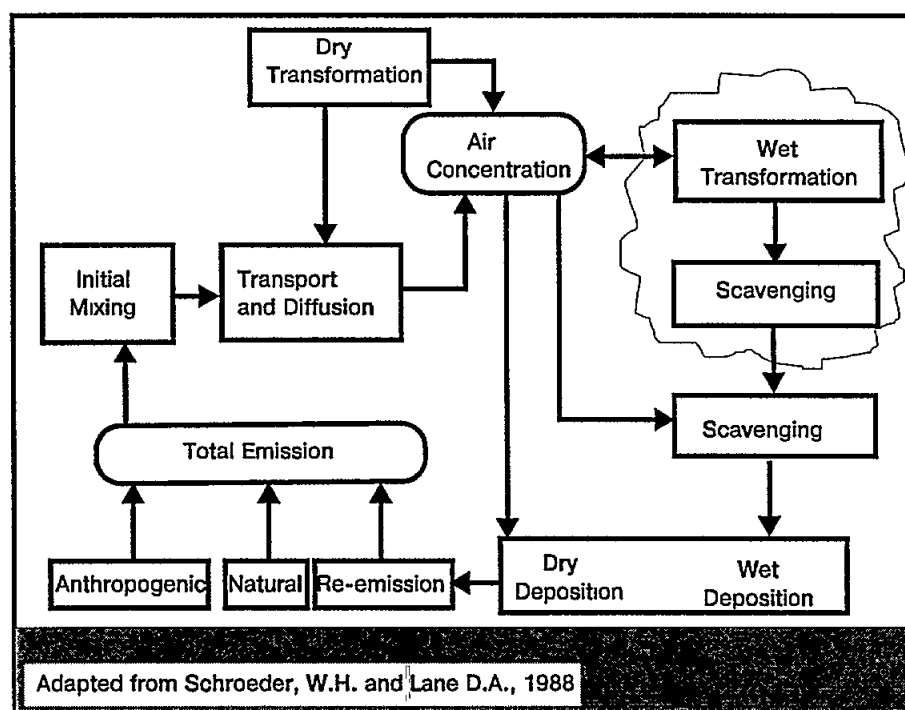
**Figure 3.1** The scheme of processes in liquid-drop phase with allowance for the input of gaseous  $\text{Hg}^0$  from air (figures in brackets - reaction number from table 3.1)

*Ryaboshapko and Korolev (1997)* believe that the role of soot particles in atmospheric mercury chemistry is not completely clear.

Very little is known about a solid-phase reaction of mercury and its compounds.

### 3.2 Removal from the atmosphere

Mercury removal from the atmosphere takes place due to dry and wet deposition. Figure 3.2 [adapted from *Schröder and Lane, 1988*] shows the mercury atmospheric cycle from emission from natural and anthropogenic sources to deposition on the underlying surface.



**Figure 3.2** Mercury Emissions-To-Deposition Cycle

Wet deposition is executed by washout processes which can be both reversible and irreversible [*Ryaboshapko and Korolev, 1997*]. In case of reversible scavenging (in the scheme - scavenging in the cloud) mercury is captured by a cloud drop/fog and remains in the atmosphere. Later, the drop is most probably evaporated producing an aerosol particle which eventually enters a drop again. *Rodhe (1992)* estimated that, before being irreversibly scavenged, on the average each drop experiences such a cycle 5 times. In case of irreversible

scavenging (in the scheme - scavenging in the atmosphere) mercury with snow and rain falls out to the underlying surface.

Dry deposition (though as applied to fine particle and gases it is more correct to use the term "dry absorption" [Ryaboshapko and Korolev, 1997]) is defined by the intensity of an atmospheric substance flux in the turbulent layer and laminar sublayer, and by the physical-chemical properties of the underlying surface.

Ryaboshapko and Korolev (1997) consider a set of data on dry deposition rates provided by various authors for different mercury species. The dry deposition rate of  $\text{Hg}^0$  for forests varies within 0-0.03 cm/s, for other types of the landcover it is zero. It is considered that scavenging rates for  $\text{Hg}(\text{Cl})_2$  and  $\text{Hg}(\text{P})$  are similar to those of nitric acid and  $\text{SO}_4$ .

Lindqvist *et al.* (1991) consider that about 30% of total global deposition (2500 of 7500 t/y) is due to dry scavenging while Petersen (1992) calculates the amount at 50% (4000 of 8000 t/y). The uncertainty of calculations is within one order of magnitude. At the regional and local levels the input of dry scavenging varies within wide ranges depending on climate, underlying surface types, relative content of mercury forms emitted by local sources, etc.

Scavenging rates of various mercury forms are very different. The scavenging rate of total mercury is also different at local, regional and global scales. Near sources this scavenging rate of mercury species can be as much as hours. According to data of [Expert Panel ..., 1994] about 5-10% of the primary emission of  $\text{Hg}(\text{II})$  is deposited within a radius of 100 km therefore, the life-time of  $\text{Hg}(\text{II})$  is less than 24 hours. Depending on atmospheric concentrations and tree species, substantial absorption of  $\text{Hg}^0$  by the foliage takes place. According to Ebinghaus and Krüger (1996) 30% of mercury emitted by a powerful source is washed out by precipitation within 5-km zone. This corresponds to life-time that is not more than 1-2 hours.

At the regional level the scavenging rate is considerably lower but is still high for emitted  $\text{Hg}(\text{II})$  compounds and particle bound mercury [Expert Panel ..., 1994] which are subject to both wet and dry scavenging. The life-time of the aerosol mercury constituent is about 5 days (approximately 1 week) similar to other chemical compounds [Expert Panel ..., 1994].

At the global level the scavenging rate is mainly determined by the transition rate of gaseous elemental mercury to more easily scavenged compounds. Using several different methods Slemr *et al.* (1985) obtained a life-time for mercury of 0.6-1.4 years. Later, Slemr (1996) confirmed these estimates.

### 3.3 Mercury concentration in the atmosphere and precipitation

#### 3.3.1 Background data

A reliable determination of individual mercury forms is a rather difficult problem. Iverfeldt (1992) notes that "the history of mercury speciation in air ... is also, in many cases, a history of biased or reproducible results". A NATO expert group [Pacyna *et al.*, 1996] considers that sampling and analysis methods of total mercury give reliable estimates (standard deviation - 10-15%). At the intercalibration of these methods an acceptable agreement of the results was obtained for 8 of 13 leading laboratories of the USA, Canada and Germany [Schröder *et al.*, 1995]. Standard deviation can reach 100% [Pacyna *et al.*, 1996] when the aerosol component is measured. No consistency has been obtained for aerosol fraction [Schröder *et al.*, 1995]. Porcella *et al.* (1996) believe that data obtained before 1990 are doubtful due to methodological problems.



The first measurements of atmospheric mercury were carried out in 1934 [Stock and Cucuel, 1934]. Since then a great number of measurement data have appeared. The greatest numbers of measurements have been carried out in Sweden, Germany, Norway, the USA and Canada. During the 80s many measurements were made on the USSR territory [Fursov, 1983,1988]. Observation results in remote areas were published by Brosset (1982,1987); Fitzgerald (1986); Iverfeldt (1992); Iverfeldt et al. (1995); Schröder (1994); Gill et al. (1995). These represent only some of the works over the last 15 years. Substantial information is discussed in the papers by Lindqvist and Rodhe (1985); Lindqvist et al. (1991); Petersen et al. (1996); Slemr (1996). The PARCOM network measurements are presented in OSPARCOM (1994). Some data are provided by Berg et al. (1996).

Mainly air concentrations of TGM (total gaseous matter) were measured, then separately - Hg(II), mercury on particles Hg(P) and methyl- and dimethylmercury. In precipitation total concentrations of HgTot, then Hg(IIa) and the particulate fraction Hg(P) as well as MMHg were determined.

Total concentrations and the contribution of various forms varied with regions depending on the effect of local and regional emissions. Lindqvist et al. (1991) refers to background regions, deserts, oceans, the polar regions, remote areas over both sea and land, remote industrial regions, industrial regions and heavily polluted regions. Measurements carried out over the Atlantic ocean showed that more than 92% of mercury in air masses of oceanic origin represents elemental mercury while elemental mercury amounts to 83% of mercury in air masses of continental origin [Slemr et al., 1985].

In background regions the total mercury concentrations in air are 1-2 ng/m<sup>3</sup>, with Hg(II) and Hg(P) content being less than 2%. In industrial regions the total mercury concentrations amount to 3-6 ng/m<sup>3</sup> and Hg(II) and Hg(P) content is up to 5%. In heavily polluted areas concentrations of total mercury reach 6-30 ng/m<sup>3</sup>, Hg(II) content can be 20% and Hg(P) - 10% [Lindqvist et al., 1991; based on various publications during 1986-1990].

The total mercury concentrations in precipitation in remote and moderately polluted regions are within the range of 2-100 ng/l [Petersen et al., 1996; data of various authors published at the end of the 80s]. The mercury input with precipitation can be also characterized by wet deposition density. These densities [Lindqvist et al., 1991] are 5 g/km<sup>2</sup>/year for polar regions and the oceans and up to 80 g/km<sup>2</sup>/year for heavily polluted areas. Global estimates [Cossa et al., 1996] for coastal regions vary from 8 g/km<sup>2</sup>/year for the southern hemisphere and to 18 g/km<sup>2</sup>/year for temperate latitudes of the northern hemisphere. Mason and Fitzgerald (1996) present figures for the oceans which are two times lower. As is mentioned by Iverfeldt (1991b) the input of particle bound mercury to its total concentration in precipitation varies from <10% at remote sites to 90% in polluted regions. The fraction of MMHg to the total concentration [Lee and Iverfeldt, 1991] varies from 0.1 to 3%. According to Fitzgerald et al. (1991); Fitzgerald et al. (1994); Lamborg et al. (1995) the MMHg content in mid-continental regions of the USA reaches 7%. The origin of methylmercury in precipitation has not yet been explained.

Table 3.2 contains data on concentrations of mercury and its compounds in different regions of Eurasia and North America.

**Table 3.2** Mercury concentrations in the atmosphere and precipitation in Eurasia and North America.

|                                  | Air                           |                              |                               |                              |                 | Precipitation |               |              | References                           |
|----------------------------------|-------------------------------|------------------------------|-------------------------------|------------------------------|-----------------|---------------|---------------|--------------|--------------------------------------|
|                                  | HgTot<br>(ng/m <sup>3</sup> ) | HgII<br>(pg/m <sup>3</sup> ) | Hg(P)<br>(pg/m <sup>3</sup> ) | MMHg<br>(pg/m <sup>3</sup> ) | HgTot<br>(ng/l) | HgIIa<br>ng/l | Hg(P)<br>ng/l | MMHg<br>ng/l |                                      |
| Europe, Sweden                   | 2.2 - 2.8                     | 90 - 190                     |                               |                              |                 | 2.2 - 3.0     | 3.4 - 10      |              | <i>Brosset, 1987</i>                 |
| Sweden                           | 2.8 - 3.7                     |                              | 50 - 60                       |                              | 13 ± 4          |               |               |              | <i>Iverfeldt, 1991 a,b</i>           |
| Sweden                           | 2.5 - 2.8                     |                              |                               |                              | 9 - 35          | 1.0 - 2.4     |               |              | <i>Petersen et al., 1995</i>         |
| Sweden                           |                               |                              | 0.1                           |                              |                 | 0.15 - 0.3    |               |              | <i>Munthe, 1993</i>                  |
| Norway, south                    | 1 - 4                         | 50 - 150                     | 1 - 86                        | < 1 - 8                      | (2 - 100)       |               |               |              | <i>Foltescu et al., 1995</i>         |
| Central and                      | 2.5 - 8.2                     |                              | 50 - 60                       |                              | 9 - 462         | 1.0 - 29.4    |               |              | <i>Petersen et al., 1996</i>         |
| Northern Europe                  |                               |                              |                               |                              | 5 - 50          |               |               |              | <i>Pleijel &amp; Munthe, 1995a,b</i> |
| Industrial part                  |                               |                              |                               |                              |                 |               |               |              | <i>Fursov, 1983</i>                  |
| European part of the former USSR | 1.1 - 4.2                     |                              |                               |                              |                 |               |               | 0.05 - 0.5   |                                      |
| Middle Asia & Kazakhstan,        | 2 (1.5 - 3)                   |                              |                               |                              |                 |               |               |              | <i>Fursov, 1983, 1988</i>            |
| lake Baikal, summer              | 0.7 - 2.3                     |                              | 5 - 20                        |                              | 2.9 - 20        |               |               | 0.1 - 0.25   | <i>Leermakers et al., 1996</i>       |
| winter                           | 1.2 - 6.2                     |                              | 20 - 90                       |                              | 8.6 - 60        |               |               | 0.09 - 0.29  |                                      |
| USA, Florida                     | 2 (1.5 - 3)                   |                              | 44 (10 - 120)                 |                              |                 |               |               |              | <i>Dvonch et al., 1995</i>           |
| Florida                          | 1.6 ± 0.8                     |                              |                               |                              |                 |               |               |              | <i>Gill et al., 1995</i>             |
| Wisconsin                        | 1.6 ± 0.4                     |                              | 22 ± 19                       | 12 ± 13                      | 6 - 5           |               |               | 0.16 ± 0.07  | <i>Fitzgerald et al., 1991</i>       |
| N.-E. of USA                     |                               | 0.05 - 0.15                  | 75                            |                              | 15              |               |               |              | <i>Stratton &amp; Lindberg, 1995</i> |
| Ontario                          | 2.5 (2.2 - 3.7)               |                              |                               |                              |                 |               |               |              | <i>Schröder, 1996</i>                |
| USA                              |                               | 0.05 - 160                   |                               |                              | 14              |               |               |              | <i>Schröder et al., 1987</i>         |
| USA and Canada                   |                               |                              |                               |                              |                 |               |               |              | <i>Vandal et al., 1991</i>           |
| Canada, Alert                    | 1.5                           |                              |                               |                              |                 |               |               |              | <i>Schröder et al., 1995</i>         |

In the oceanic atmosphere mercury is distributed rather uniformly. Normal concentrations are 1-3 ng/m<sup>3</sup>. Mean concentrations in the Atlantic Ocean in the northern hemisphere are 1.96 ng/m<sup>3</sup> (data from 1977-1980) and 2.25 ng/m<sup>3</sup> (data from 1990) and in the southern hemisphere - 1.33 ng/m<sup>3</sup> and 1.5 ng/m<sup>3</sup> respectively [Slemr *et al.*, 1995]. In the Pacific Ocean from 40°S to the equator the mean concentration is about 1 ng/m<sup>3</sup> and from the equator to 20°N about 1.8 ng/m<sup>3</sup> [Fitzgerald, 1996; Fitzgerald *et al.*, 1991]. Experimental data for the Indian and southern oceans are virtually non-existent [Slemr, 1996]. Measurement data on gaseous mercury concentrations obtained in 1990 for the Atlantic Ocean and for the Pacific Ocean in 1980-86 are presented in the paper by Fitzgerald and Mason (1996).

In a clean oceanic atmosphere elemental mercury accounts for 99% of gaseous mercury and the remaining fraction is accounted for by MMHg [Mason *et al.*, 1992]. Gaseous inorganic compounds Hg<sup>2+</sup> are absent due to their high solubility [Fitzgerald and Mason, 1996]. Particle bound mercury is 1% of the total mercury concentration in air [Slemr *et al.*, 1995; Lamborg *et al.*, 1995].

Measured concentrations [Slemr *et al.*, 1985; Millward and Griffin, 1980] of particle bound mercury are 11-13 pg/m<sup>3</sup> in the northern Atlantic and 7 pg/m<sup>3</sup> in its southern part. Measured concentrations of particle bound mercury at Enewetak Atoll (11°N) and American Samoa (13°S) (0.4-2 pg/m<sup>3</sup>) [Fitzgerald *et al.*, 1991] show that the aerosol fraction content in the Pacific Ocean is lower than in the Atlantic.

Total mercury concentrations in precipitation falling in the Pacific Ocean are from 1.2 to 17 ng/l [Mason and Fitzgerald, 1996]. Total mercury concentrations in the northern part of the Atlantic Ocean are 9 and 26 ng/l at 37°N and 34°N [Fitzgerald, 1989]. No measurements of mercury in precipitation in the South Atlantic, Indian Ocean and in high southern latitudes were carried out [Mason and Fitzgerald, 1996]. Very scarce information on the content of individual mercury species in oceanic rain is available. In the equatorial Pacific MMHg has not been detected (the detection limit is 10 pg/l), i.e. a priori methylmercury content does not exceed 1%, but in its north-western part 2-5% of MMHg was recorded. It was assumed that methylmercury was produced as a result of demethylmercury decomposition in the atmosphere [Mason and Fitzgerald, 1996]. The bulk of mercury in precipitation is presented as a soluble fraction.

### 3.3.2 Mercury over regional seas and coastal zones

Regional seas and coastal zones are seen as the transition zones between continental and oceanic regions. Data on the Baltic Sea obtained within the framework of the Swedish national monitoring programme [Iverfeldt *et al.*, 1996] show that during 1992-94 the density of total wet deposition at coastal sites was 6-11 g/km<sup>2</sup>/year, and MMHg content in precipitation from 1 to 3%.

Data on the North Sea obtained by the PARCOM network [OSPARCOM, 1994] during 1987-92 demonstrated that concentrations in precipitation monitored at coastal sites amounted to 50 ng/l (English stations) and 10-30 ng/l (other stations). Air concentrations measured in 1992 at Norwegian coastal stations were 2 ng/m<sup>3</sup> (data for Spitsbergen obtained in 1994, 1995 [Berg *et al.*, 1996] indicate values 1.6-1.8 ng/m<sup>3</sup>). At the Mace Head station on the western coast of Ireland showed concentrations of 1.5 ng/m<sup>3</sup>.

According to the data from a number of authors [UNEP/FAO/WHO, 1987, p.16] air concentrations over the Tyrrhenian Sea are 2.1 ng/m<sup>3</sup>, near the coast - 3 ng/m<sup>3</sup> and on the Ligurian Beach Sea coast - 6 ng/m<sup>3</sup>. Total concentrations in precipitation in the urban area near

the coast were 70 ng/l at the beginning of a rain event and fell to 18 ng/l late in the event [Ferrara et al., 1986a].

Slemr (1996) reviewed some measurement data on the intrusion of oceanic air masses to the coastal zone. In San-Francisco air concentrations were 1-2 ng Hg/m<sup>3</sup> [Williston, 1968], and on the Pacific coast of Japan, 1 ng Hg/m<sup>3</sup> [Matsunaga and Goto, 1976]. Observations carried out by the Netherlands and Norway in the Atlantic showed air concentrations equal to 1.8-2.3 ng Hg/m<sup>3</sup> [Van der Sloot and Das, 1974] and 0.4-3.5 ng Hg/m<sup>3</sup> [Thrane, 1978]. These data are well correlated with total mercury concentrations in the clean oceanic atmosphere of the Pacific and Atlantic Oceans presented above.

High concentrations of total mercury in precipitation together with an elevated relative content of particle bound mercury in such precipitation testify to the continental origin of the air masses. According to data provided by Mason and Fitzgerald (1996) observed mercury concentrations in precipitation in Chesapeake Bay were 17 ng/l, and 3 ng/l on the eastern coast of the Pacific (Washington State), suggesting that in the latter case the precipitation was of oceanic origin. In Chesapeake Bay the relative content of particle bound mercury was found to be 75% testifying to the continental origin of the precipitation.

### 3.3.3 Gradient regions

Regions containing different levels of pollution give rise to graduated concentrations and relative contents of various pollutants in zones of transition. The first example, the coastal zone as a transition zone between more polluted continental region and cleaner oceanic zones has been described above.

The second example is described by Ebinghaus and Krüger (1996). Measurements were conducted at three sites: heavily polluted factory area; moderately polluted Langenbrugge; and the background site at Mace Head in Ireland. A drastic decrease of total mercury concentration in air (from 10-580 ng/m<sup>3</sup> to ~4ng/m<sup>3</sup>) and in precipitation (from 15 to 12700 ng/l to ~50 ng/l) from the factory area to Lanenbrugge is observed. The relative content of particulate matter in precipitation did not actually change and amounts to 90%. It is appropriate to call this region as a region of local gradient. The decrease of total air concentrations (from 4 to 1.5 ng/m<sup>3</sup>) and concentrations in precipitation (from ~50 to 17 ng/l) between Langenbrugge and Mace Head is less marked but the reduction of Hg(P) content is important (from ~90% to 30-35%).

Variability of the gradient in Sweden is a classical example. Observations from the south to the north show a decrease in mercury concentrations in air (weak), concentrations in precipitation (strong) and of the relative content in particulate matter (drastic) [Brosset, 1987]. See also Table 3.4. The lower boundaries of the range correspond to the northern part of Sweden, and the upper boundary to the southern one). It is reasonable to consider this gradient as a regional one.

A similar gradient is observed in the Arctic region. Here mercury concentrations decrease from the south to the north [Schröder et al., 1995]. Obviously its origin is the same as in Sweden but it shows the transition (character) from regional to global gradient.

Finally, the concentration gradient in the oceans [Slemr, 1996; Fitzgerald and Mason, 1996] is manifested by concentration reductions in the oceanic atmosphere from the north to the south. This gradient is certainly of a global character and can be explained, on the one hand, by the fact that the bulk of pollution is concentrated in the northern hemisphere and on the other (it is highly probable) natural emissions from the northern hemisphere due to relatively large land masses as compared to the southern hemisphere.

## Chapter 4 MODELLING OF MERCURY ATMOSPHERIC TRANSPORT AND ITS DEPOSITION

Spatial and temporal distributions of mercury concentration and deposition are determined by a number of atmospheric and physical-chemical processes. Physical-chemical transformations of mercury compounds (including  $\text{Hg}^0$ ) are of particular importance. Designing measurement programmes and interpreting the results is impossible without a transparent conceptual model of mercury behaviour in the atmosphere. When selecting cost-effective strategies for the abatement of mercury pollution, direct application of measurement data to a considerable extent is of no sense, since understanding individual processes occurring in the atmosphere does not automatically lead to understanding the total complex of these processes. A sufficiently comprehensive pattern of individual processes and their interaction can be reproduced by numerical modelling.

### 4.1 Modelling approaches

At present there are mercury models of various types which have been developed or are under development. They include global models which describe input/accumulation of mercury in different environmental compartments and exchanges among them. These models are useful for understanding the mercury cycle, evaluation of the impact on the cycles by anthropogenic emissions as well as the detection of mercury pollution trends and the efficiency of measures taken. Transport processes and mercury transformations are described by regional and local models with spatial resolution hundreds-thousands of kilometers and hundreds of kilometers respectively.

In modelling, a receptor-oriented approach is possible when the model evaluates the input from different sources using measurements made at sampling sites or "receptors" thus allowing characterization (so-called source signature or profile) of possible sources. Hybrid receptor models are also used which consider in addition the transport of air masses to a "receptor" from other sources [*Expert panel...*,1994].

Source oriented models are the most widely used ; some of them will be described below. There are two basic approaches - Lagrangian and Eulerian. Lagrangian models or trajectory models describe turbulent processes and reactions of the first order. Models of this type, requiring less computer resources are suitable for the explanation of processes without non-linear phenomenon and/or interactions.

Eulerian models directly simulate non-linear processes and, at the same time, consider a number of cloud and subcloud wet and dry removal processes, as well as the vertical distribution of mercury compounds.

Among Lagrangian models worthy of mention is the model of *Petersen et al.* (1995) and local-scale models with more complicated chemical schemes of *Pleijel and Munthe* (1995a,b).

The basic model of *Petersen et al.* (1995) is similar to Lagrangian models describing photo-oxidant transport and particle-carried heavy metals. This model considers three mercury forms: elemental  $\text{Hg}^0$ , gaseous divalent  $\text{Hg(II)}$  and particle bound mercury  $\text{Hg(P)}$ .

Wash-out ratio and dry deposition velocity are considered for gaseous divalent mercury  $\text{Hg(II)}$  - by analogy with lead and are constant over the whole calculation domain. Dry deposition velocity of  $\text{Hg}^0$  is taken to be zero, washout ratio variable in time and space is calculated on the basis of only liquid-phase reactions including  $\text{Hg}^0$  oxidation by ozone, reduction by sulphite-ions  $\text{SO}_3^{2-}$  and absorption of reaction products on soot carbon particles in a drop (see chapter 3).

Calculation results using this simple model demonstrated the difference in concentrations between summer and winter air ; south-north reductions in concentrations in air and precipitation

in Scandinavia: the reductions were smaller for air concentrations compared to those for precipitation [Petersen et al., 1995]. More complicated schemes of physical-chemical transformations were tested and evaluated in Pleijel and Munthe (1995a,b). Testing results prepared the ground for design of a generalized physical-chemical scheme (see Figure 4.1) adapted from Petersen et al (1996). It contains 14 mercury species and 21 reactions. This scheme is simpler than those considered in Pleijel and Munthe (1995a,b), but is complemented by gas-phase reaction of  $\text{Hg}^0$  oxidation by ozone taken from Hall (1995).

Scheme presented in Figure 4.1 was incorporated in the improved Eulerian transport model ADOM (Acid Deposition and Oxidation Model [Venkatram et al., 1988]).

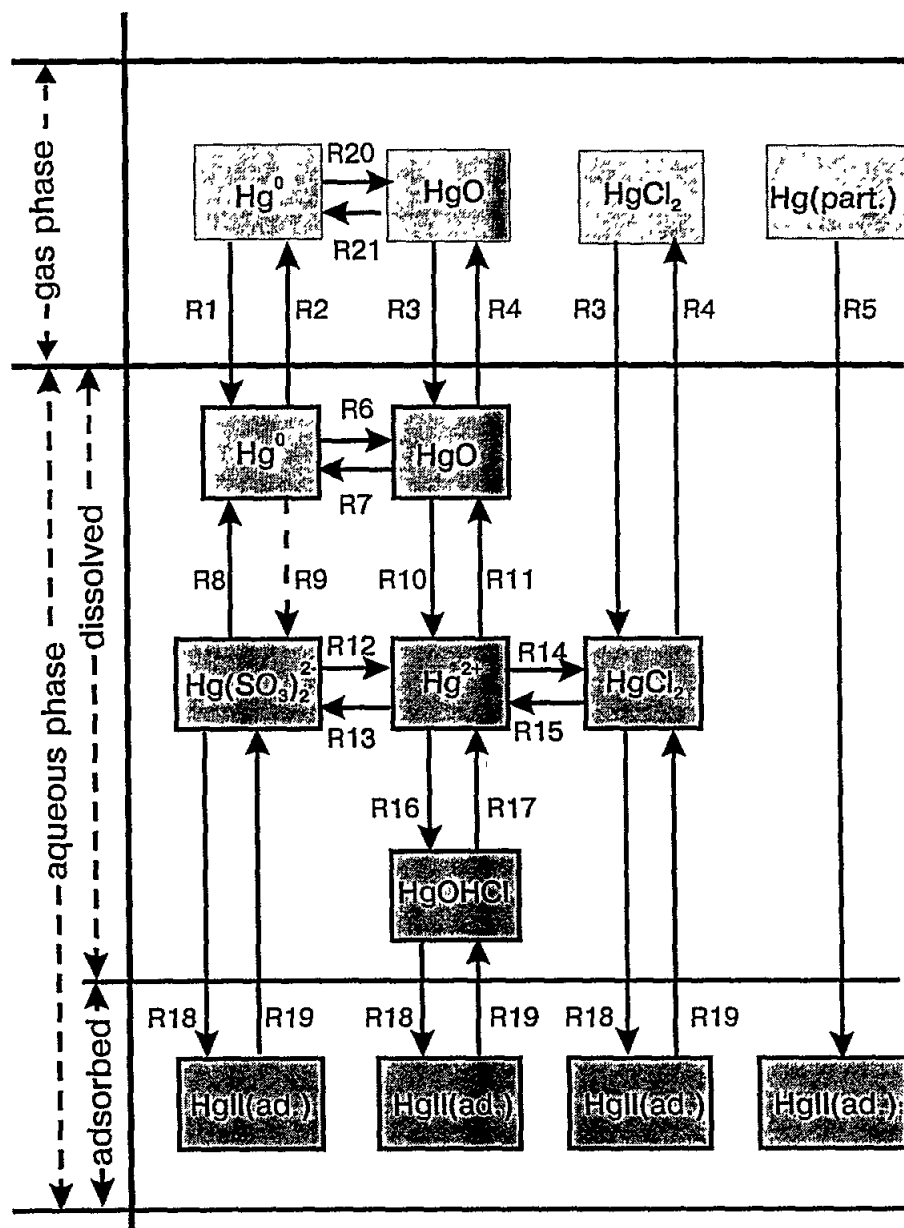


Figure 4.1 Atmospheric mercury chemistry scheme (R1-R19 denote rate constants and equilibrium constants) (adapted from [Petersen et al., 1996])

The input data for modelling include:

Meteorological data (horizontal and vertical wind speed, eddy diffusivity, temperature, humidity, cloud distribution and data from a high resolution boundary layer model); geographical data (terrain height, 8 categories of land use, 12 soil categories, snow season); emission data on  $\text{Hg}^0$ ,  $\text{HgCl}_2$  and  $\text{Hg(P)}$  (point and area sources);

initial and boundary concentrations.

The difference operator is split in such a way:

$$C^{n+1} = B \cdot B^T \cdot C^n; \quad B = A_x \cdot A_y \cdot A_z \cdot A_c,$$

where  $A_x, A_y$  - operators of horizontal transport and diffusion;

$A_z$  - operator of vertical transport and diffusion, input from sources and physical depletion;

$A_c$  - operator including cloud mixing, dry removal and all chemical transformations;

$B^T$  - operator transposed to B;

$C^{n+1}$  and  $C^n$  - species concentrations at  $n+1$  and  $n$  time steps.

Symmetric form of the operator is used to cancel errors built up at each calculation time-step [Marchuk, 1975].

Dry removal is determined by its velocity and is inversely proportional to the sum of weighted area resistance: aerodynamic, surface and canopy. Dry removal for  $\text{Hg}^0$  is not zero only for forests.

The removal from clouds is considered for two cloud types: stratus (layer cloud) and cumulus (convective clouds). Reactions occurring in the liquid-phase in stratiform cloud are considered only during a precipitation event, in cumulus clouds they are considered during their life-cycle beginning with cloud formation when mercury species are injected to the cloud, dwell phase when liquid-phase reactions take place and cloud dissipation when mercury species are ejected from the decaying cloud. The ADOM system was developed for calculations in north-western and central Europe and eastern regions of North America.

The Eulerian model MODIS (MOment DISpersion) [Eppel *et al*, 1991] is also worthy of mention and was applied [Ebinghaus and Krüger, 1996] to the evaluation of mercury emission intensity from powerful sources using measurement data. The MODIS model is an extended version of a simple Gaussian model. To determine the desired set of source strengths the cost function minimization method is used. The cost function depends on simultaneously measured and calculated concentrations. Minimization is an iteration process. Each incremental step uses a set of sought source strengths and calculations of concentrations at measurement sites are made. The next set of source strengths is determined by the simplex-method. Iteration is repeated until a minimum cost function is obtained. In this study the source-oriented model was used rather than the less useful receptor-oriented approach.

## 4.2 MSC-E Model

The model used for the evaluation of mercury transport was developed at MSC-E on the basis of the ASIMD (ASymmetric Improved MoDel) model [Pekar, 1996] and the physical-chemical module described in [Ryaboshapko and Korolev, 1997].

#### 4.2.1 Transport

The Eulerian multilayer ASIMD model was used for calculations of lead and cadmium transport and participated in the intercomparison study of long-range transport of lead carried out under EMEP [EB.AIR/GE.1/28, item VIII (31)]. The model calculation results were compared with Pb and Cd measurements of the PARCOM network [Pekar, 1996] and with data from Berg *et al.* (1996) and OSPARCOM (1994) (see [Pekar *et al.*, 1997]). These comparisons demonstrated reasonable agreement between calculated and measured data.

The model version used has 4 layers with the upper boundaries at 100, 400, 1100 and 2100 m. The layer depths were influenced by the meteorological data available. Horizontal transport in ASIMD is realized using an asymmetric advection scheme. Compensation for numerical diffusion accomplished by correcting advection velocity, depending on local gradients.

Vertical diffusion is calculated using an explicit scheme with the conservation of 3 moments developed for unequal grid intervals.

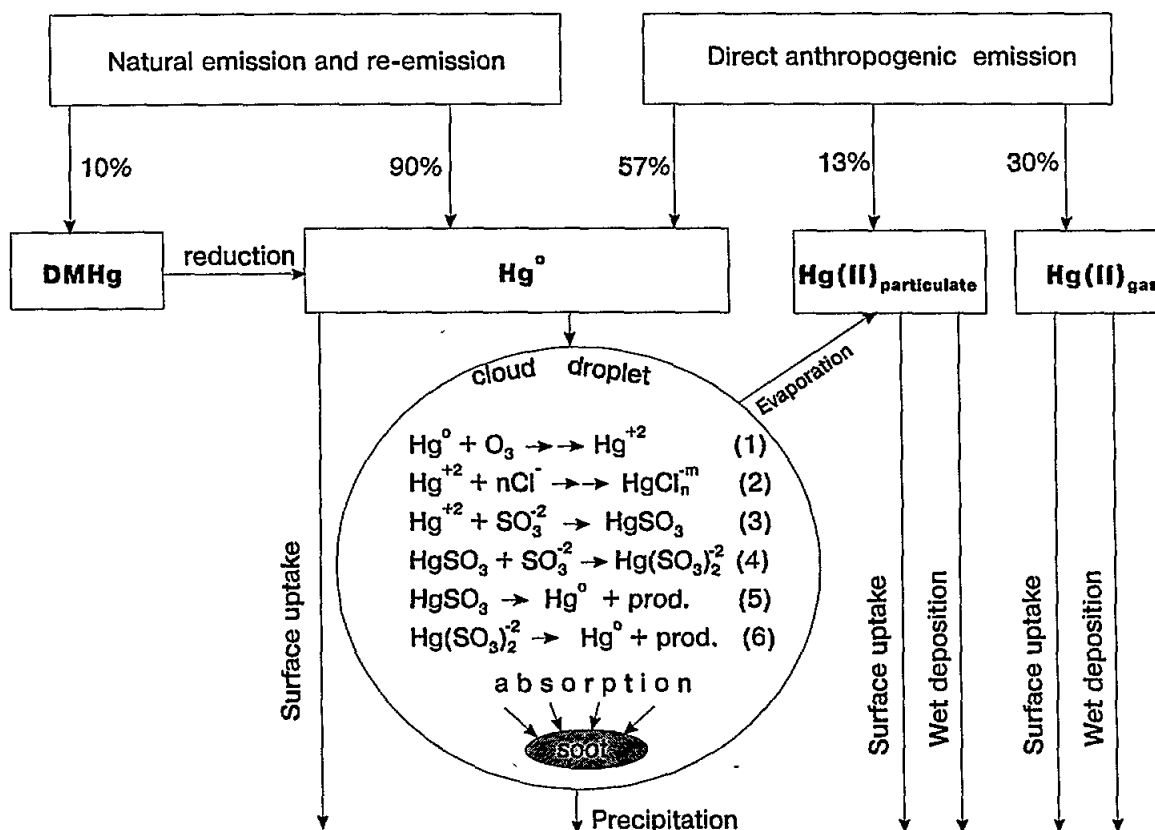
Parameters required for the description of local pollution dispersion conditions consists of friction velocity  $u_*$  (m/sec), Monin-Obukhov length scale  $L$ (m), mixing layer height  $h$ (m), vertical diffusion coefficient profiles  $K_z(z)$  ( $m^2/sec$ ) devised on the basis of the 1000 mb wind, temperature and roughness  $z_0$ .

The calculation region covers the domain of the EMEP grid with a spatial resolution of  $150 \times 150$  km<sup>2</sup>. Temporal resolution is 1 hour. Summing/averaging of calculated values was made for each month.

Three components  $Hg^0$ ,  $Hg(II)$  and  $Hg(P)$  were considered. Their dry and wet scavenging was calculated using a physical-chemical scheme for transformation/scavenging.

#### 4.2.2 Physical-chemical scheme for transformation and scavenging

A general scheme of mercury scavenging is presented in Figure 4.2 [Ryaboshapko and Korolev, 1997].



**Figure 4.2** Modelling scheme of chemical transformations and removal of mercury from the atmosphere (from [Ryaboshapko and Korolev, 1997])



Hg<sup>0</sup> oxidation in the gas phase is not considered. It is assumed that DMHg removal from the atmosphere takes place due only to chemical reactions of mercury reduction. The removal (wet and dry scavenging) accounts for Hg(P) and gaseous inorganic mercury compounds Hg(II). The reduction reaction of oxidized gaseous compounds to Hg<sup>0</sup> and the dependence of redistribution between gaseous and aerosol fractions on temperature were neglected.

It is assumed that dissolution of Hg<sup>0</sup> follows Henry's law. The most important reactions in the liquid-drop phase are: Hg<sup>0</sup> oxidation by ozone (reaction 1), formation of a set of compounds with chlorine and possibly with other halogens (reaction 2), and reduction of Hg<sup>2+</sup> to Hg<sup>0</sup> via reactions (3-6). The distribution of oxidized dissolved mercury between liquid and solid phases is described by the Langmuir isotherm [Petersen *et al.*, 1995].

It is assumed that clouds occur only in the third and fourth layer (above 400 m). The bulk of cloud water is evaporated and does not fall out. At the same time, aerosol particles are formed replenishing the atmospheric aerosol pool. It is assumed that evaporation takes place in the absence of precipitation.

#### 4.2.3 Model parameters

Ozone concentration is assumed to be constant in space and varies from month to month as elevated sinusoid with minimum 20 ppb in January and maximum 40 ppb in July.

Soot particle concentration in air is taken to be equal to 0.1 of sulphur dioxide concentrations [Feichter *et al.*, 1996] and were taken from data representing 1987 with a spatial resolution 150×150 km<sup>2</sup> [Sofiev *et al.*, 1994].

Dissolution of gaseous elemental mercury and ozone in the liquid phase of clouds and rain was taken to follow Henry's law [Ryaboshapko and Korolev, 1997]. Washout is prescribed by washout ratio  $1.4 \cdot 10^6$  for inorganic gaseous Hg(II) as for nitric acid [Jonsen and Berge, 1995], by  $7 \cdot 10^5$  for particles containing mercury as for sulphate particles [Iversen *et al.*, 1989], and by 1 for organic gaseous mercury (i.e. in the latter case the washout process is absent).

Dry absorption rate by the underlying surface of the elemental gaseous mercury for the land is taken to be 0.03 cm/s during May-October and 0.01 cm/s during the rest of the year at positive near-surface air temperature. At negative near-surface air temperatures and for the sea surface this rate is assumed to be zero.

Reaction rates in the liquid-drop phase were taken from Table 3.2.

The process of cloud evaporation is described by constants of mercury transition from the liquid reservoir to the aerosol one. They are 0.2, 0.1 and 0.05 h<sup>-1</sup> for summer, spring-autumn and winter seasons. It corresponds to life-time of 5, 10 and 20 hours in clouds relative to the evaporation process.

Generalized rate constant of elemental mercury reduction from its organic compounds is  $2.3 \cdot 10^{-5} \text{ s}^{-1}$ .

#### 4.2.4 Input data

Meteorological data. Wind speed at 1000 and 850 mb levels, precipitation amount, turbulent diffusion coefficient  $K_z$ , temperature, humidity and cloudiness are used. Meteorological information for 1987, 1990, 1992 and 1994 were used. The synoptic analysis for the Mediterranean area for 1990 similar to that made for 1991 [Erdman *et al.*, 1994] has been

performed. The meteorological situation for 1990 was compared with that one for 1991 and climatic data.

Emission. Data on anthropogenic emissions for 1987 [Axenfeld *et al.*, 1991] and for 1990 [Berdowski *et al.*, 1997] were used. Emissions for countries for these years is presented in Table 2.3 (Chapter 2). Natural emissions (total pre-industrial emissions and re-emissions) is taken from Moisseev (1997) (see Table 2.3).

In each grid cell the distribution of sources with components/height was taken to be constant: relationship between  $\text{Hg}^0$ ,  $\text{Hg(II)}$ ,  $\text{Hg(P)}$  is 57 : 30 : 13 [Axenfeld *et al.*, 1991; Pacyna and Münch, 1991]; it was also assumed that emissions enter only two layers: 100 m and 400 m in a 65 : 35 ratio.

## Chapter 5 EVALUATION OF MERCURY DEPOSITION ON THE SEAS

### 5.1 Results of mercury deposition calculation (MSC-E model test runs)

First of all it should be mentioned that data discussed are the results of the mercury model [Ryaboshapko and Korolev,1997] test runs, and therefore should be considered as very approximate.

Deposition of mercury and its compounds were calculated for 1987 (with emission data of 1987 [Axenfeld *et al.*, 1991]), for 1990 (with emission data for 1987 [Axenfeld *et al.*, 1991] and 1990 [Berdowski *et al.*, 1997]) and for 1994 (with emission data of 1990 [Berdowski *et al.*, 1997]). Emission data of 1987 and 1990 are noticeably different because a number of powerful sources in East Germany were closed after unification.

Figure 5.1 shows the region where calculations were made (the EMEP region) which does not cover a part of the Levantin region.

Figures 5.2-5.9 show mercury deposition in 1990; Figures 5.2 and 5.3 present deposition of total mercury (emission of 1987 and 1990 respectively), Figures 5.4 and 5.5 - elemental mercury  $Hg^0$ , Figures 5.6 and 5.7 - divalent gaseous  $Hg(II)$ , Figures 5.8 and 5.9 - particulate  $Hg(P)$ .

Figures 5.6-5.9 show evidence that gaseous divalent and particulate mercury deposition significantly decreases from the north to the south, i.e. in the direction of transport from European sources. This pattern is especially pronounced since we do not consider sources from Turkey, the Middle East and North Africa which could slightly distort the results as was the case while modelling other pollutants (sulphur and nitrogen and some heavy metals [Erdman *et al.*,1994]).

Deposition of elemental mercury  $Hg^0$  (Figures 5.4 and 5.5) on land also decreases from the north to the south due to peculiarities in the distribution of elemental mercury sources (mainly anthropogenic ones) and the prevailing transport direction. Deposition of elemental mercury on marine areas are small enough, since elemental mercury proper is poorly scavenged with wet deposition and its dry deposition on water is assumed to be negligible. Over North Africa the deposition of elemental mercury due to dry scavenging is about 10  $g/km^2/year$ .

Tables 5.1-5.6 contain data on total, oxidized and particulate mercury deposition on the Mediterranean Sea and its subbasins (Tables 5.1-5.3) as well as deposition densities (Tables 5.4-5.6) (for notations mt1-mt11 see Figure 2.1).

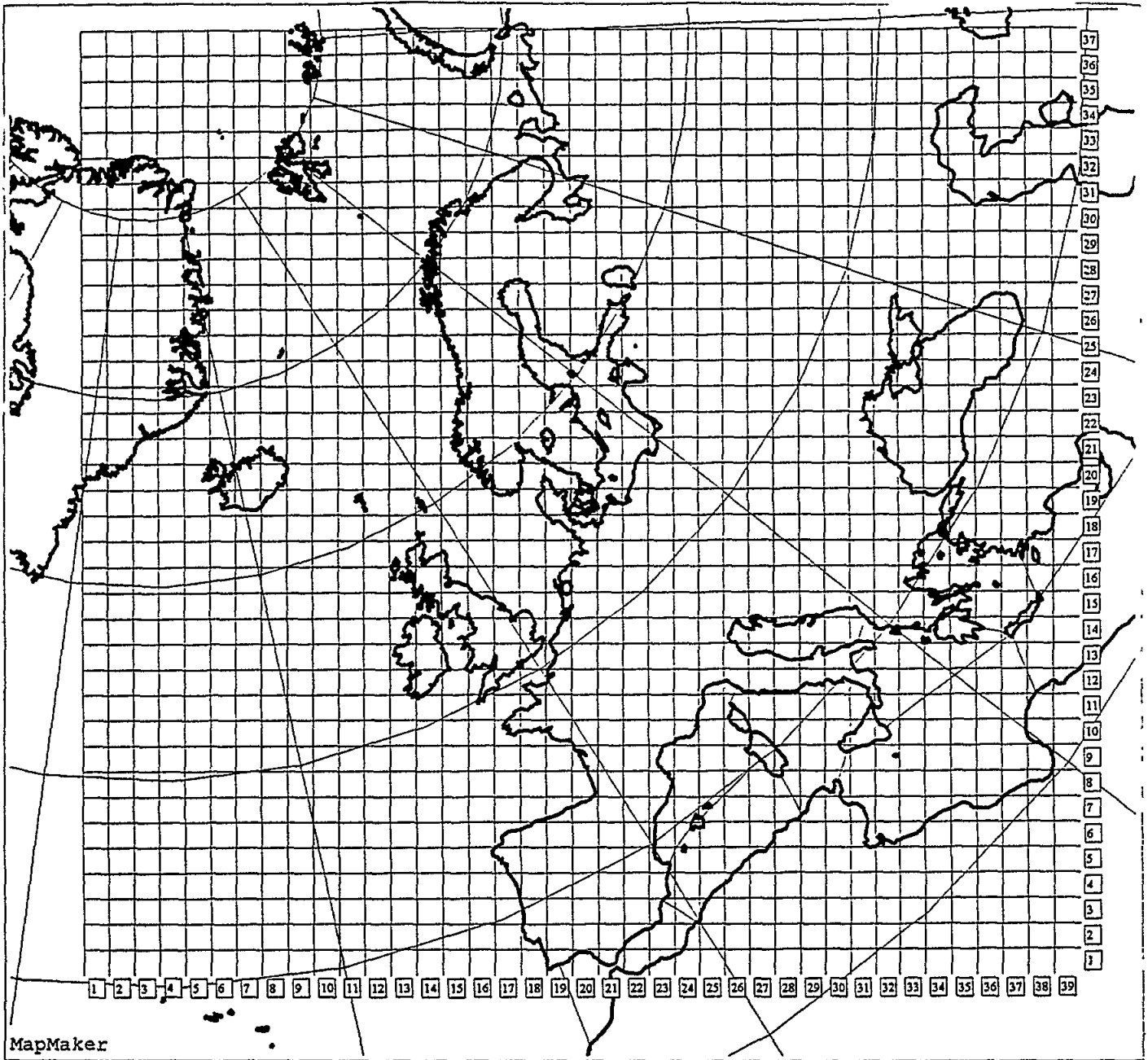
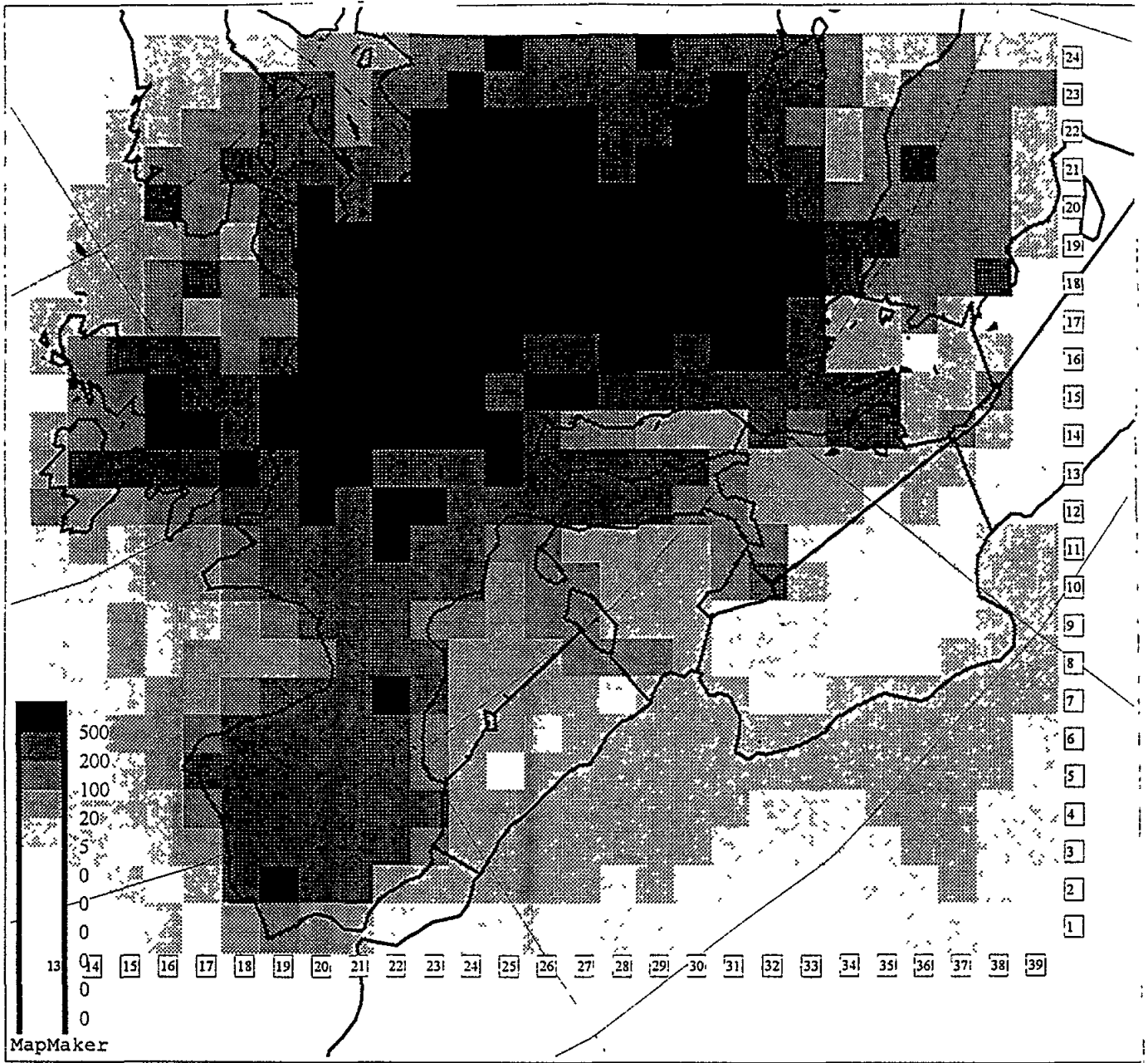
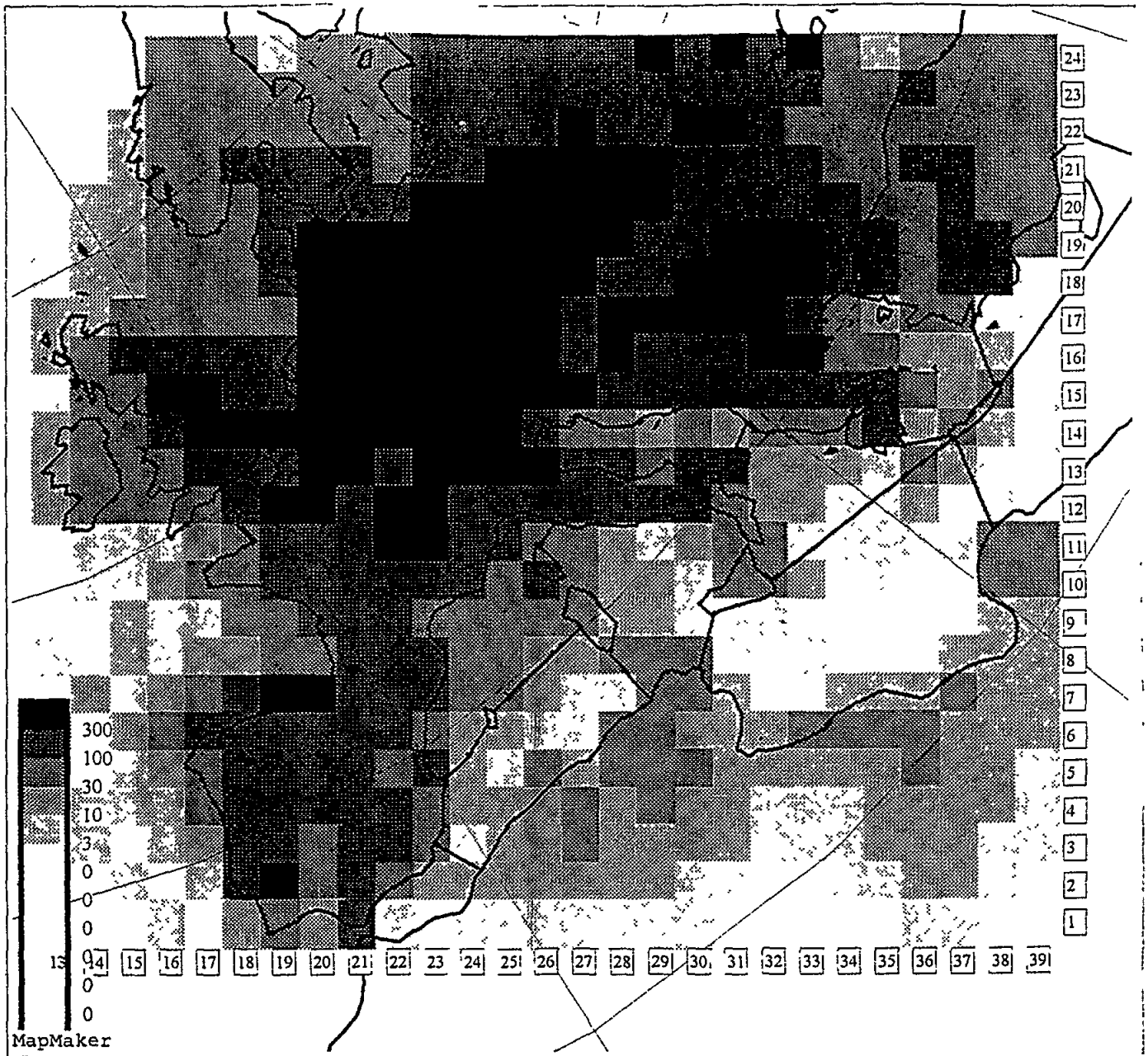


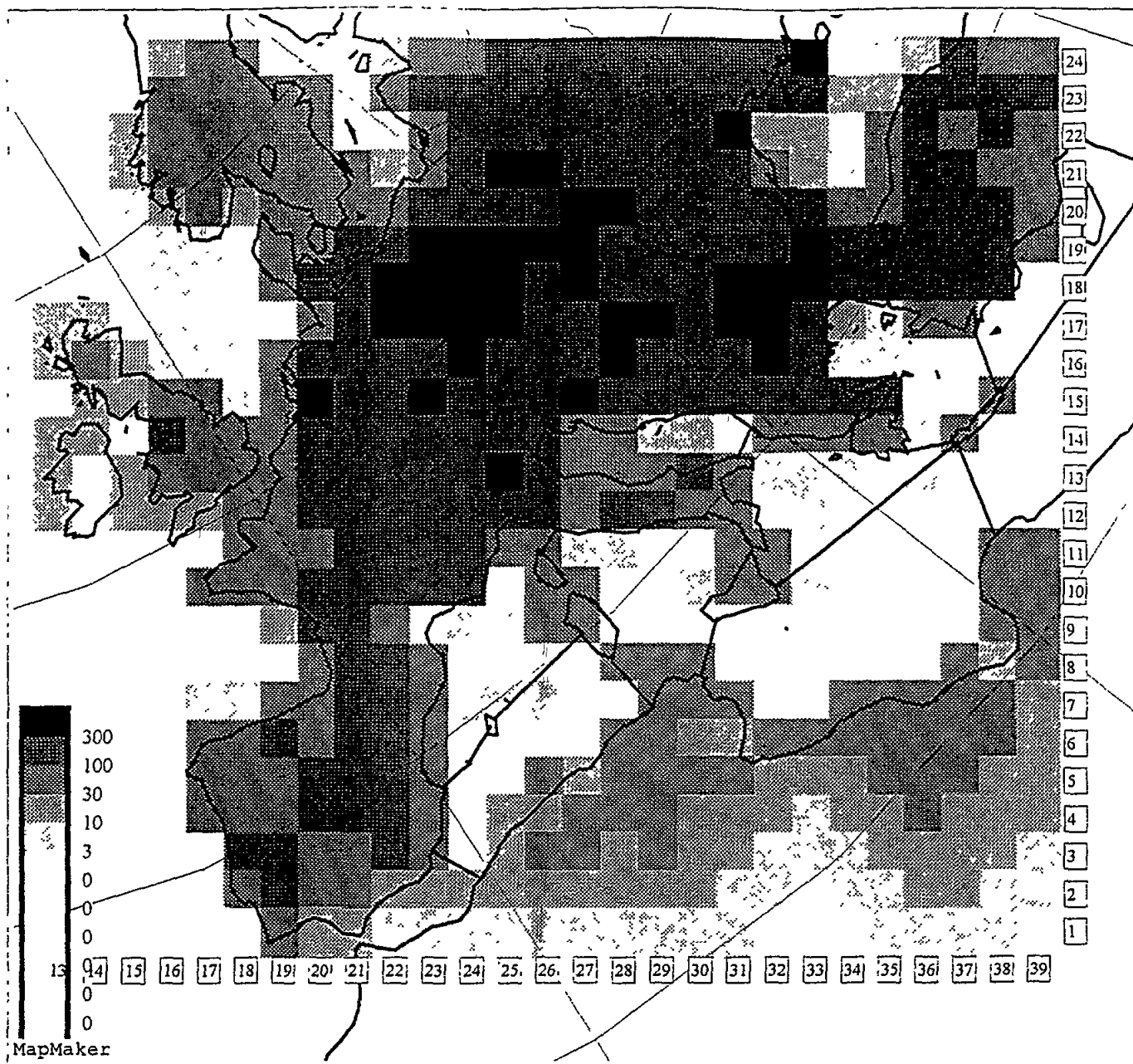
Figure 5.1 Calculation region



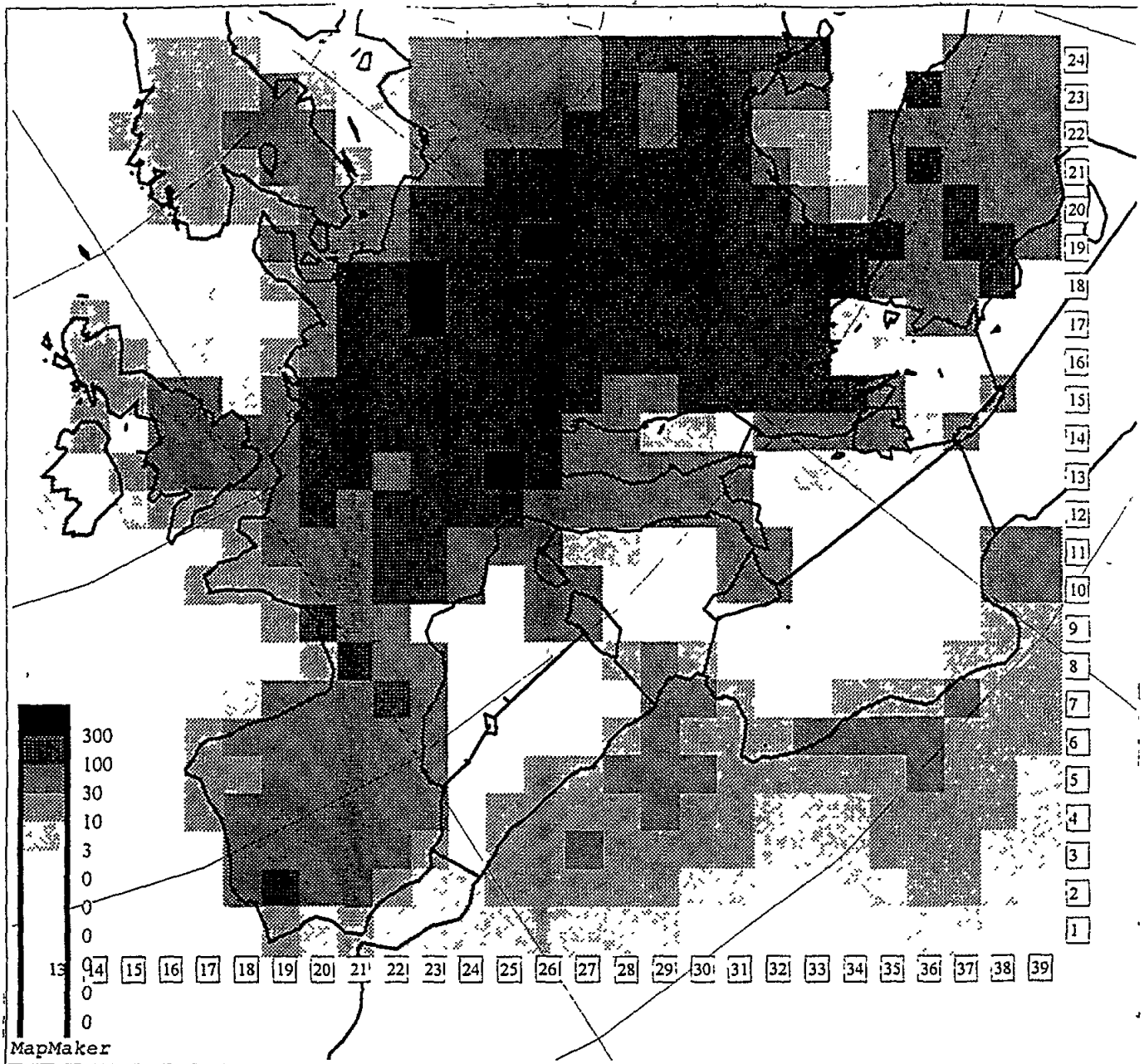
**Figure 5.2** Calculated total deposition of mercury for 1990 (emission data of 1987)  
 Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$



**Figure 5.3** Calculated total deposition of mercury for 1990 (emission data of 1990).  
Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$

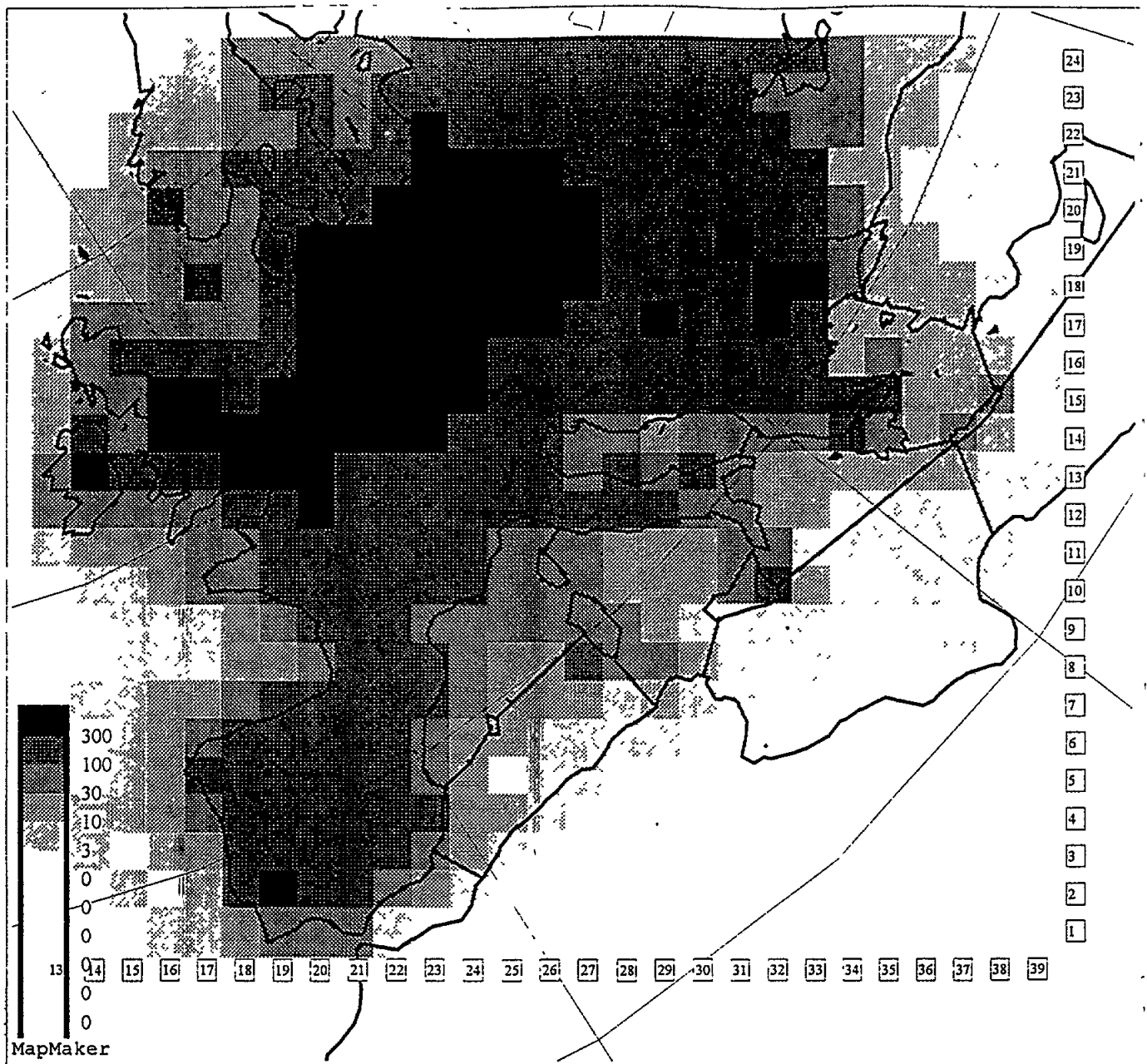


**Figure 5.4** Calculated total deposition of elemental mercury  $\text{Hg}^0$  for 1990 (emission data of 1987). Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$

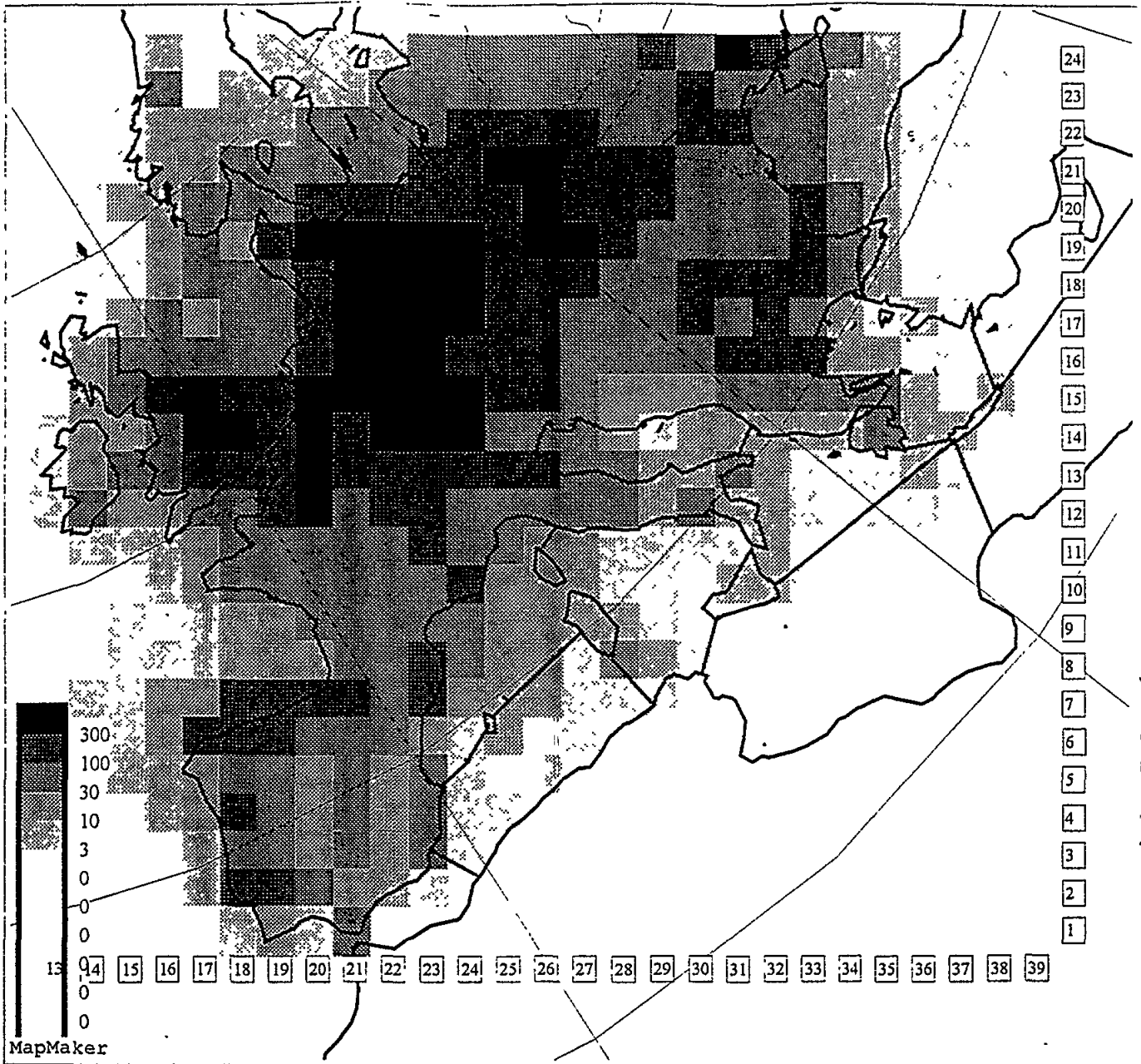


**Figure 5.5** Calculated total deposition of elemental mercury Hg<sup>0</sup> for 1990 (emission data of 1990). Unit: 0.1  $\mu\text{g m}^{-2} \text{y}^{-1}$

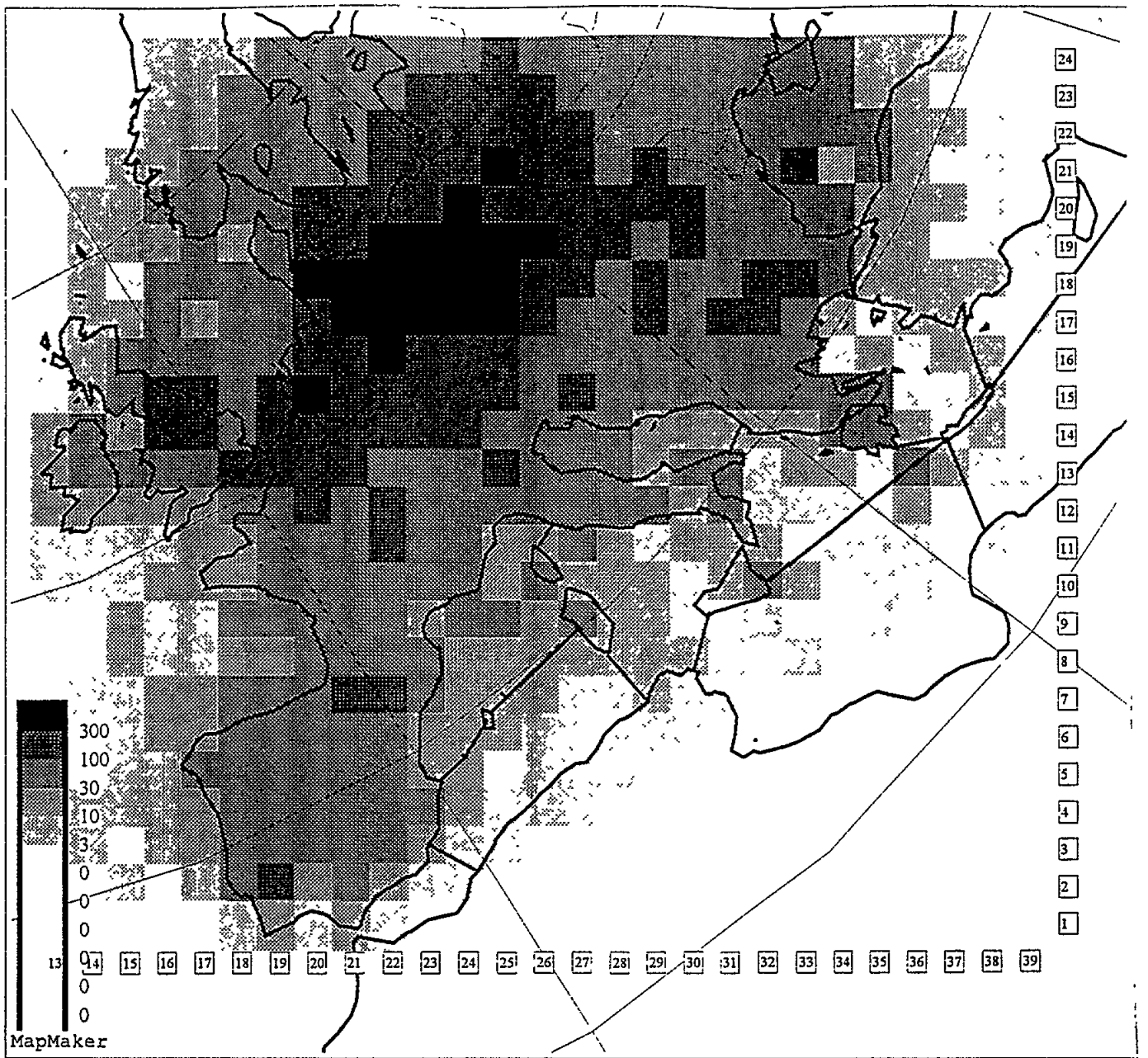




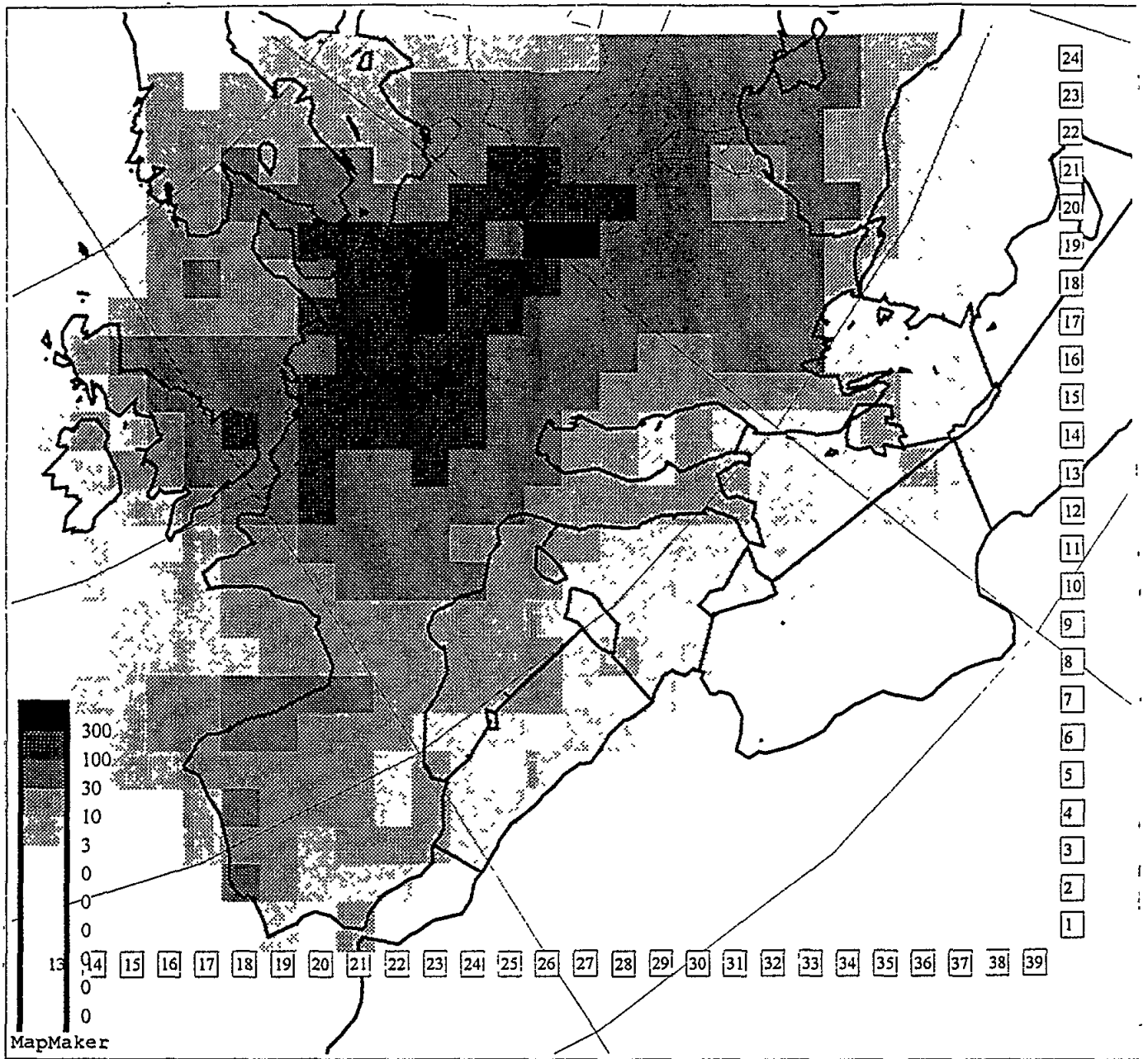
**Figure 5.6** Calculated total deposition of oxidized gaseous mercury compounds Hg(II) for 1990 (emission data of 1987). Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$



**Figure 5.7** Calculated total deposition of oxidized gaseous mercury compounds Hg(II) for 1990 (emission data of 1990). Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$



**Figure 5.8** Calculated total deposition of particle bound mercury for 1990 (emission data of 1987). Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$



**Figure 5.9** Calculated total deposition of particle bound mercury for 1990 (emission data of 1990). Unit:  $0.1 \mu\text{g m}^{-2} \text{y}^{-1}$

**Table 5.1** Total deposition of mercury on the Mediterranean Sea and its subbasins (in kg Hg/y)

|       | 90/87 | 90/90 | 87/87 | 94/90 |
|-------|-------|-------|-------|-------|
| mt1   | 406   | 267   | 501   | 327   |
| mt2   | 3055  | 2021  | 3129  | 1754  |
| mt3   | 1500  | 633   | 1522  | 502   |
| mt4   | 1644  | 626   | 1618  | 417   |
| mt5   | 2091  | 947   | 2090  | 789   |
| mt6   | 1679  | 669   | 1627  | 549   |
| mt7   | 742   | 305   | 559   | 154   |
| mt8   | 1477  | 975   | 1562  | 1040  |
| mt9   | 140   | 70    | 111   | 42    |
| mt10  | 373   | 176   | 264   | 116   |
| mt11  | 134   | 80    | 112   | 63    |
| total | 13240 | 6770  | 13095 | 5752  |

**Table 5.2** Deposition of oxidized gaseous mercury on the Mediterranean Sea and its subbasins (in kg Hg/y)

|       | 90/87 | 90/90 | 87/87 | 94/90 |
|-------|-------|-------|-------|-------|
| mt1   | 273   | 193   | 339   | 235   |
| mt2   | 1900  | 1290  | 1910  | 1140  |
| mt3   | 934   | 354   | 963   | 302   |
| mt4   | 951   | 293   | 934   | 204   |
| mt5   | 1250  | 487   | 1230  | 409   |
| mt6   | 1020  | 364   | 1010  | 329   |
| mt7   | 337   | 120   | 272   | 63    |
| mt8   | 927   | 640   | 923   | 637   |
| mt9   | 60    | 28    | 56    | 18    |
| mt10  | 209   | 92    | 169   | 70    |
| mt11  | 64    | 38    | 48    | 26    |
| total | 7925  | 3900  | 7855  | 3434  |

**Table 5.3** Deposition of particle bound mercury on the Mediterranean Sea and its subbasins (in kg Hg/y)

|       | 90/87 | 90/90 | 87/87 | 94/90 |
|-------|-------|-------|-------|-------|
| mt1   | 113   | 56    | 138   | 77    |
| mt2   | 954   | 573   | 966   | 481   |
| mt3   | 486   | 216   | 476   | 165   |
| mt4   | 538   | 212   | 511   | 131   |
| mt5   | 606   | 282   | 600   | 228   |
| mt6   | 483   | 182   | 454   | 138   |
| mt7   | 319   | 127   | 226   | 70    |
| mt8   | 403   | 231   | 400   | 249   |
| mt9   | 67    | 32    | 41    | 19    |
| mt10  | 139   | 64    | 72    | 38    |
| mt11  | 52    | 28    | 36    | 21    |
| total | 4159  | 2003  | 3919  | 1619  |

**Table 5.4** Deposition density of total mercury on the Mediterranean Sea and its subbasins  
(in  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ )

|      | 90/87 | 90/90 | 87/87 | 94/90 |
|------|-------|-------|-------|-------|
| mt1  | 4.88  | 3.20  | 6.01  | 3.92  |
| mt2  | 11.91 | 7.88  | 12.20 | 6.84  |
| mt3  | 5.79  | 2.45  | 5.88  | 1.94  |
| mt4  | 7.66  | 2.92  | 7.54  | 1.94  |
| mt5  | 16.76 | 7.60  | 16.76 | 6.33  |
| mt6  | 7.62  | 3.04  | 7.39  | 2.49  |
| mt7  | 1.53  | 0.63  | 1.15  | 0.32  |
| mt8  | 8.42  | 5.56  | 8.90  | 5.93  |
| mt9  | 2.10  | 1.04  | 1.65  | 0.63  |
| mt10 | 3.22  | 1.52  | 2.28  | 1.00  |
| mt11 | 13.84 | 8.23  | 11.57 | 6.47  |
| mean | 6.58  | 3.37  | 6.51  | 2.86  |

**Table 5.5** Deposition density of oxidized gaseous mercury on the Mediterranean Sea and  
its subbasins (in  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ )

|      | 90/87 | 90/90 | 87/87 | 94/90 |
|------|-------|-------|-------|-------|
| mt1  | 3.28  | 2.31  | 4.07  | 2.82  |
| mt2  | 7.41  | 5.03  | 7.45  | 4.45  |
| mt3  | 3.61  | 1.37  | 3.72  | 1.17  |
| mt4  | 4.43  | 1.37  | 4.35  | 0.95  |
| mt5  | 10.02 | 3.91  | 9.86  | 3.28  |
| mt6  | 4.63  | 1.65  | 4.59  | 1.50  |
| mt7  | 0.69  | 0.25  | 0.56  | 0.13  |
| mt8  | 5.28  | 3.65  | 5.26  | 3.63  |
| mt9  | 0.90  | 0.41  | 0.84  | 0.26  |
| mt10 | 1.80  | 0.80  | 1.46  | 0.60  |
| mt11 | 6.64  | 3.97  | 4.95  | 2.70  |
| mean | 3.94  | 1.94  | 3.91  | 1.71  |

**Table 5.6** Deposition density of particle bound mercury on the Mediterranean Sea and  
its subbasins (in  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ )

|      | 90/87 | 90/90 | 87/87 | 94/90 |
|------|-------|-------|-------|-------|
| mt1  | 1.36  | 0.67  | 1.65  | 0.93  |
| mt2  | 3.72  | 2.23  | 3.77  | 1.88  |
| mt3  | 1.88  | 0.83  | 1.84  | 0.64  |
| mt4  | 2.51  | 0.99  | 2.38  | 0.61  |
| mt5  | 4.86  | 2.26  | 4.81  | 1.83  |
| mt6  | 2.19  | 0.83  | 2.06  | 0.63  |
| mt7  | 0.66  | 0.26  | 0.47  | 0.15  |
| mt8  | 2.30  | 1.31  | 2.28  | 1.42  |
| mt9  | 1.00  | 0.48  | 0.61  | 0.28  |
| mt10 | 1.19  | 0.55  | 0.62  | 0.33  |
| mt11 | 5.34  | 2.88  | 3.70  | 2.21  |
| mean | 2.07  | 1.00  | 1.95  | 0.81  |

As can be seen from the tables, deposition of total mercury on the Mediterranean Sea is about 13 t/y using emissions from 1987 and about 7 t/y with emissions from 1990, i.e. about 1% of the total European emissions used in the calculations.

Maximum deposition (about 25% of the total) is observed in the north-western part of the Mediterranean sea (mt2) and in the Adriatic Sea (about 15%) (mt5) and minimum in the North and South Levantin.

Maximum deposition densities of total mercury are about 10 g/km<sup>2</sup>/y and are observed in the north-western part of the sea (mt2) and 15 g/km<sup>2</sup>/y in the Adriatic Sea (mt5). Minimum densities of 1 g/km<sup>2</sup>/y are evident in the central part of the sea (mt7). This distribution of densities is explained by the distance from major European sources and prevailing atmospheric transport directions.

## 5.2 Synoptic analysis

Pressure and surface wind fields, 850 hPa wind field, monthly averaged precipitation field (1990 year data) over the Mediterranean basin were analysed and types of atmospheric circulation were identified on the basis of the Hess-Brezowsky classification [*Hess and Brezowsky*, 1969]. A similar analysis was performed earlier for 1991 [*Erdman et al.*, 1994] and results can be compared with climatic data [*UNEP/WMO*, 1989].

Let us briefly describe types of synoptic situations according to *Hess and Brezowsky* (1969) (see also [*UNEP/WMO*, 1989]).

Type A: Blocking anticyclone or ridge stays over the north-eastern Atlantic and British Isles. East of the block in the mid-troposphere (level 500 hPa) a quasistationary depression exists with the axis directed across the central Mediterranean.

Type B: Anticyclone stays over northern Europe. Low pressure system covers most of the Mediterranean.

Type C: The westerly type. Deep depression or series of depressions prevail in mid latitudes over Europe. Westerly winds prevail over the Mediterranean.

Type D: The easterly type. Anticyclone located over central and southern Europe, resulting in easterly winds over most of the Mediterranean. Low pressure systems are located over northern Europe.

Type E: The anticyclonic type. Anticyclone or ridge of high pressure system situated over most of the Mediterranean, with prevailing westerly winds in the north, easterly winds in the south and northerly winds in the east of the region.

In *Erdman et al.* (1994) two additional types of frequently occurring synoptic situations were included. Firstly,  $E_w$  - strong blocking anticyclone over the whole Europe with the centre in Austria or Hungary. Low pressure is observed only in the northern and eastern parts of the region where fast-moving Atlantic depressions traverse along the anticyclone edge bringing short periods of precipitation. This type is more characteristic of winter. Secondly, type  $E_1$  - strong blocking anticyclone over northern Europe with the centre over the north-western part of Russia. Between this blocking high and the Azores anticyclone, cold low pressure areas move towards the Mediterranean from the northern Atlantic.

Comparing analyses of synoptic situations for 1990 and 1991 the following can be noted. On the whole, the situations for both years are similar. Types A, B, C and  $E_w$  predominate in winter and D, E and  $E_1$  - in summer as is normal although in the 1991 summer, type D was never observed. It should be noted that non-typical situations in 1990 occurred more often. There were, however, significant differences in spring and autumn. Comparing 1990 with 1991 type A was more frequent and B, less frequent in spring, while type D was prevalent in all seasons.

In 1990, surface wind speed and direction fields generally corresponded well with the climate (although there were substantial departures with the climate record in autumn and spring). In 1991, the most substantial differences were observed in winter and were also noteworthy in October and July.

In 1990, the 850 hPa field had the highest deviation from the climate during winter and autumn.

Thus, surface and 850 hPa wind fields in 1990 during spring and autumn and, in 1991 also during the winter significantly differ from climate. For example, in May 1990 because of anticyclonic weather over the Mediterranean Sea (type D) easterly winds very often brought a decrease in depositions over the region studied in comparison with climatic ones. In more common cases, it can be expected that winds directed from Europe will increase depositions, since the main sources of mercury are located there. North-westerly winds prevail over the Mediterranean thus, for most of the Mediterranean Sea, increases of northerly or westerly winds will lead to deposition increases. For the Adriatic and Aegean Seas, one can predict decreases in deposition with south-easterly or southerly winds.

As to the precipitation fields, normal amounts are observed relatively seldom for the whole region; as a rule, in every month there are some areas with excess rainfall and others suffering a lack of precipitation. For the Pyreneas and Appenins such situations occur most often. Precipitation, like the wind field, affects pollution deposition to a great extent through the wet deposition mechanism. Therefore deposition increases with precipitation and vice versa.

In order to exclude the effect of interannual meteorological variability and to obtain a more realistic pattern of mercury deposition on the Mediterranean region, it is necessary to make multiannual calculations using a more advanced model.

### **5.3 Comparison with measurements and other estimates**

#### *5.3.1 Comparison of modelling results with measurements*

Regular measurements in the Mediterranean Sea region are virtually non-existent. In particular, in the summarizing paper dealing with measurements of heavy metals and persistent organic pollutants [Berg *et al.*, 1996] there are no measurement data on mercury for this region. Therefore the comparison has been made using 1987 data from several stations in the Baltic/North Seas region. In addition, and for comparison the model calculation results presented in Petersen *et al.* (1995) were also used. Tables 5.7 and 5.8 taken from Ryaboshapko and Korolev (1997) compare concentrations of total and aerosol mercury in air (Table 5.7) and concentrations in precipitation and wet deposition (Table 5.8).

The comparison shows that calculated and observed mercury air concentrations are in good agreement at some distance from European sources (Windeln and Oberbirg stations). The closer to the sources the greater the discrepancy, but it remains within a factor of 2. Since there are no measurement data in the vicinity of major sources the comparison was made with



calculation results of *G.Petersen et al. (1995)*. The discrepancy is not more than 4 times which appears reasonable due to the very high gradients in concentrations in this region. The difference in concentrations of aerosol bound mercury is within an order of magnitude that is also acceptable when making allowances for measurement accuracy and current knowledge on parameters of aerosol scavenging.

**Table 5.7** Comparison of modelled by (G.Petersen et al. [1995] and A.Ryaboshapko and V.Korolev [1997]) and measured concentrations of mercury in air, ng/m<sup>3</sup>.

| EMEP cell<br>(X-Y) | Monitoring stations | Observed in 1987-1988 |             | Modelled by G.Petersen et al. [1995] for 1988 |             | Modelled by A.Ryaboshapko and V.Korolev [1997] |             |                  |
|--------------------|---------------------|-----------------------|-------------|---|-------------|--|-------------|------------------|
|                    |                     | Hg <sup>0</sup>       | Particulate | Hg <sup>0</sup>                               | Particulate | Hg <sup>0</sup>                                | Particulate | Oxidized gaseous |
| 22-17              | -                   | -                     | -           | 10.1  | 0.28        | 40   | 4.4         | 2.6              |
| 22-18              | -                   | -                     | -           | 4.9   | 0.21        | 16   | 0.5         | 0.4              |
| 21-17              | Landenbrügge*       | 4.2                   | -           | 4.1   | 0.11        | 8  | 0.5         | 0.2              |
| 21-19              | -                   | -                     | -           | 3.6   | 0.11        | 6  | 0.1         | 0.05             |
| 19-20              | Rörvik              | 2.8                   | 0.06        | 2.5   | 0.025       | 3.8  | 0.1         | 0.05             |
| 20-22              | -                   | -                     | -           | 2.5   | 0.019       | 2.6  | 0.01        | 0.05             |
| 17-26              | Vindeln             | 2.5                   | 0.05        | 2.1   | 0.005       | 2.4  | <0.01       | <0.01            |
| 14-28              | Overbygd            | 2.6                   | -           | 2.1   | 0.002       | 2.6  | <0.01       | <0.01            |

\* observations of 1992

**Table 5.8** Comparison of measured and modelled by (G.Petersen et al. [1995] and A.Ryaboshapko and V.Korolev [1997]) total concentrations in precipitation (ng/l) and wet deposition (g/km<sup>2</sup>/yr) of mercury

| EMEP cell<br>(X-Y) | Monitoring stations | Observed in 1987-1988 |            | Modelled by G.Petersen et al. [1995] for 1988 |            | Modelled by A.Ryaboshapko and V.Korolev [1997] |            |
|--------------------|---------------------|-----------------------|------------|---|------------|--|------------|
|                    |                     | Concentrat            | Deposition | Concentrat                                    | Deposition | Concentrat                                     | Deposition |
| 22-17              | -                   | -                     | -          | 331   | 114        | 1380   | 772        |
| 22-18              | -                   | -                     | -          | 234   | 95         | 409  | 255        |
| 21-17              | Landenbrügge*       | 52                    | -          | 66  | 39         | 93   | 117        |
| 21-19              | -                   | -                     | -          | 62  | 46         | 47   | 60         |
| 19-20              | Rörvik              | 35                    | 27         | 17  | 15         | 16   | 18         |
| 20-22              | -                   | 18                    | 10         | 17  | 10         | 18   | 11         |
| 17-26              | Vindeln             | 11                    | 7.3        | 7.0   | 4.9        | 7  | 4          |
| 14-28              | Overbygd            | 9                     | 5.0        | 3.9   | 2.1        | 2  | 3          |

\* observations of 1992

Data discrepancies on concentrations of total mercury in precipitation and wet deposition are as much as 3-4 times. It seems reasonable that the comparison results on the whole be considered satisfactory. In so far as direct measurements for the Mediterranean Sea are not available the comparison with data on other pollutants is considered below.

### 5.3.2 Comparison with deposition modelling results of other pollutants

*Erdman et al.* (1994) have estimated the quantity of various pollutants (sulphur, nitrogen compounds and some heavy metals) deposited on the Mediterranean Sea. It was demonstrated that for various species it is 4-8% of the emission within the calculation grid. It was also shown that these results agree well with calculation results on heavy metals obtained by the TRACE [*Alcamo et al.*, 1993] and TREND [*Van Jaarsveld*, 1993] models. Calculation results of Cd and Pb also correlate well with these data [*Pekar et al.*, 1997]. For a correct comparison of these results with calculations of mercury pollution it is necessary to take into account a number of factors. First, *a*) The deposition calculations of *Erdman et al.* (1994) were performed for the whole Mediterranean basin including the North and South Levantin regions but only a part of these regions is considered in this work. Deposition of acid pollutants and heavy metals in this region is 10% of the total deposition on the Mediterranean Sea; *b*) The contribution of emissions and deposition from Turkey, the Middle East and North Africa on the sea is about 10%, whereas the contribution of these sources to the total emission within the calculation region does not exceed 2-3%.

Thus the contribution of acid pollutants and HM total emission (without indicated sources) to deposition on the Mediterranean Sea (ignoring the main part of the Levantin) is 3.5-7%.

On the other hand, on the basis of assumptions used in calculations the anthropogenic mercury emission comprises mainly (57%) long-lived elemental mercury,  $Hg^0$ , 30% is accounted for by the relatively short-lived divalent gaseous mercury,  $Hg(II)$ , and the content of particulate mercury is 13%. The bulk of natural emission (90%) is composed of elemental mercury  $Hg^0$ . The contribution to emission of 1987 (1020 tonnes in total) of relatively short-lived forms is 247 tonnes of divalent gaseous mercury  $Hg(II)$  (including DMHg) and 94 tonnes of particulate mercury. For 1990 emission (734 tonnes in total) the input of  $Hg(II)$  is 161 tonnes and  $Hg(II)$ , 57 tonnes.

Comparing deposition values of individual forms of mercury with their emissions we obtain that the fraction of emission of 1987 deposited on the Mediterranean Sea is 4% for particulate mercury and more than 3% for divalent mercury. This correlates reasonably with emission fractions of other pollutants. An even better correlation is obtained in the comparison with similar fractions of reduced nitrogen emissions deposited on the subbasins of the Mediterranean Sea (Table 5.9). (In recalculations of reduced nitrogen, the sources from Turkey, the Middle East and North Africa are not considered. Deposition on the Levantin is not included in the comparison because of a discordance between the calculation regions).

**Table 5.9** Fractions of European emission deposited on the Mediterranean subbasins

| Year |          | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|------|----------|-----|-----|-----|-----|-----|-----|-----|-----|
|      | $NH_x^*$ | 0.1 | 0.8 | 0.4 | 0.6 | 0.6 | 0.4 | 0.4 | 0.4 |
| 1987 | Hg(P)    | 0.1 | 1.0 | 0.5 | 0.6 | 0.6 | 0.5 | 0.3 | 0.4 |
|      | Hg(II)   | 0.1 | 0.8 | 0.4 | 0.4 | 0.5 | 0.4 | 0.1 | 0.4 |
| 1990 | Hg(P)    | 0.1 | 1.0 | 0.4 | 0.4 | 0.5 | 0.3 | 0.2 | 0.4 |
|      | Hg(II)   | 0.1 | 0.8 | 0.2 | 0.2 | 0.3 | 0.2 | 0.1 | 0.4 |

\* Recalculated from [*Erdman et al.*, 1994]

The table data show that calculated results for particulate mercury are in better agreement than those for divalent mercury, and calculated data for 1990 emissions, on the whole demonstrate a worse correlation.

In general the comparison shows that scavenging parameters of relatively short-lived forms of mercury are properly selected.

### 5.3.3 Comparison with other estimates of mercury deposition on the Mediterranean Sea

No reliable assessments of mercury input from the atmosphere on the Mediterranean Sea are available for the moment [UNEP, 1996]. Direct and indirect rough estimates available in the literature are given below.

1. According to *Copin-Montegut et al.* (1984) the value is 125 t/y (deposition density 50 g/km<sup>2</sup>/y).
2. Deposition maps resulting from model calculations of *Galperin et al.* (1994) show that deposition density of mercury compounds over the Mediterranean Sea is between 15-20 g/km<sup>2</sup>/y (with allowance for only anthropogenic emission) to 100 g/km<sup>2</sup>/y (with allowance for anthropogenic emission as well as re-emission from land and evasion from seas and oceans) i.e. the Mediterranean Sea appears to receive from 40 to 250 tonnes of mercury per year.
3. *Cossa et al.* (1996) estimated the mean deposition density of mercury on the shelf zone of the world oceans as 16 g/km<sup>2</sup>/y. Adapting this value to the Mediterranean Sea we find deposition amounts to 40 t Hg/y.
4. As estimated by *Mason and Fitzgerald* (1996) for latitudes between 10°N and 70° N the mean density of mercury wet deposition is 18 g/km<sup>2</sup>/y for land and 8,5 g/km<sup>2</sup>/y for oceans. Based on these data deposition on the Mediterranean Sea should be about 20 t/y.
5. According to *UNEP* (1989) the total precipitation amount per year in the Mediterranean Sea area amounts to 850 km<sup>3</sup>/y. Assuming that the mean concentration of mercury in precipitation over the whole Mediterranean basin is not more than 20 kg/l (data on the late rain over the urban area in Italy - 17.5 ng/l [*Ferrara et al.*, 1982]), the upper estimate of wet deposition is 20 t Hg/y.

Let us discuss these assessments. If we take that the value of 125 t/y [*Copin-Montegut et al.*, 1984] was obtained using only wet deposition values, then with allowance for the precipitation amount, mean concentration in precipitation is 150 ng/l. This value seems to be overestimated by at least an order of magnitude. In case of the value of 125 t/y is conditioned only by dry deposition (dry deposition rate was taken to be 1 cm/s [*UNEP/FAO/WHO*, 1987]) then it corresponds to mean concentrations of aerosol bound mercury over the Mediterranean Sea equal to 0.15 ng/m<sup>3</sup>, in its turn it corresponds to 5-10% of its total mercury concentration in air. This value is likely to be also overestimated by several times. Hence the value of 125 t Hg/y should be reduced several times, i.e. it should not exceed 40 t/y. In conclusion it may be stated that mercury deposition on the Mediterranean Sea amounts to 10 - 40 t/y with a corresponding deposition density of 4-15 g/km<sup>2</sup>/y.

### 5.3.4 Comparison with calculation results of mercury deposition on the North and Baltic Seas

According to various estimates [*Petersen*, 1992] mercury deposition on the North Sea is 5-36 t/y that corresponds to a deposition density of 10-70 g/km<sup>2</sup>/y. *Petersen* (1992) considers that a reliable estimate is 5-12 t/y corresponding to a deposition density of 10-25 g/km<sup>2</sup>/y. Deposition on the Baltic Sea is estimated within the narrower range, 6-13 t/y with deposition density of 15-30 g/km<sup>2</sup>/y. According to data from the Swedish national network, the total deposition of mercury compounds is 6-11 g/km<sup>2</sup>/y. This decrease compared to previous assessments can, to a certain extent, be explained by the abrupt reduction of mercury

emissions in East Germany. Thus, at present, the mercury deposition density on the Mediterranean Sea is approximately of the same order of magnitude as on the Baltic and North Seas.

## Chapter 6 POTENTIAL MEASURES FOR REDUCTION OF MERCURY LOAD ON THE SEAS

### 6.1 Assimilative capacity

#### 6.1.1 General

To evaluate negative consequences of mercury input to the Mediterranean Sea it is worthy to invoke the concept of assimilative capacity of a marine ecosystem. By definition, [Izrael and Tsyban, 1989] "assimilative capacity of a marine ecosystem with respect to a given pollutant is maximum dynamic capacity to hold such amount of pollutant (recalculated for the whole volume or per unit of marine ecosystem volume) which can be accumulated, destructed, converted (biological and/or chemical transformations) and removed per time unit outside the ecosystem limits without violation of its normal functioning due to processes of sedimentation, diffusion or any other process". This definition implies that assimilation capacity has the dimension of a flux (i.e. mass related to time unit) or concentration variation rate (i.e. concentration related to time unit).

Scavenging rate of a pollutant from system  $A_{out}$  (t/y) is described by relationship

$$A_{out} = k \cdot V / \tau \cdot \bar{C} \quad \text{where}$$

$k$  - so-called safety factor,

$V$  - ecosystem volume,

$\bar{C}$  - mean concentration of a pollutant,

$\tau$  - residence time of pollutant in ecosystem.

Assimilative capacity  $A$  is determined by the same formula at  $\bar{C} = C_0$  where  $C_0$  is the threshold concentration of pollutant, i.e.

$$A = k \cdot V / \tau \cdot C_0$$

In the work by *Izrael and Tsyban* (1989) calculation results for the Baltic Sea assimilative capacity relative to persistent organic pollutants and heavy metals including mercury are presented. Using field measurements and literature data, a balance of the mercury input/removal was estimated as well as its concentration in water and sediments. These data are given in Table 6.1, adapted from *Izrael and Tsyban* (1989).

**Table 6.1** Balance of mercury for the Baltic Sea

| Input (t/year) |           | Output (t/year)  |           | Stock (t)                 |            |
|----------------|-----------|------------------|-----------|---------------------------|------------|
| Atmosphere     | 13        | Sedimentation    | 45        | Water:                    |            |
| Rivers         | 10        | Water exchange   | 6         | soluble                   | 60         |
| Discharges     | 31        | in the North Sea |           | particulate               | 134        |
| Other          | 1         |                  |           | sediments (0-5 cm depths) | 100        |
| <b>Total</b>   | <b>55</b> | <b>Total</b>     | <b>51</b> | <b>Total</b>              | <b>294</b> |

Residence time  $\tau$  is 3.8 years. With allowance for the Baltic Sea volume (in the calculations -  $21 \cdot 10^3 \text{ km}^3$ ) and threshold mercury concentration in water (100 -1000 ng/l) the assimilative capacity of the sea was estimated as 550-5500 t/y (in terms of total mercury input to the sea per year) or 26-260  $\text{ng l}^{-1} \text{ year}^{-1}$  (in terms of the increase of mean concentrations over the whole sea basin corresponding to this input). The authors concluded that the current input of mercury to the Baltic Sea is several times less than its assimilative capacity [Izrael and Tsyban, 1989].

### 6.1.2 Mediterranean Sea

A similar very rough balance can be made for the Mediterranean Sea. The evaluation is considered only with biologically accessible dissolved mercury.

#### Water balance

The Mediterranean Sea water balance is represented [UNEP, 1989] by the following components (in 1000 km<sup>3</sup>/y)

| Input                |      | Output      |     |
|----------------------|------|-------------|-----|
| Through Gibraltar*   | 1.2  | Evaporation | 2.9 |
| Through Dardanelles* | 0.18 |             |     |
| Precipitation        | 0.9  |             |     |
| Rivers               | 0.5  |             |     |

\* net inflow

The Sea volume is  $3.7 \cdot 10^6$  km<sup>3</sup>.

Water exchange takes place mainly with the Atlantic Ocean. The inflow/outflow of marine water through Gibraltar is about  $5 \cdot 10^4$  km<sup>3</sup>/year [UNEP, 1989]. Consequently the time of exchange with the Atlantic Ocean is not less than  $3.7 \cdot 10^6$  km<sup>3</sup> :  $5 \cdot 10^4$  km<sup>3</sup>/year = 75 years. Obviously this value is drastically underestimated, since, within these temporal intervals, the Mediterranean Sea as a whole is not well mixed.

#### Inputs

Mercury input to the Mediterranean Sea comes from:

a) Rivers. During a year about  $350 \cdot 10^6$  tonnes of particulates are transported to the Mediterranean Sea with 430 km<sup>3</sup> of river water, therefore the mean turbidity of all the rivers is 0.8 g/l. The mean mercury concentration on particles is 400 µg/kg, which is approximately equal to the mercury concentration on particles in the Rhone river (mean value is 480 µg/kg [Cossa et al., 1996]), and the mean mercury concentration in water is about 300 ng/l (including mercury on particles). Previous estimates [UNEP, 1989] showed that about 130 tonnes of mercury were discharged to the Mediterranean Sea from rivers (range is 50-200 t/y) including both soluble and insoluble fractions. According to Cossa et al. (1996) about 10% of mercury on particles is converted to soluble forms. Assuming that 10% of mercury supplied from rivers can originally be in the dissolved form, the total input of soluble forms is 10-40 t/y (or about 20% of the total amount of 50-200 t/y).

b) Atmosphere. The estimates obtained in chapter 5 vary from 10-40 t/y. It should be noted that mercury coming from the atmosphere is mainly in the dissolved state (contrary to mercury discharged with rivers).

c) Inflow from the Atlantic. The assessment is made on the basis of the inflow of surface water ( $5 \cdot 10^4$  km<sup>3</sup> of water/year) [UNEP, 1989]. Assuming that the possible range of dissolved mercury concentration near Gibraltar is 0.2-0.4 ng/l [Mason and Fitzgerald, 1996] then the inflow with the surface water from the Atlantic is 10-20 tonnes of mercury per year.

d) Input from sediments. Reliable data are not available. The input of dissolved mercury from riverine particulate matter is estimated as 5-20 t/y.

## Removal

a) Evasion (re-emission) to the atmosphere. According to data for the north-western Mediterranean [Cossa *et al.*, 1996] evasion to the atmosphere is about 10 g/km<sup>2</sup>/y. It amounts to 25 t/y if this value is extrapolated to the whole Mediterranean Sea. Obviously this assessment is the highest one.

b) Biosedimentation. Reliable data are not available. However, Cossa *et al.* (1996) calculate biosedimentation in the world ocean coastal zone to be 140 t/y. Accounting for areas of the world ocean coastal zone ( $2.6 \cdot 10^7$  km<sup>2</sup>) [Cossa *et al.*, 1996] and of the Mediterranean Sea ( $2.5 \cdot 10^6$  km<sup>2</sup>), biosedimentation in the Sea can be estimated as 14 t/y. The uncertainty of this assessment is high but obviously it is a low estimate. Following estimates [Cossa *et al.*, 1996] for deep waters of the Mediterranean and extrapolating data on biosedimentation of mercury in the Baltic Sea ( $4 \cdot 10^4$  km<sup>2</sup>) [Izrael and Tsyban, 1989] to the Mediterranean shelf zone (depth - not more than 200 m, area - 500 thous. km<sup>2</sup>, volume - approximately  $5 \cdot 10^4$  km<sup>3</sup> [UNEP, 1989]) we obtain a value of 70 t/y for biosedimentation of dissolved mercury in the Mediterranean Sea. Obviously, this is an overestimate.

The inflow of Atlantic surface water is compensated by the outflow of deep waters from the Mediterranean Sea (as it was indicated above the value of these flows in opposite direction is  $5 \cdot 10^4$  km<sup>3</sup> of water/year). Unfortunately there are no reliable data on dissolved mercury concentrations in the deep water of the Mediterranean Sea. Presumably they do not exceed units of ng/l. Mercury outflow from the Mediterranean Sea can be described in such a way: each ng/l of dissolved mercury concentration in deep marine waters corresponds to the outflow of 50 tonnes of dissolved mercury from the Mediterranean Sea).

## Stock

Mean concentrations of dissolved mercury in the whole sea volume ( $3.7 \cdot 10^6$  km<sup>3</sup>) being within the range from tens of ng/l to units of ng/l then the total stock of mercury in the Mediterranean Sea is  $10^3$ - $10^4$  tonnes. For comparison purposes we indicate that the dissolved mercury stock in the upper 100 m of the world oceans is 11,000 tonnes [Mason and Fitzgerald, 1996]. Thus the balance of dissolved mercury in the Mediterranean can be roughly described as follows:

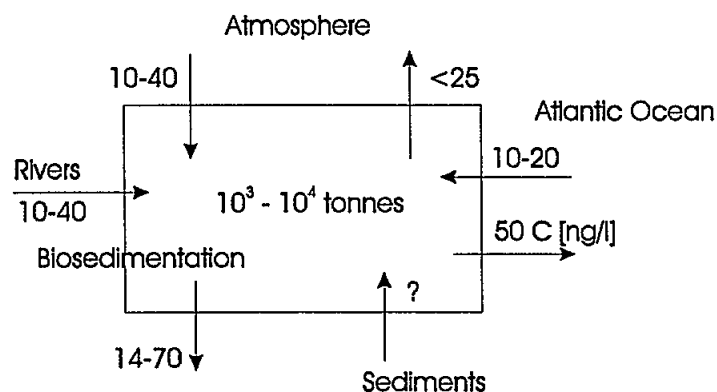


Figure 6.1 Rough balance of dissolved mercury in the Mediterranean Sea (inputs/outputs in t/year)

Assuming a mean critical concentration of dissolved mercury in the Mediterranean of 10 ng/l then critical stock will be  $37 \cdot 10^3$  tonnes. In this case the outflow to the Atlantic is 500 t/y which appreciably exceeds mercury inflow from all the sources. Therefore, in view of the assimilation capacity of marine ecosystems, the Mediterranean Sea is on average relatively

safe ("safety range" is several times). It does not mean that in some "hot spots" the situation is quite safe. The availability of fish with mercury concentrations exceeding maximum permissible ones established by legislation in both France and Italy (0.5 mg HgTot kg<sup>-1</sup> FW (Fresh Weight) for France and 0.7 mg HgTot kg<sup>-1</sup> FW for Italy) is indicative of trouble. Therefore measures to lower mercury pollution have to be taken without delay.

## 6.2 Measures undertaken by some countries

Mediterranean countries have already adopted a number of measures to protect the Mediterranean Sea from pollution (Barcelona,1975). The Barcelona Convention became its legislative framework. One of protocols approved in 1983, and amended in 1996 concerns land-based sources (LBS protocol). In accordance with this protocol the countries agreed to take all possible measures to prevent, mitigate and regulate Mediterranean Sea pollution caused by riverine discharge, coastal installations and other sources (including atmospheric deposition) on their territories.

Also in accordance with this protocol, the parties pledged to reduce emissions of a number of pollutants including mercury and its compounds from state enterprises. Reports [UNEP/FAO/WHO, 1987; UNEP, 1989; UNEP, 1996] contain the evaluation of pollution in the Mediterranean Sea, in particular by mercury and its compounds. The report issued by UNEP (1989) indicated that, in the Mediterranean Sea, fish are both "slightly" and "heavily" polluted by mercury. Among strongly polluted fish there are some species with recorded mercury concentrations exceeding the legal standard (0.5 mg HgTot/kg FW - French standard, 0.7 mgTot/kg FW - Italian standard).

In UNEP (1996) it was pointed out that according to data for the 1970s, human health was in danger, but further investigations showed that, in general, with regard to mercury pollution the Mediterranean was not at risk. The parties to the Barcelona Convention agreed to set up national standards for maximum residue levels (MRLS) making allowances for FAO requirements for permissible weekly consumption of mercury compounds amounting to 0.3 mg/week (of which not more than 0.2 mg/week are in the form of methylated mercury). At the same time the maximum permissible concentration for waste water (50 µg/l) was also established.

Countries of the North Sea have moved on further in protection of the sea from mercury pollution.

In 1980 the Council of Environmental Advisors made a decision that, in spite of the difficulty to evaluate empirically the ecological situation as it stands, together with poor knowledge of long-term irreversible consequences of the impact of persistent organic pollutants on the environment, the increasing input of pollutants to the North Sea requires specific measures.

It was decided that:

- a successful policy for North Sea protection should be based on the precautionary principle;
- North Sea protection can be realized only on the basis of international co-operation;

The following conferences specified priority species, sources and measures to be taken.

The Hague Conference approved a list of 36 pollutants whose emissions are to be reduced by 50%. Mercury and its compounds were assigned to the most harmful pollutants category. Together with dioxins, cadmium and lead it was decided to reduce mercury emissions by



70%. To a great extent this decision was based on the "precautionary principle". Results of the planned reduction are considered in *Progress Report* (1995).

In Great Britain it was estimated that mercury riverine runoff and its direct discharges to estuaries and coastal zone would be decreased by 75% by 1995. This reduction has been achieved due to the introduction of mercury-free technology in the chlor-alkali industry, stringent standards for emissions and changes in existing industrial practices.

It was planned to reduce municipal waste water discharges and industrial emissions into the atmosphere by 50 to 95% by 1995 in all countries of the North Sea region. This reduction is to be achieved by regulation of chlor-alkali plants, manufacturing industry and phosphate fertilizer production. In particular in France though there are no precise data on major sources the reduction will exceed 50%.

It is more difficult to evaluate diffuse sources. Presumably input from diffuse sources such as dentistry, thermometer breaking, consumption of fertilizers and mercury atmospheric deposition is also to be reduced. Substitution of mercury in consumer products will lead to a gradual decrease of emission from diffuse sources. Total reductions of mercury input to water in the PARCOM countries is presented in Table 6.2 along with emission reductions of mercury and its compounds to the atmosphere.

**Table 6.2:** Reduction of mercury input to water and emission to the atmosphere from the PARCOM countries from 1985 to 1995 (%)\*

|       | Belgium | Denmark | France | Germany | Netherlands | Norway | Sweden | Switzerland | Great Britain |
|-------|---------|---------|--------|---------|-------------|--------|--------|-------------|---------------|
| Water | 45      | 60      | 50     | 75      | 60          | 95     | 50     | 65          | 75            |
| Air   | 45      | 80      | ?      | 25      | 55          | 75     | 65     | 50          | 30            |
| Total | 38      | 80      | ?      | 27      |             | 86     | 65     |             | 60-65         |

\* According to data of [*Progress report*, 1995]

Let us consider measures which led to successful reductions using examples from several countries. The reduction of atmospheric emission in Belgium has been achieved by substituting other less harmful products than mercury in thermometers, batteries, barometers, etc. and by reductions in emissions from municipal waste facilities. Note that according to a decision of the Hague Conference (1990), batteries with a mercury content of more than 0.025% were prohibited for sale. Application of mercury-free technologies was extended in the chlor-alkali industry. Stringent standards were set up in various source sectors.

In Germany atmospheric emissions were cut down due to compliance with technical instructions for air quality, and ordinances dealing with large combustion installations and incinerators for wastes. Further reductions are planned within the framework of compliance with these instructions and ordinances for power plants.

In Denmark, atmospheric emission reductions were brought about due to ordinances concerning waste incineration and the installation of more efficient gas treatment facilities at coal-fired power plants, as well as substituting for mercury in final products.

Emission reductions in other countries presented in the Table 6.2 were attained by applying all the measures discussed, or a part of them. According to data presented by Sweden, a 70% reduction in mercury emissions had been achieved by 1995 making allowances for the uncertainty of emission data for 1985, but further reduction is obviously impossible even with

the application of the best available technology [*Progress report*,1995]. A detailed description of measures applied is given in *Mercury in the Environment* (1991).

In accordance with the Swedish Government Environment Bill (1991) mercury should be excluded from use. In the chlor-alkali industry mercury-free methods should be introduced (e.g. membrane technique). It is expected that mercury-free technology would be fully utilized by 2010. Batteries containing large amounts of mercury would be replaced by air-zinc and silver oxide ones. The sale of mercuric oxide batteries should be prohibited by 2000. In dentistry the use of mercury amalgams will be reduced by substituting alternative materials. Since 1985, each dental chair has been equipped with a separator and wastes containing amalgam have been collected. It is considered that all mercury thermometers (medical and industrial) can be replaced by digital and liquid ones. The sale of medical mercury thermometers has been prohibited since 1992 and other mercury thermometers - since 1993. There are fully acceptable substitutes for mercury in relays. The sale of mercury switches, relays etc. has been prohibited since 1993. Although, at present, it is impossible to produce fluorescent lamps without using mercury, one should expect reduced amounts of mercury in their manufacture. It is expected that, not later than 2010, the bulk of mercury will be withdrawn from circulation both as a raw material and as components of final products.

Note that the Helsinki Commission has made the decision to reduce mercury emissions into the atmosphere in Baltic countries by 50%.

## Chapter 7 GENERAL REMARKS

Emission. Mercury enters the atmosphere from anthropogenic sources (fossil fuel combustion, waste destruction, chemical production, non-ferrous metallurgy and gold mining, etc.) and natural sources (soil outgassing including soils polluted due to human activity; vegetation transpiration, evasion from seas, volcanic activity and forest fires etc.). Expert estimates of emissions have been made for Europe and North America.

Presence in the atmosphere. Mercury basically occurs in the elemental gaseous form especially far away from anthropogenic and/or natural sources. Near anthropogenic sources mercury content in the form of particulate mercury Hg(P) and gaseous Hg(II) increases (to 10-20%). Hg(P) life-time in the atmosphere is about one week, and Hg<sup>0</sup> life-time (in the global cycle) is about one year. The life-time of gaseous Hg(II) requires further investigation.

Basic reactions. The basic reaction of Hg<sup>0</sup> in air is oxidation by ozone (the reaction constant is continually being refined), in the liquid-drop phase Hg<sup>0</sup> oxidation by ozone and reduction of Hg(II) to Hg<sup>0</sup> with sulphite ions takes place. Constants of these reactions are known from laboratory experiments. Henry constants versus temperature and salinity are available.

Deposition. The scavenging of mercury and its compounds from the atmosphere take place due to wet and dry deposition. Over the marine surface wet deposition plays a dominant role. Over the land dry deposition can amount to 35% of total scavenging and even more in the MEDPOL region. In precipitation mercury occurs due to cloud and subcloud washout. Judging from data [Ferrara *et al.*, 1986a] sub-cloud washout is more important than incloud one. In precipitation mercury is present as Hg(II), Hg(P) and MMHg. The ratio of dissolved/particulate fraction varies from 10:1 in remote regions and 1:10 in heavily polluted ones. The origin of MMHg in precipitation remains unclear.

Sea water. Mercury enters the seas and oceans from the atmosphere, rivers and from sediments. In water mercury occurs as Hg(II), Hg(P), MMHg, DMHg and Hg<sup>0</sup>. The relative content of various mercury compounds fluctuates considerably. Hg<sup>0</sup> content varies from 1 to 30% in the open sea and it is less than 1% in the coastal zone, DMHg - from 1 to 25% in the open sea (there is no reliable data for the coastal zone), MMHg comprises less than 10% in the open sea and in coastal zones [Horvat, 1996]. Basic reactions are mercury methylation and reduction of mercury compounds to elemental mercury. The bulk of reactions occur with participation of the biota. Removal of mercury from sea water takes place due to evasion (re-emission to the atmosphere), sedimentation and biosedimentation. In a number of oceanic regions evasion to the atmosphere exceeds the input from the atmosphere.

Measurements. It is considered that gaseous mercury measurements in air provide reliable results [Pacyna *et al.*, 1996]. Measurements of an aerosol-bound constituent have not been standardized and there is no possibility of specifying individual forms of mercury [Ryaboshapko and Korolev, 1997]. Concentrations of total gaseous mercury in the clean oceanic atmosphere are from 1.5 ng/m<sup>3</sup> (the southern Atlantic) to 2.25 ng/m<sup>3</sup> (the northern Atlantic), and in the background atmosphere over land, 1-2 ng/m<sup>3</sup>. Over polluted regions concentrations increase to 3-4 ng/l, and in heavily polluted regions, 6-30 ng/m<sup>3</sup>. Relative content of Hg(II) and Hg(P) also increases and amounts to less than 2% in background regions, to 5% in polluted regions, to 20% Hg(II) and 10% Hg(P) in heavily polluted regions. Concentrations in precipitation measured over the urban area of Tuscany [Ferrara *et al.*, 1982] were 80 ng/l for early rain and 20 ng/l - for late rain.

The content of dissolved mercury in the Mediterranean Sea is a few ng/l and not exceeding 50 ng/l in heavily polluted regions [UNEP, 1996]. According to estimates [Horvat, 1996] in the open sea, in particular in Gulf of Lions [Cossa *et al.*, 1996] the concentration of dissolved mercury is a few tenths of ng/l.

Modelling. At present several models (Lagrangian and Eulerian) of mercury atmospheric transport are under development. The Lagrangian model EMERC [Petersen *et al.*, 1995] was used to evaluate depositions on the Baltic and North Seas. The results obtained demonstrated reasonable agreement between measured and calculated values. The model described seasonal variation of air concentrations and the gradient in concentrations, decreasing from the south to the north. Test runs of an Eulerian model [Ryaboshapko and Korolev, 1997] manifest a satisfactory consistency of calculated and measured data for regions of the North and Baltic Seas. This model version is only at an initial stage of development.

Model development. It is desirable to develop local, regional and global models. As far as parametrization is concerned it is necessary to determine:

- the life-time of gaseous species of mercury within the global cycle;
- mechanisms and reaction rates of (in gaseous and liquid phases) basic mercury species;
- source and/or origin of methylated mercury present in precipitation;
- constants of Hg<sup>0</sup> oxidation by oxidants other than ozone and equilibrium constants for Hg(II) adsorption on particles in clouds and rain drops;
- the amount and proportion of mercury compounds (Hg<sup>0</sup>, MMHg and DMHg, Hg(II), Hg(P)) emitted from sources of various types (anthropogenic, natural and re-emission);
- the effect of underlying surface and vegetation on dry deposition rates.

## CONCLUSIONS

On the basis of published data and modelling results of the present study it is possible to make the following conclusions and suggestions:

- the pollution of the Mediterranean Sea by mercury and its compounds is brought about mainly via the atmosphere and riverine runoff;
- the total input from anthropogenic sources through the atmosphere is 10-40 tonnes per year. The contribution of riverine runoff varies within the range of 50-200 tonnes per year (mainly in particulate form);
- a part of riverine runoff of mercury (about 10-40 tonnes per year) and the bulk of atmospheric deposition come to the Mediterranean Sea as soluble mercury compounds which can be assimilated by the marine biota and thus would affect the marine life.

A special attention should be paid to coastal zones where higher concentrations of mercury are observed due to riverine runoff, intensive sedimentation and atmospheric deposition. In addition these zones are characterized by enhanced biological productivity. The Western Mediterranean, the Tyrrhenian and Adriatic Seas are believed to be the most vulnerable regions.

According to the modelling results of the present study, the total deposition of mercury on the Mediterranean Sea varies from 5.8 to 13.2 t/y depending on emission estimates (for 1987 or 1990) and meteorological conditions (for 1987, 1990 and 1994).

The deposition density correspondingly varies from 2.86 to 6.58  $\mu\text{g}$  of  $\text{Hg}/\text{m}^2/\text{y}$  with highest deposition density occurring in the following sub-basins : North-Western (mt2)(6.8-11.9  $\mu\text{g}/\text{m}^2/\text{y}$ ), Adriatic (mt5)(6.3-16.8), Marmara (mt11)(6.5-13.8) and Aegean (mt8)(5.9-8.4).

Taking into account other estimates (see paragraph 5.3.3) based on modelling and measurements it could be assumed that the total atmospheric deposition of soluble mercury on the Mediterranean Sea would amount to 10-40 t/y with its riverine input amounting to almost the same value.

The validation of the obtained results was made taking into account the results of global estimates, model results for other pollutants and available results for the North and Baltic Seas.

To improve estimates of the Mediterranean Sea pollution by mercury and its compounds it is necessary to evaluate:

- mercury input to/from the watershed;
- mercury removal due to sedimentation and biosedimentation;
- input/output through Gibraltar and Dardanelles;
- contribution of mercury to the marine water from sediments and thermal sources;
- evasion to the atmosphere;
- mercury vertical distribution in the sea water;

and in addition:

- to refine emission data including sources in Turkey, Middle East and North Africa;
- to make calculation for the whole Mediterranean Sea and its watershed;
- to consider peculiarities of the Mediterranean: enhanced insolation, prolonged dry period, effects of dust storms.

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