

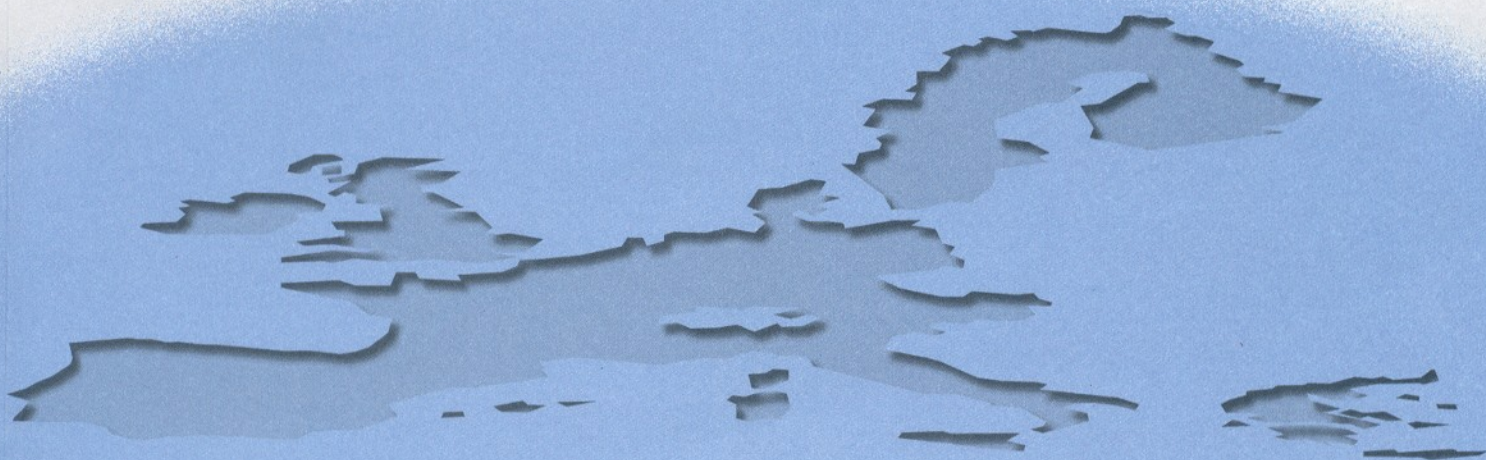


European Commission

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# **Ambient Air Pollution by Mercury (Hg) Position Paper**



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# **Ambient Air Pollution by Mercury (Hg)**

## **Position Paper**

17 October 2001

**Prepared by the Working Group  
On Mercury**

A great deal of additional information on the European Union is available on the Internet.  
It can be accessed through the Europa server (<http://europa.eu.int>).

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## EXECUTIVE SUMMARY

The **Position Paper on Mercury** is a Technical Report prepared by a number of experts (see attached list) nominated by Member States as part of the “Working Group on Mercury”. It fulfils the requirement of the **Council Directive** on Ambient Air Quality Assessment and Management, better known as the Framework Directive (FD) (Council Directive, 1996) and it is aimed to support the preparation of the Daughter Directives (DD) as reported in *Art. 2* of the FD. The Position Paper (PP) on mercury is based on *state-of-the-art knowledge* of European sources (natural and anthropogenic) and major processes/mechanisms that influence the cycle of mercury in Europe and in the global environment, and ultimately its impact on human health, following the requirement of an integrated approach to the protection of air, water and soil ecosystems as dictated in *Art. 7.2* of the FD. As the *state-of-the-knowledge* on different aspects involved in mercury pollution is continuously and rapidly evolving, this PP should be considered as a “snapshot” of our current understanding of temporal and spatial patterns of processes/mechanisms of mercury (and its compounds) in the European environment and its impact on human health and sensitive ecosystems.

The **Position Paper on Mercury** is structured in **seven chapters** that report on natural and anthropogenic emissions of mercury on local and regional scales in Europe (Chapter-2) and provides an overview of Best Available Technology (BAT) that can be used to reduce the emission to the atmosphere (Chapter-7). A detailed presentation of major chemical and physical processes involved in the dynamic of mercury in the atmosphere and modeling techniques currently available in Europe to assess spatial and temporal patterns of ambient concentrations and deposition fluxes are discussed in Chapter-3, whereas monitoring and analytical techniques along with ambient concentration data currently available for gaseous and particulate mercury observed at industrial, urban and rural areas in Europe are presented in Chapter-4. Detailed information on major exposure patterns to elemental mercury and mercury compounds (organic and inorganic) are discussed in Chapter-5, whereas Chapter-6 reports on the risk associated to mercury exposure for major population groups in Europe.

It is well known that mercury is a natural element that cannot be created or destroyed and the same amount has existed on the planet since the earth was formed. A significant amount of research indicate that natural and human (anthropogenic) activities can redistribute this

element in the atmospheric, soil and water ecosystems through a complex combination of different chemical and physical mechanisms. During the industrial times due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), it has been employed in a wide array of applications (i.e., manufacturing, dentistry, metallurgy) and as result of its uses the amount of mercury mobilised and released into the atmosphere has increased compared to the pre-industrial levels. The atmosphere is the major transport (re-distribution) media of mercury in the environment, it is released from a variety of point and diffuse sources, is dispersed and transported in the air, deposited to the earth and stored in or redistributed between water, soil and atmospheric compartments. Wet deposition plays a major role in the transfer of mercury from the atmosphere to surface waters and land. Even after it deposits, mercury is partly emitted back to the atmosphere either as a gas or associated with particles, to be re-deposited elsewhere. It has been extensively demonstrated that mercury accumulates most efficiently in the aquatic food web. Predatory species at the top of the food web generally have higher mercury concentrations. Therefore, mercury cycling and mercury partitioning between different environmental compartments and its impact on human health depend upon the combination of complex phenomena that are related to numerous environmental parameters as described in detail in this PP.

**Important findings and remarks** highlighted in each chapter of the PP are summarised below, whereas the recommendation of the WG addressed to the Commission are reported in a separate (“Recommendation”) chapter of this PP.

1. Studies of occupationally exposed humans have shown slight adverse effects on the CNS and kidneys, and probably also on the thyroid, from inhalation of *elemental mercury* ( $\text{Hg}^0$ ) at long-term air levels of 25-30  $\mu\text{g m}^{-3}$ . Starting from this lowest observed adverse effect level (LOAEL), we propose a conversion factor of 10 for the continuous exposure of the general population during a whole lifetime, an uncertainty factor of 5 for the use of a LOAEL (instead of a no observed adverse effect level), and 10 for variability in toxicokinetics and individual susceptibility. The limit value will then be 0.05  $\mu\text{g m}^{-3}$ , as an annual average for the general population (Chapter-6).
2. The developing brain is considered the most sensitive target organ for *methyl mercury*, which occurs in the human diet. For a risk assessment the US Environmental Protection

Agency (EPA) uses a reference dose (RfD) at which no adverse effects should occur. The RfD has recently been re-evaluated by the National Research Council. It is now derived from an analysis of data from the Faroe Islands study of children and their mothers exposed to methyl mercury during pregnancy.

3. A **benchmark dose analysis** was performed on cord blood Hg from the Faroe Islands study and neuropsychological tests at seven years of age. The cord blood data were converted to maternal intakes. The EPA chose an uncertainty factor of 10 accounting for inter-individual variability in pharmacokinetics, gaps of knowledge on possible long term effects, and uncertainty concerning the relationships between cord and maternal blood mercury concentration. No new information has emerged that would change the risk assessment. Moreover, the considerations made for the US should be valid also for the European population.

We therefore consider the **US EPA RfD of 0.1 µg per kg body weight and day** to be appropriate for **Europe**. It should be noted that it is mainly relevant for fertile women. The reference dose will be exceeded if the diet is contaminated with mercury, this mainly applies to fish. As an example, if the weekly intake is about 100 g (one typical fish meal per week) of fish with roughly 0.4 mg kg<sup>-1</sup>, the RfD will be exceeded. Since one fish meal per week should be possible, an aim of keeping fish Hg levels below this limit seems appropriate. If this is not possible, dietary restrictions with respect to fish with high mercury content should be considered. However, fish also is a source of proteins, selenium, and fatty acids. As a consequence risk management of mercury exposure, e.g. dietary restrictions, should be based on a risk-benefit analysis (Chapter 6).

4. Numerous **animal experiments** have shown interactions between nutrients and methyl mercury, no human data has been provided, but a modifying effect of nutrients e.g. selenium is likely to occur.
5. The proposed **limit value** for Hg<sup>0</sup> of 0.05 µg m<sup>-3</sup> is rarely exceeded in ambient air in Europe. Exposure to elemental Hg from dental amalgams in most cases represents a daily uptake higher than this level would give rise to (Chapter-5).
6. In **European populations** where fish and other seafood represent a considerable part of the diet, the value of 0.1 µg MeHg kg<sup>-1</sup>-body weight per day could be considerably

- exceeded. Models for the population exposure to MeHg have been developed, but owing to scarcity of input data like dietary surveys and data on fish Hg, a quantification of the extent of exposure to MeHg in Europe is not available (Chapter-5).
7. Since **exposure to methyl mercury** via diet is the critical mercury problem in Europe, the reduction of potential exposure to this Hg species should be the focus for the steps to be taken in Europe (Chapter-1, -5 and -6).
  8. The **origin of methylmercury in fish** is to a large extent anthropogenic emissions of mercury to air which is subjected to long-range transport, transformations and deposition to terrestrial and aquatic systems. Mercury is accumulated in forest soils from where it only slowly is transported to aquatic ecosystems. In aquatic ecosystems, a fraction of the mercury deposited directly and transported from surrounding catchments is transformed into methylmercury compounds which are readily taken up and bioaccumulates in aquatic food-chains. *Industrial discharges of mercury directly to water systems will have the same effect.* Accumulation of mercury in forest soils may also lead to adverse effects on soil micro-organisms, which has a potential impact on mineralisation processes (Chapter-1).
  9. Due to the complexity of the biogeochemistry involved in transfer and transformation of mercury from the atmospheric deposition to methylmercury in fish, a **universal relationship between mercury input and methylmercury levels in fish does not exist**, but will be dependent on local conditions. However, research performed in Sweden has proven a general link between atmospheric deposition and methylmercury levels in fish, along a south-to-north decreasing deposition gradient. A decrease of fish methylmercury levels following reduction of the atmospheric input has also been observed. Thus, reduction of mercury emissions to the atmosphere is an important measure to reduce methylmercury levels in fish and thus reducing human exposure in Europe (Chapter-1)
  10. **Atmospheric mercury** exists mainly in the form of elemental mercury vapour ( $\text{Hg}^0$ ) (90 to 99%), particle bound mercury (< 5%) and gaseous divalent mercury (*e.g.*  $\text{HgCl}_2$ ) (<5%). Emissions from anthropogenic sources can occur in all three forms. Atmospheric deposition occurs mainly via dry deposition or wash-out of particle bound and gaseous divalent mercury. Elemental mercury contributes to the deposition via

oxidation in air or in cloud droplets. Mercury in the form of elemental vapour ( $\text{Hg}^0$ ) has a long atmospheric lifetime which makes transport on hemispheric and global scales feasible. In the northern Hemisphere, anthropogenic emissions have increased the background concentrations of mercury in air by a factor of 2-3 since before industrialisation (Chapters-1, -2 and -3).

11. There is a fairly good understanding of major anthropogenic and natural sources and source regions in Europe at present. Various factors affecting the amount of emissions from these sources are also well defined. However, quantitative assessment of the emissions is not always complete and accurate to the extent requested by major users of emission inventories, such as policy makers preparing emission reduction strategies at local, regional, and even global scale, and modellers providing input to these strategies (Chapter-2 and Chapter-3).

Current estimates of **mercury emissions** from anthropogenic sources in Europe indicate that as much as 340 tonnes of this element can be emitted annually, with 33% (~112 tonnes) released in EU-15 member countries, 26% (88 tonnes) in accession candidate countries and 41% (138 tonnes) in other European countries. More than half of these emissions are generated during the combustion of coal in utility, industrial and residential boilers. Another 200 tonnes of mercury annually is emitted to the European atmosphere from natural sources, including the re-emission of mercury emitted previously from the anthropogenic sources and deposited to the aquatic and terrestrial surfaces. The accuracy of emission estimates for anthropogenic sources is within 30% except for waste incineration (it could be as high as a factor of 5). No assessment of the accuracy of natural source emissions has been made so far but it is believed that emission estimates for natural sources are much less accurate than the emission estimates for anthropogenic sources (Chapter-2).

Information on **chemical speciation** of mercury by source category is crucial for modellers simulating the fate, behaviour, and transport of mercury in the environment and policy makers using the information on environmental human health effects of this element. As much as 60% of anthropogenic emissions of mercury in Europe is estimated to be in a gaseous elemental form, 30% as gaseous bivalent mercury and 10% as elemental mercury on particles. A majority of emissions from natural sources is believed to be in a gaseous elemental form. At present, anthropogenic mercury

- emissions in Europe are estimated to be nearly 15% of the total mercury that annually is released in the world to the global atmosphere (Chapter-2).
12. A number of different **atmospheric modeling tools** have been developed within European and national research projects and within the UN-ECE framework. In particular integrated mercury modeling systems have been developed and tested for North and Central Europe, and Mediterranean region. The main differences in these modeling tools are related to the type of approach used to model different chemical and physical processes on local and regional scales, spatial and temporal resolution and accuracy of input data. Further development of modelling tools is needed to accurately determine source-receptor relationships for mercury deposition in Europe. At present, lack of monitoring data for atmospheric mercury species is one of the main limiting factors for the evaluation and further refinement of models for policy and environmental (regulatory) planning applications (Chapter-3).
  13. **Monitoring** of wet deposition is an efficient measure of overall impact of atmospheric deposition and is useful to follow up time-trends and results of control measures on a regional scale. Wet deposition monitoring of mercury in Scandinavia has shown decreasing levels since the early nineties, which is mainly the results of emission reductions in northern and central Europe. Monitored wet deposition can also be used to assess the overall input to aquatic and terrestrial ecosystems. Monitoring of  $\text{Hg}^0$  (or TGM = Total Gaseous Mercury =  $\text{Hg}^0$  + small fractions of other gaseous species) may provide important information on the effectiveness of emission control measures adopted at local scales on a short-time basis compared to the regional background contributions. Monitoring of gaseous divalent mercury (or RGM = Reactive Gaseous Mercury, an operational definition) and particle bound mercury (or TPM = Total Particulate Mercury) is necessary for an increased understanding of atmospheric transport and transformation processes as well as for model evaluation and testing (Chapter-4).
  14. **There is a lack of standard methods** in Europe for assessing the levels of mercury (and its compounds) in ambient air and precipitation, which does not allow a comparison of mercury concentration data obtained at different sites by different laboratories using different sampling and analytical procedures. For **wet deposition and TGM monitoring**, quite similar methods are currently used by a number of

European laboratories and a standardisation could be achieved with relatively moderate efforts. For **TPM and RGM**, promising methods have been employed in European research projects but further testing and evaluation is needed before a standardisation can be achieved (Chapter-4).

15. A number of **control options** are available for mercury emission reductions. Mercury emissions are also reduced by systems for reducing emissions of other pollutants such as sulphur and fine particles although the efficiency may vary considerable depending on emission source (Chapter-7).



## RECOMMENDATIONS

Since **exposure to methyl mercury** via diet is the critical mercury problem in Europe, the reduction of potential exposure to this Hg species should be the focus for the steps to be taken in Europe. The daily reference dose of 0.1 µg methylmercury per kg body weight is often exceeded in certain population groups in Europe. To reduce the risk to human health and to ensure that this reference dose is not exceeded, a long-term strategy for the reduction of the methylmercury levels in fish from European waters should be adopted. As a part of this strategy, **the WG proposes a specific action plan** for reduction of the atmospheric input of mercury to terrestrial and aquatic ecosystems in Europe which includes reductions of mercury emissions from major anthropogenic sources and a complete phase-out of the use of mercury in major goods. Other actions such as dietary guidelines may be needed to reduce the human health risks in the short term.

The WG recommends that the European Commission adopts the following action plan as apart of the Air Quality directive:

1. **A mandatory monitoring network** for Total Gaseous Mercury (TGM) in ambient air and mercury in precipitation (wet deposition) should be established in the Europe Union.
2. The European Commission should encourage Member States to promote a voluntary monitoring network for **mercury species** in ambient air (total particulate mercury and gaseous divalent mercury).
3. To ensure data comparability and quality, the European Commission should support **standardisation** of methods for sampling and analysis of atmospheric mercury species within CEN.
4. Member States should be requested to make an **inventory** of current mercury emissions from anthropogenic sources.
5. **To reduce the uncertainty** associated to anthropogenic emission estimates there is a need that Member States promote measurements of speciated mercury emissions at the emission source (in the flue gases at the stack).
6. The European Commission should support studies that may lead to a better assessment of mercury emissions from major natural sources (i.e., surface waters, soil). It would

- improve our understanding of the **relative contribution** of natural vs. anthropogenic sources in Europe and would provide an important information on the European contribution (anthropogenic + natural sources) to the atmospheric mercury budget that annually is released into the global atmosphere (European emissions vs. emissions from the rest of the world).
7. Member states should be requested to present an inventory of what **actions** can be taken **to reduce anthropogenic mercury emissions** including a ban on use of mercury in products.
  8. The European Commission is urged to provide support for the development of **atmospheric models** to be used as (regulatory) tool in the implementation of the policy at Member State and European level.
  9. The European Commission should encourage Member States to generate **dietary exposure data** for critical population groups.
  10. To improve the **risk assessment** related to mercury exposure, the European Commission should encourage and support studies of interactions between methyl mercury and nutrients in humans.
  11. The **benefits derived from fish consumption** should be taken into account in risk assessment and risk management.
  12. The European Commission should encourage/take initiative to strengthen the **co-operation of Member States** in the current activities of the UN ECE on atmospheric modelling, monitoring and development of models for critical loads/limits assessment scenarios for atmospheric deposition of mercury.
  13. Results of the above activity should be used to establish a **target value for the long-term atmospheric deposition of mercury** in Europe and for the development of strategies for a cost-efficient implementation of the limit value.
  14. Since the actions needed are derived from assessment of human exposure in Europe and potential health risks, the European Commission should encourage research and surveys on the population exposure to mercury in Europe, and on the associations between exposure and health effects.

## **CHAPTER-1. INTRODUCTION ON THE MERCURY CYCLE AND ITS IMPLICATIONS ON HUMAN HEALTH AND THE ENVIRONMENT**

### **1.1 THE BIOGEOCHEMISTRY OF MERCURY**

### **1.2 ATMOSPHERIC EMISSIONS AND LONG-RANGE TRANSPORT**

#### 1.2.1 EMISSIONS

#### 1.2.2 ATMOSPHERIC TRANSPORT AND TRANSFORMATIONS

#### 1.2.3 LONG-RANGE TRANSPORT

### **1.3 IMPACT OF MERCURY IN AQUATIC AND TERRESTRIAL ECOSYSTEMS**

#### 1.3.1 MERCURY IN TERRESTRIAL ECOSYSTEMS

#### 1.3.2 MERCURY IN THE AQUATIC ECOSYSTEMS

#### 1.3.3 IMPACT OF MERCURY IN AQUATIC AND TERRESTRIAL ECOSYSTEMS

### **1.4 IMPACT ON HUMAN HEALTH AND THE ENVIRONMENT**

#### 1.4.1 ROUTES OF EXPOSURE

#### 1.4.2 PUBLIC HEALTH IMPACT

#### 1.4.3 ENVIRONMENTAL IMPACT

### **1.5 POLICY IMPLICATIONS**

### **1.6 REFERENCES**

This introductory chapter is devoted to a broader introduction to the characteristics of the environmental cycling of mercury and the pathways from emissions to ecological impact and human exposure. Considerable more details on some of the main aspects of mercury pollution are given in the following chapters.

## 1.1 THE BIOGEOCHEMISTRY OF MERCURY

Mercury is a natural element that cannot be created or destroyed and the same amount has existed on the planet since the earth was formed. A significant amount of research indicates that natural and human (anthropogenic) activities can redistribute this element in the atmospheric, soil and water ecosystems through a complex combination of transport and transformations. During the industrial times due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), it has been employed in a wide array of applications (i.e., manufacturing, dentistry, metallurgy) and as result of its uses the amount of mercury mobilised and released into the atmosphere has increased compared to the pre-industrial levels.

Research on atmospheric emissions, transport and deposition mechanisms to terrestrial and aquatic receptors, chemical transformations of elemental mercury to more toxic species i.e., methylmercury, studies on the bioaccumulation of mercury in the aquatic food web as well as exposure and risk assessments has driven the scientific and political communities to consider this toxic element as a pollutant of global concern (i.e., Nriagu, 1989; Mason *et al.*, 1994, Pleijel and Munthe, 1995; Pacyna and Keeler, 1995; Porcella *et al.*, 1995; Pirrone *et al.*, 1996; Pirrone *et al.*, 1998; Petersens, *et al.*, 1998; Pirrone *et al.*, 2000; Pacyna *et al.*, 2000; Munthe *et al.*, 2000; Wängberg *et al.*, 2000; Munthe *et al.*, 2001a,b).

Figure 1.1 shows a conceptualisation of the global mercury cycle in the biosphere. As indicated in Figure 1.1 mercury is emitted to the atmosphere from a variety of point and diffuse sources, is dispersed and transported in the air, deposited to the earth and stored in or redistributed between water, soil and atmospheric compartments. Therefore, mercury cycling and mercury partitioning between different environmental compartments are complex phenomena that depend on numerous environmental parameters. In principle, the following points generally describe the key factors that affect the fate and transport of mercury in the environment:

- ❑ The chemical and physical form of mercury in air affects the mechanisms by which it is transferred to the earth surface and ultimately influence the depositional fluxes.
- ❑ Wet deposition is the primary mechanism for transferring mercury and its compounds from the atmosphere to aquatic and terrestrial receptors, though in dry regions, particle dry deposition fluxes may be significant.
- ❑ Once in aquatic ecosystems, mercury can exist in dissolved and/or particulate forms and can undergo chemical/microbial transformation to methylmercury as summarised in Figure 1.1.

- ❑ Contaminated sediments at the bottom of surface waters can serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer.
- ❑ Mercury has a long retention time in soil and as a result, the mercury accumulated in soil may continue to be released to surface waters and other media for long periods of time, possibly hundreds years.

An increase in ambient air levels of mercury will result in an increase of direct human exposure and in an increase of mercury flux entering terrestrial and aquatic ecosystems leading to elevated concentrations of methylmercury in freshwater fish and marine biota. Such a contingency might have an important bearing on acceptable levels of mercury in the atmosphere. Although the different processes affecting the global atmospheric cycle of mercury and the mechanisms driving the methylation and bioaccumulation pathways in the aquatic food-chain are not completely understood, a preliminary quantitative estimates of risks from these post-depositional processes is possible. In order to prevent possible health effects of exposed populations in the near future, a strategy for emission reductions of mercury is strongly needed.

## 1.2 ATMOSPHERIC EMISSIONS AND LONG-RANGE TRANSPORT

### 1.2.1 Emissions

It is well known that mercury is emitted to the atmosphere from a variety of natural and anthropogenic sources (Nriagu and Pacyna 1988; Pirrone *et al.*, 1996; Pacyna, 1996; Pirrone *et al.*, 1998; Pacyna *et al.*, 2000; Pacyna and Pacyna, 2001). The primary natural processes that release Hg to the atmosphere include volatilisation of Hg from marine and aquatic environments, volatilisation from vegetation, volcanic emissions, degassing from geological materials, and releases associated with wind-blown dust (Nriagu, 1989; Lindqvist *et al.* 1991).

Mercury emissions to the atmosphere from wind-blown dusts, weathering of mercury-containing rocks and release of mercury from abandoned mercury mines may represent an important diffuse source of mercury in the environment. Cinnabar represents the principal ore containing mercury, which has been known since the last 3000 years. The world most abundant deposits are located in Almadén (Spain), Idrjia (Slovenia) and Monte Amiata (Italy) which have been exploited since ancient times for gold and silver extractions in Europe and North America (Nriagu 1989; Pirrone *et al.*, 1996; Pirrone *et al.*, 1998).

Emissions of mercury from water and land surfaces may occur both as natural emissions (as is the case in areas of high mineral content of mercury) or as re-emissions of previously deposited mercury with anthropogenic origin. These two processes are difficult to separate but together make up a significant flux of mercury from natural surfaces to the atmosphere.

Major anthropogenic sources of atmospheric Hg include area and point sources. Area sources includes emissions from small scale fuel burning, electric lamp breakage, laboratory use, dental preparation, landfills, and sludge application. Point sources include combustion processes, manufacturing industries and a wide range of minor sources. Coal and oil burning

in electric utilities as well as in residential, commercial and industrial facilities, incineration of solid waste (namely municipal solid waste and medical waste) and sewage sludge, and primary non-ferrous metal smelters are major combustion sources categories. Estimates of mercury emissions to the global atmosphere suggest that the contribution from industrial sources ranges between 2200 t yr<sup>-1</sup> (1992 estimate by Pirrone *et al.*, 1996) to 1660 t yr<sup>-1</sup> (1990 estimate by Pacyna and Pacyna, 1996).

A detailed description of the state-of-the-art on emissions of mercury is given in Chapter 2.

### 1.2.2 Atmospheric Transport and Transformations

Mercury is emitted in three main forms: elemental vapour (Hg<sup>0</sup>), gaseous divalent (Hg(II)) and particulate phase mercury (Hg(p)). The temporal and spatial scales of mercury transport in the atmosphere and its transfer to aquatic and terrestrial receptors depends primarily on the chemical and physical characteristics of the three main forms of atmospheric mercury which drive their chemical and physical interactions with other atmospheric contaminants (i.e., Schroeder and Munthe, 1998; Pacyna and Keeler, 1995; Petersen, *et al.*, 1998; Pirrone *et al.*, 2000; Munthe *et al.*, 2000; Wängberg *et al.*, 2000; Munthe *et al.*, 2001a).

Elemental mercury vapour is relatively inert to chemical reactions with other atmospheric constituents, and is only sparingly soluble in pure water. This gives elemental mercury an atmospheric residence time of approximately one year (Slemr *et al.*, 1985; Lindqvist and Rodhe, 1985). Therefore, once released to the atmosphere mercury can be dispersed and transported for long distances over hemispheric and global scales before being deposited to terrestrial and aquatic receptors. The concentration of Hg<sup>0</sup> in ambient air is mainly determined by the background concentration of around 1.3 – 1.5 ng m<sup>-3</sup> in the Northern Hemisphere and 0.9 – 1.2 ng m<sup>-3</sup> in the Southern. Hg(II) and Hg(p) are typically present in concentrations less than 1 % of the Hg<sup>0</sup>. Large variations may occur especially in the vicinity of sources.

The most important gas phase oxidation pathways are the reactions with ozone (Hall, 1995) and OH radicals (Sommar *et al.*, 2001). Oxidation of Hg<sup>0</sup> leads to Hg(II) species which are notably less volatile than Hg<sup>0</sup> and will tend to condense onto atmospheric particulate matter or be deposited to marine or terrestrial surfaces. In the presence of liquid water in the atmosphere (fog or cloud water or precipitation) small amounts of Hg<sup>0</sup> are dissolved and can be oxidised in the aqueous phase by e.g. ozone (Munthe, 1991) or OH radicals (Gårdfeldt *et al.*, 2001). The reactions in the aqueous phase occur at a significantly higher rate than in the gas phase but due to the low solubility of Hg<sup>0</sup> in water and the low liquid water content in the atmosphere, the overall rate of oxidation is comparable to the gas phase oxidation rate. Reduction back to Hg<sup>0</sup> and subsequent transfer back to the gas phase may also occur via reactions with dissolved sulphur dioxide and HO<sub>2</sub> radicals. The rate of reduction is to some extent governed by the complexation chemistry of Hg(II) in the liquid phase. There is a range of possible complexation products of more or less importance depending on the pH of the aqueous phase and on the chemical composition of the original aerosol particle. Hg(II) in the fog and raindrops may adsorb to particulate matter scavenged by the droplets. This is particularly likely if the particulate matter is rich in elemental carbon (soot) as the adsorption coefficient for Hg on soot is high.

Mercury in the atmosphere associated with suspended particulate matter most likely derives from two principal sources. The first source is mercury on particulate matter directly emitted

by industries and power generation plants. The second source of Hg associated with particulate matter is adsorption of  $\text{Hg}^0$  or  $\text{Hg(II)}$  from the gas or aqueous phase.

Information on concentrations of mercury in ambient and available techniques for sampling and measurements is given in Chapter 4. In Chapter 3, atmospheric models describing the emissions, transformations and long-range transport are presented.

### 1.2.3 Long-Range Transport

Long-range transport of mercury in Europe was first observed in the late seventies in Sweden (Brosset, 1982). Since then long-term monitoring activities carried out in Scandinavia have shown a clear gradient in wet deposition of mercury with elevated fluxes in the south-western part of the region, i.e. closer to the main emission sources in Central Europe (Iverfeldt, 1991; Munthe et al., 2001a). Similar patterns have been shown in North America. The Scandinavian studies have also revealed a significant decrease in wet deposition after a reduction of mercury emissions around 1990 (Iverfeldt et al., 1995; Munthe et al., 2001a).

Recent research projects conducted within the Environment and Climate Research Programme have revealed that the anthropogenic influence on atmospheric mercury levels in Europe are still considerable despite reductions in emissions during the last decade (Pirrone et al., 2000; Munthe et al., 2001b). These research projects have also clearly shown the influence of the hemispherical/global cycling of mercury. The authors concluded, that despite of the significant decreases in mercury emissions during the last decade, the atmospheric deposition is still significantly increased in comparison to pre-industrial times. Further reductions are needed to protect sensitive ecosystems and to prevent and decrease levels of methylmercury in freshwater fish in Scandinavia and elsewhere. A significant influence from background contributions was also noted. The authors assume that a large portion of the mercury present in the global atmosphere today is a result of decades of emissions from anthropogenic activities. They state, that the natural component of the total atmospheric burden is difficult to estimate, but is probably on the order of 20 to 40%. Anthropogenic activities have thus increased the levels of mercury in background air by roughly a factor of 3. This calls for actions for mercury emission reductions on European as well as global scales.

## 1.3 IMPACT OF MERCURY IN AQUATIC AND TERRESTRIAL ECOSYSTEMS

### 1.3.1 Mercury in Terrestrial Ecosystems

Metal concentrations in soil vary greatly, and depend on the location of emission sources and on local geology. Away from local pollution sources, metal levels in soils depend on the type of bedrock, soil pH, cation exchange capacity, movement of water, weathering and biological processes. Suggested permissible levels of mercury in soil were found to be  $17 \text{ mg Kg}^{-1}$  on calcareous and  $6 \text{ mg Kg}^{-1}$  on acidic soil (Wang et al., 1982). The critical value of mercury is 0.5 ppm. High pH values, high lime content, and accumulated salt in soil reduce its uptake by plants (Xuexum and Linhai, 1991). Considerable amounts of mercury may be added to agricultural land with fertilisers, lime, and manure (Andersson, 1979). The use of metal-contaminated sludge or fertilisers as soil treatments may cause significant contamination of

agricultural soils and crops. Important sources of contamination of agricultural soil include the use of organic mercurials as a seed-coat dressing to prevent fungal diseases in seeds, the use of mercury sulphate as a root dip, and the use of phenyl mercuric acetate (PMA) for the treatment of apple scab (Frank et al., 1976a, 1976b). Organomercury compounds are highly effective but directly contaminate the soil, as mercury complexes with the soil's organic humic acid component. In general, the effect of the treatment on germination is favourable when recommended dosages are used. The use of mercury compounds as agricultural seed dressing has resulted in mercury accumulation and toxicity in avian and mammalian seed eaters and in avian predators of these herbivores (Fimreite, 1970; Johnels et al., 1979).

In most soils, mercury content varies with depth, particularly in virgin soils (Anderson, 1979). Organic soils commonly have higher average mercury contents than do mineral soils. A highly significant correlation exists between mercury and organic matter content in the top layer of forest soils (Lag and Steinnes, 1978). Total concentrations of mercury in the contaminated soil do not indicate the amount of mercury taken up by plants; the absorption of organic and inorganic mercury from soil by plants is, in fact low, and there is a barrier to mercury translocation from plant roots to tops. Thus large increases in soil mercury levels produce only modest increases in plant mercury levels by direct uptake from soil. Mercury salts in soil may be reduced by biological and chemical reactions to mercury metal or methylated compounds, which may volatilise and be taken up through the leaves, a much more efficient process than via the roots.

Forest soils and other natural soils with a surface layer rich in organic matter, e.g. podsollic soils with a more or less well-developed mor horizon, are especially sensitive to anthropogenic deposition of heavy metals. The organic matter in the topsoil layer absorbs mercury and other heavy metals very effectively and can therefore be regarded as a filter between the supply from the atmospheric deposition and soil layers at deeper depths. Decomposition of the organic layer is slow. Therefore the concentrations of mercury found in surface layers of soils, like the mor layer of podsollic soils, will reflect the total atmospheric deposition over many decades. In Europe, these kinds of soil profiles are predominantly found in the central and northern parts of the region.

Although mercury acts as powerful toxin, particularly in respect of microorganisms, data of mercury in soils in Europe are very limited. In Sweden the concentrations of mercury in the organic top horizon (mor layer) of forest soils shows a regional distribution, indicating a marked impact from long range transport in the atmosphere and increased accumulation. Concentrations and amounts in the mor layer are highest in south Sweden and decrease gradually towards the north, though with considerably local variations (Alriksson 2001). Regional means of mercury vary from 0.5 mg/kg in south Sweden to 0.2 mg/kg in the northernmost parts of the country. This large-scale pattern is in good agreement with the present and past deposition pattern (Lindqvist et al. 1991, Munthe et al. 2001a). Since there is no correlation between concentrations in the mor layer and in the parent till material, the distribution pattern of mercury in the mor layer is mainly the result of deposition due to long-range atmospheric transport. The natural background levels of the mor layer is estimated at about 0.07 mg/kg, assessed from concentrations in the least affected regions of northern Scandinavia and from concentrations in deep sediments layers (Johansson et al. 1995). Also in Norway a large-scale pattern of mercury is found in the humus layer of podsollic soils with higher concentrations in the south compared to the north. The concentration varies from 0.25 mg/kg to 0.15 mg/kg (Steinnes et al. 1993).



Indications of increased concentrations of mercury are also found in central Europe. In the humus layer from six different areas in Germany, the concentrations of mercury were about 0.5 mg/kg (Ilgen and Fiedler 1983, cited in Rundgren et al. 1992) and in two other areas in northern Germany the concentrations were 0.5-0.9 mg/kg. The latter values have been estimated to exceed the natural background level by about a factor of 10. (Lambersdorf et al. 1991). Godbold (1991) suggested that in forest sites in Germany, for example in Solling, mercury in soils might pose a risk for tree vitality.

Increased concentrations of metals in forest soils, especially in the mor layer, imply risks of adverse effect on vital microbial processes and indirectly, of disturbance of ecosystem functioning. Most of the decomposition of organic matter takes place in the mor layer, including the release of nutrients important for maintaining the productivity of forests. Most plant roots are also found in the mor, which moreover is the most important soil layer for organisms that form the base for food chains ending in mammals and birds. Disturbance of the functioning of the mor may therefore have considerable ecological consequences that may be difficult to prognosticate without a thorough knowledge of the entire system.

Adverse effects on microbial processes in forest soils can be expected at increased concentrations by a factor of about 3 (Rundgren et al. 1992, Tyler 1992). In accordance, recent studies from observations in field and laboratory studies has also shown that mercury induced reduction in microbiological activity is likely in south Sweden (Bringmark and Bringmark 2001a, 2001b; Palmborg et al. 2001). Preliminary critical limits to prevent ecological effects for mercury in organic soils has been set to 0.07 –0.3 mg/kg for the total content in soil by an international expert group on effect-based critical limits for heavy metals working within the framework of UN ECE Convention on Long-range Transboundary Air Pollution (CLRTAP), (Curlic et al. 2000).

Hence, there are strong indications that the present concentrations of mercury over large areas in Europe are increased to levels that may affect the decomposition of organic matter and have an adverse effect on recycling of important nutrients. Although the deposition of mercury has decreased substantially during the last decades, the reduction is not enough to stop a further accumulation of mercury in the topsoil layer. The current mercury concentrations in the mor layer of forest soil in south Sweden is increasing at about 0.5 per cent per year (Johansson et al. 1991, Aastrup et al. , 1991, 1995).

### 1.3.2 Mercury in Aquatic Ecosystems

Once entered into the aquatic environment, the inorganic mercury is transformed into methylmercury through microbial activity, which is the most toxic and most bioavailable form of mercury for living organisms (Xun et al., 1987; Korthals and Winfrey, 1987; Kerry et al., 1991; Horvat et al., 1997; Horvat et al., 1993-a; Horvat et al., 1993-b). The levels of methylmercury may build up in the food chain to a point that pose risk to fish eating wildlife and humans. Therefore, one of the keys to understanding risk to mercury is to determine the linkage between atmospheric inputs of mercury and methylation and bioaccumulation.

Due to the low solubility of  $Hg^0$  in water, almost all the aqueous mercury is present as  $Hg(II)$  in the inorganic form and organic methylmercury. Recent research shows that methylmercury is produced in lakes by microorganisms, and sulphate-reducing bacteria as well as enzymes in

other bacteria can remove the methyl group in a process called demethylation. Recent research suggests that ultraviolet radiation can also play an important role in the demethylation process. Usually demethylators also reduce mercury to  $\text{Hg}^0$  at a rate which depends on several factors included sulphate concentrations, dissolved organic carbon (DOC) and other water quality parameters (Hudson et al., 1994; Gilmour et al., 1992; Winfrey and Rudd, 1990). Although some methylmercury can be deposited from the air (Bloom and Watras, 1989; Fitzgerald et al., 1991) this fraction is probably largely of marine origin. Therefore, net methylation in the aquatic environment is by far the main source of the mercury accumulated in biota.

The increased deposition and pools of mercury has resulted in an increased influx of mercury to lakes. In Europe this has been documented mainly in Scandinavia where lakes unaffected from local sources are abundant.

Analysis of mercury in lake sediments shows clearly a regional pattern with enhanced concentrations of mercury in the top layers of the sediment in the southern parts of Finland, Sweden and Norway and gradually decreasing values towards the north (Verta 1990; Johansson 1985; Rognerud and Fjeld 2001). Compared to pre-industrial background concentrations in deeper layers of the sediments, the concentrations of the surface sediments are increased by a factor of about 5 in southern Scandinavia compared to about a factor of 2 or less in the northernmost part of the region. Also the regional distribution of mercury in sediments shows the marked impact on the environment from long range transport in the atmosphere and increased deposition.

As a result of the increased transport of mercury to the lakes, the concentrations in fish have also increased during the last century. In the south part of Finland, Sweden and Norway the concentration of mercury in one-kilo pike (*Esox lucius*) is about 0.5 – 1.0 mg/kg compared to the natural background value estimated to about 0.2 mg/kg. (Verta 1990; Johansson et al 2001; Rognerud et al. 1996). These enhanced concentrations of mercury in fish might endanger human health. The Hg concentration limit of 0.5 mg/kg in fish, recommended by WHO/FOA, is exceeded for one-kilo pike (*Esox lucius*) in about half of the lakes in Sweden (40 000 lakes) and in 85 per cent of the lakes in southern and central Finland (22 000 lakes), (Lindqvist et al., 1991; Verta 1990). As a consequence, the National Food Administration of Sweden has recommended that pregnant women and women planning to have children should not consume species like pike and perch (*Perca fluviatilis*) from freshwater. Other people should not consume these species more than once a week. Consumption should be limited even more if concentrations exceed 1 mg/kg

## 1.4 IMPACT ON HUMAN HEALTH AND THE ENVIRONMENT

### 1.4.1 Routes of Exposure

Human exposure to the three major forms of mercury present in the environment is summarised in Table 1.1. Although the choice of values given is somewhat arbitrary, the Table 1.1 nevertheless provides a perspective on the relative magnitude of the contributions from various media. Humans may be exposed to additional quantities of mercury occupationally and in heavily polluted areas, and to additional forms of mercury, e.g. to aryl and alkoxyaryl compounds widely used as fungicides.

The ambient air and dental fillings represent the two major sources of human exposure to the vapour of metallic mercury (WHO, 1997). From the atmosphere the daily amount absorbed as a result of respiratory exposure into the bloodstream in adults is about 32 ng Hg in rural areas and about 160 ng-Hg in urban areas, assuming rural concentrations of 2 ng m<sup>-3</sup> and urban concentrations of 10 ng m<sup>-3</sup> (absorption rate 80%). Depending upon the number of amalgam fillings, the estimated average daily absorption of mercury vapour from dental fillings vary between 3,000 and 17,000 ng-Hg (WHO, 1991; Clarkson et al., 1988; Skare and Engqvist, 1994). Tracheal measurements of mercury have found concentrations in range of 1,000-6,000 ng-Hg m<sup>-3</sup> during inhalation and less than 1,000 ng-Hg m<sup>-3</sup> when subjects breathed through their noses (Longworth et al, 1988). However, these figures have been questioned by some authors, and their recalculations reduce the estimated daily mercury intake from dental fillings to about 2,000 ng-Hg (Olsson and Bergman, 1992).

Very little data is available on indoors human exposure due to mercury vapour. Fatalities and severe poisonings have resulted from heating metallic mercury and mercury-containing objects in the home. Incubators used to house premature infants have been found to contain mercury vapour at levels approaching occupational threshold limit values; the source was mercury droplets from broken mercury thermostats. The exposure to mercury vapour released from paint containing mercury compounds used to prolong shelf-life of interior latex paint can reach levels of 300-1500 ng-Hg m<sup>-3</sup> (Beusterien *et al.*, 1991). Indoor air pollution caused by central-heating thermostats and by the use of vacuum cleaners after thermometer breakage, etc., also needs attention. Release of mercury from amalgam fillings has been reviewed by Clarkson et al. (1988). It was concluded that amalgam surfaces release mercury vapour into the mouth, and this is the predominant source of human exposure to inorganic mercury in the general population.

Mercury in drinking water is usually in the range of 0.5-100 ng-Hg L<sup>-1</sup>, the average value being about 25 ng Hg/l. The forms of mercury in drinking water are not well studied, but Hg(II) is probably the predominant species present as complexes and chelates with ligands.

Concentrations of mercury in most foodstuffs are often below the detection limit (usually 20 ng-Hg per gram fresh weight) (USEPA, 1997). Fish and marine mammals are the dominant sources, mainly in the form of methylmercury compounds (70-90% of the total). The normal concentrations in edible tissues of various species of fish cover a wide range, from 50 to 1400 ng-Hg/ g-fresh weight depending on factors such as pH and redox potential of the water, species, age and size of the fish. Large predatory fish, such as pike, trout and tuna, as well as seals and toothed whales contain the highest average concentrations. Furthermore, exposure to organomercurials might occur through the use of mercury-containing skin-lightening cremes and other pharmaceuticals. Thiomersal is used for preservation of vaccines and immunoglobulins (an amount of 100 µg thiomersal per injection).

The intake from drinking water is about 50 ng mercury per day, mainly as Hg(II); only a small fraction is absorbed. Intake of fish and fish products, averaged over months or weeks, results in an average daily absorption of methylmercury variously estimated to be between 2,000 and 4,700 ng mercury (EHC, 1976). The absorption of inorganic mercury from foodstuffs is difficult to estimate because levels of total mercury are close to the limit of detection in many food items and the chemical species and ligand binding of mercury have not usually been identified. The intake of total dietary mercury has been measured over a number of years for various age groups. The intake of total dietary mercury (ng/day) measured during a market basket survey (1984-1986) of the Food and Drug Administration (FDA) in the USA (WHO, 1990), according to age group was: 310 ng (6-11 months); 900 ng (2 years) and 2,000-3,000 ng in adults. In Belgium,

two surveys estimated the total mercury intake from all foodstuffs to vary between 6,500 and 13,000 ng mercury (Fouasuin and Fondu, 1978; Buchet et al., 1983).

A detailed description and evaluation of human exposure routes is given in Chapter 5.

### 1.4.2 Public Health Impact

The impact of mercury on human health and the environment depends upon several mechanisms primarily dependent on the toxicokinetic of its major chemical forms present in different environmental media including elemental mercury ( $\text{Hg}^0$ ), inorganic mercury (i.e.,  $\text{HgCl}_2$ ) and organic mercury (i.e., methylmercury). This toxicokinetic mechanisms include absorption, distribution, metabolism and excretion. Therefore, depending on the chemical form of mercury the combination of these mechanisms will determine the risk associated to the exposure of humans to mercury and its compounds. For instance, the absorption of  $\text{Hg}^0$  vapour occurs rapidly through the lungs, but it is poorly absorbed from the gastrointestinal tract. Once absorbed, elemental mercury is readily distributed throughout the body, it crosses both placental and blood-brain barriers (Bormann et al., 1970; Hursh, 1985; Berlin, 1986). Elemental mercury is oxidised to inorganic divalent mercury by the hydrogen peroxidase-catalase pathway, which is present in most tissues. The distribution of absorbed elemental mercury is limited primarily by the oxidation of elemental mercury to the mercuric ion as the mercuric ion has a limited ability to cross the placental and blood-brain barriers. Once elemental mercury crosses these barriers and is oxidised to mercuric ion, return to the general circulation is impeded, and mercury can be retained in brain tissue. The elimination of elemental mercury occurs via urine, faeces, exhaled air, sweat and saliva. The pattern of excretion is dependent on the extent to which elemental mercury has been oxidised to mercuric mercury (WHO, 1990; US-EPA, 1997).

Absorption of inorganic mercury through the gastrointestinal tract varies with the particular mercuric salt involved and decreases with increasing solubility and be as high as up to 20% (Clarkson, 1989). Available data indicate that absorption of mercuric chloride from the gastrointestinal tract results from an electrostatic interaction with the brush border membrane and limited passive diffusion. Increases in the intestinal pH, high doses of mercuric chloride causing a corrosive action, a milk diet and increases in pinocytotic activity in the gastrointestinal tract have all been associated with increased absorption of inorganic mercury. Inorganic mercury has a limited capacity of penetrating the blood-brain and placental barriers. There is some evidence indicating that mercuric mercury in the body following oral exposures can be reduced to elemental mercury and excreted via exhaled air. Because of the relatively poor absorption of orally administered inorganic mercury, the majority of the ingested dose in humans is excreted through the faeces.

Methylmercury is rapidly and extensively absorbed through the gastrointestinal tract (Alberg et al., 1969; Fang, 1980; US-EPA, 1997 and ref. herein). Absorption information following inhalation exposure is limited. Epidemic of mercury poisoning following high-dose exposures to methylmercury in Japan and Iraq demonstrated that neurotoxicity is the health effect of greatest concern when methylmercury exposure occurs to the developing foetus (US-EPA, 1997 and ref. herein). Dietary methylmercury is almost completely absorbed into the blood and distributed to all tissues including the brain, it also readily passes through the placenta to the foetus and fetal brain. Methylmercury in the body is considered to be stable and is only

slowly demethylated to form mercuric mercury in rats. It has a relatively long biological half-life in humans (44-80 days) and it excreted through faeces, breast milk and urine (Stopford et al., 1978; Cheriarn et al., 1978).

Effects of mercury and methylmercury on humans is described and evaluated in detail in Chapter 6.

### 1.4.3 Environmental Impact

The pattern of mercury deposition over a country or continent determines which eco-regions and eco-systems will be more highly exposed. Piscivorous (fish-eating) birds and mammals are more highly exposed to mercury than any other known component of the aquatic ecosystems. Adverse effects of mercury on fish, birds and mammals include death, reduced reproductive capacity, impaired growth and development and behavioural abnormalities. Fish appear to bind methylmercury strongly, indeed nearly 100% of mercury that bioaccumulates in fish tissues is methylated and its biological half-life in fish is on the order of two years (Wiener and Spry, 1996). It is through fish consumption that mercury exposure in fish-eating birds and mammals occurs. The methylation link is important part of the mercury contamination process and responses between changes in inputs and mercury concentrations in biota are not straight forward (Bloom, 1992; Watras and Bloom, 1992). Fish-eating birds in regions with high mercury in fish may be at risk of reproductive and behavioural affects (Scheuhammer, 1995). Mercury concentrations between 0.3-0.4 ppm, wet weight (ww) in 20 to 50 gram fish are considered to be above the critical level that cause reproductive impairment in fish eating birds (Scheuhammer et al., 1998).

Archived biological specimens have been used to evaluate trends in mercury levels in biota. A decrease of mercury levels over 25 year period was observed by Newton et al. (1993) by analysing archived bird livers from Britain. The decrease was strongly related to the decline of in industrial use of mercury observed in several regions of the world. (Lindqvist et al., 1991; Engstrom and Swain, 1997). Therefore, species with an aquatic-based food web (grey heron) showed greater decrease in mercury than the terrestrial based species (sparrowhawk and kestrel).

## 1.5 POLICY IMPLICATIONS

Since anthropogenic emissions of mercury are transported over wide areas the long-term effects of the regional atmospheric deposition are of special concern. Mercury deposited from the atmosphere is accumulated in soils and transported to watercourses and lakes in increased amounts. The risks for adverse effects in the environment and for human health are mainly related to the accumulation of mercury in top layers of forest soils and to the bioaccumulation in aquatic ecosystems.

The ongoing accumulation of mercury in soils is *a large-scale environmental problem*. Large areas of Europe are most probably affected and there is an evident need to reduce the emissions of mercury both to protect forest environment and to enable human fish consumption without limitations. In addition, the environmental effects of mercury are closely

related to other large-scale environmental impacts like acidification, altered land use and the effects of climate change. In accordance, measures should be taken to reduce all anthropogenic influence, known or suspected, to cause adverse effects on the environment.

The accumulation of heavy metals in forest soils is also a *long-term environmental problem*. The present ongoing accumulation of mercury in soils is difficult to reverse. Only 0.1 % of the Hg present in the mor layer is released annually from the drainage areas (Aastrup et al., 1991). Therefore, reduced emissions have only significant effects on the pools in the perspective of decades or centuries. The strategy of environmental protection has to be based on precautionary principles and continuous assessment.

In 1998 a Protocol within the UN ECE Convention on Long-range Transboundary Air Pollution (CLRTAP) was signed by 36 parties in Europe and North America to reduce emissions of some heavy metals including mercury. The protocol is mainly based on best available technology (BAT) and on emission principles. After the implementation of the protocol it is estimated that the reduction of mercury emission will be 21 per cent in Europe compared to 1990 (Berdowski et al. 1998). However, this is not enough to stop a further accumulation of mercury in soils. The concentrations in the soils will still increase but at a slower rate. To stop a further increase of mercury in soils and to reduce the concentrations of fish to less than 0.5 mg/kg an 80 per cent reduction is needed in south Sweden (Johansson et al. 1991).

The efforts to reduce mercury emissions in Europe continue within CLRTAP towards a possible second Protocol on heavy metals. In the first Protocol, participating countries were requested to support activities to develop effect-based approaches for emission control strategies. Considerable improvement in the field of critical limits and effect based approaches for mercury, lead and cadmium has also been reported in three workshops. Potentially applicable products for the work under the Convention in the forms of critical loads for heavy metals should be available by 2004/2005. (Gregor et al. 1997, 1999; Curlic et al. 2000).

## 1.6 REFERENCES

- Aastrup M., Johnson J., Bringmark E. and Bringmark L. 1991. Occurrence and transport of mercury within a small catchment area. *Water, Air and Soil Pollution*:55: 155-167
- Aastrup M., Iverfeldt Å., Bringmark L., Kvarnäs H., Thunholm B., and Hultberg H. 1995. Monitoring of heavy metals in protected forest catchments in Sweden. *Water, Air and Soil Pollution*, 85: 755-760
- Alderice, D. F. 1967. The detection and measurement of water pollution: Biological assays. Canadian Fisheries Report No. 9: 33-39. Canadian Department of fisheries, Ottawa.
- Alessio, L. et al. Inorganic mercury. In: Roi, R and Sabbioni, E. eds. CEC criteria document for occupational exposure limit values - Inorganic mercury. Ispra, Italy: Joint Research Centre (1993).
- Alriksson A. 2001. Regional variability of contents and distribution of Cd, Hg, Pb and C in different horizons of Swedish forest soils. *Water, Air and Soil Pollution* (in print).
- Andersson, A. 1979. Chapter 4. Pp.79-112 in J.O. Nriagu (ed.), *The biogeochemistry of mercury in the environment*. Elsevier/North-Holland Biomedical Press. Amsterdam.
- Berdowski J.J M., Pulles M.P.J. and Visschedijk A.J.K. 1998. Incremental cost and remaining emission in 2010 of Heavy Metals (HM) resulting from the implementation of the draft HM Protocol under the UN/ECE Convention on Long Range Transboundary Air Pollution. TNO Institute of Environmental Sciences and Process Innovation, TNO.report R 98/020, pp 69.
- Bencko, V. et al. Immunological profiles in workers occupationally exposed to inorganic mercury. *Journal of Hygiene, Epidemiology, Microbiology and Immunology*, 34: 9-15 (1990).
- Berlin, M. 1986. Mercury. Pp 2: 387-435 in L. Friberg, G.F. Nordberg and V.B. Vouk (eds.), *Handbook on the toxicology of metals*. Elsevier, Amsterdam.
- Beusterien, K.M. et al. Indoor air mercury concentrations following application of interior latex paint. *Archives Environment and Contamination Toxicology*, 21(1): 62-64 (1991).
- Bloom, N.S., Prestbo, E.M., Hall, B. and Von der Geest, E.J. 1995. Determination of atmospheric mercury by collection on iodated carbon, acid digestion and CVAFS detection. *Water, Air, Soil Pollution* 80, 1315-1318.
- Bowen, H.J.M. 1979. *Environmental chemistry of the elements*. Academic Press. London.
- Bringmark L. and Bringmark E. 2001a. Soil respiration in relation to small -scale patterns of lead and mercury in mor layers of South Swedish forest sites. *Water, Air and Soil Pollution* (in print).
- Bringmark L. and Bringmark E. 2001b. Lowest effect levels of lead and mercury added to mor layer in a long-term experiment. *Water, Air and Soil Pollution* (in print).
- Buchet, J.P. et al. Oral daily intake of cadmium, lead, manganese, chromium, mercury, calcium, zinc, and arsenic in Belgium. A duplicate meal study. *Food and Chemical Toxicology*, 21: 19-24 (1983).
- Clarkson, T.W. et al. Mercury. In: Clarkson, T.W. et al. eds. *Biological monitoring of toxic metals*. New York, Plenum, 1988 pp. 199-246.

- Cherian, M.G. et al. Radioactive mercury distribution in biological fluids and excretion in human subjects after inhalation of mercury vapour. *Archives of Environmental Health*, 33: 109-114 (1978).
- Curlic J., Sefcik P. and Viechova Z. (eds) 2000. Proceedings from meeting of the ad hoc international expert group on effect-based critical limits for heavy metals. Report from Soil Science and Conservation Research Institute, Bratislava.
- Druet, P. et al. Nephrotoxin-induced changes in kidney immunobiology with special reference to mercury-induced glomerulonephritis. In: Bach, P.H. et al., ed. *Nephrotoxicity assessment and pathogenesis*. New York, Wiley, 1982, pp. 206-221.
- Daston, G.P. et al. Toxicity of mercuric chloride to the developing rat kidney. I. Post-natal ontogeny of renal sensitivity. *Toxicology and applied pharmacology*, 71: 24-41(1983).
- Ebinghaus, R., S.G. Jennings, W.H. Schroeder, T. Berg, T. Donaghy, J. Guentzel, C. Kenny, H.H. Kock, K. Kvietkus, W. Landing, J. Munthe, E.M. Prestbo, D. Schneeberger, F. Slemr, J. Sommar, A. Urba, D. Wallschläger, Z. Xiao (1999): International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, *Atmospheric Environment* **33**, 3063-3073
- EHC 101. WHO Task Group on Environmental Health Criteria for Methylmercury. Geneva: WHO (1990).
- EHC 118. WHO Task Group on Environmental Health Criteria for Inorganic Mercury. Geneva: WHO (1991).
- EHC 1. WHO Task Group on Environmental Health Criteria for Mercury. Geneva: WHO (1976).
- Eyssen, G.E.M. et al. Methylmercury exposure in northern Quebec II. Neurologic findings in children, 118: 470-478 (1983).
- Fimreite, N. 1970. Mercury uses in Canada and their possible hazard as sources of mercury contamination. *Environ. Pollut.* 1: 119-131.
- Frank, R., K. Ishida and P. Suda. 1976a. Metals in agricultural soils of Ontario. *Canad. J. Soil Sci.* 56:181-196.
- Frank, R., H.E. Braun, K. Ishida and P. Suda (1976b) Persistent organic and inorganic pesticide residues in orchard soils and vineyards of southern Ontario. *Canad. J. Soil Sci.* 56:463-484.
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N. (2000) Temporal trends in gaseous mercury evasion from the Mediterranean Seawaters. *Science of the Total Environment*, 259, 183-190.
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N. (2000) Volcanoes as Emission Sources of Atmospheric Mercury in the Mediterranean Basin. *Science of Total Environment*, 259, 115-121.
- Fitzgerald W F, Mason R P, Vandal G M. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *Water, Air and Soil Poll* 1991; 56, 745-767.
- Fitzgerald W F, Mason R P, Vandal G M, Dulac F. Air-water cycling of mercury in lakes. Chapt. II.3. In: *Mercury Pollution. Integration and Synthesis* (eds. Watras C J, Huckabee J W). Lewis Publishers 1994; 203-220.



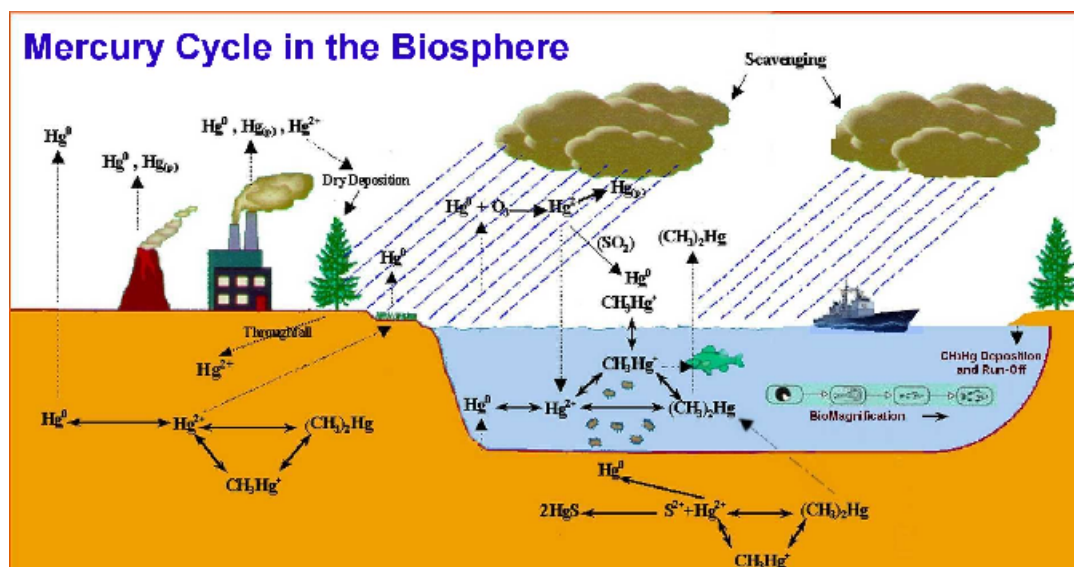
- Foa, V. (1976) Patterns of some lysosomal enzymes in the plasma and of proteins in urine of workers exposed to inorganic mercury. *International archives of occupational and environmental health*, 37: 115-124.
- Forlano, L., Hedgecock, I., Pirrone, N. (2000) Elemental Gas Phase Atmospheric Mercury as it Interacts with the Ambient Aerosol and its Subsequent Speciation and Deposition. *Science of the Total Environment*, 259, 211-222.
- Fouassin, A. and Fondu, M. (1978) Evaluation de la teneur moyenne en mercure de la ration alimentaire en Belgique. *Archives Belges de Medecine Sociale, Hygiene, Medecine du Travail et Medecine Legale*, 36: 481-490.
- Godbold D.L. 1991. Mercury -induced root damage in spruce seedlings. *Water, Air and Soil Pollution* 56:823-831.
- Gregor H.D., Spranger T. and Honerbach F. 1997. Critical limits and effect based approaches for metals and persistent organic pollutants. *Proceedings of the workshop Texte 5/98*, Bad Harzburg, Umweltbundesamt, Berlin.
- Gregor H.D., Mohaupt-Jahr B. and Honerbach F. 1999. Workshop on effect-based approaches for heavy metals. *Proceedings of the workshop Texte 87/99*, Schwerin, Umweltbundesamt, Berlin.
- Gårdfeldt, K., Sommar, J., Strömberg, D., Feng, X. 2001. Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury species in the aqueous phase. *Atmospheric Environment* 35, 3039-3047.
- Hall, B. (1995) The Gas-Phase Oxidation of Elemental Mercury by Ozone. *Water Air and Soil Pollution* 80, 301-315.
- Hedgecock, I., Pirrone, N. and Forlano, L. (2000) Mercury and Photochemistry in the Marine Boundary Layer – Evidence for the production of Reactive Gas Phase Mercury. *Atmos. Environ.* 35, 3055-3062.
- Hursh, J.B. et al. (1976) Clearance of mercury (Hg-197, Hg-203) vapor inhaled by human subjects. *Archives of Environmental Health*, 31: 301-309.
- Horvat, M., Liang, L. and Bloom, N.S. (1993b) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part I Sediments. *Anal. Chim Acta* **281**: 153
- Horvat, M., Bloom, N.S. and Liang, L. (1993a) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II Water. *Anal. Chim Acta* **282**, 153-168.
- Horvat, M., Liang, L., Azemard, S., Mandi, V., Villeneuve, J., Coquery, M. (1997) Certification of total mercury and methylmercury concentrations in mussel homogenate (*Mytilus edulis*) reference material, IAEA-142. *Fresenius' j. anal. chem.*, 1997, letn. 358, str. 411-418.
- Hultman, P. and Eneström, S. The induction of immune complex deposits in mice by peroral and parenteral administration of mercuric chloride; strain dependent susceptibility. *Clinical Experimental Immunology*, 67: 283-292 (1987).
- IARC Monographs on the Evaluation of Carcinogenic Risk to Humans, Volume 58. Mercury and mercury compounds. Lyon 1994.
- Iverfeldt, Å. 1991a. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water, Air, Soil Pollut.* 56, 251-265.

- Iverfeldt, Å. 1991b. Mercury in canopy throughfall water and its relation to atmospheric deposition. *Water, Air, Soil Pollut.* 56, 553-542.
- Iverfeldt, Å., Munthe, J., Brosset, C. and Pacyna, J. Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia. *Water, Air, Soil Pollution* **80**, 227-233, 1995.
- Johnels, A., G. Tyler and T. Westermark. 1979. A history of mercury levels in Swedish fauna. *Ambio* 8: 160-168.
- Kabata-Pendias, A. and Pendias. 1984. Trace elements in the soils and plants. CRC Press, Boca Raton, FL.
- Keeler, G.J., Glinsorn, G. and Pirrone, N. (1995) Particulate Mercury in the Atmosphere: Its Significance, Transport, Transformation and Sources. *Water, Air and Soil Pollution*, 80, 159-168.
- Kimura, Y.; Miller, V. L. *Anal. Chem.* 1960, 32, 4240-4244.
- Kjellström, T. et al. Physical and mental development of children with prenatal exposure to mercury from fish. Stage 1. Preliminary tests at age 4 (Report 3080). Stockholm: National Swedish Environmental Protection Board (1986).
- Johansson K. (1985) Mercury in sediment in Swedish forest lakes, *Verh. Internat. Verein. Limnol.* 22, 2359-2363.
- Johansson K., Aastrup M. Andersson A. Bringmark L. and Iverfeldt Å. 1991. Mercury in Swedish forest soils. Assessment of critical load. *Water Air and Soil Pollution* 56:267 - 281.
- Johansson K., Andersson A. and Andersson T. 1995. Regional accumulation pattern of heavy metals in lake sediments and forest soils in Sweden. *Sci. Total Environ.* 160/161, 373-380
- Lag, J. and E. Steinnes. 1978. *Acta Agric. Scand.* 28: 393.
- Lamersdorf, N.P., Godbold, D.L. & Knoche, D. 1991. Risk assessment of some heavy metals for the growth of Norway spruce. *Water, Air and Soil Pollution* 57-58, 535-543.
- Lindqvist, O., Johansson K., Aastrup M., Andersson A., Bringmark L., Hovsenius G., Håkanson L., Iverfeldt Å., Meili M. and Timm B. 1991. Mercury in the Swedish environment - recent research on causes, consequences and corrective methods. *Water, Air and Soil Pollution*:55.
- Landis, M.S. and Keeler, G.J. 1996 A critical evaluation of a wet only precipitation collector designed for network operation for mercury and trace elements. Presented at the Fourth International Conference on mercury as a global pollutant, Hamburg, august 1996.
- Langworth, S. et al. (1988) Mercury exposure from dental fillings. II. Release and absorption. *Swedish Dental Journal*, 12: 71-72.
- Langworth, S. et al. (1993) Minor effects of low exposure to inorganic mercury on the human immune system. *Scandinavian Journal of Work Environment and Health*, 19: 405-413.
- Lorscheider, F.L. et al. The dental amalgam mercury controversy - inorganic mercury and the CNS; genetic linkage of mercury and antibiotic resistances in intestinal bacteria. *Toxicology*, 97: 19-22 (1995).

- Lu, J. Y., Schroeder, W. H., Berg, T., Munthe, J., Schneeberger, D. and Schaedlich, F. "A Device for Sampling and Determination of Total Particulate Mercury in Ambient Air", *Anal. Chem.* 1998, 70, 2403-2408.
- Marsh, D.O. et al. Fetal methylmercury poisoning; clinical and toxicological data on 29 cases. *Annals of neurology*, 7: 348-355 (1980).
- Munthe, J., Kindbom, K., Kruger, O., Petersen, G., Pacyna, J.M. and Iverfeldt, Å.(2001a): Emission, deposition, and atmospheric pathways of mercury in Sweden, accepted for *Water, Air and Soil Pollution*.
- Munthe, J., Wangberg, I., Pirrone, N., Iverfeldt, A., Ferrara, R., Ebinghaus, R., Feng, R., Gerdfeldt, K., Keeler, G.J., Lanzillotta, E., Lindberg, S.E., Lu, J., Mamane, Y., Nucaro, E., Prestbo, E., Schmolke, S., Schroder, W.H., Sommar, J., Sprovieri, F., Stevens, R.K., Stratton, W., Tuncel, G., Urba, A. (2000) Intercomparison of Methods for Sampling and Analysis of Atmospheric Mercury Species. *Atmos. Environ.* 35, 3007-3017.
- Munthe J., Wängberg I., Iverfeldt Å., Petersen G., Ebinghaus R., Schmolke S., Bahlmann E., Lindquist O., Strömberg D., Sommar J., Gårdfeldt K., Feng X., Larjava K. and Siemens V. (2001b): Mercury species over Europe (MOE). Relative importance of depositional methylmercury fluxes to various ecosystems. FINAL REPORT FOR the European Commission, Directorate General XII. September, 2001.
- Munthe, J. The aqueous oxidation of elemental mercury by ozone. *Atmospheric Environment* **26A**, 1461 - 1468, 1992.
- Nielsen J.B. & Andersen O. Time dependent disposition of mercury after oral dosage. In: E. Merian and W. Haerdi (eds.), *Metal compounds in environment and life*, Science and Technology Letters, Middlesex, UK, 1992, pp 341-348.
- Nielsen, J.B. and Andersen, O. Evaluation of mercury in hair, blood and muscle as biomarkers for methylmercury exposure in male and female mice. *Archives of Toxicology*, 68: 317-321 (1994).
- Nriagu J. O. and Pacyna J. M. (1988) Quantitative assessment of worldwide contamination of air water and soils by trace metals. *Nature* **333**, 134-139.
- Nriagu J. O. (1989) A global assessment of natural sources of atmospheric trace metals. *Nature* **338**, 47-49.
- Ochiai, E. I. 1987. General principles of biochemistry of the elements. Plenum Press, New York.
- Olsson, S and Bergman, M. (1992) Daily dose calculations from measurements of intra-oral mercury vapor. *Journal of Dental Research*, 71: 414-423.
- Pacyna, E., Pacyna, J.M. and Pirrone, N. (2000) Atmospheric Mercury Emissions in Europe from Anthropogenic Sources. *Atmos. Environ.* 35, 2987-2996.
- Pacyna J. M. and Keeler G., (1995) Sources of mercury in the Arctic. *Water Air Soil Pollut.*, 80, 621-632.
- Pacyna J. M. and Pacyna P.E, (1996) Global emissions of mercury to the atmosphere. Emission from anthropogenic sources . A report for the arctic monitoring and assessment programme (AMAP), Oslo, June 1996.
- Pacyna J. M., (1996) Emission inventories of atmospheric mercury from anthropogenic sources . In Baeyens W., Ebinghaus R, Vasiliev O (eds) *Global and regional mercury*

- cycles: sources, fluxes and mass balances. NATO-ASI Series 2. Environment vol. 21. Kluwer, Dordrecht, The Netherlands, pp 161-178.
- Pacyna J. M., (1998) Environmental and health impacts of selected hazardous air pollutants from utility boilers. Keynote paper. Hazardous air pollutants Workshop. The U.S. Clean Air Task Force, Washington, DC, 23 March, 1998.
- Pacyna, J.M., Scholtz, T. and Pirrone, N. (1999) Global Emissions of Anthropogenic Mercury to the Atmosphere. In Proceedings of the 5<sup>th</sup> International Conference on Mercury As a Global Pollutant, May 23-27, 1999, Rio de Janeiro, Brazil.
- Palmborg C., Bringmark L. and Bringmark E. 2001. Microbiological activity in relation to small-scale patterns of heavy metals and substrate quality in spruce mor layers (Of) in southern Sweden. Water, Air and Soil Pollution (in print)
- Petersen, G., J. Munthe, K. Pleijel, R. Bloxam, and A. Vinod Kumar (1998) A comprehensive eulerian modeling framework for airborne mercury species: Development and testing of the tropospheric chemistry module (TCM). *Atmospheric Environment*, 29, 829-843.
- Pirrone, N., Keeler, G.J. and Allegrini, I. (1996) Particle Size Distributions of Atmospheric Mercury in Urban and Rural Areas. *Journal of Aerosol Science*, 27, 13-14.
- Pirrone, N., Keeler, G.J. and Nriagu, J.O (1996) Regional Differences in Worldwide Emissions of Mercury to the Atmosphere. *Atmospheric Environment*, 30, 2981-2987.
- Pirrone, N., Keeler, G.J., Nriagu, J.O. and Warner, P.O. (1996) Historical Trends of Airborne Trace Metals in Detroit from 1971 to 1992. *Water, Air and Soil Pollution*, 88, 145-165.
- Pirrone, N., Allegrini, I., Keeler, G.J., Nriagu, J.O., Rossmann, R. and Robbins, J.A. (1998) Historical Atmospheric Mercury Emissions and Depositions in North America Compared to Mercury Accumulations in Sedimentary Records. *Atmospheric Environment*, 32, 929-940.
- Pirrone, N., Costa, P., Pacyna, J. (1999) Past, Current and Projected Emissions of Trace Elements in the Mediterranean Basin. *Water Science and Technology*, 39, 1-7.
- Pirrone, N., Hedgecock, I., Forlano, L. (2000) The Role of the Ambient Aerosol in the Atmospheric Processing of Semi-Volatile Contaminants: A Parameterised Numerical Model (GASPAR). *Journal of Geophysical Research*, 105, D8, 9773-9790.
- Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R. (2001) Atmospheric mercury emissions from anthropogenic sources in the Mediterranean Region. *Atmos. Environ.* 35, 2997-3006.
- Rognerud S., Fjeld E., and Eriksen G.S. 1996. Nationwide survey of mercury in fish from inland waters and human effects at consumption. NIVA report 673/96, pp 21 (In Norwegian)
- Rognerud S. and Fjeld E. 2001. Trace element contamination of Norwegian lake sediments. *Ambio* Voll.1, 11-19.
- Rundgren S., Rühling Å, Schlüter K. and Tyler G. 1992. Mercury in soil; distribution, speciation and biological effects. *Nord* 1992:3. Pp 89.
- Schroeder, W. H.; Munthe, J., 1998) Atmospheric Mercury – An Overview. *Atmospheric Environment* 29, 809-822.
- Skare, I. and Engqvist A. (1990) Urinary mercury clearance of dental personnel after a longterm intermission in occupational exposure. *Swedish Dental Journal*, 14: 255-259.

- Skare, I. and Engqvist, A. (1994) Human exposure to mercury and silver released from dental amalgam restorations. *Archives of Environmental Health*, 49(5): 384-394.
- Slemr, F.; Seiler, W.; Eberling, C.; Roggendorf, P. (1979) *Analyt. Chim. Acta*, 110, 35-47.
- Sommar, J., Gårdfeldt, K., Strömberg, D., Feng, X. 2001. A kinetic study of the as-phase reaction between the hydroxyl radical and atomic mercury. *Atmospheric Environment* 35, 3049-3054
- Steinnes E., Andersson E.M. and Jakobsen. 1993. Atmospheric deposition of mercury in Norway. In Allan and Nriagu (eds.) *Proceedings International Conference of Heavy Metals in the Environment*, Toronto september 1993; 70-73.
- Task Group on Lung Dynamics (1966) Deposition and retention models for internal dosimetry of the human respiratory tract. *Health physics*, 12: 173-208.
- Tejning, S. and Ohman, H. (1966) Uptake, excretion and retention of metallic mercury in chlor-alkali workers. *Proceedings of the 15th. International Congress on Occupational Health*, 239.
- Thomas D.J. et al. Sexual differences in the distribution and retention of organic and inorganic mercury in methyl mercury-treated rats. *Environmental Research*, 41: 219-234 (1986).
- Tyler G., 1992. Critical concentrations of heavy metals in the mor horizon of Swedish forests. *Swedish Environm. Prot. Agency. Report 4078*.
- Urba, A., Kvietskus, K., Sakalys, J., Xiao, Z. and Lindqvist O. (1995) A new sensitive and portable mercury vapor analyzer GARDIS-1A. *Water, Air and Soil Pollut.* **80** 1305-1309.
- Verta, M. 1990. Mercury in Finnish forest lakes and resevoirs: Anthropogenic contribution to the load and accumulation in fish. Doctoral dissertation, Univ. of Helsinki. Public. of the Water and Environ. Research Inst., Nat. Board of Waters and the Environ. Finland. 6, 1990.
- Xiao, Z., Sommar, J., Wei, S., Lindqvist, O. (1997) Sampling and Determination of Gas Phase Divalent Mercury in the Air using a KCl coated Denuder", *Fresenius J. Anal. Chem.* 358, 386-391.
- Xuexum, Z. and G. Linhai. 1991. Studies on the heavy metals pollution of soil and plants in Tianjin waste-water irrigated area. *Ekologia* 10: 87-97.
- Webb, J. *Enzyme and metabolic inhibitors*. Vol. 2, Academic Press, New-York.
- Wang, H. K., B. Y. Liv, G. Z. Feng and Q. M. Wang 1982. A Study of the permissible level of mercury due to the utilisation of sludge on land. *Acta Agric. Univ. Pekinensis* 8: 69-75.
- Wängberg, I., Munthe, J., Pirrone, N., Iverfeldt, Å., Bahlman, E., Costa, P., Ebinghaus, R., Feng, X., Ferrara, R., Gårdfeldt, K., Kock, H., Lanzillotta, E., Mamane, Y., Mas, F., Melamed, E., Osnat, Y., Prestbo E., Sommar, J., Spain, G., Sprovieri, F., Tuncel, G. (2001) Atmospheric Mercury Measurements in Europe during MAMCS and MOE. *Atmos. Environ.* 35, 3019-3025.
- Wood, J.M. and Wang, H.K. (1983) Microbial resistance to heavy metals. *Environmental Science and Technology* 17, 82-90.



**Figure 1.1** - Conceptualisation of major processes/mechanisms involved in the global mercury cycle in the biosphere.

**Table 1.1** - Estimated average daily intake (retention) of elemental mercury and inorganic and organic mercury compounds (WHO, 1997 and ref. herein).

Estimated average daily intake (retention) <sup>a</sup> in ng of mercury per day			
Media	Elemental Mercury	Inorg. Mercury Comp	Methylmercury
Atmosphere	40-200 <sup>b</sup> (30-160)	0 <sup>c</sup>	0 <sup>c</sup>
Food: fish	0	600 <sup>d</sup> ( 60)	2400 <sup>d</sup> (2300)
non-fish	0	3600 (360)	?
Drinking water	0	50 (5)	0
Dental amalgam	3800-21000 (3000-17000)	0	0
<b>Total</b>	3900-21000 (3100-17000)	4200 (420)	2400 (2300)

- (a) Figures in parentheses are the amounts retained that were estimated from the pharmacokinetic parameters; i.e. 80% of inhaled vapour, 95% of ingested methylmercury and 10% of inorganic mercury is retained.
- (b) Assumes an air concentration of 2-10 ng/m<sup>3</sup> and a daily respiratory volume of 20 m<sup>3</sup>.
- (c) For the purposes of comparison, it is assumed that in the atmospheric concentrations of species of mercury other than mercury vapour are negligible.
- (d) It is assumed that 80% of the total mercury in edible fish tissues is in the form of methylmercury and 20% in the form of inorganic mercury compounds. It should be noted that fish intake may vary considerably between individuals and across populations. Certain communities whose major source of protein is fish may exceed this estimated methylmercury intake by an order of magnitude or more.

## **CHAPTER-2. MERCURY EMISSIONS FROM NATURAL AND ANTHROPOGENIC SOURCES**

### **2.1 OVERVIEW**

### **2.2 NATURAL SOURCES**

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### **ANNEX-1**

### **ANNEX-2**



## 2.1 OVERVIEW

Processing of mineral resources at high temperatures, such as combustion of fossil fuels, roasting and smelting of ores, kilns operations in cement industry, as well as incineration of wastes and production of certain chemicals result in the release of several volatile trace elements to the environment. Mercury is one of the most important trace elements emitted to the environment due to its toxic effects on the environmental and human health, as well as its role in the chemistry of the atmosphere and other environmental compartments.

Our knowledge of mercury emissions on a global and regional scale is still incomplete. Recent estimates of global emission estimates by Pacyna and Pacyna (2000) indicate that Europe and North America seem to contribute less than 25 % to the global anthropogenic emissions of the element to the atmosphere. The majority of the emissions originate from combustion of fossil fuels, particularly in the Asian countries including China, India, and South and North Korea. Combustion of coal is and will remain in the near future as the main source of energy in these countries. An increase of energy demands in this region is clearly foreseen. It is therefore of utmost importance that the combustion of fuels in the Asian countries will be carried out in installation with efficient emission control, also for mercury. These installations are expensive (e.g. Pacyna, 1997) but the expenses on the purchase and maintenance are fully justified taking into account large emissions of mercury with its adverse effects on the environment. The expenses on emission control of mercury in the Asian countries are so large that international community would need to be called for finding proper solutions to the problem.

It is difficult to compare the emission estimates in this work with the estimates of Hg emissions from natural sources, mostly due to a lack of reliable data on the natural emissions. Assuming that annual emissions from natural sources are about 3000 tonnes, it can be concluded that the anthropogenic emissions contributed about 40 % to the total emissions of mercury from all sources worldwide in 1995.

Information on chemical and physical species of mercury emitted from various sources is needed for the development of models of transport and transformations of the element in the environment and the assessment environmental and human health risks. First approaches to assess emissions of various chemical forms of mercury to the atmosphere have recently been made (e.g. Pacyna and Pacyna, 2000). More than half of mercury is emitted as gaseous elemental mercury, while only 10 % emissions occur on particles. The rest of mercury is emitted as gaseous bivalent mercury.

Various international and national organizations and programs have been involved in assessing the current status of environmental contamination by mercury and in developing strategies and policies to reduce emissions of this pollutant. Major international activity to assess source - receptor relationships for mercury in the environment has been carried out within the UN Economic Commission for Europe (ECE) Convention on Long-range Transboundary Air Pollution Transmission (LRTAP). The aim of this activity is to assess major sources of mercury emissions in Europe, the environmental impact of these emissions, and eventually the emission reductions. There are also at least three other conventions in Europe working on the basis of international agreements which aim at the reduction of environmental fluxes of various pollutants to the marine environment, including mercury. These three conventions include: Oslo and Paris Commissions (OSPAR) program on reduction of land-based pollutants transported to the North Sea and the sister programs for the

Baltic Sea (Helsinki Commission - HELCOM) and for the Mediterranean Sea (Barcelona Convention). There are also national programs in the European countries aiming at the assessment of emissions of mercury and elaboration of emission reduction strategies for this pollutant.

## 2.2 NATURAL SOURCES

Natural sources can be very important contributors to the total budgets of atmospheric mercury. However, they are very difficult to assess and even to define. Two major source categories would include the sources related to the geological presence of mercury in various minerals and evasion of mercury from aquatic and terrestrial ecosystems. The latter source category is very much related to the historical atmospheric deposition of mercury to these ecosystems, emitted originally also from anthropogenic activities. It is extremely difficult with the current status of our knowledge to differentiate between the re-emission of mercury originally from anthropogenic and natural sources. However, some assumptions need to be made in this respect.

Emissions from volcanoes seem to be one of the major geological sources of mercury globally and in Europe together with evasion of the element from land containing Hg minerals. Southern Europe is the most affected region in Europe in this respect. A number of studies have been carried out in the Mediterranean Sea area to assess emission rates from these sources and eventually to estimate a contribution of natural emissions of Hg to the total emissions of the element in Europe. One of the major studies was recently completed within the EU project on the Mediterranean Atmospheric Mercury Cycle System - MAMCS (Pirrone *et al.*, 2000). The emission rates estimated within this project are presented in Table 2.1 (also discussed in Chapter-4).

Estimates of Hg emission rates within MAMCS can be used to calculate natural source emissions of the element in Europe. An amount of 200 tonnes per year can be proposed as an average value, which corresponds quite well with the earlier estimates of 265 tonnes per year carried out by Axenfeld *et al.* (1991) for the beginning of the 1980's. It should be admitted that both estimates include the total re-emission of Hg from aquatic and terrestrial surfaces.

## 2.3 ANTHROPOGENIC SOURCES

Processing of mineral resources at high temperatures, such as combustion of fossil fuels, roasting and smelting of ores, kilns operations in cement industry, as well as incineration of wastes and production of certain chemicals result in the release of several volatile trace elements into the atmosphere. Although substantial information has been collected on environmental effects of mercury and its behavior in the environment much less data is available on atmospheric emissions of the element. There are four major groups of parameters affecting emission of mercury to the atmosphere:

- ❑ contamination of raw materials by mercury,
- ❑ physico-chemical properties of mercury affecting its behavior during the industrial processes,
- ❑ the technology of industrial processes, and
- ❑ the type and efficiency of control equipment.

### 2.3.1. Contamination of Raw Materials

Concentrations of mercury in coals and fuel oils vary substantially depending on the type of the fuel and its origin, as well as the affinity of the element for pure coal and mineral matter. The sulfide-forming elements, with mercury included, are consistently found in the inorganic fraction of coal.

Although it is very difficult to generalize on the impurities in coal, the literature data (Gluskoter et al., 1977; Smith, 1987; Pacyna, 1987) seem to indicate that the mercury concentrations in coals vary between 0.01 and 1.5 ppm and that the lignites are somewhat less contaminated than bituminous and subbituminous coals. It should be noted, moreover, that concentrations of mercury within the same mining field might vary by one order of magnitude or more.

There is only limited information on the content of mercury in oils. In general, mercury concentrations in crude oils are about 0.01 ppm. However, on some sporadic occasions these concentrations were as high as 30.0 ppm (Pacyna, 1987). It is expected that mercury concentrations in residual oil are higher than those in distillate oils being produced at an earlier stage in an oil refinery. Heavier refinery fractions, including residual oil, contain higher quantities of ash containing mercury.

Natural gas may contain small amounts of mercury but the element should be removed from the raw gas during the recovery of liquid constituents, as well as during the removal of hydrogen sulfide. Therefore, it is believed that mercury emissions during the natural gas combustion are insignificant.

The most frequently measured concentrations of mercury in coals from various countries, crude oil and natural gas are presented in Table 2.2 after several studies summarized for this document.

Wood and wood wastes are used as fuel in both the industrial and residential sectors. In the industrial sector, wood waste is fired in industrial boilers to provide process heat, while wood is used in fireplaces and wood stoves in the residential sectors. As indicated in the Hg assessment in the United States (US EPA, 1995), wood and wood wastes may contain mercury. Insufficient data are available, however, to estimate the typical mercury content of wood and wood wastes.

Mercury appears as an impurity of copper, zinc, lead, and nickel ores. Obviously, there are also mercury minerals, particularly cinnabar. The element is also present in the gold ores. It is very difficult to discuss the average content of mercury in the copper, zinc, lead, nickel and gold ores as very little information is available in the literature on this subject. On the basis of the review by Pacyna (1983) it can be suggested that on average zinc ores contain larger amounts of the element compared to copper and lead ores.

Chemical composition of input material for incineration is one of the most important factors affecting the quantity of atmospheric emissions of various pollutants from waste incineration. Very limited information exists on mercury concentrations in various types of wastes. Another difficulty is that it is almost impossible to calculate an average value for these concentrations due to the high variability in the content and origin of wastes to be incinerated,

even in the same incinerator. Therefore, it is rather difficult to extend the information on the mercury content measured in one incinerator for another one.

### **2.3.2 Physico-Chemical Properties of Mercury Affecting its Behavior during the Industrial Processes**

Most of the processes generating atmospheric emissions of mercury employ high temperature. During these processes, including combustion of fossil fuels, incineration of wastes, roasting and smelting operations in non-ferrous and ferrous metallurgy, and cement production, mercury introduced with input material volatilizes and is converted to the elemental form. It has been confirmed in various investigations that almost 100 % of the element is found in exhaust gases in a gaseous form (Smith, 1987; Pacyna, 1980). However, mercury in the exhaust gases may be oxidized by HCl and oxygen in the presence of soot or other surfaces as the temperature drops (Hall et al., 1991). Methods capable of determining the exact speciation in exhaust gases from various industrial processes are not readily available, however, a number of reasonable assessments have been made.

### **2.3.3 Technology of Industrial Processes**

Various technologies within the same industry may generate different amounts of atmospheric emissions of mercury. It can be generalized for conventional thermal power plants that the plant design, particularly the burner configuration has an impact on the emission quantities. Wet bottom boilers produce the highest emissions among the coal-fired utility boilers, as they need to operate at the temperature above the ash -melting temperature (Pacyna, 1989).

The load of the burner affects the emissions of trace elements including mercury in such a way that for low load and full load the emissions are the largest (Bakkum and Veldt, 1986). For a 50 % load the emission rates can be lower by a factor of two.

The influence of plant design or its size on atmospheric emissions of mercury from oil-fired boilers is not as clear as for the coal-fired boilers. Under similar conditions the emission rates for the two major types of oil-fired boilers: tangential and horizontal units are comparable (Pacyna, 1982).

Non-conventional methods of combustion, such as fluidized bed combustion (FBC) were found to generate comparable or slightly lower emissions of mercury and other trace elements than the conventional power plants (Carpenter, 1979; Abel et al., 1981). However, a long residence time of the bed material may result in increased fine particle production and thus more efficient condensation of gaseous mercury. Tests carried out in the former Federal Republic of Germany have shown that the residence time of the bed material can be regulated by changing the operating conditions of a given plant, the reduction of combustion temperature, coal size, moisture content, and bed flow rates (Munzner and Schilling, 1985). A literature review of information on the influence of various FBC techniques on emissions of trace elements has been presented by Sloss and Smith (2000).

Among various steel making technologies the electric arc (EA) process produces the largest amounts of trace elements and their emission factors are about one order of magnitude higher than those for other techniques, e.g., basic oxygen (BO) and open hearth (OH) processes. The

EA furnaces are used primarily to produce special alloy steels or to melt large amounts of scrap for the reuse. The scrap which often contains trace elements, and on some occasions mercury, is processed in electric furnaces at very high temperatures resulting in volatilization of trace elements. This process is similar from the point of view of emission generation to the combustion of coal in power plants. Much less scrap is used in other furnaces, where mostly pig iron (molten blast-furnace metal) is charged. It should be noted, however, that the major source of atmospheric mercury related to the iron and steel industry is the production of metallurgical coke.

Quantities of atmospheric emissions from waste incineration depend greatly on the type of combustor and its operating characteristics. The mass burn/waterwall (MB/WW) type of combustor is often used. In this design the waste bed is exposed to fairly uniform high combustion temperatures resulting in high emissions of gaseous mercury and its compounds. Other types of combustors seem to emit lesser amounts of mercury as indicated by the comparison of the best typical mercury emission factors for municipal waste combustors (MRI, 1993). It is also suggested that fluidized-bed combustors (FB) emit smaller amounts of mercury to the atmosphere compared to other sewage sludge incineration techniques, and particularly multiple hearth (MH) techniques.

### 2.3.4 Type and Efficiency of Control Equipment

The type and efficiency of control equipment is the major parameter affecting the amount of trace elements released to the atmosphere. Unlike other trace elements, mercury enters the atmosphere from various industrial processes in a gas form. This section discusses the latest progress in developing the techniques to remove gaseous pollutants from exhaust gases with focus on the removal of mercury and its compounds. Major emphasis is placed on the removal of mercury and its compounds by the application of flue gas desulfurisation (FGD).

The distribution of trace elements in coal-fired boilers with wet and dry FGD was reviewed by Moberg et al. (1982) within the Swedish KHM project. Halogens, mercuric chloride and selenium dioxide, were removed with SO<sub>2</sub> absorption. Large variations of mercury removal were found, probably due to differences in the behavior of specific mercury compounds. Formation of particles of chloride and sulfate salts was considered to be an important removal mechanism for mercury in the FGD process. This would be promoted by high Cl content in the coal and for mercury sulfate, by low temperatures combined with the catalytic effect of activated carbon.

Two major types of FGD systems can be distinguished: wet and dry FGDs.

#### Wet FGD Systems

Distribution of mercury within various streams of the wet FGD system was studied in various countries (1984). As much as 70 % of mercury in exhaust gases has remained in the gas stream after passing through the FGD. In general, the trace element content of the gypsum and sludge is influenced by the solubility of the elements upstream, the settling behavior of solids in the thickener, and the waste water volume. In the waste water cleaning plant, the solubility of the trace elements is decreased by increasing the pH to the range of 8.0 to 9.5 so the waste

water contains only very small amounts of the elements. Their concentrations in the waste sludge are at low levels (e.g. 6 ppm for Hg).

Wet FGD systems improve retention of trace elements from coal combustion where the elements have not already been retained by particulate control (e.g. mercury). The concentrations of trace elements in scrubber waste products depend largely on the amount of fly ash collected with the FGD wastes. The waste from dual collection FGD systems will resemble fly ash very closely, but for systems with efficient particulate removal, gypsum will contain very low or undetectable amounts of trace elements.

Removal of trace elements from exhaust gases by the wet FGD systems has also been studied in the Netherlands (Meij, 1989; 1992), where only pulverized coal-fired dry-bottom boilers are used, equipped with high-efficiency electrostatic precipitators (ESP) and FGD using a wet lime/limestone-gypsum process with prescrubber. Mostly bituminous coals imported mainly from US and Australia are burnt. In one study (Meij, 1992) the Hg concentration upstream of FGD was  $3.4 \mu\text{g}/\text{m}^3$  and downstream was  $1.0 \mu\text{g}/\text{m}^3$ . The relative distribution of mercury between bottom ash, collected pulverised-fuel ash and fly-ash in the flue gases and in the vapor phase was about 10% on fine particles and about 90% in vapor phase. Flue gases contained 87% of the mercury concentration found in coal, and up to 70% of that was removed by the wet FGD. About 60% of mercury removal takes place in the prescrubber and about 40% in the main scrubber.

In summary, the relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapor phase and thus to be removed from the flue gases. In general, removal efficiency for mercury ranges from 30 to 50%.

### Dry FGD Systems

Retention of vapor phase mercury by spray dryers has been investigated in Europe and the United States for coal combustors and for incinerators (e.g. a review by Sloss and Smith, 2000). The following conclusions have been reached:

Brosset (1983): Water soluble mercury (40 to 80%) was partly bound in lime slurry and so mostly retained by the lime.

Bergstrom (1983): 50–70% of the mercury from coal was retained in the ESP ash preceding the FGD spray dryer; 75% of the mercury from coal was retained overall, so the major portion of removal was by the ESP.

Nilsson (1981): 30–40% of gas phase mercury was retained.

Karlsson (1986): 52–63% of mercury was removed, with 15–33% retained in the FGD unit (including baghouse).

Moller and Christiansen (1985): inlet gas phase mercury concentrations of  $0.2\text{--}0.7 \text{ mg}/\text{m}^3$  reduced to  $0.1\text{--}0.01 \text{ mg}/\text{m}^3$  through the FGD unit.

An excellent retention of trace elements by spray dryer systems implies that fly ash or dry end product might contain high concentrations of mercury. Karlsson (1986) showed that

precollection was beneficial for some elements. The pattern for carry over of trace elements from the ESP to the dry end product is complicated by condensation of some constituents and varying degrees of enrichment, and interactions among the elements. For example, a high Ca concentration led to high As, Cr and Hg concentrations but low concentrations of other elements.

In summary, the overall removal of mercury in various spray dry systems varies from about 35 to 85%. The highest removal efficiencies are achieved from spray dry systems fitted with downstream fabric filters.

### Low NO<sub>x</sub> Technologies

Low NO<sub>x</sub> technologies are also likely to reduce mercury emission in the exhaust gases due to the lower operating temperatures. Very limited information on this subject is inconclusive. While some sources indicate that the reduction can be achieved, preliminary results of staged combustion in atmospheric fluidized bed combustion (AFBC) units indicated that low NO<sub>x</sub> had only little effect on trace element emissions (Sloss and Smith, 2000). It should be noted, however, that low NO<sub>x</sub> technologies are far less used compared to the FGD systems.

### Technologies to Control Emissions of Mercury on Particles

Coal-fired power plants and municipal incinerators are mostly equipped with either electrostatic precipitators (ESPs) or fabric filters. The ESPs are particularly efficient in removing all types of particles with diameter larger than 0.01  $\mu\text{m}$ , including those bearing mercury after condensation within exhaust gases. The ESPs can tolerate operating temperatures as high as 720 K (Pacyna, 1987). The applicability of conventional precipitators is, however, limited by the electric resistivity of the particles. For example, low sulfur coals produce high-resistivity fly ash, and in such case the control efficiency of the ESPs drops off. The problem can be overcome by applying wet-type ESPs, which have the advantage of treating the exhaust gases under relatively cool saturated conditions.

Concerning the particle size distribution from the ESPs in coal-fired power plants, it has been concluded that the particle mass containing trace elements is concentrated mostly in two size ranges: 1) at ca. 0.15  $\mu\text{m}$  dia., and 2) between 2 and 8  $\mu\text{m}$  dia. Mercury can be found on particles in both size ranges.

Fabric filters are also used in coal-fired power plants. The particle collection efficiency is always very high, and even for particles of 0.01  $\mu\text{m}$  dia. exceeds 99%. However, the life time of fabric filters is very dependent upon the working temperature and their resistance to the chemical attack by corrosive elements in exhaust gases. The temperature of exhaust gases often exceeds the temperature tolerance for fabric filter material and therefore limits the fabric filter application. A bimodal particle size distribution has been measured at the outlet of fabric filters, similarly to the size distribution of particles at the outlet of ESPs.

Summarizing the information on removal of mercury from exhaust gases generated during the combustion processes in power plants and incinerators, it can be concluded that between 30% and 60% of mercury is retained by high efficiency ESPs or fabric filters and FGD systems

capture further 10 to 20 %. If coal cleaning is applied prior to combustion, preliminary data from the U.S. Department of Energy indicate 10% to 25% removal of mercury from coal in the case of commercial cleaning (MRI, 1993).

Various techniques to remove mercury from exhaust gases generated by industries other than the production of electricity and heat, as well as during waste incineration have been developed, particularly for metallurgical processes. A selenium filter has been applied at both steel and non-ferrous plants. In this dry media process, the volatilized mercury is reacting with red amorphous selenium forming mercury selenide. Mercury removal of 90 % has been achieved through this technique reducing the mercury concentrations to below 10  $\mu\text{g}/\text{m}^3$ . Carbon filter is also used showing the removal effects similar to those reached with the selenium filter (SNV, 1991).

Lead sulfide process is another dry media technique used to remove mercury from flue gases generated in non-ferrous metal smelters. The gases containing volatile mercury are passed through a tower packed with lead sulfide coated balls. One study at a Japanese smelter in Naoshima indicates reduction of mercury concentrations from 1–5  $\text{mg}/\text{m}^3$  in the feed to the absorption tower to 0.01-0.05  $\text{mg}/\text{m}^3$  at the outlet (SNV, 1991).

The two major wet media processes to remove mercury from flue gases include selenium scrubber and so-called Odda chloride process. The selenium scrubber method is in principle similar to the selenium filter technique except for that activated amorphous selenium is circulating in a scrubber with 20–40 % sulfuric acid. The mercury reduction is about 90–95 %.

In the Odda chloride process mercury vapors are oxidized to form mercuric chloride which then precipitates. Mercury is recovered and mercury chloride is regenerated. The mercury concentrations of the treated gases are 0.05-0.1  $\text{mg}/\text{m}^3$ .

## 2.4 PAST AND CURRENT MERCURY EMISSIONS IN EUROPE

The first European-wide emission survey for atmospheric mercury has been elaborated in the mid 1980s (e.g. Pacyna et al., 1990). The reference year of this survey was 1982. The emission of total Hg from anthropogenic sources was estimated about 390 tonnes with 69 % contribution from the combustion of fossil fuels and 18 % from caustic soda production. The latest source was considered as underestimated, mostly due to the underestimation of Hg emission factor for this source.

The first update of the 1982 emissions was made for the reference year 1987 (Axenfeld et al., 1991). The emission of total mercury in 1987 was estimated about 726 tonnes, thus almost double of that in 1982. Emissions from combustion of fossil fuels have increased by 30 % in the period from 1982 through 1987, mostly due to increase of coal consumption to produce electricity and heat. The largest increase, however, was estimated for the production of inorganic chemicals (chlor-alkali production), mainly caustic soda from about 71 tonnes of Hg in 1982 to more than 235 tonnes in 1987. The reasons for this increase are twofold: 1) increased production of these chemicals, and 2) improvement in estimation of emission factors of Hg, taking account emissions from ventilation and stacks.



The 1987 update was also important because for the first time emissions from natural sources in Europe were assessed, as well as first attempt to present chemical speciation of Hg in emissions from major source categories was made. Natural emissions were estimated concluding that their total amount is about 265 tonnes per year contributing about 27 % to the total emissions in 1987 (Axenfeld et al., 1991). Volcanic eruptions and venting, as well as re-emission from terrestrial and aquatic surfaces were found to be the most important natural sources of Hg in Europe.

It was also concluded that as much as 60 % of the anthropogenic emissions in Europe were in gaseous elemental form, 30 % as gaseous bivalent mercury and 10 % as elemental mercury on particles.

The second update of European emissions of Hg was prepared for the reference year 1990 (Pacyna, 1997). While preparing the 1990 update, special emphasis was placed on:

- ❑ improvement of information on mercury emissions during the coal and waste combustion through application of data on the reduction of mercury concentrations in the exhaust gases passing through various kinds of control equipment removing particles and gaseous pollutants (mostly sulfur dioxide),
- ❑ review of information on mercury removal with fly and bottom ashes in the European power plants,
- ❑ review of information on possible changes in the production quantities of chlorine and caustic soda, as well as in coal consumption, particularly in Eastern Europe after a switch to the free-market economies, and
- ❑ revision of information on mercury emissions from major "large point sources" in Europe.

An assessment of atmospheric emissions of mercury from anthropogenic sources in Europe in 1990, including the European part of Russia, concluded that the total atmospheric emission of mercury from anthropogenic sources in Europe was estimated to 627 tonnes. Large portion of the European emissions of mercury in the late 1980's was estimated for the VEB Chemische Werke Buna in Schkopau and for the chemical plants in Bitterfeld in the former German Democratic Republic. These large emissions were related mostly to the production of chlorine and caustic soda using so-called mercury method. The year 1990 was the beginning of the economical decline in these factories. During the last few years mercury emission from these sources has decreased drastically and is nowadays about 2 orders of magnitude lower than in the late 1980's.

Combustion of fuels, particularly coal, was still an important source category for atmospheric mercury in Europe. In some countries where combustion of coal is the predominant technology to produce heat and electricity, the contribution of mercury emission from fuel combustion to the total national emission of the element is more than half of the total emissions. For example, the fuel combustion in Poland has generated more than 75% of the atmospheric mercury in the country.

Emissions from waste incineration were still underestimated in the 1990 survey. They represent emission data collected from 8 European countries only.

Anthropogenic emissions of mercury in Europe in 1990 were then spatially distributed using the 150 km by 150 km grid system. Emissions from more than 900 point sources were allocated according to their geographical location. Emissions from area sources were allocated using population density data. The highest emissions were estimated in Central and Eastern Europe, particularly in the Black Triangle area of south-western Poland, south-eastern Germany and north western Czech Republic, as well as in the Upper Silesia in Poland and in the region of Bitterfeld in Germany. High emissions were also estimated for Central United Kingdom and certain regions of Western Europe.

Concerning emission trends, an anthropogenic emission decrease of 14 % has been estimated between 1987 and 1990 in Europe, mostly due to the decrease of emissions during fuel combustion. The fuel combustion emissions have decreased by 30 % in this period. Further reduction of mercury emissions has occurred in the period from 1990 to 1993, particularly in Eastern Europe due to further decline of the production of industrial goods. This conclusion can be confirmed by 16 % decrease of average concentrations of total gaseous mercury measured over Scandinavia (Iverfeldt et al., 1995) in the period 1985-1989 as compared to the period 1990-1992.

The latest update and improvement of the mercury emissions from anthropogenic sources in Europe was made for the reference year 1995 (Pacyna et al., 2000). The estimates of total atmospheric mercury from anthropogenic sources in Europe in 1995 are presented in Table 2.3. Three sets of emission data are presented in this table: national estimates with their authors listed in Annex 1, estimates presented to the UN ECE European Monitoring and Evaluation Programme (EMEP) by national authorities (EMEP, 1999), and the estimates by Pacyna et al. (2001). The total amount of Hg emissions was estimated to 342 tonnes. The largest emissions were estimated for Russia (the European part of the country), contributing with about 25 % to the European emissions, followed by Ukraine, Poland, Germany, Romania, and the United Kingdom. All of these countries use coal as a major source of energy in order to meet the electricity and heat demands. In general, countries in the Central and Eastern Europe generated the main part of the European emissions in 1995.

Contributions from various source categories to the total emissions in Europe are presented in Figure 2.1. Combustion of coal in power plants and residential heat furnaces generates more than half of the European emissions, followed by the production of caustic soda with the use of the Hg cell process (12 %). Major points of mercury emission generation in the mercury cell process include: byproduct hydrogen stream, end box ventilation air, and cell room ventilation air. This technology is now being changed to other caustic soda production technologies and further reduction of Hg emissions is expected in this connection. A category called "Other Sources" in Figure 2.1 contributes about 15 % of Hg to its total emission in Europe. This category includes various uses of mercury, and particularly: primary battery production, production of measuring and control instruments, and production of electrical lighting, wiring devices, and electrical switches. All of these uses of mercury decrease and lower emissions of Hg are expected from these sources in the future.

Changes of the Hg emissions from anthropogenic sources in Europe between 1980 and 1995 are presented in Table 2.4. A continuous decrease of emissions can be explained by the installation of efficient abatement technologies, particularly in Western Europe and a change in the production pattern of various industrial goods in Eastern Europe following the switch of their economies from centrally planned to market oriented at the beginning of the 1990's.

## 2.5 SPECIATION OF MERCURY EMISSIONS

Accurate information on emissions of various chemical forms of Hg is needed by the modelers simulating long-range transport and atmospheric deposition of the element to the marine and terrestrial surfaces. Studies carried out at the end of the 1980's on the chemical speciation of Hg emissions have continued within the EU projects, including the MAMCS project and the Mercury species over Europe: relative importance of depositional methylmercury fluxes to various ecosystems (MOE). Emission profiles of Hg for major anthropogenic source categories in Europe in 1995 have been elaborated and are presented in Table 2.5. These profiles were used to estimate emissions of various Hg species to the atmosphere in 1995.

The major chemical form of mercury emitted from the anthropogenic sources in Europe to the atmosphere is gaseous elemental mercury, contributing with about 205 tonnes in 1995 (about 61 %) to about 342 tonnes of the total Hg. Gaseous bivalent mercury contributed about 108 tonnes (about 32 % of the total), and the emissions of Hg on particles were about 25 tonnes (7 % of the total). Gaseous elemental mercury contributes the most to the total emissions of Hg from all source categories presented in Table 2.5 except for waste disposal. In the latter case, contribution of gaseous bivalent mercury is the highest. It is probably due to the high content of chlorine in wastes resulting in the formation of chlorides of mercury.

Contributions of emissions from various source categories to the total gaseous elemental mercury, gaseous bivalent mercury and emissions on particles are presented in Figures 2.2-2.4, respectively. Combustion emissions contributed the most to the emissions of various Hg species. However, while this contribution was about 45 % in the case of gaseous elemental mercury, it is between 66 and 68 % in the case of the two remaining species.

It should be admitted that more studies are needed to better understand the emission of various chemical and physical forms of Hg to the atmosphere. This information is needed for the assessment of environmental chemistry of the element, its transport pathways with air masses and water currents, cycling through the environmental compartments, and environmental and human health effects.

## 2.6 MAPS OF POINT AND DIFFUSE SOURCES IN EUROPE

Lists of major point sources and emissions of Hg from these sources in 1995 were prepared for individual countries in Europe. These lists are available from the emission data base at the Norwegian Institute for Air Research (NILU), Kjeller, Norway.

The basis for the lists was a set of similar lists prepared by Pacyna and Pacyna (1996) in an earlier work for the year 1990. These 1990 lists of emission sources were checked for the completeness of sources and their location (new countries in 1995 after the political division of the former Soviet Union, Yugoslavia and Czechoslovakia, as well re-unification of Germany). Then, the estimates of 1995 emissions within major categories were adjusted into major point sources within these categories, using the 1990 emission split as a basis.

The following information is presented within the lists of major point sources:

- ❑ name of the source,
- ❑ geographical position of the source, including latitude and longitude,
- ❑ codes, indicating the type of industry and industrial technology (installation code), and
- ❑ emission of total mercury.

Information on emission from "Other sources" is also included in the lists. These sources include major area sources (or diffuse sources) related to the combustion of fuels to produce heat in small residential and commercial furnaces.

The top ten point sources of anthropogenic mercury emissions in Europe in 1995 are presented in Table 2.6.

Information on the geographical location and Hg emissions for point sources was used to prepare spatial distribution of Hg emissions in Europe within the EMEP grid system of 50 km x 50 km. Diffuse emissions were distributed within this system using the information on population density within the grid system. The map of total emissions of Hg in Europe in 1995 within the EMEP grid system of 50 km x 50 km is presented in Figure 2.5. This map was prepared as a joint activity between the EU projects MAMCS (at NILU) and MOE (at the GKSS in Germany).

## 2.7 GLOBAL VS. EUROPEAN MERCURY EMISSIONS

The 1995 global emissions of total mercury from anthropogenic sources are presented in Table 2.7. It should be added that information of Hg emissions from caustic soda production and "other sources" is not included in Table 2.7. About 1900 tonnes of total Hg was emitted in 1995, which is in the upper part of the range between 1270 (minimum estimate) and 2140 tonnes (maximum) estimated earlier by Pacyna and Pacyna (1996) for the year 1990. The authors of the 1990 emission inventory concluded that the maximum emission estimate is close to the reality (close to the best estimate) rather than the minimum estimate. It should be admitted that the 1995 do not contain emissions from the use of mercury for the gold production. These data are highly speculative and therefore it was decided not to include them in this paper. They can be, however, high as it was speculated that as much as 325 tonnes of

Hg can be emitted from this process annually. More than half of these emissions were assumed to occur in Africa.

A summary of the 1990 maximum emission data is also included in Table 2.7 for comparison with the 1995 data. It can be concluded that no major changes were observed between 1990 and 1995 estimates of global Hg emissions from anthropogenic sources worldwide. Somewhat bigger is, however, contribution of stationary combustion of fuels to the total emissions in 1995. This contribution is as high as 77 % in 1995, compared to 60 % in 1990. Larger Hg emissions from combustion of fossil fuels, particularly coal in 1995 compared to 1990 are due to their increased combustion for the production of electricity and heat in the compared period of time.

There have been major changes in emissions in 1995 compared to 1990, with respect to the location of major emission regions contributing the most to the global emission survey of the element. Whereas the Hg emissions in Europe and North America have decreased quite substantially during the period from 1990 through 1995, emissions in Asia, particularly in China and India, have increased significantly. The Asian sources contributed about 30 % to the total emissions of mercury in 1990, compared to 56 % in 1995. An increase of more than 250 tonnes was estimated for China between the years 1990 and 1995. The increase of Hg emissions in China from 1990 through 1995 is clearly related to the increased of coal combustion in the country. The Hg emission increase due to the increased combustion of coal has overcome a slight reduction of emission of air pollutants in the country due to the installation of high efficient emission control devices starting in the mid 1990's.

Decrease of Hg emissions in Western Europe, the United States, and Canada can be explained by further installation of emission control equipment, particularly various flue gas desulfurisation (FGD) technologies, as already mentioned. Relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapor phase and thus to be removed from the flue gases.

Decrease of Hg emissions from combustion sources, as well as other industrial sources in Central and Eastern Europe from 1990 to 1995 was also caused by a general decrease of industrial activities and resulting decrease of the consumption of raw materials. These decreases are related to the switch of economies from centrally planned to market oriented in this part of Europe. It is very difficult to assess to what extent the emission decrease can be accounted for the change of economies and what is the contribution of more efficient control equipment. Informal discussions of the authors with emission expert in Poland seem to indicate that as much as three quarters of emission reductions can be accounted for the decrease of industrial activities in the countries. However, this statement needs to be verified.

The national emission estimates for the incineration of wastes have been available from only a few countries in Western Europe and the United States. These estimates were used directly in this work. Then, statistics on the amount of wastes incinerated were available for another small group of countries. These statistics were used together with emission factor information to assess Hg emissions from waste incineration. These emission data are very much incomplete and therefore largely underestimated. The incompleteness of data has been caused by a lack of information from most countries on emissions of mercury during waste incineration and/or on the amount of wastes incinerated.

Emissions of Hg from pig iron and steel production, as well as the production of cement are very much related to the amount of the production of these industrial goods and the efficiency

of emission control installations employed in these plants. No major changes in the Hg emissions have been observed between for these industries between the 1990 and 1995.

## 2.8 QA/QC AND UNCERTAINTY IN MERCURY EMISSION ESTIMATES

It is very difficult to assess the accuracy of currently available emission data for mercury mostly due to limited information on the accuracy of emission factor estimates, and specific statistical data in various countries. Ideally, emissions from at least major sources, such as large power plants, waste incinerators, smelter, steel and iron plants and cement kilns should be measured. Emission measurements would generate the most accurate data on emissions assuming that the proper sampling methods and analytical techniques are applied and the samples are collected at representative sites along the path of flue gases in the stack. However, to measure emissions at so many point sources is for many reasons impossible to accomplish in many countries. Therefore, less accurate methods, based on emission factors and material balances are applied to assess the emissions.

Anthropogenic mercury has been a subject of a few emission estimates, mentioned earlier in this work. Major sources of Hg emissions are fairly well defined and emission factors established. An emission estimation accuracy of less than 50 % can be assigned for this element in Europe, as proved by the comparison of air concentrations calculated by models using emission data and those measured. Very recent study carried out at the Meteorological Synthesizing Centre-East (MSC-E) of EMEP (EMEP MSC-E) concluded that an agreement between the model estimates of Hg concentrations in the air based on the emission data for Europe, used in this paper and air measurements at various EMEP stations in Europe was as good as within 6 % (Ryaboshapko et al., 1999).

Only single numbers of emissions are often presented instead of emission ranges. In the case that emissions were estimated using emission factors, these factors were the ones selected as the most relevant for a given industrial technology, an industrial development in a given country or region, a progress and improvements in application of advanced emission control equipment, the content of mercury in raw materials, etc. However, emission estimates for one category can be more accurate and complete than the estimates for another source category. It can be concluded that the following accuracy of emission estimates can be assigned to the estimates for individual source categories in Europe:

- ❑ stationary fossil fuel combustion:  $\pm 25$  %,
- ❑ non-ferrous metal production:  $\pm 30$  %,
- ❑ iron and steel production:  $\pm 30$  %,
- ❑ cement production:  $\pm 30$  %, and
- ❑ waste disposal: a factor of up to 5

## 2.9 CONCLUSIONS AND RECOMMENDATIONS

In recent years our knowledge on the contribution of major anthropogenic and natural sources and source regions in Europe to the regional mercury budget has improved. Various factors affecting the amount of emissions from these sources are also well defined. However, quantitative assessment of the emissions is not always complete and accurate to the extent requested by major users of emission inventories, such as policy makers preparing emission reduction strategies at local, regional, and even global scale, and modelers providing input to these strategies.

Estimates of current emissions of mercury from anthropogenic sources indicate that as much as 340 tonnes of this element can be emitted annually, with more than half of these emissions generated during the combustion of coal in utility, industrial, and residential boilers. A continuous decreasing trend of these emissions in the period from 1980 to 1995 as a result of the introduction of emission control installations (mainly in Western Europe) and the decrease of consumption and production of energy and industrial goods at the beginning of the 1990's (mainly in eastern Europe). Another 200 tonnes of mercury annually is emitted to the European atmosphere from natural sources, including the re-emission of mercury emitted previously from the anthropogenic sources and deposited to the aquatic and terrestrial surfaces. The accuracy of emission estimates for anthropogenic sources is within 30 % except for waste incineration (it could be as high as a factor of 5). No assessment of natural source emissions has been made so far but it is believed that emission estimates for natural sources are much less accurate than the emission estimates for anthropogenic sources.

Information on chemical speciation of mercury in the element emissions is crucial for modelers simulating the fate, behavior, and transport of mercury in the environment and policy makers using the information on environmental human health effects of this element. As much as 60 % of anthropogenic emissions of mercury in Europe is estimated to be in a gaseous elemental form, 30 % as gaseous bivalent mercury and 10 % as elemental mercury on particles. A majority of emissions from natural sources is believed to be in a gaseous elemental form.

At present, the European anthropogenic sources are estimated to contribute below 15 % of the mercury emissions to the total anthropogenic emissions of the element in the world.

It is important to point out that the mercury emission estimates reported in this chapter are based on the official emission data provided by national authorities to the UN-ECE in the framework of EMEP. However, in the review process of this chapter by the member of the Air Quality Steering Group (AQSG) an external contribution was received from the European Cement Association concerning mercury emissions from cement production. Although this data do not represent the official estimates reported by the national authorities, the WG decided to acknowledge this contribution which can be found in Annex-1.

## 2.10 REFERENCES

- Abel, W.T., Rice, R.L., Shang, J.Y., Turek, D.G., and Ayers, W.J. (1981) Combustion of western coal in a fluidized bed. Morgantown, WV. U.S. Department of Energy, Morgantown Energy Technology Center (DOE Report No. DOE/METC/RI-178).
- Axenfeld, F., Munch, J. and Pacyna, J.M., 1991. Europäische Test-Emissionsdatenbasis von Quecksilber-komponenten für Modellrechnungen. Umweltforschungsplan des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit, Luftreinhalung: 104 02 726, Friedrichshafen, Germany.
- Bakkum, A. and Veldt, C. (1986) Emission factors for combustion processes. In: *Proc. OECD Workshop on comparison of emission inventory data*, Schauinsland, Germany, 22-24 October.
- Bergstrom, J. (1983) Separation of mercury in electrostatic filters and by flue gas desulfurization. Vallingby, The Swedish State Power Board (KHM Technical Report No. 89) (in Swedish).
- Brosset, C. (1983) Emission s of mercury compounds from flue gases. Vallingby, The Swedish State Power Board (KHM Technical report No. 76) (in Swedish).
- Carpenter, R.L. (1979) Fluidized bed combustion emissions toxicology program. Status report, October 1979. Albuquerque, NM. Lovelace Biomedical and Environmental Research Institute (LMF-74 Report).
- EMEP (1999) EMEP Emission Data. The UN ECE European Monitoring and Evaluation Programme, Meteorological Synthesizing Centre - West, EMEP/MSC-W Report 1/1999, Oslo Norway.
- Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B., and Kuhn, J.K. (1977) Trace elements in coal: occurrence and distribution. Urbana, IL. (Illinois State Geological Survey Circular. 499)
- Gutberlet, H. (1984) Measurement of heavy metal removal by a flue gas desulfurization plant working by the lime scrubbing method. Luxembourg, Commission of the European Communities, (Research report ENV-492-D (B)).
- Hall, B., Schager, P., and Lindqvist, O. (1991) Chemical reactions of mercury in combustion flue gases. *Water Air, Soil Poll.* 56, 3-14.
- Iverfeldt, Å., Munthe, J., Brosset, C. and Pacyna, J.M. (1995): Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia. *Water, Air & Soil Poll.*, 80, 227-233.
- Karlsson, H.T. (1986) Spray dry scrubbing of secondary pollutants from coal burning. In: *Proceedings of 3rd Annual Pittsburg Coal Conference*, Pittsburg, PA.
- Kotnik, J., Horvat, M., Mandic, V. (2000) Influence of the Šoštanj coal-fired thermal power plant on mercury and methylmercury concentrations in lake Velenje, Slovenia. *Sci. Tot. Environ.*, **259**, 85-95.
- Kotnik, J., Horvat, M., Izhodišca za izdelavo analize onesnaženosti z živim srebrom in predlog ukrepov na podlagi Evropskih direktiv, Report for the Ministry of Environment, of the Republic of Slovenia, IJS DP – 8290, October 2000 (in Slovenian).
- MAMCS (2000) The Mediterranean Atmospheric Mercury Cycle System (MAMCS) Project Report. The EU Environment and Climate Research Programme, Contract No. ENV4-CT97-0593, coordinated by N. Pirrone, Rende Italy.



- Meij, R. (1992) A mass balance study of trace elements in a coal-fired power plant with a wet FGD facility. In: *Elemental analysis of coal and its by-products*, G. Vourvopoulos, ed. Singapore, World Scientific, pp. 299-318.
- Meij, R. and Alderliesten, P.T. (1989) The emission of inorganic trace compounds at coal-fired power plants equipped with wet flue gas desulfurization plants. In: *Man and his Ecosystem, Proc. 8th World Clean Air Congress*. Amsterdam, Elsevier.
- Moberg, P.-O., Westermark, M., and Noling, B. (1982) Migration of trace elements during flue gas desulfurization. Vallingby, The Swedish State Power Board (KHM Report TR 28).
- Moller, J.T. and Christiansen, O.B. (1985) Dry scrubbing of MSW incinerator flue gas by spray dryer absorption: new developments in Europe. Presented at 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI.
- MRI (1993) Locating and estimating air emissions from sources of mercury and mercury compounds. Midwest Research Institute Report for the U.S. Environmental Protection Agency, Draft Rep. Research Triangle Park, NC. (EPA-454/R-93-023).
- Munzner, H. and Schilling, H.-D. (1985) Fluorine and chlorine emissions from FBC enrichments in fly-ash and filter dust. In: *8th Inter. Conf. on Fluidized Bed Combustion: Options and Issues*, Houston, TX.
- Nilsson, B. (1981) Secondary cleaning effects in dry FGD scrubbing. Studsvik Energiteknik AB, Sweden (KHM Technical Report No. 07) (in Swedish).
- Nriagu, J.O. and Pacyna, J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333, 134–139.
- Pacyna, J. (1987) Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry. In: *Lead, Mercury, Cadmium and Arsenic in the Environment*, T.C. Hutchinson and K.M. Meema (eds.). Chichester, Wiley, pp. 69-87.
- Pacyna, J.M. (1980) Coal-fired power plants as a source of environmental contamination by trace metals and radionuclides. Technical University of Wroclaw, Poland (Monographs Series No.17) (in Polish).
- Pacyna, J.M. (1982) Estimation of emission factors of trace metals from oil-fired power plants. Lillestrøm, Norwegian Institute for Air Research. (NILU Technical Report No. 2/82).
- Pacyna, J.M. (1983) Trace element emission from anthropogenic sources in Europe. Lillestrøm, Norwegian Institute for Air Research (NILU Technical Report No. 10/83).
- Pacyna, J.M. (1987) Methods for air pollution abatement. In: *Atmospheric Pollution*, E.E. Pickett, (ed.), Washington, Hemisphere Publishing Corp.
- Pacyna, J.M. (1989) Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources. In: *Control and fate of atmospheric trace metals*, J.M.Pacyna and B.Ottar, (eds.), Dordrecht, Kluwer Academic Publishers , pp. 15-32.
- Pacyna J.M. (1997) Practical opportunities and technologies available to reduce anthropogenic emissions of mercury to the environment and to reduce the risks of mercury exposure to humans and the environment. A report for the North American Commission for Environmental Cooperation, Hagan, Norway, May.

- Pacyna, J.M., Munch, J., Axenfeld, F., Duiser, J., and Veldt, C., 1990. Europäische Modell - Emissionsdatenbasis für die Spurenelemente As, Cd, Hg, Pb, Zn und für spezielle organische Verbindungen Lindan, HCB, PCB und PAK. Umweltforschungsplan des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit, Luftreinhalteplan: 104 02 588, Berlin, Germany.
- Pacyna, J.M. and Pacyna, E.P. (1996) Global emissions of mercury to the atmosphere. Emissions from anthropogenic sources. A Report for the Arctic Monitoring and Assessment Programme (AMAP), Oslo, June.
- Pacyna, J.M., and Pacyna, E.G., (2000). Assessment of emissions/ discharges of mercury reaching the Arctic environment. The Norwegian Institute for Air Research, NILU Report OR 7/2000, Kjeller, Norway.
- Pacyna E.G., Pacyna J.M. and Pirrone N. (2000) Anthropogenic emissions of atmospheric mercury from anthropogenic sources in Europe in 1995. *Atmos. Environ.* **35**, 2987-2996.
- Pirrone, N. (Coordinator), Pacyna, J.M., Mamane, Y., Munthe, J., Ferrarea, R. (2000) Mediterranean Atmospheric Mercury Cycle System (MAMCS). Technical Final Report, European Commission (Contract No. ENV4-CT97-0593).
- Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R. (2001) Atmospheric mercury emissions from anthropogenic and natural sources in the Mediterranean Region. *Atmos. Environ.* **35**, 2997-3006.
- Ryaboshapko, A., Ilyin, I., Gusev, A., Berg, T. and Hjellbrekke A.-G., 1999. Monitoring and Modelling of Lead, Cadmium and Mercury Transboundary Transport in the Atmosphere of Europe. EMEP Report 3/99. The UN ECE Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). Meteorological Synthesizing Centre – East, Moscow and Chemical Coordinating Centre, Kjeller, Norway.
- Sloss L. and Smith I. (2000) Trace element emissions. IEA Coal Research, the Clean Coal Centre, London, the UK.
- Smith, I.M. (1987) Trace elements from coal combustion – emissions. London. International Energy Agency Coal Research.
- SNV (1991) Guidelines on measures and methods for heavy metal emissions control. Solna, The Swedish Environmental Protection Agency – Naturvårdsverket.
- US EPA (1995) Mercury Study report to Congress. U.S. Environmental Protection Agency, Office of Research and Development, EPA/600/P-94/002Aa Report, Washington, DC.

## ANNEX-1

### Source of information on Hg emissions from national experts

#### 1. Austria:

Abschätzung der Schwermetallemissionen in Österreich, Umweltbundesamt, UBE Rept.-95-108, Wien, 1995, and

Winiwarter, W. Emission of Cd, Hg and Pb in Austria in 1985, 1990 and 1995. Austrian Research Centers, Seibersdorf, December 10, 1998.

#### 2. Belarus

Belarusian Contribution to EMEP, Annual Report, 1996. Belarusian National Academy of Sciences, Meteorological Synthesizing Center – East, Minsk – Moscow, January 1997.

#### 3. Bulgaria

Syrakov, D. 1997 Annual Report on Bulgarian Contribution to EMEP. National Institute of Meteorology and Hydrology, Sofia, January 30, 1998.

#### 4. The Czech Republic:

Data reported to the UN ECE Task Force on Heavy Metals,

Machalek, P. Emissions estimates data –HMs in Czech Republic (1990-1995). Czech Hydrometeorological Institute, Emission Inventory Section, Division of Air Quality Protection, Prague, January 28, 1999, and

CHI: Air Pollution in the Czech Republic in 1997. The Czech Hydrometeorological Institute (CHI), Air Quality Protection Department, Prague, 1998.

#### 5. Denmark:

Data reported to the UN ECE Task Force on Heavy Metals, and to the PARCOM/ATMOS program,

#### 6. Finland:

Data reported to the UN ECE Task Force on Heavy Metals

#### 7. France:

Fontelle, J.P. Heavy Metals emissions based on the 11 CORINAIR/MNECE/EMEP groups (take care of version SNAP 1997). CITEPA (Centere Interprofessionnel Technique D'Etudes De La Pollution Atmospherique), Paris, February 02, 1999.

**8. Germany:**

Schwermetallemissionen in die Atmosphäre, TUV Rheinland, Köln, EP 10/93, 1993, and

Jockel, W., Hartje, J. Report on the Development of the Emissions of Heavy Metals in Germany 1985-1995. Umweltforschungsplan Des Bundesministers für UMWELT, Naturschutz und Reaktorsicherheit, Köln, July 1997, letter of Jockel, W. Environmental Protection/Air Pollution Control, Köln, December 02, 1998.

**9. The Netherlands:**

Emission inventory in the Netherlands. Emissions to air and water in 1992. The Ministry of Housing, Spatial Planning and the Environment, Directorate-General for the Environment, Gravenhage, Publ. No. 22, December 1994, and

Berdowski, J.J.M. et al. Emissions to air for the Inventories of CORINAIR, EMEP and OSPARCOM 1990-1996. Ministry of Housing, Spatial Planning and the Environment, January 1998.

**10. Norway:**

Miljøgifter i Norge. Statens forurensningstilsyn (SFT), Rept. 92/103, Oslo, 1993.

Statens forurensningstilsyn (SFT), Mercury emission in Norway, 1995. SFT and INKOSYS data.

**11. Poland:**

Report on Heavy Metals Emissions in Poland for 1990. The Institute for Ecology of Industrial Areas, Katowice, November 1993,

Mitosek, G. National annual total anthropogenic emissions of heavy metals 1990-1995. Institute of Environmental Protection, Air Protection Division, Warsaw, October 1997, and

Hlawiczka, S. Report on heavy metals emission in Poland for the year 1996. Institute for Ecology of Industrial Areas, Katowice, March 1998.

**12. Slovenia:**

Rode, B. Heavy Metals emission estimations of Cd, Hg and Pb based on Technical Paper to the OSPARCOM-HELCOM UNECE Emission Inventory, 1990-1996. Ministry of the Environment and Physical Planning Hydrometeorological Institute of Slovenia, Ljubljane, December 29, 1998.

**13. Slovakia:**

Heavy Metals in Slovakia. Ministerstvo Zivotneho Prostredia Slovenskej Republiky, Bratislava, December 1994.

**14. Sweden:**

Heavy Metal Emissions to Air in Sweden in 1992. Swedish Environmental Protection Agency, Industrial Department, Stockholm, December 1993.

**15. Switzerland:**

Vom Menschen Verursachte Schadstoff-Emissionen in der Schweiz 1950-2010. Bundesamt für Umweltschutz, Schriftenreihe Umweltschutz No. 76, Bern, and

**16. The United Kingdom:**

The UK Atmospheric Emissions of Metals and Halides 1970-1991. National Atmospheric Emissions Inventory. Department of Environment, London, September 1993.

## ANNEX-2

### Contribution by the European Cement Association

#### Comment on Table 2.3 “Hg Emissions from Anthropogenic Sources in Europe”

CEMBUREAU has strong indications that the total Hg emissions from the cement industry in the EU15 countries are estimated far too high. This conclusion is based on measured emission data from Austria, Germany, the United Kingdom and Spain as shown below (table-A).

**TABLE-A:** Austrian Hackl-Study “Emissionen aus Anlagen der österreichischen Zementindustrie (Emissions from the Austrian Cement Plants) II+III - Jahresreihen 1994-1996 +1997-1999 ”.

Year	Total Emissions [t/a]	Average Exhaust Gas Volume [Nm <sup>3</sup> /kg Clinker]	Average Emissions [µg/Nm <sup>3</sup> ]
1994	0.123	2.309	14.0
1995	0.077	2.408	10.9
1996	0.070	2.376	10.2
1997	0.090	2.254	12.8
1998	0.072	2.200	11.5
1999	0.077	2.133	12.7

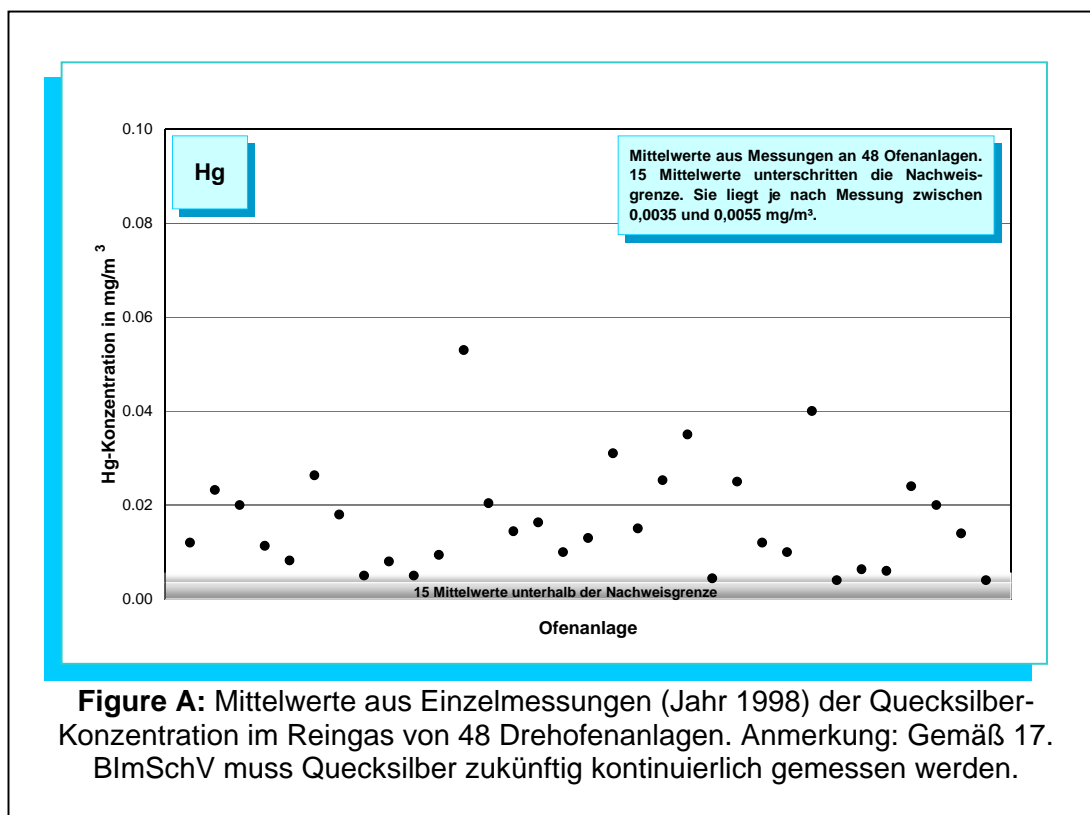
The given data confirm a range of total Hg emissions of 0.07 to 0.08 t/a corresponding to an average Hg emission of about 12 µg/Nm<sup>3</sup>

**Umweltdaten der deutschen Zementindustrie 1998” (“Environmental data of the German Cement Industry 1998”) published by the Verein deutscher Zementwerke (VDZ), September 2000.**

This survey provides an extensive overview of relevant environmental data and is covering 90% of the German cement industry and can therefore be regarded as representative. Figure A presents the average values of Hg measurements.

With respect to the mercury concentration in the stack of cement kilns the available data result in an average mercury concentration of about 13 µg/Nm<sup>3</sup>. (Values below the detection limit were very conservatively counted as the detection limit).

Taking into account the German clinker production of about 28 million tons over the last years and the conservative approach for the exhaust gas volume in German cement kilns of 2 000 Nm<sup>3</sup> per ton clinker, our calculation is leading to a value for the mercury emissions of 0.72 tons per year.



### A. Current Data from the United Kingdom

Recent data provided by 2 plants of Castle cement in the UK (wet kiln and a dry kiln with wet slurry induction to the kiln; each of them burning waste) show emission levels in the range of 1.1 to 6 µg/Nm<sup>3</sup> with a weighted average of 3.7 µg/Nm<sup>3</sup> for mercury. These very low figures lead to a specific emission of about 12.8 mg Hg/t Clinker being even lower than the corresponding values of Austria and Germany.

The British Cement Association has collected recent data from 1999 for the all 21 plants operating 34 kilns in the UK. These data provide the most reliable and comprehensive update for the mercury emissions in the UK and has been submitted to the Environmental Agency by each plant. All figures summed up lead to the total mercury emission in the UK by the British cement industry for 1999 of 0.154 t/a. The data are publicly available on the website of the Environmental Agency under <http://www.environment-agency.gov.uk>.

### B. Current Data from Spain

A recent internal study performed by the Spanish Cement Association OFICEMEN produced results of mercury emissions from 13 different cement kilns (representing more than 20 % of the total Clinker production of Spain). The weighted average emission level is given as 6.7 µg/Nm<sup>3</sup>.

Using the figure of  $6.7 \mu\text{g}/\text{Nm}^3$  for the total clinker production of 28 106 kt for the year 2000 and the very conservative figure for the exhaust gas volume of  $2.400 \text{ Nm}^3/\text{t}$  Clinker, the annual load of mercury in Spain can be calculated to 0.452 t for the year 2000.

Based on the examples of Austria and Germany, the United Kingdom and Spain CEMBUREAU is of the opinion that there is a big discrepancy between the measurement data and the data provided by Table 2.3 of Chapter 2 of the “Position Paper on Mercury”. The following table-B compares the results based on measurements with the results based on the data provided in the current Draft of the “Mercury Position Paper”.

**Table-B:** Comparison between the date reported in table 2.3 with that provided by CEMBUREAU.

Country	Current Clinker Production [kt]	Position Paper values [t/a]	CEMBUREAU values [t/a]
Austria 1996	2 916	0.20	0.08
Germany 1998	27 520	5.60	0.72
United Kingdom 1999	11 410	0.60	0.154
Spain 2000	28 106	2.70	0.452

It may be worthwhile noting that the Hg emission for the EU15 countries given in the “Position Paper” correlate much better to a worst case scenario (emission level of  $50 \mu\text{g}/\text{Nm}^3$  = current national emission limit value + Exhaust Gas Volume of  $2\,300 \text{ Nm}^3$  per tonne Clinker). This observation raises the question whether national data provided for international inventories could be based on similar estimations as mentioned above rather than on real measurements. CEMBUREAU would like to emphasize that these figures and examples may indicate a general error in the level of emissions in the “Position Paper”. This needs to be checked also for the other EU15 countries.



**Table 2.1** - Emission rates of mercury ( $\text{ng m}^{-2}\text{h}^{-1}$ ) from volcanoes, surface waters and top soils in Europe and in the Mediterranean region (Pirrone *et al.* 2001).

Country	Method	Surface type	Period		Hg Emiss. rate	References
North-Western Mediterranean	N.A.	Sea surface	N.A.		$1.16 \text{ ng m}^{-2}\text{h}^{-1}$	Cossa <i>et al.</i> , 1996 and reference herein
Scheldt outer estuary (Belgium)	N.A.	Sea surface	N.A.		$5.8 \text{ ng m}^{-2}\text{h}^{-1}$	Cossa <i>et al.</i> , 1996 and reference herein
Grand Estuaire de la Loire (France)	N.A.	Sea surface	N.A.		$0.4\text{-}2.5 \text{ ng m}^{-2}\text{h}^{-1}$	Cossa <i>et al.</i> , 1996 and reference herein
Baie de la Seine (France)	N.A.	Sea surface	N.A.		$1.7\text{-}3.3 \text{ ng m}^{-2}\text{h}^{-1}$	Cossa <i>et al.</i> , 1996 and reference herein
Northern-Tyrrhenian Sea (Poll. Coastal zone)	FC	Sea surface	Summer	Day	$11.25 \text{ ng m}^{-2}\text{h}^{-1}$	Ferrara <i>et al.</i> , 2000
				Night	$2.4 \text{ ng m}^{-2}\text{h}^{-1}$	
Northern-Tyrrhenian Sea (Off-shore)	FC	Sea surface	Summer	Day	$2.5 \text{ ng m}^{-2}\text{h}^{-1}$	Ferrara <i>et al.</i> , 2000
				Night	$1.16 \text{ ng m}^{-2}\text{h}^{-1}$	
Northern-Tyrrhenian Sea (Unpoll. Coastal zone)	FC	Sea surface	Summer	Day	up to $10.1 \text{ ng m}^{-2}\text{h}^{-1}$	Ferrara <i>et al.</i> , 2000
				Night	$1 \text{ ng m}^{-2}\text{h}^{-1}$	
			Winter	Day	$0.7\text{-}2.0 \text{ ng m}^{-2}\text{h}^{-1}$	
Sweden	FC	Lake surface	N.A.		$2.05\text{-}20.5 \text{ ng m}^{-2}\text{h}^{-1}$	Schoeder <i>et al.</i> 1989, Xiao <i>et al.</i> , 1991
North Sea	N.A.	Sea surface	N.A.		$1.6\text{-}2.5 \text{ ng m}^{-2}\text{h}^{-1}$	Cossa <i>et al.</i> , 1996 and reference herein
Etna, Stromboli, Vulcano (Med. Sea)	MN/ Gardis		Fall/Spring		$0.6\text{-}1.3 \text{ t y}^{-1}$	Ferrara <i>et al.</i> , 2000
Mercury mine in Almaden, Spain (*)	LIDAR	Ambient air	Summer & Winter		$2 \text{ t y}^{-1}$	Edner <i>et al.</i> , 1994
South Europe	FC	Top soil	Summer		Day: $4\text{-}5 \text{ ng m}^{-2} \text{ h}^{-1}$ Night: $1 \text{ ng m}^{-2} \text{ h}^{-1}$	Pirrone <i>et al.</i> 2000

N.A.= not available; FC = Flux Chamber; LD=LIDAR Technique; MN = Manual Technique.

(\*) Almaden mine is active 3 months per year; The Idjia and Mt. Amiata mines are closed since 1994 and 1980, respectively.

**Table 2.2** - Concentrations of Hg in various fossil fuels.

<b>Fuel</b>	<b>Unit</b>	<b>Concentration</b>
<b>Bituminous coals:</b>	g/tonne	
- Australia		0.03-0.4
- Germany		0.70-1.4
- Japan		0.03-0.1
- New Zealand		0.02-0.6
- Poland		0.01-1.0
- South Africa		0.01-1.0
- United Kingdom		0.20-0.7
- USA		0.01-1.5
- Russia		0.02-0.6
<b>Lignite coals:</b>		
<b>Crude oil</b>	g/tonne	~ 0.01 <sup>(1)</sup>
<b>Natural gas</b>	mg/m <sup>3</sup>	0-5.0 <sup>(2)</sup>

- (1) However, on sporadic occasions the concentrations can be as high as 30.0 g/tonne.
- (2) A reduction of Hg to below 10 µg/m<sup>3</sup> has to be obtained before the gas can be used.

**Table 2.3** - Total Hg Emissions from Anthropogenic Sources in Europe, 1995 (metric ton).

Country	Coal Combustion		Oil Combustion	Cement Production	Non-Ferrous Metals		Pig & Iron	Caustic Soda	Waste Incineration	Other	Total	Source
Sub-country	Power Plants	Residential Heat			Lead	Zinc						
<b>EU-15 countries:</b>												
<b>Austria</b>	0.40			0.20		0.10	0.10	0.10	0.40	0.90	<b>2.20</b>	(1994) National
<b>Belgium</b>	1.70			0.20	0.10	0.40	0.10	0.70	0.10		<b>3.30</b>	EMEP
<b>Denmark</b>	0.70	0.20		0.20					1.00	0.30	<b>2.40</b>	National
<b>Finland</b>	0.10	0.40		0.10		0.30	0.10	0.50		0.10	<b>1.60</b>	EMEP
<b>France</b>	1.50	0.10		2.50	0.50	1.30	1.00	7.20	1.90	1.60	<b>17.60</b>	National
<b>Germany</b>	5.70	4.40	1.20	5.60		7.00	1.31	3.00	3.00	0.09	<b>31.30</b>	National
<b>Greece</b>	0.70	0.60		1.20	0.10		0.20		0.20		<b>3.00</b>	Pacyna et al., 2000
<b>Ireland</b>	0.20			0.10	0.10						<b>0.40</b>	Pacyna et al., 2000
<b>Italy</b>	0.50	2.80		3.00	0.10	0.70	0.60	4.00	1.00	0.50	<b>13.20</b>	(1994) EMEP
<b>Luxembourg</b>	0.10						0.10				<b>0.20</b>	EMEP
<b>The Netherlands</b>	0.10	0.10		0.30			0.30		0.20		<b>1.00</b>	National
<b>Portugal</b>	0.20			0.70				0.50		0.10	<b>1.50</b>	Pacyna et al., 2000
<b>Spain</b>	2.60	2.10		2.70	0.20	1.20	0.50	2.40		1.50	<b>13.20</b>	Pacyna et al., 2000
<b>Sweden</b>	0.10	0.10					0.10	0.10	0.40	0.10	<b>0.90</b>	EMEP
<b>U.K</b>	7.80	1.40		0.60	0.20	0.20	0.30	2.20		7.40	<b>20.10</b>	EMEP
<b>Total EU-15</b>	<b>22.40</b>	<b>12.20</b>	<b>1.20</b>	<b>17.40</b>	<b>1.30</b>	<b>11.20</b>	<b>4.71</b>	<b>20.7</b>	<b>8.20</b>	<b>12.59</b>	<b>111.90</b>	

Table 2.3 - cont'd.

Country	Coal Combustion		Oil Combustion	Cement Production	Non-Ferrous Metals		Pig & Iron	Caustic Soda	Waste Incinerat.	Other	TOTAL	Source
Sub-country	Power Plants	Residential Heat			Lead	Zinc						
<b>Countries in accession to the EU:</b>												
<b>Bulgaria</b>	2.70	2.70	0.10	0.10	0.10	0.10	0.10	0.80		0.20	<b>6.90</b>	National
<b>Cyprus</b>										0.10	<b>0.10</b>	Pacyna and Pacyna, 2000
<b>Czech Republic</b>	7.00	7.00	0.10	0.20			0.30	0.40			<b>15.00</b>	National
<b>Estonia</b>										0.20	<b>0.20</b>	Pacyna and Pacyna, 2000
<b>Hungary</b>	1.60	0.50	0.10	0.30			0.10	0.90		1.30	<b>4.80</b>	EMEP
<b>Latvia</b>										0.20	<b>0.20</b>	EMEP
<b>Lithuania</b>										0.10	<b>0.10</b>	EMEP
<b>Poland</b>	20.60	11.30		0.10		0.10		0.10	1.40		<b>33.60</b>	National
<b>Romania</b>	7.00	6.00	0.40	1.40	0.20	0.20	0.80	7.00			<b>23.00</b>	Pacyna and Pacyna, 2000
<b>Slovakia</b>	0.80	0.80		0.20			0.20			1.20	<b>3.20</b>	National
<b>Slovenia</b>	0.40	0.03	0 0.003							0.30	<b>0.73</b>	Kotniz et al. (2000)
<b>Total Access into EU</b>	<b>40.10</b>	<b>28.33</b>	<b>0.703</b>	<b>2.30</b>	<b>0.30</b>	<b>0.40</b>	<b>1.50</b>	<b>9.20</b>	<b>1.40</b>	<b>3.60</b>	<b>87.83</b>	

Table 2.3 - cont'd.

Country	Coal Combustion		Oil Combustion	Cement Production	Non-Ferrous Metals		Pig & Iron	Caustic Soda	Waste Incinerat.	Other	TOTAL	Source
Sub-country	Power Plants	Residential Heat			Lead	Zinc						
<b>Other countries:</b>												
<b>Albania</b>	0.20									0.10	<b>0.30</b>	Pacyna and Pacyna
<b>Belarus</b>	0.10										<b>0.10</b>	National
<b>Bosnia-Herzegovina</b>	0.20										<b>0.20</b>	Pacyna and Pacyna, 2000
<b>Croatia</b>				0.20						0.30	<b>0.50</b>	EMEP
<b>Iceland</b>											<b>0.00</b>	
<b>Macedonia</b>										1.50	<b>1.50</b>	Pacyna and Pacyna, 2000
<b>Moldovia</b>										1.50	<b>1.50</b>	Pacyna and Pacyna, 2000
<b>Norway</b>		0.10		0.10			0.10		0.10		<b>0.40</b>	National
<b>Russia</b>	16.00	33.00	5.00	3.80	0.20	1.70	1.80	8.00		18.20	<b>87.70</b>	Pacyna and Pacyna, 2000
<b>Switzerland</b>	0.10	0.10		0.20						2.90	<b>3.30</b>	National
<b>Ukraine</b>	7.00	15.00		2.00			2.00	3.00		7.00	<b>36.00</b>	Pacyna and Pacyna, 2000
<b>Yugoslavia</b>	3.20	0.60	0.10	0.30	0.10	0.20	0.10	0.40		1.60	<b>6.60</b>	Pacyna and Pacyna, 2000
<b>Total Other Countries</b>	26.80	48.80	5.10	6.60	0.30	1.90	4.00	11.40	0.10	33.1	138.1	
<b>Total EUROPE</b>	<b>89.30</b>	<b>89.33</b>	<b>7.00</b>	<b>26.30</b>	<b>1.90</b>	<b>13.50</b>	<b>10.21</b>	<b>41.30</b>	<b>9.70</b>	<b>49.29</b>	<b>337.83</b>	

\* See also Annex-2 from CEMBUREAU.

**Table 2.4** - Changes in total anthropogenic emissions of mercury in Europe since 1980 ( in tonnes/year).

<b>Source category</b>	<b>1980</b>	<b>1985</b>	<b>1990</b>	<b>1995</b>
Combustion of fuels	350	296	195	186
Industrial processes	460	388	390	93
Other sources	50	42	42	59
<b>TOTAL</b>	<b>860</b>	<b>726</b>	<b>627</b>	<b>338</b>

**Table 2.5** - Emission profiles (fraction of the total) of Hg from Anthropogenic Sources, 1995.

Species	Coal Combustion		Oil Combustion	Cement Production	Non-Ferrous Metals	Pig & Iron	Caustic Soda	Waste Incineration	Other	Average of all sources	Information/ Source
	Power Plants	Residential Heat									
Hg <sup>0</sup> (gas)	0.5	0.5	0.5	0.8	1.6	0.8	0.7	0.2	0.8	0.64	Pacyna et al., 2000
Hg(II)	0.4	0.4	0.4	0.15	0.3	0.15	0.3	0.6	0.15	0.285	Modified by Pacyna, 1998
Hg (partic.)	0.1	0.1	0.1	0.05	0.1	0.05	0	0.2	0.05	0.075	Pacyna et al., 2001

**Table 2.6** - Top ten point sources of anthropogenic mercury emissions in Europe in 1995 ( in tonnes).

Source name	Country	Source category	Emission
Belchatow	Poland	Coal combustion	2.14
Turow	Poland	Coal combustion	2.05
St. Petersburg	Russia	Coal combustion	1.90
Woloszilograd	Russia	Coal combustion	1.80
Starobeszewskaya	Ukraine	Coal combustion	1.50
Novoczerkassk	Russia	Coal combustion	1.40
Perm	Russia	Coal combustion	1.40
Siekierk – Warsaw	Poland	Coal combustion	1.32
Jaworzno II	Poland	Coal combustion	1.32
Marita	Bulgaria	Coal combustion	1.30

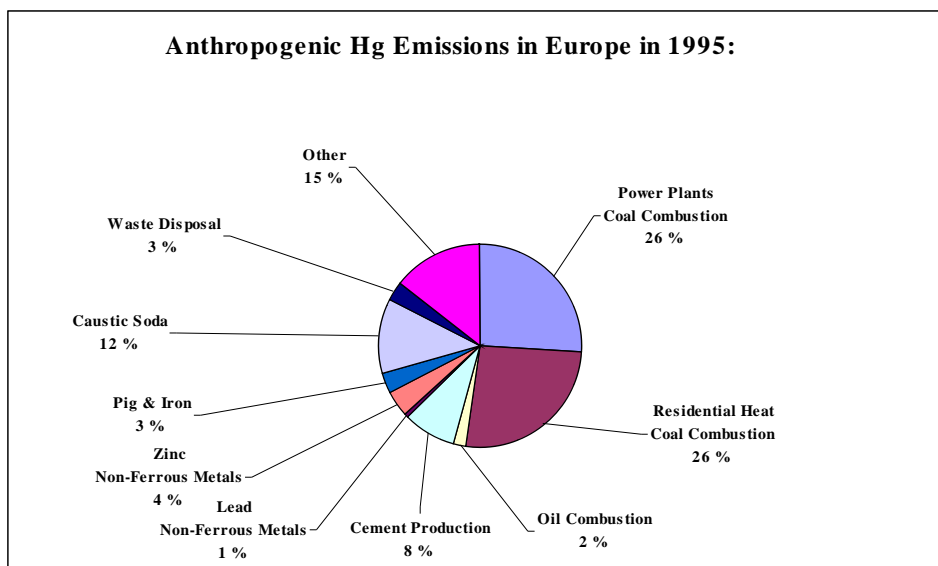


**Table 2.7 - Global Emissions of Total Mercury from Major Anthropogenic Sources in 1995 (Tonnes/ year) (Pirrone et al. 1996).**

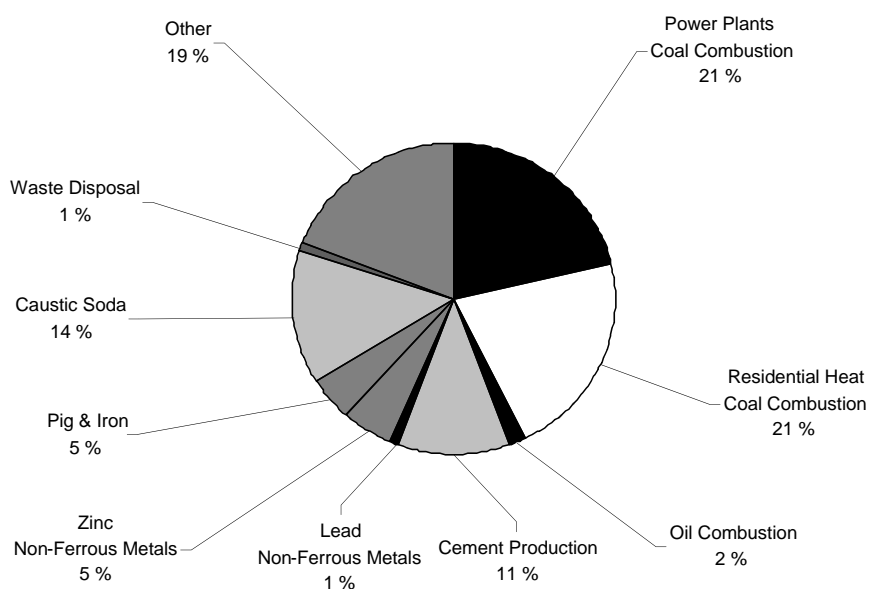
<b>Continent</b>	<b>Stationary combustion</b>	<b>Non-ferrous metal production</b>	<b>Pig iron and steel production</b>	<b>Cement production</b>	<b>Waste disposal</b>	<b>Total</b>
Europe	185.5	15.4	10.2	26.2	12.4	249.7
Africa	197.0	7.9	0.5	5.2		210.6
Asia	860.4	87.4	12.1	81.8	32.6	1 074.3
North America	104.8	25.1	4.6	12.9	66.1	213.5
South America	26.9	25.4	1.4	5.5		59.2
Australia&Oceania	99.9	4.4	0.3	0.8	0.1	105.5
<b>TOTAL 1995</b>	<b>1 474.5</b>	<b>165.6</b>	<b>29.1</b>	<b>132.4</b>	<b>111.2</b>	<b>1 912.8</b>
<b>TOTAL 1990<sup>(1)</sup></b>	<b>1 295.1</b>	<b>394.4</b>	<b>28.4</b>	<b>114.5</b>	<b>139.0</b>	<b>2 143.1<sup>(2)</sup></b>

(1) Estimates of maximum values, which are regarded as close to the best estimate value.

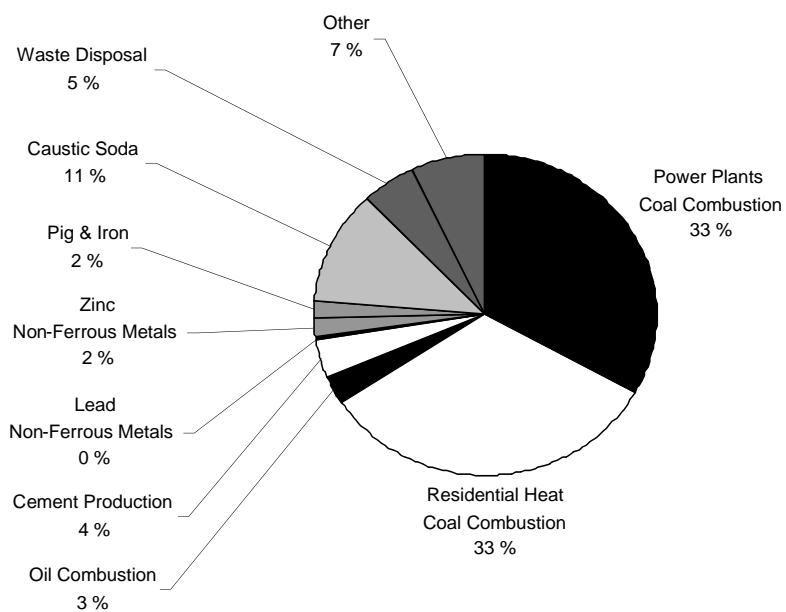
(2) The total emission estimate for 1990 includes also 171.7 tonnes of Hg emission from chlor-alkali production and other less significant sources.



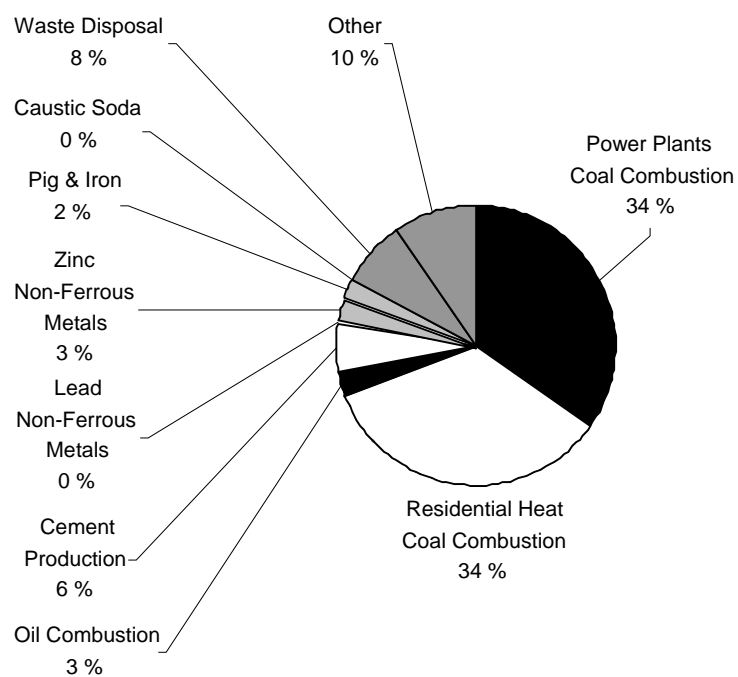
**Figure 2.1** - Contributions of the various source categories to the total mercury emitted from anthropogenic sources in Europe in 1995.



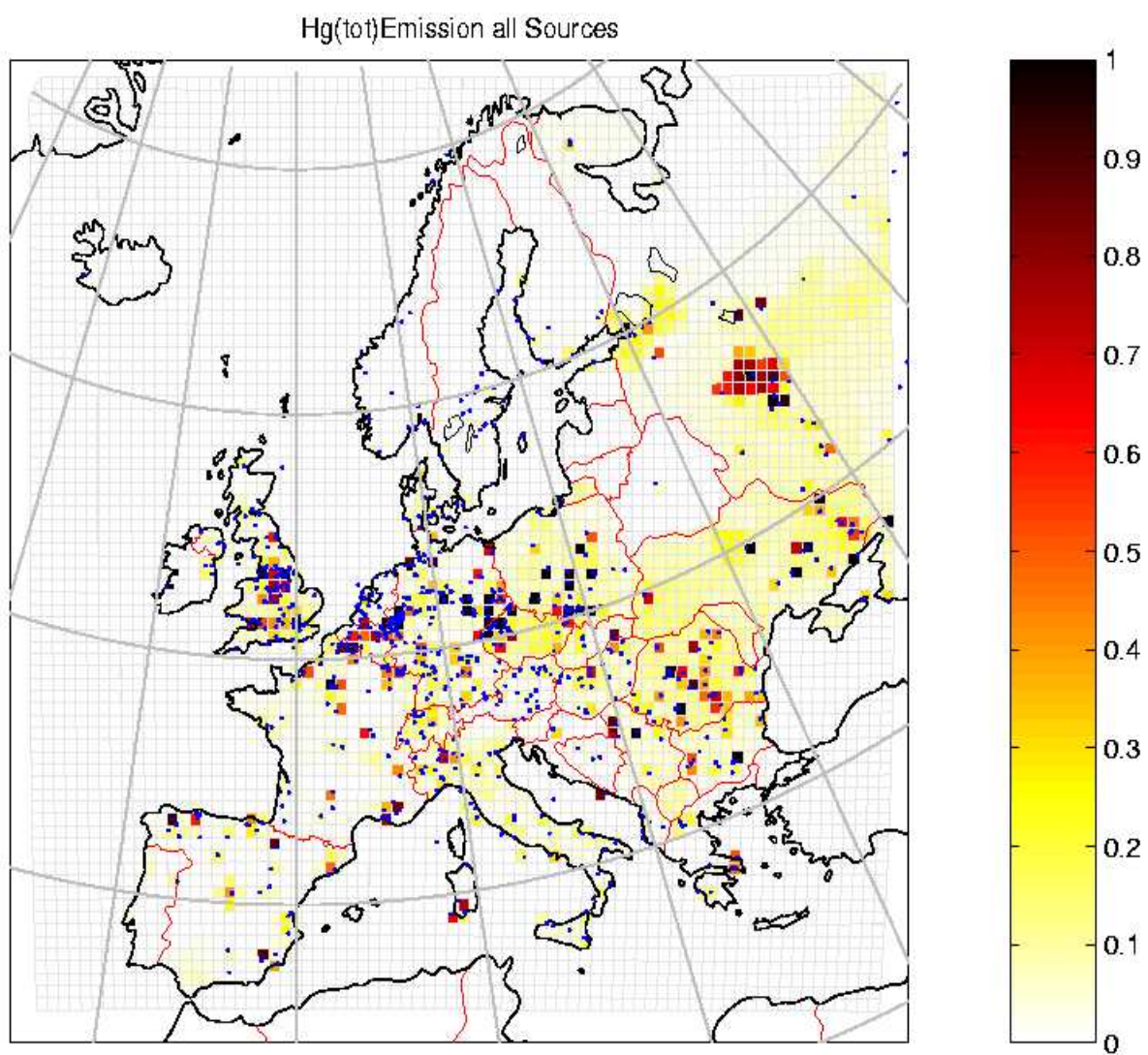
**Figure 2.2** - Contributions of the various source categories to the 204.6 tonnes of gaseous elemental mercury emitted by anthropogenic sources in Europe in 1995.



**Figure 2.3** - Contributions of the various source categories to the 108 tonnes of gaseous bivalent mercury emitted by anthropogenic sources in Europe in 1995.



**Figure 2.4** - Contributions of the various source categories to the 25 tonnes of particulate mercury emissions emitted by anthropogenic sources in Europe in 1995.



**Figure 2.5** - Emissions of total Hg from anthropogenic sources in Europe in 1995 distributed within the EMEP grid system of 50 km x 50 km (Pacyna *et al.* 2001).

## **CHAPTER-3. MODELING THE CYCLE OF ATMOSPHERIC MERCURY**

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### 3.1 INTRODUCTION

It is well known that since the industrial revolution, due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), mercury has been employed in a wide variety of applications (i.e., manufacturing, dentistry, metallurgy). As a result of its use the amount of mercury mobilised and released into the atmosphere has increased compared to the pre-industrial levels. Several advances in theoretical and experimental techniques have been made in recent years to assess spatial and temporal distributions of ambient concentrations and deposition fluxes of mercury and its compounds in Europe. Temporal and spatial scales of mercury transport in the European atmosphere and its transfer to aquatic and terrestrial receptors were found to depend primarily on the chemical and physical characteristics of the three main forms of atmospheric mercury (Munthe, 1992; Petersen, *et al.*, 1998; Pirrone *et al.*, 2000; Petersen *et al.* 2001; Hedgecock and Pirrone, 2001). Therefore the outcome of experimental and theoretical research indicates that natural and human (anthropogenic) activities can redistribute this element in the atmospheric, soil and water ecosystems through a complex combination of chemical, physical and biological mechanisms.

Regional scale modeling of major atmospheric transport and removal mechanisms of Hg(0), Hg(II) and Hg-bound to particulate have been performed within the framework of MOE and MAMCS projects. Model results suggest that up to 75% of mercury in cloud and rain droplets is associated with particles in polluted areas of Europe due to adsorption on to soot particles (Petersen *et al.*, 2001), and that the sea salt aerosol and spray droplets play an important role in the production of Hg(II) in the Marine Boundary Layer (MBL), possibly accounting for up to 20% of the total Hg(II) observed in coastal areas, with higher values expected in open sea (Forlano *et al.*, 2000; Hedgecock and Pirrone, 2001). Preliminary assessments of spatial distributions of atmospheric deposition fluxes of Hg(0), Hg(II) and particulate Hg over Europe have been based on the up-to-date Mercury Emission Inventory (MEI) (Pacyna *et al.*, 2001) developed for Europe, North Africa and the Middle East and executed for different seasons as discussed in Petersen *et al.* (2001) and Pirrone *et al.* (2000a).

Different modeling techniques are currently used to assess the emission source areas (receptor models) as well as spatial and temporal distribution of mercury transported for long distances from the emission sources (Lagrangian and Eulerian modeling approaches). In this chapter, an overview on major chemical and physical processes affecting the dynamics of mercury in the atmosphere and its cycle between air, water and terrestrial ecosystems is provided. In particular, major modeling techniques currently used in Europe to assess spatial and temporal distributions of ambient concentrations and deposition fluxes with changing meteorological conditions are briefly highlighted and recommendations on future research needs for implementing the New European Directive on Mercury will be discussed.

## 3.2 ATMOSPHERIC PROCESSES

### 3.2.1 The Chemistry of Mercury

Gas phase elemental mercury makes up the bulk of mercury emitted from industrial and natural sources and is also the most common form of mercury in the gas phase. The reason for this is that elemental Hg reacts slowly with atmospheric oxidants. The most important gas phase oxidation pathway is the reaction with ozone. This reaction is slower than some other gas phase reactions, but the relatively high concentrations of ozone found in the troposphere with respect to other oxidant compounds makes it the most important. Oxidation of Hg(0) leads to Hg(II) species which are notably less volatile than Hg(0) and will tend to condense onto atmospheric particulate matter or be deposited to marine or terrestrial surfaces.

The partitioning of Hg(0) between the gaseous, dissolved and adsorbed states generally provides a sink for a part of the Hg(0) present in the gas phase. Hg(0) may dissolve into rain water or adsorb onto the atmospheric aerosol and subsequently be precipitated or deposited. These deposition processes provide the major removal pathways for atmospheric mercury.

Elemental mercury is present in atmospheric water, whether it be fog or cloud water or the water associated with deliquesced aerosol particles. The Henry's Law constant for mercury is low so the elemental mercury concentration in atmospheric water should reach equilibrium with the gas phase concentration rapidly, if no particularly rapid reactions of elemental mercury occur in the aqueous phase. In fact this is the case for mercury because even though the oxidation of mercury in the aqueous phase is significantly more rapid in the aqueous phase than the gas phase, the mass transfer of Hg(0) from the gas phase is faster for the droplet radius range found in fogs and clouds.

Oxidised Hg in atmospheric water is usually found complexed with  $\text{SO}_3^{2-}$ ,  $\text{OH}^-$  or  $\text{Cl}^-$  ions, the concentrations of the various complexes depending on the origin of the aqueous phases. In most cases, apart from sea-salt aerosol, the concentration of chloride ions is low and  $\text{OH}^-$  and  $\text{SO}_3^{2-}$  complexes are predominant. The greater solubility and lower volatility of Hg(II) with respect to Hg(0) means that Hg(II) does not generally outgas from the aqueous phase in any significant fashion, although recent research suggests that  $\text{HgCl}_2$  outgassing from the marine aerosol may be an important process in the marine boundary layer (Hedgecock and Pirrone, 2001).

Hg(II) in fog and raindrops may adsorb to particulate matter scavenged by the droplets. This is particularly likely if the particulate matter is rich in elemental carbon (soot) as the adsorption coefficient for Hg on soot is high (Petersen et al., 1998, Pirrone et al., 2000)

Mercury associated with particulate matter in the atmosphere may be the result of direct emissions from industry where the small amount of Hg present in fossil fuels is emitted bound to particulate matter, usually soot. This mercury is unlikely to be released or react in the atmosphere and is deposited together with the particulate. The other possibility for Hg association with particulate matter is the adsorption of elemental Hg present in the atmosphere, the amount of Hg adsorbed will depend on the composition of the aerosol and the gas phase concentration of Hg. There is also the possibility that particulates which undergo cycling through droplets or periods of deliquescence contain Hg(II) compounds which remain after the evaporation of the water.



### 3.2.2 Gas-Particle Partitioning

The modeling of the atmospheric aerosol is fundamental for many questions involving the quality of the environment in which we live. Aerosols directly affect health when inhaled, they reduce visibility [see Seinfeld, 1986, and references therein] and provide surfaces for the heterogeneous production of gaseous pollutants [Dentener and Crutzen, 1993]. Aerosols are also intimately involved in the transport of pollutant species and in the chemical and physical transformation of hazardous atmospheric pollutants (HAPs). The transport and dispersion of pollutants via the particulate matter emitted in industrial plumes has been studied and modeled [Shannon and Voldner, 1995; Constantinou et al., 1995, Pirrone et al., 1995ab]. The ambient aerosol population is not a very well defined entity, and is constantly changing, adsorption isotherms of Hg for the various types of aerosol are unavailable and the interaction of gaseous pollutants with aerosol particles is dependent on the chemical composition of the particle. Although the composition is at least partially known in some instances or can be modeled, in others it remains nevertheless an obstacle to the rigorous treatment of adsorption processes.

### 3.2.3 Dry deposition to Terrestrial and Aquatic Receptors

Dry deposition of Hg may occur via two processes. One is the direct deposition of elemental gas phase Hg, the other is the deposition of atmospheric particulate matter to which Hg is reversibly or irreversibly adsorbed. The first process is extremely difficult to quantify depending as it does on meteorological phenomena such as temperature and wind speed, but also on the type and geomorphology of the surface in consideration. Most regional scale studies have assumed that the gaseous flux of Hg(0) the land/water surface is zero, (Pai et al., 1997). Recently a number of flux chamber experiments, especially on water surfaces have been performed to test the validity of this assumption and to determine whether it is possible to parameterise net fluxes as a function of air and sea temperature and solar irradiation (Atmos. Env. special issue 2001).

The second process, that of Hg deposition together with particulate matter has until recently only been considered in terms of Hg irreversibly bound to particulate matter emitted with flue gases from industrial installations. The role of the atmospheric aerosol as a vehicle for Hg deposition was recently investigated by Pirrone et al., (2000). This preliminary investigation sought to consider the various possible aerosol sources, urban, continental, marine and desert individually and also to take into account the possible deliquescence of the particles during periods of high humidity with the consequent aqueous phase chemistry and altered deposition velocity due to the increase in mass and diameter resulting from the adsorption of water vapour. Their results suggest that where rainfall is relatively frequent this process is secondary to wet deposition. However in regions with prolonged periods of dry weather it could be the major deposition process for part of the year. This would be particularly true of coastal areas where the sea is a constant source of deliquesced aerosol particles capable of adsorbing Hg(0), which undergoing oxidation to Hg(II) in the aqueous phase would result in continuing adsorption of Hg(0).

### 3.2.4 Wet Scavenging by Precipitation Events

Wet removal processes concern soluble chemical species (Hg(II) and its compounds, and some Hg(0)), and also particulate matter scavenged from below the precipitating clouds.

The total wet deposition flux is made up of two contributory factors. The first derives from the continuous transfer of mercury to cloud water, described by chemistry models. There are two limiting factors here, the rate of uptake of gas phase elemental mercury, which is regulated by Henry's constant, and the subsequent oxidation of Hg(0) to Hg(II) which is governed by reaction rate constants and the initial concentrations of the oxidant species. The total flux depends upon the liquid water content of the cloud and the percentage of the droplets in the cloud which reach the earth's surface.

The second contribution to the total mercury flux is the physical removal of particulate matter during precipitation events. The latter case is modelled by specifying a scavenging coefficient.

### 3.2.5 Exchange of Mercury Between Atmospheric, Aquatic and Terrestrial Compartments

The exchange of pollutants between different environmental media is a phenomenon that involves chemical and physical processes which operate on different temporal and spatial scales. It plays an important role in the cycle of all semi-volatile contaminants due to the propensity of these contaminants to be partitioned between the gas, aqueous and solid phases depending on the Henry's Law constant and ambient conditions. Although the exchange of contaminants between the atmospheric, water and terrestrial compartments is considered a critical mechanism in the overall biogeochemical cycle for a wide array of semi-volatile contaminants including mercury and several organic compounds (i.e., PAHs, PCBs, pesticides) in the last two decades not very much progress has been made in understanding its magnitude, its possible variation over time and space, of the different processes/mechanisms involved (Cossa et al. 1996; Rasmussen 1994; Schroeder et al. 1989; Xiao et al. 1991; Ferrara, et al. 2000). Recently attempts have been made to develop a comprehensive model to assess the role of sea spray aerosol in the overall cycling of atmospheric mercury over the Mediterranean Sea. The relative contribution of sea spray at different wind speeds with respect to the exchange of gas phase Hg at low wind speeds has been investigated. The latter phenomena is driven primarily by the concentration gradient between the top-water microlayer and lower atmosphere (Pirrone 1998; Trombino *et al.* 2000) and solar irradiation (Hedgecock and Pirrone, 2001).

There are not many models that describe the air-water exchange mechanisms and those that exist are mostly used to estimate the rate of air-water exchange of Persistent Organic Pollutants (POPs) (Deacon, 1977; Liss and Slater, 1974; Kerman, 1984; Schwartzenbach *et al.*, 1993). The two-film model (Liss and Slater, 1974; Schwartzenbach et al., 1993) is the most commonly used to describe air-water exchange, although surface renewal (Daenkwerf, 1951; Asher and Pankow, 1991) and boundary layer (Deacon, 1977; Kerman, 1984) models are sometimes employed. The model is used to assess the dynamics of gaseous mercury via sea spray formation in the Marine Boundary Layer (MBL) and its magnitude compared to other mechanisms. Wind stress at the sea surface generates droplets in the size range 37.5 to 400  $\mu\text{m}$ . The droplet radius is of great importance as it determines whether gas phase

elemental mercury is removed from or released to the atmosphere. When the sea water top micro-layer Hg concentration is high ( $C_0=0.1 \text{ ng L}^{-1}$ ) the aerosol which is eventually re-deposited on the sea surface releases mercury whilst it remains in the air. Conversely when the Hg concentration in the sea top micro-layer is low ( $C_0=0.001 \text{ ng L}^{-1}$ ) the trend is inverted and the aerosol absorbs Hg before re-deposition.

### 3.3 TIME SCALE AND UNCERTAINTY ANALYSIS

#### 3.3.1 Introduction

Atmospheric processes occur over a very wide range of time scales, varying from almost instantaneous in the case of chemical reactions involving radicals, to the hours sometimes required to establish gas-aqueous phase equilibria and the days or even weeks required for atmospheric transport. The impact of any one equilibria or a particular reaction on the speciation, deposition or transport of mercury therefore requires an in depth analysis of the result of variations of the parameters that determine the time scale of the equilibrium or reaction. The parameters involved could be many, meteorological factors such as temperature, pressure, relative humidity and atmospheric liquid water content are clearly important, as are the concentrations of atmospheric chemical species which react with mercury itself or compete with mercury to react with complexing ligands or oxidants. The most common method used to assess the importance of specific reactions and equilibria or initial model concentrations is to run the model a large number of times, varying initial concentrations or reaction and equilibrium constants to obtain an idea of the sensitivity of the model's output to these parameters.

A more rigorous and quantitative approach to the analysis of a model's sensibility to initial concentrations, reaction rate constants and equilibrium constants is to obtain the derivative of a species' concentration with respect to initial concentrations and individual rate constants. This is less easy to achieve but once performed may save time and produce less ambiguous results than the empirical approach of varying individual concentrations and rate parameters. The other advantage is that the sensitivity of a given species concentration to an initial concentration or rate constant may change over time, and this is easily seen in a plot of sensitivity against time.

#### 3.3.2 Initial Results with a Condensed Chemical Reaction Scheme

A condensed gas and aqueous phase chemistry scheme for mercury was prepared for use with a model describing the interactions of gas phase mercury with the ambient aerosol based on the condensed scheme used by Petersen et al., (1998), which in turn had been derived from the much more comprehensive reaction set used by Pleijel and Munthe (1995). The aqueous phase chemistry was included originally to account for mercury chemistry fog and rain droplets and then in gas-particle interaction model to describe the chemistry in deliquesced aerosols. Sensitivity analysis was performed on this condensed mercury chemistry scheme using the Direct Decoupled Method (DDM) devised by Dunker (1984), and incorporated in the freely available Fortran programme ODESSA which uses a Gear based integration routine to solve the system of Ordinary Differential Equations (ODEs) which mathematically represents the ensemble of reactions in the chemistry scheme.

The sensitivity to initial concentrations revealed that the mercury compound concentrations which are initially dependent on the concentration of aqueous phase elemental mercury become entirely dependent on the gas phase elemental mercury concentration after 100s. The concentration of elemental mercury itself establishes its gas-aqueous phase equilibrium in approximately a microsecond. Thus the gas phase concentration is by far the most important parameter in the determination of final mercury compound concentrations in the atmospheric aqueous phase, and the quantity of mercury adsorbed on particles which deliquesce or are scavenged has little impact on the final steady state concentration of the mercury compounds. The most important factor in determining the eventual steady state mercury compound concentrations proved to be the initial concentration of chloride ions. Mercury is oxidised rapidly in the aqueous phase by dissolved ozone and also by OH and HOCl, but the total concentration of mercury in the aqueous phase is determined by the concentration of ions present which may form complexes with mercury. The most important are OH<sup>-</sup>, SO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup>. The sensitivity analysis showed clearly that the initial concentration of chloride ion was fundamental in determining the eventual total mercury content of the aqueous phase. In the presence of high chloride concentrations the total concentration of dissolved mercury compounds could be 100 times that in conditions with low chloride ion concentration. This fact illustrated the difference between sea-salt and other types of aerosol, where the chloride concentration is very high in the former and thus is able to have high concentrations of dissolved mercury compounds, and other particles where the chloride concentration is determined by the gas phase HCl concentration, which is generally low. In the low chloride concentration case the major mercury containing complexes are Hg(SO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and Hg(OH)<sub>2</sub>, both of which are dependent on pH so that their concentration is sensitive to the concentration of acidic species in the gas phase and aqueous phases. The sensitivity of the mercury compound concentrations to individual reaction rates was shown to be dependent on gas and aqueous phase oxidation rates as would be expected, because of the necessity of this first step to provide Hg<sup>2+</sup> for complexation by Cl<sup>-</sup>, OH<sup>-</sup> and SO<sub>3</sub><sup>2-</sup>.

### 3.3.3 Recent Advances

The importance of the role of the sea-salt aerosol as a possible carrier of oxidised mercury due to its ability to complex relatively large quantities of oxidised mercury due to its high chloride concentration, prompted more detailed studies of the role of the sea-salt aerosol in mercury chemistry in the marine boundary layer. Preliminary results show that the most important oxidation pathway is gas phase oxidation of elemental mercury by ozone. It had been suggested that in low ozone regimes, typically regions where there is little anthropogenic production of nitrogen oxides, such as those prevailing in the remote marine boundary layer that a two-step oxidation of mercury by OH radical in the aqueous phase would also become a major pathway, Lin and Pekkonen (1997). This has been shown not to be the case, and it is the gas phase oxidation of elemental mercury by ozone and the subsequent scavenging of HgO by deliquesced aerosol which makes the largest contribution overall to the oxidation process in the marine boundary layer in non-cloudy conditions. Current work is focussing on the sensitivity of mercury oxidation and speciation to atmospheric liquid water content and photolysis rate constants which are behind the diurnal photooxidant concentration variations in the atmosphere.

## 3.4 MODELLING FRAMEWORKS

A variety of modelling techniques have been developed for exploration of atmospheric mercury processes. These include relative simple mass balance models that examine the pooling and exchange of mercury species between various environmental compartments as well as complex deterministic atmospheric dispersion models attempting to simulate the transport and transformation of mercury over domains of hundreds to thousands of kilometers, while detailed chemical transformation models incorporate the most sophisticated treatment of atmospheric mercury chemical processes. In addition to source-based models, receptor models show promise for explaining source-receptor relationships. It is expected that improved modelling techniques and increasing monitoring data bases will enable detailed source attribution determination for the EU region within the next several years.

### 3.4.1 Modelling Local Scale and Near Source Transport

Local scale models for mercury are used to predict concentrations and deposition fluxes downwind of point sources over a few hours or days in an array of grid cells which range in horizontal size from about 1 to 2000 km<sup>2</sup>. They require detailed understanding of chemical reactions and atmospheric processes on the order of minutes or hours. Such models can be employed to predict worst-case episode conditions and are typically used by regulatory agencies as a basis for control strategies. Local scale models can be described as simple or advanced based on the assumptions with which the important variables are treated. Relative simple models based on Gaussian diffusion assume that concentrations of pollutants will be normally distributed and do not undergo significant chemical reaction and removal as they travel away from the source. In extended versions of the elementary Gaussian model transport equations are solved numerically using a momentum reduction in cross-wind direction in order to reduce the three-dimensional problem to a two-dimensional one. This procedure preserves a high resolution of the plume structure even far from sources. As the vertical grid is oriented vertically in the mean wind direction, a high cross-wind resolution can be used over the entire model domain.

### 3.4.2 Modelling Long-Range Transport

The major European marine environment protection conventions (OSPAR, HELCOM and MEDPOL), the Arctic Monitoring and Assessment Program (AMAP), and the recently signed UN-ECE protocol on reducing the atmospheric transboundary transport of mercury in Europe have intensified the scientific interest in relating the spatial and temporal information on the release of mercury into the atmosphere to the pattern of atmospheric deposition fluxes to various ecosystems by means of long-range transport modelling on regional European scales. In this context, efforts have been made to simulate the atmospheric transport and fate of mercury and to derive estimates of ambient concentrations and dry and wet deposition fluxes of mercury over Europe (Petersen et al., 1995; Ryaboshapko, 1998) through either relative simple Lagrangian formulations or Eulerian approaches employing extensive gas- and aqueous phase chemical mechanisms and explicitly tracking numerous species concentrations. Results from regional scale models reveal that mercury transport over Europe is significantly affected by the temporal and spatial variability of global background concentrations of

elemental mercury suggesting a need for hemispheric and global scale models to calculate time dependent boundary concentration fields as input data for European scale models.

#### **3.4.2.1 Lagrangian Modeling**

Lagrangian models developed for mercury and currently in use are variants of the so-called trajectory models. These models are usually formulated under assumptions of simplified turbulent diffusion, no convergent flows and no wind shear. In these approaches only first-order chemical reactions can be treated rigorously. However, the Lagrangian approach avoids many of the computational complexities associated with the simultaneous solution of many differential equations; this generally results in requiring significantly less computational resources and can facilitate an understanding of problems that do not require descriptions of interactive non-linear processes.

#### **3.4.2.2 Eulerian Modeling**

Further progress in understanding the atmospheric cycling of mercury has emphasised the need for direct modelling of the complex physico-chemical transformations of atmospheric mercury species by comprehensive Eulerian models. These approaches employ extensive gas- and aqueous phase chemical mechanisms and explicitly track numerous species concentrations. Also, a more detailed numerical formulation of physical and chemical processes occurring within and below precipitating and non-precipitating clouds is included. Typically, these models contain modules designed to calculate explicitly the chemical interactions that move gas-phase species into and among the various aqueous phases within clouds as well as calculate the aqueous-phase chemical transformations that occur within cloud- and precipitation droplets.

#### **3.4.2.3 Mass Balance**

Multimedia mass balance models are relatively simple mathematical descriptions of the environment designed to gain a qualitative and quantitative understanding of the behaviour of mercury species, which are likely to be found in more than one environmental medium. Such models subdivide the environment into a number of well mixed boxes which are assumed to have homogenous environmental characteristics and concentrations. The model then calculates how mercury species are distributed within that simplified system. The distribution, and thus the concentration that is established in each medium, is influenced both by the intrinsic mercury properties and emission pattern and by the characteristics of the environment into which the mercury species are released. The models thus integrate information on multiple and interacting processes of partitioning, transport and transformation into a comprehensive picture of mercury in the environment.

Compartmental box models may serve as test modules for more complex atmospheric dispersion models which can be overwhelming in their complexity and in the amount of data they require and produce. For example, the incorporation of soil, vegetation and marine

environments into an atmospheric dispersion model can make them completely impractical and non-transparent. It was therefore suggested that box models can play an important role in:

- ❑ testing which fate processes are important and thus need to be included in the atmospheric dispersion models
- ❑ attempts to understand model behaviour
- ❑ testing expressions and parameter values for air-surface exchange
- ❑ conducting sensitivity and uncertainty analysis

#### **3.4.2.4 Receptor Modeling**

In the last two decades a number of receptor models were developed and applied for different regions and for a number of trace elements and organic compounds in order to evaluate the emission source profiles in relation to ambient concentrations. There are different type of receptor models. Multivariate statistical techniques (i.e., FA, PCA) combined with backward trajectory analysis were the first to be applied to trace elements and provide the emission source profiles of emission sources from which the observed ambient concentrations at a give location originate from. Alternatively, hybrid receptor-deposition modeling techniques combine Lagrangian model with physical or/and empirical process models (Pirrone et al. 1995a; 1995b) in order to assess the relative contribution of anthropogenic emission sources to air masses crossing the monitoring site. These techniques have been used for trace elements (Pirrone et al. 1995a) including mercury (Pirrone and Keeler, 1995) and semi-volatile organic compounds (Pirrone et al. 1995b; Pirrone and Keeler 1997). However, regardless of the technique employed, the application of receptor models require continuous observations, preferably with high temporal resolution, of ambient concentrations of trace elements. It is particularly suitable for regulatory purposes when continuous and dense (spatially) monitoring network data are available.

### **3.4.3 Integrated Mercury Modeling Frameworks used in EU**

Hemispheric and global model developments are now underway based on national research efforts in Scandinavia and Canada but results are still in a preliminary stage. The major European scale mercury model developments and applications have been performed under the Heavy Metals Protocol of the UN-ECE LRTAP Convention and in the framework of two European projects, namely the Mercury Over Europe (MOE) and the Mediterranean Atmospheric Mercury Cycle System (MAMCS) funded by the European Commission-Environment and Climate Programme. In the following three subsections, the basic features of these three modeling frameworks are briefly outlined and main results in terms of model predicted concentrations and deposition fields are summarised.

#### **3.4.3.1 Integrated Modeling System developed at MSC-E, Russia**

The MSC-E model for mercury transport and deposition includes basic chemical and physical processes such as emission, advective transport, turbulent diffusion, chemical transformations, and dry and wet deposition. The MSC-E model operates within the EMEP

grid region (135×111 cells) with a grid cell size of 50×50 km<sup>2</sup> and a time step of 20 min. The basis of this version are models described by Pekar (1996) and Ryaboshapko et al. (1998; 1999). In the last model version the most essential changes concern the description of mercury gas-phase chemistry and boundary concentrations.

A detailed description of the model is given in MSC-E report for 1999 (Ryaboshapko *et al.*, 1999). The schematic representation of the model is given in Figure 3.1. The model operates with five vertical layers of 100, 300, 700, 1000 and 1800 m depth. Thus, the calculation domain covers the whole boundary layer and an essential part of the free troposphere. Emissions enter either the first or the second model layer according to the source height. Interlayer exchange is realised by vertical turbulent diffusion and ordered vertical fluxes. The latter are calculated at each time step in each cell reasoning from the condition of air mass balance. The upper boundary of the model reservoir is open for the exchange with the above atmospheric layers. The lateral margins of the model reservoir are also open for the exchange with the ambient atmosphere. Mercury and its compounds can undergo chemical reactions both in the gaseous phase and in the liquid phase of clouds. It is assumed that clouds can be present in the third, fourth and fifth model layers. The model describes heavy metal scavenging from the atmosphere due to dry uptake by the underlying surface as well as due to wet removal.

The advection scheme has been developed by Pekar (1996). Horizontal diffusion is described according to the approach suggested by Izrael et al. (1980). The model description of turbulent diffusion is based on the assumption that substance flux is proportional to the concentration gradient. The proportionality factor is the coefficient of turbulent diffusion calculated by the boundary layer parameterisation described in Pekar (1996). Vertical diffusion is described by an implicit scheme in which stability does not depend on the ratio of time-step and diffusion coefficient (Samarsky, 1977). The diffusion equation is solved by the sweep method.

Petersen et al. (1998) developed a chemical module containing only basic reactions. On the basis of this module Ryaboshapko et al. (1999) have developed a simplified scheme which does not require much computer time and can be used in operational calculations (Figure 3.2). In this scheme gaseous elemental mercury is dissolved in the liquid phase of cloud (fog) drops according to Henry's Law (equilibrium E1). In the liquid phase the process of mercury oxidation by ozone takes place (reaction R6). Products of the liquid phase oxidation react with dissolved species (reactions R13, equilibrium E2) and are absorbed by solid insoluble particles, for example, soot particles (equilibrium E3, E4). The reaction of divalent mercury with sulfite ions produces unstable mercury-sulfite complexes (reaction R13). Their decay (reaction R9) results in mercury reduction to the elemental state and in the elevation of the elemental mercury concentration in the solution. Therefore this scheme presumes a negative feedback controlling the rapidity of gaseous elemental mercury dissolution process in the liquid phase. It is possible to group mercury compounds which are in equilibrium. The first group - elemental mercury in the air and water, the second one - mercury of the mercury-sulfite complexes in the aqueous phase and on soot particles, the third - free mercury ions and mercury-chloride complexes in solution and on particles. These groups are denoted as A, B, and C respectively: A, B and C can be considered as individual "substances" and the distribution inside A, B or C can be established by equilibrium coefficients. For example, the distribution between Hg(0)(liquid) and Hg(0)(gas) within A is defined by Henry's law. Mean monthly concentration fields of sulphur dioxide were calculated by Meteorological Synthesizing Centre - West using a Eulerian model for acidifying species with spatial



resolution of 50x50 km (Olendrzynski, 1999). The equilibrium ratio between sulfite and chloride complexes in a solution drop and associated with soot particles is assumed to be 1/6 (Petersen *et al.*, 1998). Henry's law constants for ozone  $\text{H}_{\text{O}_3}$  and elemental mercury  $\text{H}_{\text{Hg}}$  depend on temperature. For temperatures below 273<sup>0</sup>K it was assumed that cloud water is partially in the super-cooled liquid state. For the liquid phase appropriate Henry's law constants both for mercury and ozone were calculated by extrapolation of known temperature dependencies into the negative temperature range. In addition to the liquid phase reactions, the gas-phase reactions of mercury and its compounds can also take place. Gas-phase elemental mercury is oxidised by ozone with a second order rate constant of 0.74E-9 ppb<sup>-1</sup>s<sup>-1</sup> (Petersen *et al.*, 1998). Since ozone is present in large excess relative to mercury the reaction may be considered as a quasi-first order process. In our calculations mean monthly ozone concentrations calculated for the boundary layer with spatial resolution 50x50 km in Meteorological Centre-West (Simpson *et al.*, 1997) are used.

It is assumed that mercury associated with particles behaves like sulfate with an equilibrium washout ratio of  $7 \times 10^5$ . Washout of inorganic gaseous oxidised mercury by the cloud liquid phase is set equal to the equilibrium washout ratio characteristic for nitric acid:  $1.4 \times 10^6$  (Petersen *et al.*, 1995).

Dry deposition of elemental mercury is taken into account by assuming a dry deposition velocity of 0.03 cm/s over land during May-October and 0.01 cm/s during the other months. On the sea surface the dry deposition velocity of  $\text{Hg}^0$  is always zero. For gaseous oxidised inorganic mercury the dry deposition velocity is always 0.5 cm s<sup>-1</sup> regardless of season and the underlying surface type.

Results from model simulations in terms of mean annual surface air TGM concentration fields for 1998 are shown in Figure 3.3. As can be seen from the figure the highest concentrations occur in central Europe with maximum values up to 7 ng m<sup>-3</sup>. The regions of northern Scandinavia however show concentrations close to the global background level. The spatial distribution of mean annual mercury concentrations in precipitation for 1998 depicted in Figure 3.4 shows pronounced peak values close to the main European emission areas with relatively high contributions from divalent mercury, which is readily transferred into the aqueous phase. The total deposition flux (Figure 3.5) consists of contributions from all mercury species in ambient air and precipitation. Maximum values in main emission areas with high concentrations and precipitation rates are in the range of 600 g m<sup>-2</sup> a<sup>-1</sup> with a pronounced decreasing gradient towards the remote European areas.

For comparison purposes model results were compared with observations of mercury concentrations in air and precipitation carried out in the framework of EMEP programme. Only a small number of EMEP stations have in the past measured mercury concentrations in air and precipitation: 5 stations in 1997 and 3 in 1998 (Figure 3.6). The situation with mercury in precipitation is somewhat better – the measurements were carried out at 8 and 6 stations (Figure 3.7). The model slightly overestimates mercury concentrations in air. This difference is quite understandable because the model is very sensitive to background concentrations of elemental mercury. The model will be able to provide a high level of agreement between measured and calculated values if reliable information on mercury background concentrations outside the modelling domain were available. However, observed and model predicted mercury concentrations in precipitation agree satisfactorily within a factor of 1.2.

### 3.4.3.2 Integrated Modeling System Developed at CNR-IIA, Italy

The mercury modeling system was developed within the framework of the Mediterranean Atmospheric Mercury Cycling System (MAMCS) project funded by the EU-Environment and Climate Program (Contr. No. ENV4-CT97-0593) in which major research and university institutions were involved (see Final MAMCS Report, Pirrone et al. 2000a). The major goal of MAMCS was to examine the cycling of atmospheric mercury in order to characterise and quantify the emission, ambient concentration and deposition flux patterns in the Mediterranean region. The climatic conditions in the Mediterranean region are such that one of the major foci of the project was the investigation and modelling of the interaction between gas phase mercury species and the ambient aerosol. The reason for this is that for relatively long periods during the year there is very little, if any, rainfall in the area. Under such conditions the major mercury deposition pathway, precipitation is unavailable, and the major deposition process will be via the ambient aerosol. This fact has important implications, particularly in the marine environment where deliquesced sea salt aerosol is present, providing both a means of deposition and of oxidation of elemental mercury.

The MAMCS integrated modelling system (see Figures 3.8-3.10) is based on two well known meteorological-dispersion models, the Regional Atmospheric Modelling System (RAMS) and the SKIRON/Eta meteorological system (Figure 3.8). RAMS is a highly versatile Eulerian model developed jointly by Colorado State University and Mission Research Inc/ASTeR Division. It is a merger of a non-hydrostatic cloud model and a hydrostatic mesoscale model. There is no lower limit to the domain size or to the mesh cell size of the model finite difference grid. The large number of RAMS applications worldwide has given valuable information about the model behaviour under different climatic conditions. RAMS has a number of features which make it extremely useful for air quality studies on various scales. It has two-way interactive nesting capabilities with any number of either telescoping or parallel fine nest grids, terrain following coordinate surfaces with Cartesian or polar stereographic horizontal coordinates and non-hydrostatic time-split time differencing. The cloud microphysics parameterization works at various levels of complexity, there are various turbulence parameterization schemes, radiative transfer parameterizations (short and long wave) through clear and cloudy atmospheres, options for upper and lateral boundary conditions and for finite operators. The surface-layer parameterization (soil, vegetation type, lakes and seas, etc) may be used with different levels of complexity depending on the users requirements. RAMS is therefore a highly versatile tool and is used in air quality studies and to study a wide variety of other atmospheric phenomena. This model is the backbone of the modeling system.

A second meteorological model (SKIRON system) can also be used, it is less time consuming with respect to RAMS because the treatment of cloud microphysics is simplified. The SKIRON system was developed at the University of Athens and is in use in several Mediterranean countries as operational weather forecast model. It is based on the Eta/NMC model originally developed at the University of Belgrade, with the specific objective of being applicable to regions with steep mountains. It therefore uses a unique "step-mountain" vertical coordinate rather than the customary pressure or sigma (or hybrid) coordinate. This model is the fully operational weather forecasting model in use in the United States and several other countries. SKIRON has several capabilities which make it appropriate for regional/mesoscale simulations. One of the more important features of this model is the use of Eta as the vertical coordinate which is a generalisation of sigma-coordinates to give a better parameterization of step-like terrain. The model uses a split-explicit time differencing scheme, a 2.5 order closure

scheme for parameterization of the boundary and surface layer, a viscous sub-layer scheme, a parameterization of surface processes, a 4th diffusion scheme in the field boundaries with diffusion coefficients dependent on deformation and turbulent kinetic energy. It also uses mass convergence and convection for the small, medium and large scale precipitation parameterization scheme, the GFDL radiation scheme with random interaction of clouds at various levels, and importantly includes a dust uptake-transport-deposition module.

The links (see Figure 3.8) between the input required by RAMS (or SKIRON), the mercury emission database, mercury boundary conditions and vertical profiles and the chemical-physical process modules are described below.

The gas and aqueous phase chemistry of mercury is modelled using a reaction scheme based on that of Pleijel and Munthe (1995), and updated to include the radical reactions in the gas and aqueous phases for which rate constants have been published in the last six years. These include the gas and aqueous phase oxidation of elemental mercury by the hydroxyl radical (Sommar et al. (2001), the aqueous phase oxidation of elemental mercury by HOCl and the aqueous phase reduction of oxidised mercury by HO<sub>2</sub> (Lin and Pehkonen, (1998)). A number of versions of the chemistry model exist, all of which may be linked to RAMS, but obviously the more complex the reaction scheme is in the model the more time consuming become the simulations. The most complex schemes treat atmospheric photochemistry in urban areas (complex volatile organic compound chemistry) and marine environments (complex halogen chemistry), both are used predominantly as box models. The advantage of these complex schemes is that by using sensitivity analysis techniques i.e., the Direct Decoupled Method (Pirrone et al. 2000), it is possible to derive a slim-line reaction scheme for mercury and its compounds whilst ensuring that no important reactions are overlooked. This has proved to be particularly important in the marine environment where the omnipresent sea salt aerosol not only provides a reservoir of complexing ligands in the form of high concentrations of halide ions (including bromide and iodide), but also provides a means by which oxidised mercury may be returned to the gas phase (Hedgecock and Pirrone, 2001). The chemistry model normally used with RAMS includes gas phase and aqueous phase oxidation pathways, and in the aqueous phase the complexation equilibria which determine the speciation and concentration of oxidised mercury compounds, this is shown schematically in Figure 3.9. In this version of the model the concentrations of the important oxidants produced by photolytic processes is calculated using a minimum and maximum value for each grid cell and varying the concentration sinusoidally with a maximum when the sun reaches its zenith.

The study of the interaction between mercury and the ambient aerosol, mentioned above, resulted in the development of the gas-particle partitioning (GASPAR) model (Pirrone et al. 2000; Hedgecock and Pirrone, 2001). GASPAR represents the ambient aerosol in a parameterised fashion, and describes the particulate in terms of its source (urban, continental, marine or desert), a maximum of three modal diameters for each source, its hygroscopicity and its soot and chloride ion content. The model calculates the diffusion of mercury into the particles and using empirically derived adsorption enthalpies from experimental data the concentration of mercury associated with particulate matter is obtained. This is not all however, one of the most important characteristics of an aerosol particle is its hygroscopicity, which determines whether or not the particle, or some of the particle, adsorbs enough water vapour to deliquesce. If deliquescence occurs there is an atmospheric aqueous phase present, providing the possibility for all the aqueous phase chemistry of mercury to take place even in the absence of fog and clouds. Deliquescence obviously depends on relative humidity, which is a fundamental parameter for any meteorological model and is therefore known for each grid

cell. The eventual fate of the ambient aerosol is either dry deposition to aquatic or terrestrial surfaces, or scavenging by fog or cloud droplets. Dry deposition velocities are calculated using the resistance method and scavenging is modelled using below and in cloud scavenging ratios. The interaction between the meteorological, chemistry and gas-particle partitioning models is shown in Figure 3.10.

Another important process in the global mercury cycle is the exchange of gaseous mercury at the air-water interface, as indicated in Figure 3.8. This may occur by gas phase diffusion to water surfaces and evasion from the top water micro-layer, or it may be provoked by the mechanical action of the wind on the water surface producing waves and thereby mechanically generating sea-water droplets which may either release or take up elemental mercury. These processes are not as yet thoroughly understood but empirical models capable of reproducing experimental data from flux chamber measurements exist, as do models to predict the size distribution of droplets produced by the action of the wind on the water surface as a function of wind speed (Pirrone et al. 2000a; Trombino et al. 2000).

The integrated MAMCS modelling system has been tested using the results of four intensive measurement campaigns carried out at five sites during the MAMCS project. As an example of MAMCS modeling system application hereafter is reported the results obtained for the fourth MAMCS intensive measurement campaigns carried out from 17 July to 3 August, 1999.

In order to understand the dynamic processes of pollutants during atmospheric transport it is important to characterise the meteorological conditions. The meteorological conditions predicted for the summer period of simulation varied between a high pressures system over the Central and West Mediterranean Regions (17 July) and weak pressure gradients over the North-East Mediterranean at the same time followed by a high-pressure system extending over the Aegean Sea and the Mediterranean Sea region (July 21). On 23 July, weak pressure gradients prevailed over the eastern Mediterranean as a result of the extension of the thermal flow of the Anatolian Plateau, while high pressures over the Northern Africa and strong northerlies and north-westerlies were predicted over the sea on the west side of Italy (23 July). These conditions could promote the long-range transport of mercury from the Central Europe towards the Central Mediterranean. As an example Figure 3.11-a shows a trough that covered the Central Mediterranean and the Balkans on 25 July while it moved towards the Anatolian Plateau on 27 July, followed by strong north-westerly winds predicted over the southeastern Mediterranean on 31 July (Figure 3.11-b). The combination of the low and high-pressure systems over northern Europe induced strong northeastern winds. During the last two days of the simulation a weak synoptic circulation was observed over the Balkans.

Examples of spatial distributions of ambient concentrations (in the first model layer) and deposition fluxes (wet and dry) of  $\text{Hg}^0$ ,  $\text{Hg(II)}$  and  $\text{Hg(part)}$  predicted with MAMCS modeling framework during the simulation period are shown in Figures 3.11-3.12. During the initial days of the simulation the weak flow towards the Mediterranean Sea region did not favour the transport of gaseous mercury. The concentration of mercury species is a function of many factors that affect chemical and physical processes, such as atmospheric reactions and deposition, but it also depends strongly on flow conditions and source locations. Therefore the  $\text{Hg}^0$  concentrations were high only around the sources during the first days of the simulation, while there is a weak mercury concentration gradient over the Mediterranean Sea region. The strengthening of the northerlies west of Italy during the next days (i.e around 23 July), led to the increase in  $\text{Hg}^0$  concentration to 2.4-2.5  $\text{ng m}^{-3}$  in the Central and Western Mediterranean

(Figures 3.11-c) from sources located in those areas. The low-pressure system that covered the Central Mediterranean and the Balkans on 25 July favoured a further increase in  $\text{Hg}^0$  concentration over the above region and over southern Greece. As the cyclone moved towards the Anatolian Plateau, followed by strong northerlies, high values (approximately  $2.3 \text{ ng m}^{-3}$ ) of  $\text{Hg}^0$  were observed over the sea and reaching the eastern Mediterranean (Figure 3.11-d). The concentration of gaseous mercury increased above the usually observed value (background value) over Europe, where most of the sources (e.g. factories, power plants etc.) are located. The opposite is observed over northern Africa and the Middle East where  $\text{Hg}^0$  concentration values are either close to, or just below background levels. The relatively high concentrations observed over the sea, are mainly due to advection of mercury from Europe, while air water exchange processes also make a small contribution.

Similar patterns were followed by the spatial and temporal distributions of  $\text{Hg}^{\text{II}}$  concentrations as illustrated in Figures 3.11-e (on 20 July 1999) during the summer experimental period. High concentrations of  $\text{Hg}^{\text{II}}$  are observed in the vicinity of sources due to its short residence time in the atmosphere, however higher concentrations events were observed on 22 July (Figure 3.11-f) far from the emission sources and over the sea. These patterns are primarily due to a combination of two synergetic factors (1) regional scale transport due to strong horizontal advection, and (2)  $\text{Hg}^{\text{II}}$  formation in the marine boundary layer as also suggested previously in Forlano et al. (2000) and Hedgecock and Pirrone (2001).

$\text{Hg}^{\text{P}}$  is usually deposited at intermediate distances from its source, therefore high concentrations are naturally observed near the sources. However, the removal of  $\text{Hg}^{\text{P}}$  from the atmosphere is mainly dependent on wash-out mechanisms. During the summer and spring experimental periods precipitation amounts were much lower than during the wet period of the year. The concentrations of  $\text{Hg}^{\text{P}}$  modelled on 28 July (as example) are higher near the sources as illustrated in Figure 3.11-g.

The wet and dry deposition of mercury over land or water is a very important issue for human activities and health. Figure 3.12 shows the wet and dry deposition patterns of  $\text{Hg}^{\text{P}}$ ,  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^0$ -adsorbed modelled for the summer MAMCS experimental period, whereas Figure 3.13 shows the total annual deposition fluxes of the three Hg species which were obtained by integrating that related to the four simulation periods (winter, spring, summer and autumn) assuming that each simulation was representative of each season.

The deposition patterns (see Figure 3.13) show that the greatest amounts of mercury are deposited in eastern Europe and in the Mediterranean region, especially in its eastern part. Taking into account the fact that the vast majority of mercury sources are located over central and northwest Europe, two main transport paths are indicated. One is from central to eastern Europe and the other is from Europe towards the Mediterranean sea, namely from north to south.

On a yearly basis the accumulated (within the 17 days of the simulation) amounts of  $\text{Hg}^{\text{P}}$  that is dry deposited are greater over the sea than over land. The deposition velocity of  $\text{Hg}^{\text{P}}$  is a weighted average of 15 deposition velocities, corresponding to the 15 size intervals over which particle radii are distributed. Over regions with high humidity (e.g. over the sea surface) greater deposition velocities are observed due to water uptake and the dependence of the deposition velocity with the size of the particles. The simulated values of  $\text{Hg}^{\text{P}}$  dry deposited, reached  $180 \text{ ng/m}^2$  over the waters surfaces of the South and East Mediterranean Sea during the summer simulation period. On the contrary, higher wet deposition of  $\text{Hg}^{\text{P}}$  is

predicted, over mountainous areas, as expected due to the higher precipitation usually occurring there.

The wet deposition pattern of  $\text{Hg}^0$ -adsorbed is similar to that of  $\text{Hg}^{\text{P}}$ , as the total amount of precipitation is higher over the Alps and the Mountains of Greece and East Turkey. The dry deposition pattern of  $\text{Hg}^0$ -adsorbed in Total Suspended Particulate (TSP) shows a seasonal variation. The dry deposition patterns also vary over the sea and over land. Higher values are observed over the sea during the cold simulated periods (13 February to 2 March and 21 November to 7 December). This dry deposition pattern can be attributed firstly to the prevailing flow and turbulence conditions in the region, and secondly to the size of the particles. Relatively strong northwesterly and northerly winds were evident over Central and Northern Europe during the winter and fall simulation periods. The above-described atmospheric circulation favoured the increase of mercury concentration over the Mediterranean region. Therefore higher amounts of the pollutant were dry deposited over water surfaces, during the cold simulation period.

During the warm periods (1 to 18 May and 17 July to 3 August) the dry deposition values of  $\text{Hg}^0$ -adsorbed, are higher over land as the total amount of aerosol is larger. The dry deposition patterns of  $\text{Hg}^{\text{P}}$  and  $\text{Hg}^0$ -adsorbed also depend on the pollutant concentration and the deposition velocity. The transport of mercury species is dependent on advective transport by wind and transport by turbulent dispersion. The wet and dry deposition patterns of  $\text{Hg}^{\text{II}}$  are highest near the sources.  $\text{Hg}^{\text{II}}$  is also highly soluble so it dominates the wet deposition pattern of gaseous mercury. The wet deposition pattern of  $\text{Hg}^{\text{II}}$  has several similarities with the wet deposition pattern of  $\text{Hg}^0$ -adsorbed, but that of  $\text{Hg}^{\text{II}}$  are four orders of magnitude greater than those of  $\text{Hg}^0$ -adsorbed.

The total annual depositions (Figure 3.13) were calculated using weighted values of the four seasonal runs. It should be remembered that  $\text{Hg}^0$  is deposited only as  $\text{Hg}^0$ -adsorbed. It can be adsorbed either on particulates (see Pirrone et al. 2001) when it is dry deposited or dissolved in raindrops during wet deposition events. Two main reasons allow the inference of seasonal and annual values of deposition from the four model runs. Firstly the four model integration for the different scenarios lasted several days (~17 days each) and secondly there were a representative of the inter-synoptic variability in them. Various synoptic patterns were present in these simulations and thus the deposition patterns and amounts can be considered as representative of their “annual” and seasonal values.

The annual wet deposition patterns of the three mercury species are illustrated in Figures 3.13-b, 3.13-d, 3.13-f. The wet deposition patterns follow the rain pattern simulated by the atmospheric model. For example, this can be understood from the fact that the highest wet deposition amounts are estimated in the vicinity of mountainous regions (e.g. Alps, Atlas mountains). The dominance of the wet processes in mountainous regions was also associated with a well-defined minima of dry deposition of  $\text{Hg}^{\text{P}}$  in these regions.

In conclusion, the wet deposition of  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^{\text{P}}$  were found in general to be one order of magnitude larger than for dry deposition, and the domain-averaged “annual” wet deposition of total mercury was found to be of the same order of magnitude as that measured by Iverfeldt (1991) in northern Europe. The “annual” wet and dry deposition of  $\text{Hg}^{\text{P}}$  are within the range simulated by Petersen et al. (1995) for selected stations in northern Europe. This agreement between our study and the literature gives confidence in the results, although further development is certainly needed. Finally, the total domain-averaged seasonal deposition

exhibited higher values during the wet season (winter, autumn) than during the dry season (summer, spring) of the year (Pirrone et al. 2000a). This is due to the fact that the total deposition is dominated by wet deposition, which is obviously greater during rainy periods. On the other hand, the highest domain-averaged dry depositions of  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^{\text{P}}$  were observed during summer. In conclusion the deposition patterns modelled in MAMCS for the Mediterranean region show that large amounts of mercury are deposited in the Mediterranean region which should be considered in the future development of the European policy for regulating the emissions and controlling the amount of mercury (and its compounds) transferred from the emission sources to terrestrial and aquatic receptors.

Figure 3.14 shows a preliminary comparison of modelled concentrations of  $\text{Hg}^0$ ,  $\text{Hg}^{\text{P}}$  and  $\text{Hg}^{\text{II}}$  with that observed at some of the MAMCS stations during the spring period.  $\text{Hg}^0$  concentrations observed in Sicily and Neve Yam were compared with those modelled with the SKIRON MAMCS based framework (Figures 3.14-a, 3.14-b). The bold line represents the 6-hour moving average. In Figure 3.14-c the  $\text{Hg}^{\text{P}}$  concentrations measured in Fuscaldo for the spring simulation period (1-18 May) are also illustrated. The thin line indicates the modelled concentrations (in 6-hour increments) in the lowest model layer (~62m above the ground) with both the background and lateral boundary concentration of  $\text{Hg}^0$  (in the lowest 2 km) equal to  $1.6 \text{ ng/m}^3$ . The model follows the trends of  $\text{Hg}^0$  in Porte Palo and Neve Yam quite satisfactorily.  $\text{Hg}^{\text{P}}$  trends in Calabria are also represented satisfactorily by model outputs. Significant differences between the model forecasts and the observations seem to appear in some relatively short periods of the simulation. Although models can simulate several phenomena effectively, it is difficult to observe or predict any peaks that might occur over short time scales. Figure 3.14-d represents the  $\text{Hg}^{\text{II}}$  concentrations, observations and model simulation, in Antalya for the same period. The measured values used are limited, however it can be assumed, that the modeled  $\text{Hg}^{\text{II}}$  concentrations are in satisfactory agreement with the observations.

Major details on the MAMCS modeling results for the period of 1998-1999 can be found in the MAMCS Final Technical Report (Pirrone et al. 2000a). It would be unrealistic to say that the cycling of mercury, its emission, transformation and deposition is perfectly reproduced by the model, there are still processes which need to be better understood, among them, the role of the ambient aerosol and air-water exchange would head the list; however it is clear that even when empirical or parameterised approaches have had to be used due to a lack of theoretical studies, the model does reproduce the trends in mercury concentration.

### 3.4.3.3 Integrated Modeling System Developed at GKSS, Germany

A comprehensive mercury modelling system using the Eulerian reference frame of the Acid Deposition and Oxidant Model (ADOM) has been developed under the Canada-Germany Science & Technology Co-operation Agreement and applied within the European Union Marine Science and Technology – Baltic Sea System Study (MAST-III-BASYS) and the Environment & Climate project Mercury Species over Europe (MOE), to study the regional transport and deposition fluxes of atmospheric mercury species. The cloud mixing, scavenging, chemistry and wet deposition modules of the Acid Deposition and Oxidants Model (ADOM), originally designed for regional-scale acid precipitation and photochemical oxidants studies (Venkatram et al., 1988; Misra et al., 1988) have been restructured to accommodate recent developments in atmospheric mercury chemistry. A stand-alone version of these modules referred to as the Tropospheric Chemistry Module (TCM) was designed to simulate the meteorology and chemistry of the entire depth of the troposphere to study cloud mixing, scavenging and chemical reactions associated with precipitation systems that generate wet deposition fluxes (Petersen et al., 1998). The TCM chemistry scheme was developed by systematic simplification of the detailed Chemistry of Atmospheric Mercury (CAM) process model, which is based on current knowledge of physico-chemical forms and transformation reactions of atmospheric mercury species (Pleijel and Munthe, 1995).

After comprehensive testing under different environmental conditions the TCM has been implemented into the full ADOM model. Within the constraints of the available computer resources and input data, these models incorporate an up-to-date understanding of the detailed physical and chemical processes in the atmosphere. The vertical grid consists of 12 unequally spaced levels between the surface and the top of the model domain at 10 km. The model is run for a grid cell size 55 by 55 km (High Resolution Limited Area Model (HIRLAM) grid) over a 76 by 76 domain.

The major modules making up the mercury version of ADOM together with the model input data sets are schematically depicted in Figure 3.15. The transport and diffusion module uses a sophisticated cell-centered flux formulation solver for the 3-dimensional advection-diffusion equation. Dry deposition is modelled in terms of a deposition velocity for gaseous and particle associated mercury species, which is calculated as the inverse of the sum of the aerodynamic, deposition layer and surface canopy resistance. The mass transfer, chemistry and adsorption component of the model is illustrated in Figure 3.16. It incorporates 14 mercury species and 21 reactions including mass transfer (R1-R5), aqueous phase (R6-R17) and gas phase (R20-R21) chemical reactions and adsorption processes on particles (R18-R19). The reaction rates are derived from published data and from assumption of the rates of complex formation. The cloud physics module simulates the vertical distribution of mercury species in clouds. Two different modules are incorporated: one describes stratus (layer) clouds and the other simulates cumulus (convective) type clouds. One or the other or a combination (cumulus deck embedded in a stratus cloud) is used in the calculation depending on the characteristics of the precipitation observed.

The details of each module comprising the original ADOM version for acid rain studies are given in ERT (1984). The development and testing of the mercury wet scavenging module consisting of cloud physics and mercury gas and aqueous phase chemistry sub-modules is described in detail in Petersen et al. (1998).



The database for anthropogenic mercury emissions in Europe employed in the model calculations has been compiled for 1995 (Pacyna et al. 2001). The emission rates and their spatial distribution in the model grid depicted in Figure 2.5 of Chapter 2 and are based on location and capacity of their dominating source categories such as combustion of fossil fuels in power plants, non-ferrous metal smelters, waste incinerators, chlor-alkaline factories and other industrial installations.

The meteorological input data needed by ADOM are three-dimensional fields of wind speed, wind direction, pressure, temperature, relative humidity, vertical velocity and vertical diffusivity, and two-dimensional fields of surface winds, surface pressure, surface air temperature, friction velocity, Monin-Obukhov length, mixing height, cloud base and top height, amount of cloud cover and the amount of precipitation at every one hour model time step. These data sets are derived diagnostically using the weather prediction model HIRLAM. The geophysical data include files for 8 land use categories (i. e. deciduous forest, coniferous forest, grassland, cropland, urban, desert, water and swamp) and 12 soil categories. The database also includes information on terrain height and the growing season. This geophysical data affects meteorology, dry deposition processes and air-surface exchange of gaseous mercury species.

Initial and boundary conditions are needed for all advected species in the model. This includes the emitted compounds and mercuric oxide ( $\text{HgO}$ ) formed by gas phase oxidation of  $\text{Hg}^0$ . A typical European background mixing ratio of 0.18 ppt corresponding to a mass per unit volume concentration of about  $1.5 \text{ ng m}^{-3}$  is used for  $\text{Hg}^0$  in the atmospheric boundary layer (layers 1-4 in the vertical model grid) with a slight vertical mixing ratio decrease of approximately 80% of the boundary layer value at the top of the modelling domain. Observations for mercury species other than  $\text{Hg}^0$  are still scarce in Europe and vertical profiles are not available at all. Therefore, initial and boundary concentrations of  $2 \text{ pg m}^{-3}$ , and  $20 \text{ pg m}^{-3}$  estimated to be average values from a limited number of observations in Europe are used for  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  in the boundary layer. Due their relative short atmospheric residence time and due to anthropogenic emissions occurring near the ground concentrations of  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  are allowed to decrease with height to a value of about 10 % of the boundary value at the model top. In addition to  $\text{HgCl}_2$ , boundary concentrations for  $\text{HgO}$  are also given.  $\text{HgO}$  is believed to be the initial product from the gas phase reaction with  $\text{Hg}^0$  and  $\text{O}_3$  and is included in the chemistry scheme employed in the model. No information on ambient air concentrations of  $\text{HgO}$  or its physical/chemical properties such as Henry's law constant are available. For this reason,  $\text{HgO}$  is treated using the same parameterisation as for  $\text{HgCl}_2$ , believed to be the main gaseous divalent species in the atmosphere. In the absence of reliable measurement data, a very low initial value of  $0.7 \cdot 10^{-6} \text{ pg m}^{-3}$  constant with height is used for  $\text{HgO}$ . The more realistic initial value for  $\text{HgCl}_2$  ( $2 \text{ pg m}^{-3}$ ) is thus assumed to represent all divalent mercury compounds in the boundary air masses. The mercury chemistry in ADOM, described in Petersen et al. 1998, requires the specification of  $\text{O}_3$ ,  $\text{SO}_2$ , and soot carbon concentrations in ambient air as well as  $\text{Cl}^-$  concentrations in cloud water and cloud water pH. For the results with the European version of ADOM, the concentrations of  $\text{O}_3$ ,  $\text{SO}_2$ , and soot carbon were fixed at 35 ppb, 1 ppb and 1 microgram per  $\text{m}^3$ . The cloudwater concentration of  $\text{Cl}^-$  and the cloudwater pH were specified as  $2 \cdot 10^{-6} \text{ mol l}^{-1}$  and 4.5, respectively.

As an example for model applications in Europe, Figures 3.17, 3.18 and 3.19 show calculated  $\text{Hg}^0$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  air concentration patterns study averaged over the entire month of November 1998. As expected the maximum concentrations of all three species are closely

related to the source areas. Concentration values of  $\text{Hg}^0$  generally range from about  $1.2 \text{ ng m}^{-3}$  in remote locations to  $2.2 \text{ ng m}^{-3}$  in the main emission area in Central Europe. The concentration pattern of  $\text{Hg}^0$  is substantially elongated towards Eastern Europe, i. e. in the direction of the mean wind during that month. In the main emission areas, concentrations of  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  are about two orders of magnitude lower than  $\text{Hg}^0$  concentrations due to lower emission rates of these species. Due to rapid dry and wet deposition close to sources the  $\text{HgCl}_2$  concentration pattern (Figure 3.17-a) clearly reflects the spatial emission distribution of that species. The  $\text{Hg}(\text{part.})$  concentration pattern (Figure 3.17-c) is influenced by both  $\text{Hg}(\text{part.})$  emissions and secondary formation of  $\text{Hg}(\text{part.})$  at the end of the life cycle of non-precipitating clouds when dissolved mercury species are evaporated back to particulate mercury.

The dry deposition fluxes shown in Figure 3.17-d denote the sum of  $\text{Hg}^0$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  deposition across the entire model domain. As can be seen, dry mercury deposition fluxes mainly occur over land surfaces with elevated levels in the major emission areas. The reason for that is twofold: First, due to its very low solubility the dry deposition rate of  $\text{Hg}^0$  to all surfaces was set to zero except forests where dry deposition velocities in the range of  $0.001$  to  $0.03 \text{ cm s}^{-1}$  have been determined from experimental studies (Iverfeldt, 1991b, Lindberg et al., 1991). Second,  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  are readily dry deposited in the vicinity of sources resulting in very minor dry deposition over sea areas.

For precipitating clouds, the total monthly wet deposition flux depicted in Figure 3.18-a is derived by summing up the product of the hourly average cloud water concentration of all aqueous species (AQ(1) – AQ(10) in Figure 3.18-c) and the hourly precipitation amount over the entire month. As expected, wet deposition is determined by the precipitation distribution (Figure 3.18-b) and to a certain extent by the concentrations of mercury species in ambient air (see Figure 3.18) yielding a deposition pattern that comprises areas of high precipitation amounts as well as areas of elevated levels of  $\text{Hg}^0$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  concentrations in ambient air.

Concerning the physicochemical composition of mercury in cloudwater and precipitation, the scheme shown in Figure 3.16 is based on the assumption, that the total wet deposition flux  $\text{Hg}(\text{tot.})$  can be divided into a dissolved fraction  $\text{Hg}(\text{diss.})$  and a fraction adsorbed on particles  $\text{Hg}(\text{ads.})$  depicted in Figure 3.18-c and Figure 3.18-d, respectively. The very distinct pattern in these two figures clearly reflect the design of two important and sensitive parts of the scheme:

In general,  $\text{Hg}(\text{diss.})$  and  $\text{Hg}(\text{ads.})$  are based on an equilibrium relation depending on gaseous and aqueous species concentration and rate expressions (R1-R21). However, in areas of relative high  $\text{HgCl}_2$  (G(2)) concentrations in ambient air (i.e. close to major sources) the equilibrium is shifted towards a higher  $\text{Hg}(\text{diss.})$  fraction and hence a relative high  $\text{Hg}(\text{diss.})$  deposition flux as shown in Figure 3.18-d, since  $\text{HgCl}_2$  is very water soluble and the mass transfer rate of this species into the aqueous phase is much higher than the adsorption rate of aqueous  $\text{HgCl}_2$  on particles. In areas of low  $\text{HgCl}_2$  concentrations in ambient air (i. e. far from sources) the  $\text{Hg}(\text{diss.})$  and  $\text{Hg}(\text{ads.})$  equilibrium relation is more determined by  $\text{Hg}^0$  (AQ(1)) and its oxidation products and by aqueous phase reactions of  $\text{Hg}^{2+}$  (AQ(8)) leading to the formation of complexes, namely  $\text{HgCl}_2$  (AQ(2)),  $\text{HgOHCl}$  (AQ(9)) and  $\text{Hg}(\text{SO}_3)^{2-}_2$  (AQ(7)). Compared to  $\text{HgCl}_2$  the concentration level of  $\text{Hg}^0$  in ambient air is almost uniform in areas far from sources and hence the deposition pattern in these areas is mainly governed by

precipitation, but elevated  $\text{Hg}^0$  concentrations in source areas are also reflected to a certain extent (see Figure 3.17-a).

A comparison of Figure 3.17 and Figure 3.18 shows, that the total mercury deposition over Central Europe is dominated by wet deposition. The dry deposition of all mercury species, shown in Figure 3.17-d, indicates that over most of the main source areas in Central Europe the model estimated monthly dry deposition is in the range of 100 to 500  $\text{ng m}^{-2}$ , whereas the wet deposition flux (Figure 3.18-a) exceeds 1000  $\text{ng m}^{-2}$  despite relatively low precipitation amounts (less than 50 mm per month) in that area.

As an illustrative example for comparisons between model predicted and observed mercury concentrations in air, Figure 3.19 shows  $\text{Hg}^0$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{part.})$  concentrations at the German monitoring stations of Zingst and Neuglobsow, respectively. The  $\text{Hg}^0$  time series at Zingst are consistent with respect to time intervals, i.e. model predicted and observed hourly averages are compared. Observations and model predictions are in reasonable agreement. However, the model predicted time series shows some peak events with calculated hourly concentrations exceeding 3.0  $\text{ng m}^{-3}$ . Almost coinciding peaks have also been observed but on a lower level, indicating that the model is capable to simulate elevated concentrations with a tendency of over-prediction most probably due to both overestimated emissions near the measurement site and underestimated vertical exchange of air masses in the grid cell in which the measurement site is located. Calculated  $\text{Hg}(\text{part.})$  and  $\text{HgCl}_2$  concentrations at Neuglobsow are also hourly averages, whereas the observed numbers are daily and 7 hours averages, respectively, due to the constraints in current measurement techniques. The agreement between model predictions and observations is fair for  $\text{Hg}(\text{part.})$  but rather poor for  $\text{HgCl}_2$ . However, the limited data material does not allow to draw any firm conclusions at present and a larger data set comprising additional time series from other measurement sites would be needed.

### 3.5 RECOMMENDATIONS

Therefore, in order to support the implementation of the new Mercury Directive in Europe there is a great need to improve our knowledge of certain specific aspects involved in the cycling of mercury on local and regional scales, these include:

- ❑ There is a strong need to promote measurement programs to assess the level of mercury and its compounds (Hg(0), Hg(II) and particulate Hg on a European scale and at major urban, industrial and remote sites.
- ❑ An improved mercury emission inventory for major anthropogenic sources, possibly on a 0.5 x 0.5 degree spatially resolved grid including North Africa and the Middle East regions.
- ❑ The role played by sea salt aerosol and sea spray formation in the cycling of mercury and its compounds in the MBL.
- ❑ Gas phase mercury and halogen containing radical kinetic studies.
- ❑ Exchange fluxes of gaseous mercury at the air-water, air-soil and air-vegetation interfaces with changing meteorological conditions and geophysical parameters.
- ❑ A better knowledge of the time-dependent vertical profile of Hg(0) concentrations at the model inflow boundaries in order to improve the modeling capability.
- ❑ To assess the relationship between the atmospheric input of mercury and its compounds to surface waters and the formation/production of the most toxic organic forms of mercury i.e., methylmercury, which have a significant impact on human health and the quality of the environment.
- ❑ There is a strong need to develop hemispherical/global models for a better assessment of the boundary conditions on regional scale.
- ❑ Intercomparison of the three modeling techniques currently used in Europe for assessing the spatial and temporal distribution of mercury and its compounds and to evaluate the relative contribution of each emission source category to the ambient level and deposition flux of mercury to terrestrial and aquatic receptors.

### 3.6 REFERENCES

- Andreas E. L., Edson J. B., Monahan E.C., Rouaul M.P., Smith S.D. 1995. The Spray Contribution to Net Evaporation from the Sea: *A Review of Recent Progress, Boundary-Layer Meteorology* 72: 3-52
- Andreas E. 1992. Sea Spray and the Turbulent Air-Sea Heat Fluxes. *J. Geophys. Res.* 97: 11, 429-11,441.
- Constantinou, E., X. A. Wu, and C. Seigneur, Development and application of a reactive plume model for mercury emissions, *Water Air Soil Pollut.*, 80, 325-335, 1995.
- Cossa, D., Coquery, M., Gobeil, C., and Martin, J.-M., (1996) Mercury fluxes at the ocean margins. In C.J. Watras and J.W. Huckabee (eds.), *Mercury as a Global Pollutant: Towards Integration and Synthesis*, Lewis Publishers, pp. 229-247.
- Crank, J., *The Mathematics of Diffusion*, 2nd ed., Oxford Univ. Press, New York, 1975.
- Dentener, F. J., and P. J. Crutzen, Reaction of  $\text{N}_2\text{O}_5$  on tropospheric aerosols: Impact on the global distributions of  $\text{NO}_x$ ,  $\text{O}_3$ , and OH, *J. Geophys. Res.*, 98 (D4), 7149-7163, 1993.
- Draxler, R. R. and Hess G. D. (1998) An overview of the HYSPLIT\_4 modelling system for trajectories, dispersion and deposition. *Aust. Met. Mag.* (1998) 295-308
- Dunker, A. M., The Direct Decoupled Method for calculating sensitivity coefficients in chemical kinetics, *J. Chem. Phys.*, B1(5), 2385-2393, 1984.
- Engstrom, D. R., E. B. Swain and M. E. Brigham, paper presented at International Conference on Mercury as a Global Pollutant, Whistler, British Columbia, 1994
- ERT (1984) ADOM/TADAP Model Development Program, Vols. 1-8. ERT No. P-B980-535, July 1984, Environmental Research and Technology, Inc., Newbury Park, California 91320, USA.
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N., (2000) Temporal trends in gaseous mercury evasion from the Mediterranean Sea Waters. *Sci. Tot. Environ.* 259, 183-190.
- Forlano, L., Hedgecock, I., Pirrone, N. (2000) Elemental Gas Phase Atmospheric Mercury as it Interacts with the Ambient Aerosol and its Subsequent Speciation and Deposition. *Science of the Total Environment*, 259, 211-222.
- Ge, Z., A. S. Wexler and M. V. Johnston, Deliquescence behavior of multicomponent aerosols, *J. Phys. Chem A.*, 102, 173-180, 1998.
- Gear C. W., *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice-Hall, Englewood Cliffs, N.J., 1971.
- Hedgecock I. and Pirrone N., (2001), Mercury and photochemistry in the marine boundary layer - modelling studies suggest the in situ production of reactive gas phase mercury, *Atmos. Environ.*, 35, 3055-3062.
- Hindmarsh, A. C., LSODE and LSODI, two new initial value ordinary differential equation solvers, *ACM Sigsum Newsl.*, 15, 10, 1980.
- Izrael Yu.A., Mikhailova J.E. and A.Ja. Pressman [1980] The model for operational calculations of transboundary fluxes of anthropogenic pollution (sulphur dioxide and sulphates) Reports of the USSR Academy of Sciences v.253, N 4, pp.848-852 (in Russian).

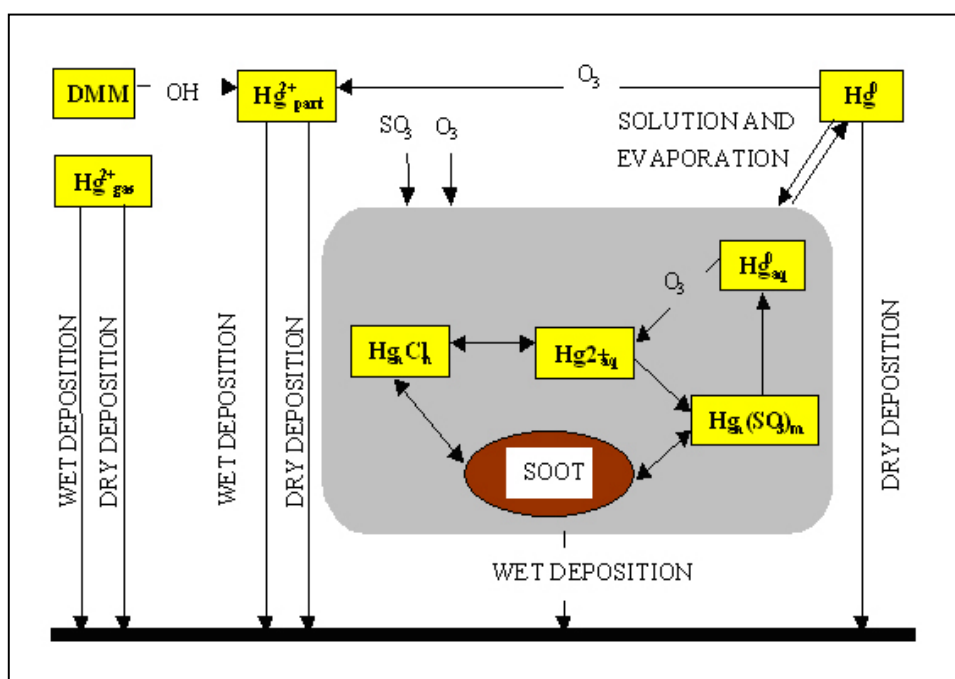
- Jacob, D. J., Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *J. Geophys. Res.* 91 (D9), 9807-9826, 1986.
- Keeler, G., G. Glinsorn and N. Pirrone, Particulate mercury in the atmosphere: its significance, transport, transformation and sources, *Water Air Soil Pollut.*, 80, 159-168, 1995.
- Leis, J. R., and M. A. Kramer, An ordinary differential equation solver with explicit simultaneous sensitivity analysis, *Trans. Math. Software*, 14, 61-67, 1988.
- Lin, C., and S. O. Pehkonen, Aqueous free radical chemistry of mercury in the presence of iron oxides and ambient aerosol, *Atmos. Environ.*, 31, 4125-4137, 1997.
- Lin, C., and S. O. Pehkonen, Two-phase model of mercury chemistry in the atmosphere, *Atmos. Environ.*, 32, 2543-2558, 1998.
- Lockhart, W. L., Implications of chemical contaminants for aquatic animals in the Canadian Arctic: Some review comments, *Sci. Total Environ.*, 160-161, 631-641, 1995.
- Misra P. K., Bloxam R., Fung C. and Wong S. (1989) Non-linear response of wet deposition to emission reductions: A case study. *Atmospheric Environment*. **23**, 671-687.
- Massman, W. J., Molecular diffusivities of Hg vapor in air, O<sub>2</sub> and N<sub>2</sub> near STP and kinematic viscosity and thermal diffusivity of air near TSP, *Atmos. Environ.*, 33 453-457, 1999.
- Munthe, J., Wangberg, I., Pirrone, N., Iverfeld, A., Ferrara, R., Ebinghaus, R., Feng, R., Gerdelt, K., Keeler, G.J., Lanzillotta, E., Lindberg, S.E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroder, W.H., Sommar, J., Sprovieri, F., Stevens, R.K., Stratton, W., Tuncel, G., Urba, A. (2001) Intercomparison of Methods for Sampling and Analysis of Atmospheric Mercury Species. *Atmos. Environ.*, 35, 3007-3017.
- Olendrzynski K. [1999] Operational EMEP Eulerian Acid Deposition Model. EMEP/MS-CW Note 4/99. Norwegian Meteorological Institute, Oslo, Norway.
- Pacyna J. M. and Pacyna E. P. (2000) Assessment of emissions/discharges of mercury reaching the Arctic Environment. The Norwegian Institute for Air Research, NILU Report OR 7/2000, Kjeller, Norway.
- Pacyna, E., Pacyna, J.M. and Pirrone, N. (2001) Atmospheric Mercury Emissions in Europe from Anthropogenic Sources. *Atmos. Environ.*, **35**, 2987-2996.
- Pandis, S. N., A. S. Wexler, and J. H. Seinfeld, Dynamics of tropospheric aerosols, *J. Phys. Chem.*, 99, 9646-9659, 1995. Pankow, J. F., Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, *Atmos. Environ.*, 21, 2275-2283, 1987.
- Pankow, J. F., An absorption model of gas/particle partitioning of organic compounds in the atmosphere, *Atmos. Environ.*, 28, 185-188, 1994.
- Pekar M. [1996] Regional models LPMOD and ASIMD. Algorithms, parametrization and results of application to Pb and Cd in Europe scale for 1990. MSC-E/EMEP, Technical Report 9/96.
- Pehkonen, S. O., and C. Lin, Aqueous photochemistry of mercury with organic acids, *J. Air Waste Manage. Assoc.*, 48, 144-150, 1998.
- Petersen G., Iverfeldt A. and Munthe J. (1995) Atmospheric mercury species over Central and Northern Europe. Model calculations and comparison with measurements from the

- Nordic air and precipitation network for 1987 and 1988. *Atmospheric Environment*, **29**, 47-67.
- Petersen G., Munthe J., Pleijel K., Bloxam R. and Kumar A. V. (1998) A comprehensive Eulerian modeling framework for airborne mercury species: Development and testing of the tropospheric chemistry module (TCM). *Atmospheric Environment*, **32**, 829-843.
- Pirrone, N., Glinsorn, G. and Keeler, G.J. (1995) Ambient Levels and Dry Deposition Fluxes of Mercury to Lakes Huron, Erie and St. Clair. *Water, Air and Soil Pollution*, **80**, 179-188.
- Pirrone, N. (1998) Modeling the dynamics of atmospheric mercury over the Mediterranean Sea: The MAMCS project, *J. Aerosol Sci.*, **29**, 1155-1156.
- Pirrone, N., G. J. Keeler, and T. M. Holsen (1995a) Dry deposition of trace elements over Lake Michigan: A hybrid receptor-deposition modeling approach. *Environ. Sci. Technol.*, **29**, 2112-2122.
- Pirrone, N., G. J. Keeler, and T. M. Holsen (1995b) Dry deposition of semivolatile organic compounds to Lake Michigan. *Environ. Sci. Technol.*, **29**, 2123-2132.
- Pirrone, N. and Keeler, G.J (1996) Modeling Atmospheric Deposition and Gas Exchange of Hazardous Air Pollutants to Lake Michigan. In: *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*, J. Baker (Editor), A Special Publication of the Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Chapter 7, pp.137-150.
- Pirrone, N., Hedgecock, I.M. and Forlano L. (2000) Role of the Ambient Aerosol in the Atmospheric Processing of semi-volatile contaminants: A parameterized numerical model (GASPAR), *Journal of Geophys. Res.*, **105**, D8, 9773-9790.
- Pirrone, N., Pacyna, J., Munthe, J., Kallos, G., Mamane, Y., Ferrara, R. (2000a) Mediterranean Atmospheric Mercury Cycle System (MAMCS)-Final Technical Report. EU-DG Research-Environment and Climate Programme, Brussels, Belgium.
- Pirrone, N. (2001) Mercury Research in Europe: Towards the preparation of the New EU Air Quality Directive. *Atmos. Environ.*, **35**, 2979-2986.
- Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R. (2001) Atmospheric mercury emissions from anthropogenic and natural sources in the Mediterranean Region. *Atmos. Environ.*, **35**, 2999-3006.
- Pleijel K. and Munthe J., (1995), Modeling the atmospheric mercury cycle - chemistry in fog droplets, *Atmospheric Environment*, **29**, 1441-1457
- Pruppacher, H. R., and J. D. Klett, *The Microphysics of Clouds and Precipitation*, 2nd ed., Kluwer Acad., Norwell, Mass., 1997.
- Rasmussen, P.E. (1994) Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* **28**, 2233-2241.
- Rounds, S. A., and J. F. Pankow, Application of a radial diffusion model to describe gas/particle sorption kinetics, *Environ. Sci. Technol.*, **24**, 1378-1386, 1990.
- Ryaboshapko A. and V.Korolev [1997] Mercury in the atmosphere: estimates of model parameters. Meteorological Synthesizing Centre - East, EMEP/MSC-E Report 7/97, August 1997, Moscow, 60 p.

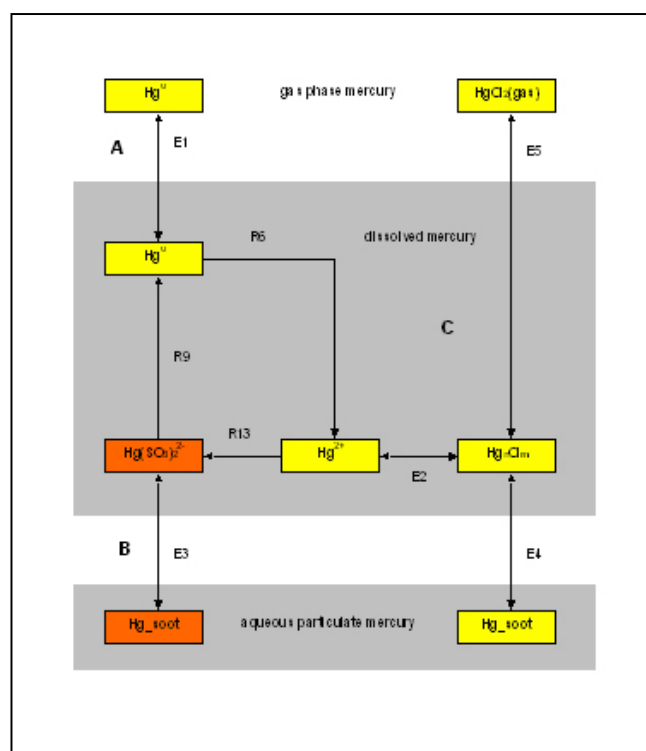
- Ryaboshapko A., Ilyin I., Gusev A. and Afinogenova O. (1998) Mercury in the atmosphere of Europe: Concentrations, deposition patterns, transboundary fluxes. EMEP Meteorological Synthesizing Center-East, EMEP/MSC-E Report 7/98.
- Ryaboshapko A., Ilyin I., Gusev A., Afinogenova O., Berg T. and A.G. Hjellbrekke [1999] Monitoring and modelling of lead, cadmium and mercury transboundary transport in the atmosphere of Europe. Joint report of EMEP centers MSC-E and CCC. MSCE report No 1/99, 1999
- Schroeder, W.H., Munthe, J., Lindqvist, O., (1989) Cycling of mercury between water, air and soil components of the environment. *Water, Air and Soil Pollut.* **48**, pp. 337-347.
- Seigneur, C., H. Abeck, G. Chia, M. Reinhard, N. S. Bloom, E. Prestbo, and P. Saxena, Mercury adsorption to elemental carbon (soot) particles and atmospheric particulate Matter, *Atmos. Environ.*, **32**, 2649-2657, 1998.
- Seinfeld, J. H., *Atmospheric Physics and Chemistry of Air Pollution*, John Wiley, New York, 1986.
- Shampine, L. F., and H. A. Watts, DEPAC - Design of a user oriented package of ODE solvers, *SAND-79-2374*, Sandia National Laboratory Report, 1979.
- Shannon, J. D., and E. A. Voldner, Modeling atmospheric concentrations of mercury and deposition to the Great Lakes, *Atmos. Environ.*, **29** (14), 1649-1661, 1995.
- Sprengard-Eichel, C., M. Kramer, and L. Schutz, Soluble and insoluble fractions of urban, continental and marine aerosol, *J. Aerosol Sci.*, **29** suppl. 1, S175-S176, 1998.
- Samarsky A. A. [1977] Theory of difference schemes. "Nauka", Moscow, 656 ps. (in Russian).
- Simpson D., Olendrzynski K., Semb A., Storen E. and S.Unger [1997] Photochemical oxidant modelling in Europe: multi-annual modelling and source-receptor relationships. Report of EMEP/MSC-W 3/97.
- Sommar J., Gardfeldt K., Stromberg D. and Feng X., (2001), A Kinetic Study of the Gas-Phase Reaction between the Hydroxyl Radical and Atomic Mercury, *Atmospheric Environment*, in press.
- Trombino, G., Forlano L., Hedgecock, I. M. and Pirrone, N. (2000) The Role of Water Wave Dynamic Processes in the Exchange of Gaseous Mercury at the Air-Sea Interface. In the Proceedings of the 25<sup>th</sup> *International Conference on Heavy Metals in the Environment*, 6-10 August, Ann Arbor, MI, USA.
- U.S. Environmental Protection Agency. Mercury study report to Congress. *EPA-452/R-97-003*, Off. of Air Qual. Plann. and Stand. and Off. of Res. and Dev., Washington, D. C., 1997.
- Venkatram A., Karamchandani P. and Misra P. K. (1988) Testing a comprehensive acid deposition model. *Atmospheric Environment*. **22**, 2717 – 2732.
- Wängberg, I., Munthe, J., Pirrone, N., Iverfeldt, Å., Bahlman, E., Costa, P., Ebinghaus, R., Feng, X., Ferrara, R., Gårdfeldt, K., Kock, H., Lanzillotta, E., Mamane, Y., Mas, F., Melamed, E., Osnat, Y., Prestbo E., Sommar, J., Schmolke, S., Spain, G., Sprovieri, F., Tuncel, G. (2001) Atmospheric Mercury Distributions in North Europe and in the Mediterranean Region. *Atmospheric Environment* **35**, 3019-3025.
- Wexler, A. S., F. W. Lurmann, and J. H. Seinfeld, Modeling urban and regional aerosols, 1, Model development, *Atmos. Environ.*, **28**, 531-546, 1994.



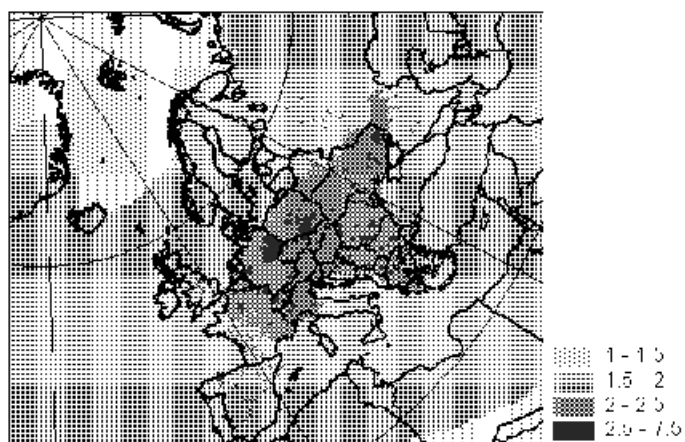
- Wild, O., X. Zhu and M.J. Prather (2000), Fast –J: Accurate simulation of in and below-cloud photolysis in tropospheric Chemical Models, *J. Atmos. Chem.*, 37, 245 – 282.
- Wilke, C. R., and C. Y. Lee, Estimation of diffusion coefficients fog gases and vapors, *Ind. and Eng. Chem.*, 47, 1253, 1955.
- Wu J. 1993. Production of Spume Drops by the Wind Tearing of Wave Crest: The Research for Quantification. *J. of Geophys. Researc.* 98: 18,221-18,227.
- Wu, S., and P. M. Gschwend, Sorption kinetics of hydrophobic organic compounds to natural sediments and soil, *Environ. Sci. Technol.*, 20, 717-725, 1986.
- Yamasaki, H., K. Kuwata, and H. Miyamoto, Effects of temperature on aspects of airborne polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, 16, 189-194, 1982.
- Xiao, Z., Munthe, J., Schroeder, WH., Lindqvist, O., (1991) Vertical fluxes of mercury over forest soil and lake surfaces in Sweden. *Tellus*, **43 B**, pp.267-279.



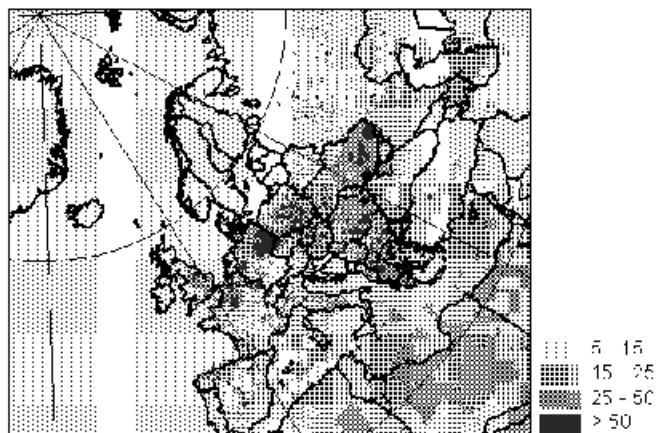
**Figure 3.1 - MSC-E mercury scheme.**



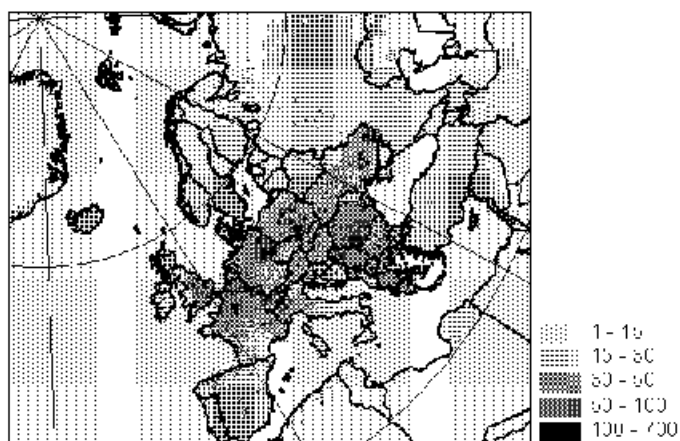
**Fig. 3.2** - MSC-E mercury chemistry scheme.



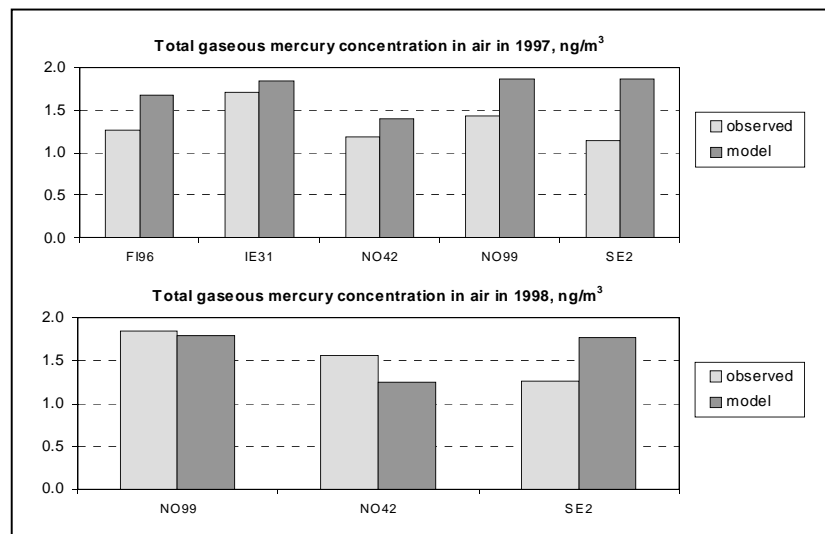
**Figure 3.3 - Gaseous mercury concentration in air 1998. [ $\text{ng m}^{-3}$ ]**



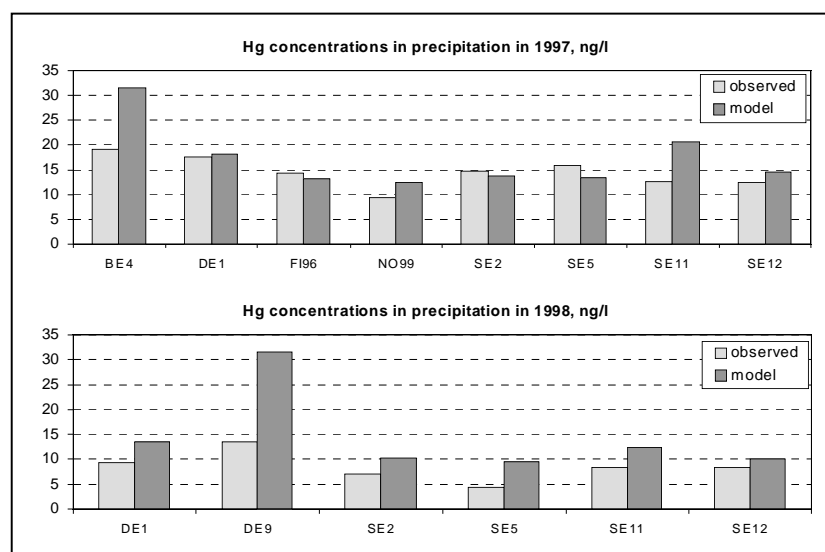
**Figure 3.4 - Mercury concentration in precipitation 1998. [ $\text{ng L}^{-1}$ ]**



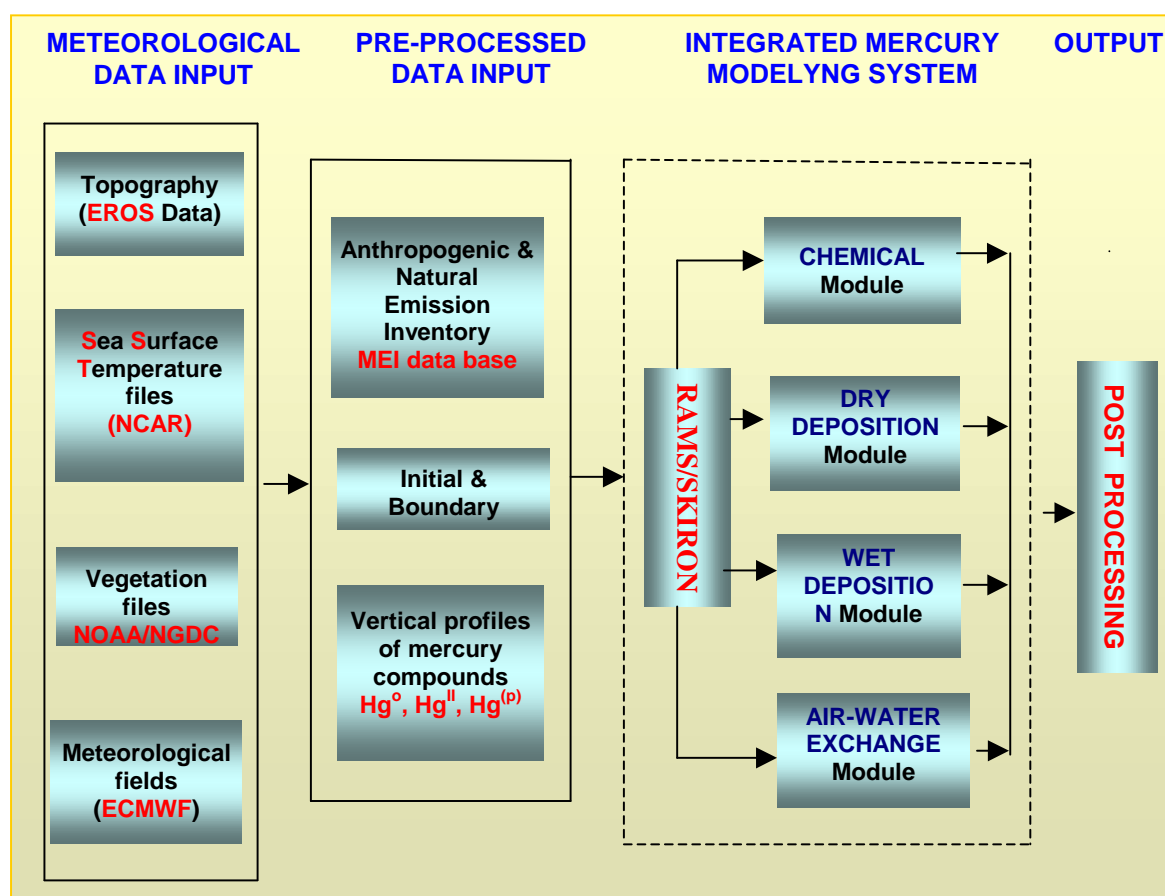
**Figure 3.5 - Mercury total deposition flux 1998 [ $\text{g km}^{-2} \text{a}^{-1}$ ].**



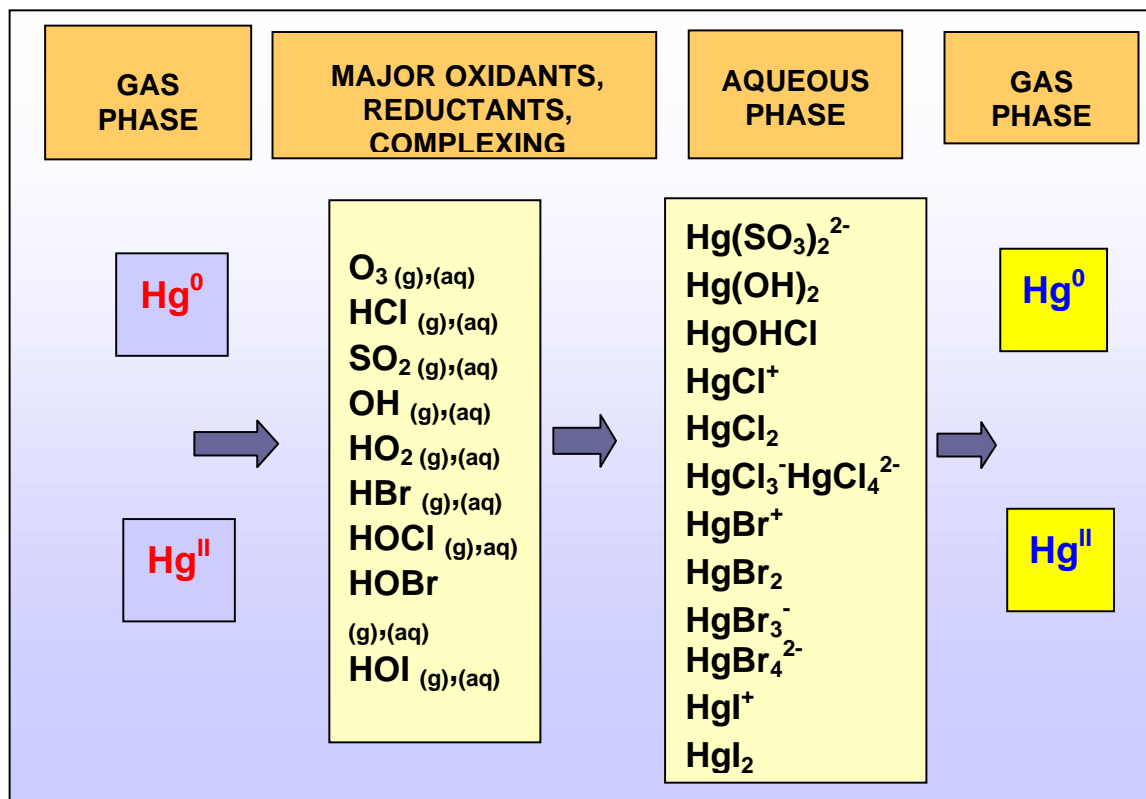
**Figure 3.6** - Observed and calculated annual means of mercury concentrations in ambient air 1997 and 1998.



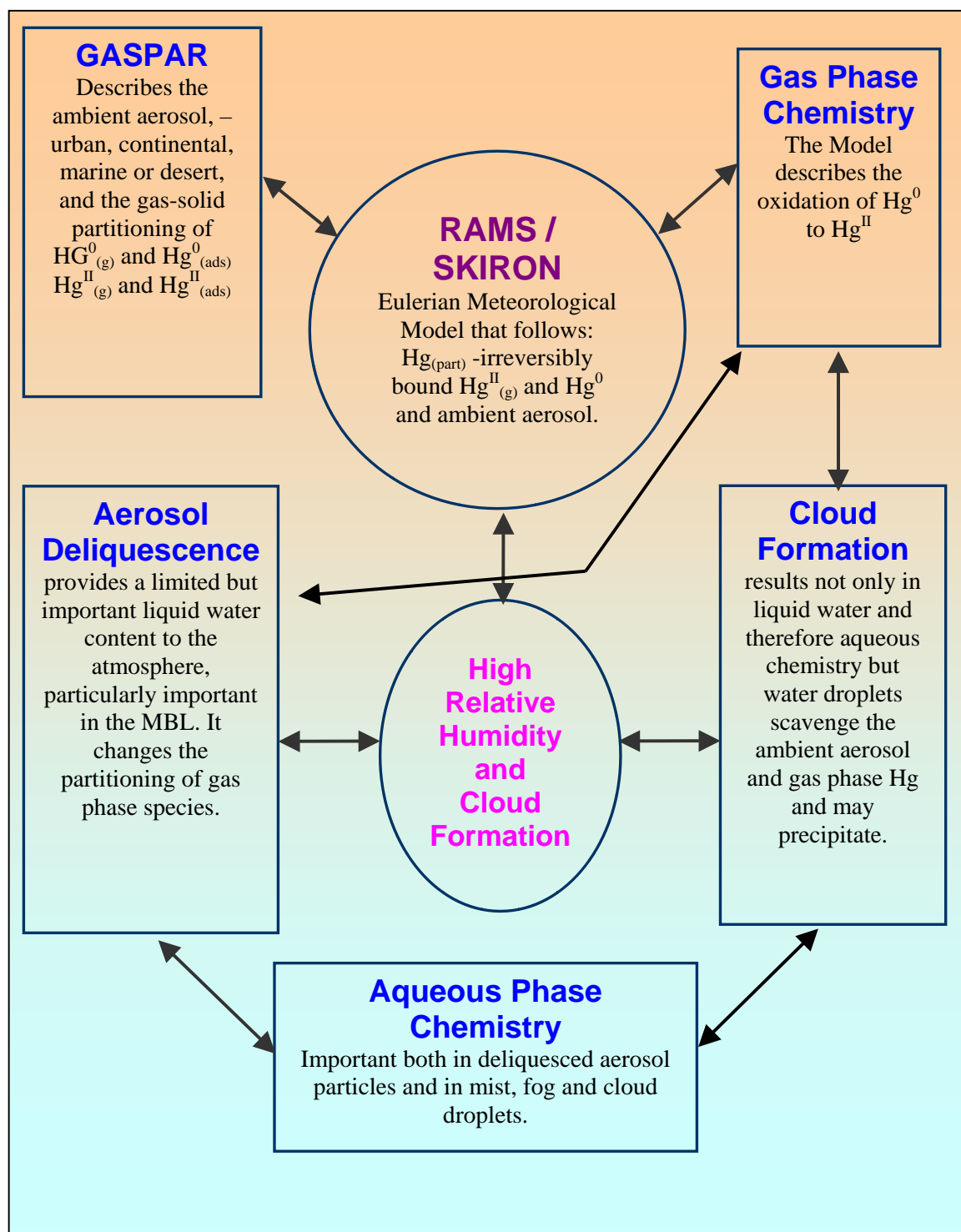
**Figure 3.7** - Observed and calculated annual means of mercury concentration in precipitation 1997 and 1998.



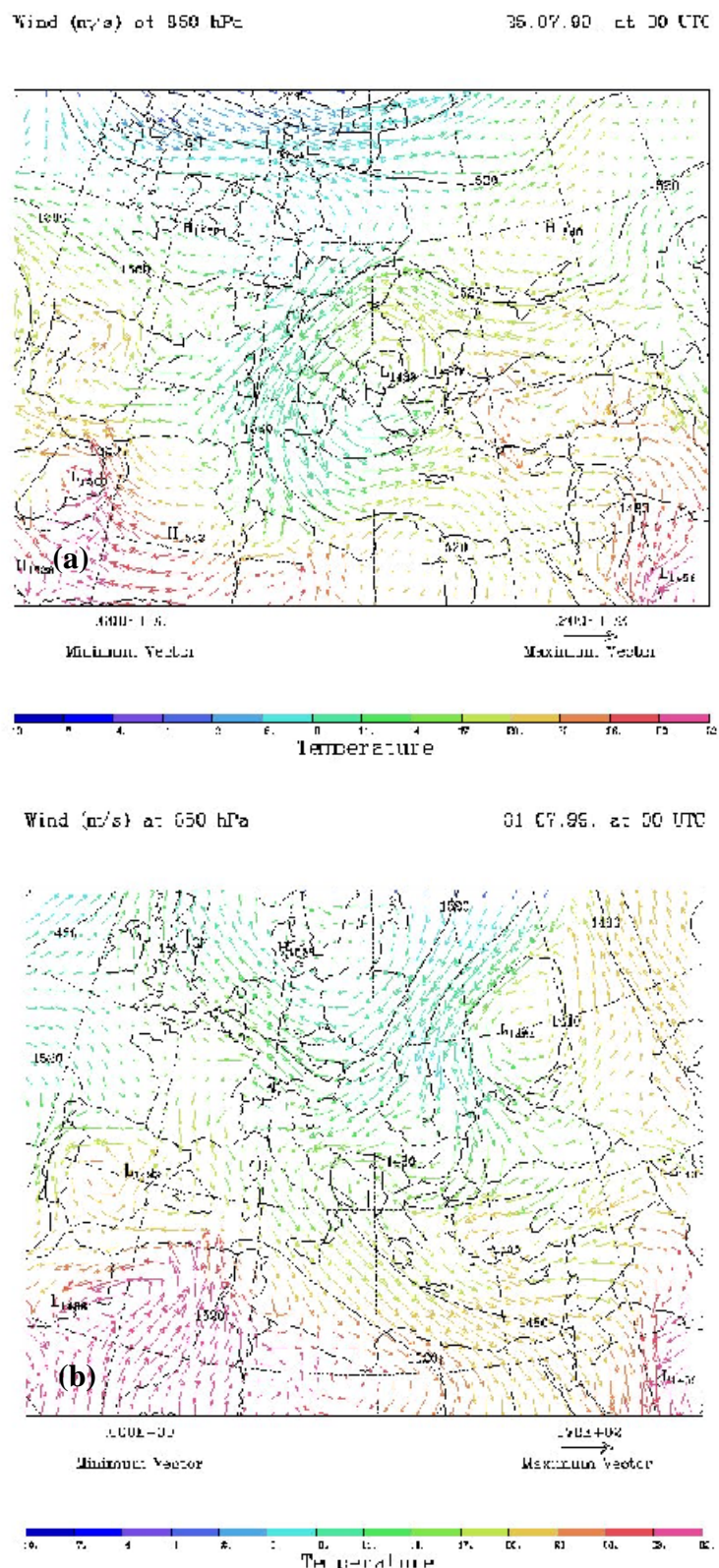
**Figure 3.8** - Integrated MAMCS framework developed for the Mediterranean region (Pirrone et al. 2000a).



**Figure 3.9** - Major chemical and physical processes considered in the chemical module of the MAMCS modeling system (Pirrone et al. 2000a).



**Figure 3.10** - Conceptual scheme showing major major links between chemical and physical process modules and RAMS e/o SKIRON meteorological systems in the overall MAMCS architecture (Pirrone et al. 2000a; Hedgecock and Pirrone 2001).



**Figure 3.11** - Example of the MAMCS modeling framework results (Pirrone et al. 2000a) Horizontal plot of geopotential heights and total winds at 850mb on 25 July **(a)** and 31 July **(b)**; Modelled ambient concentrations of  $\text{Hg}^0$  on July 22 **(c)** and July 25 **(d)**;  $\text{Hg}^{\text{II}}$  on July 22 **(e)** and July 20 **(f)** and  $\text{Hg}^{\text{P}}$  on July 28 **(g)** (Pirrone et al. 2000a).



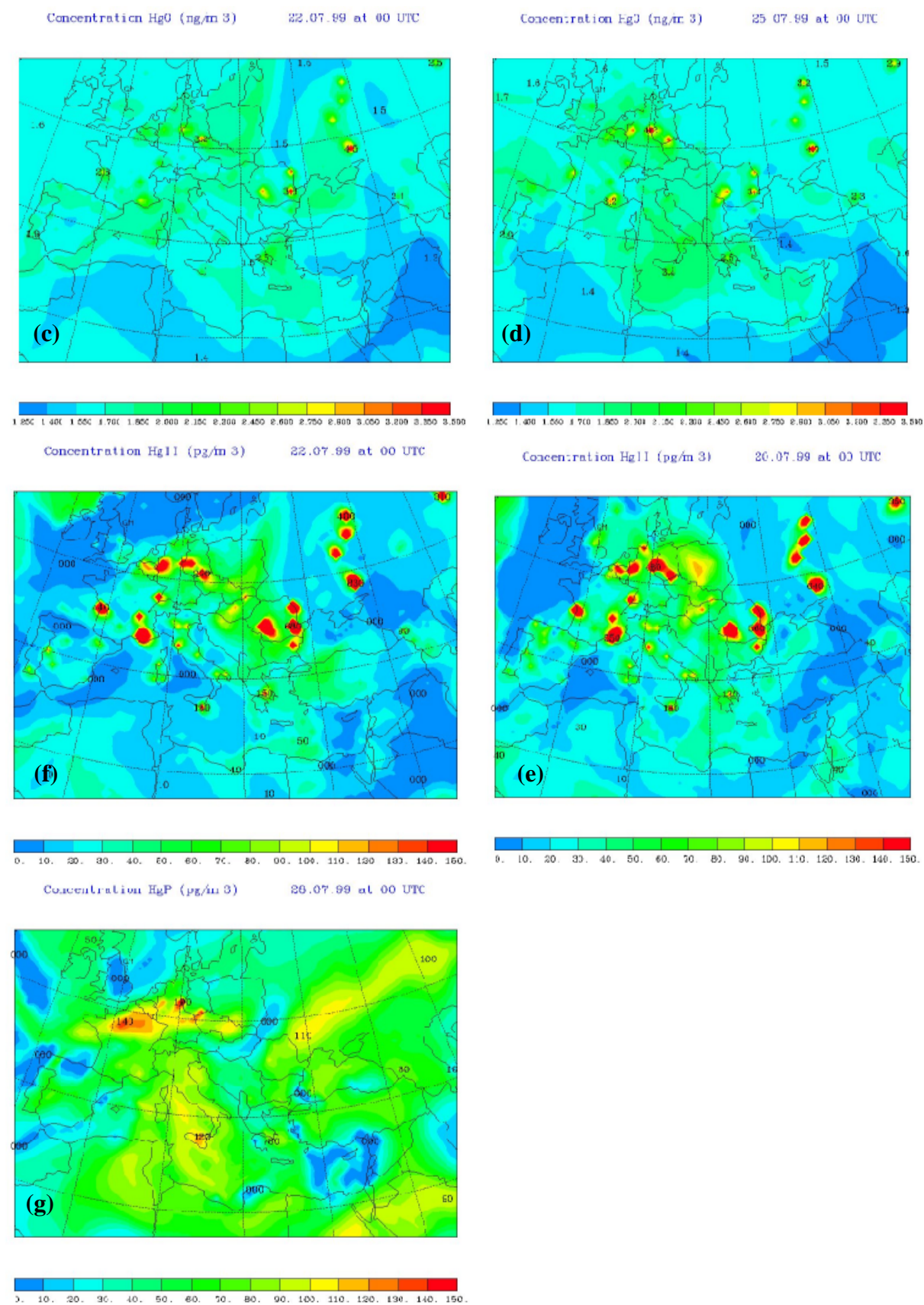
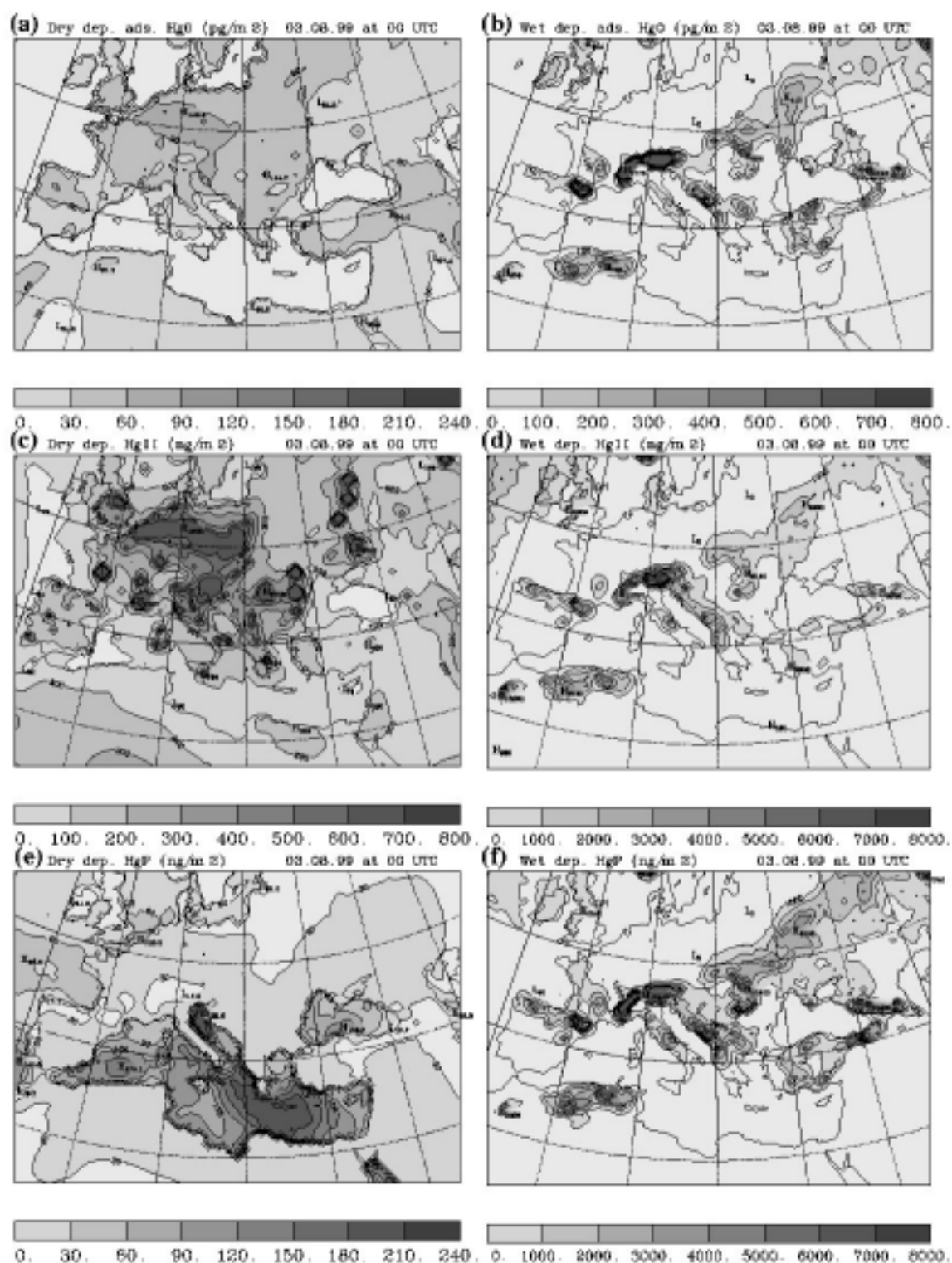
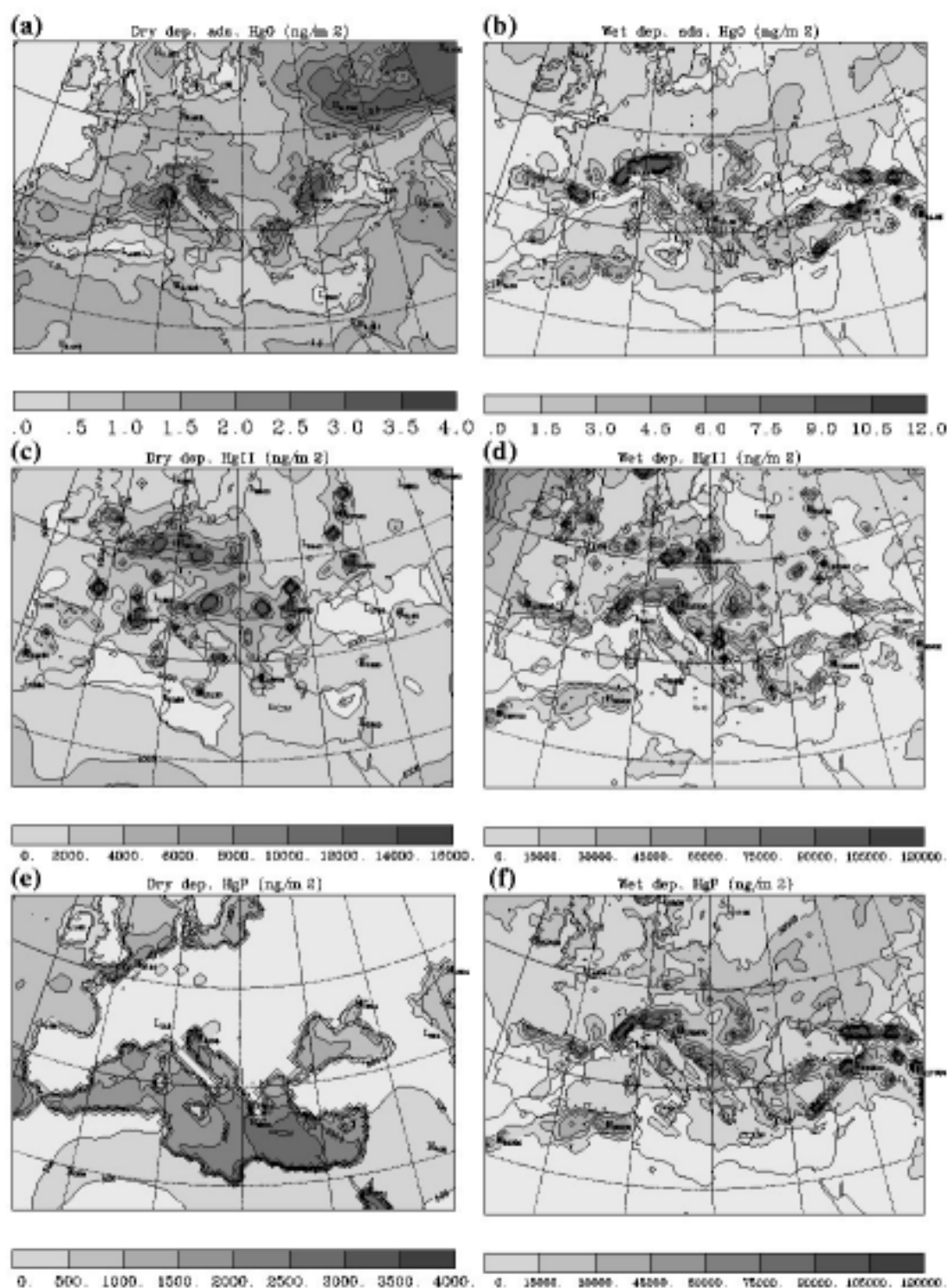


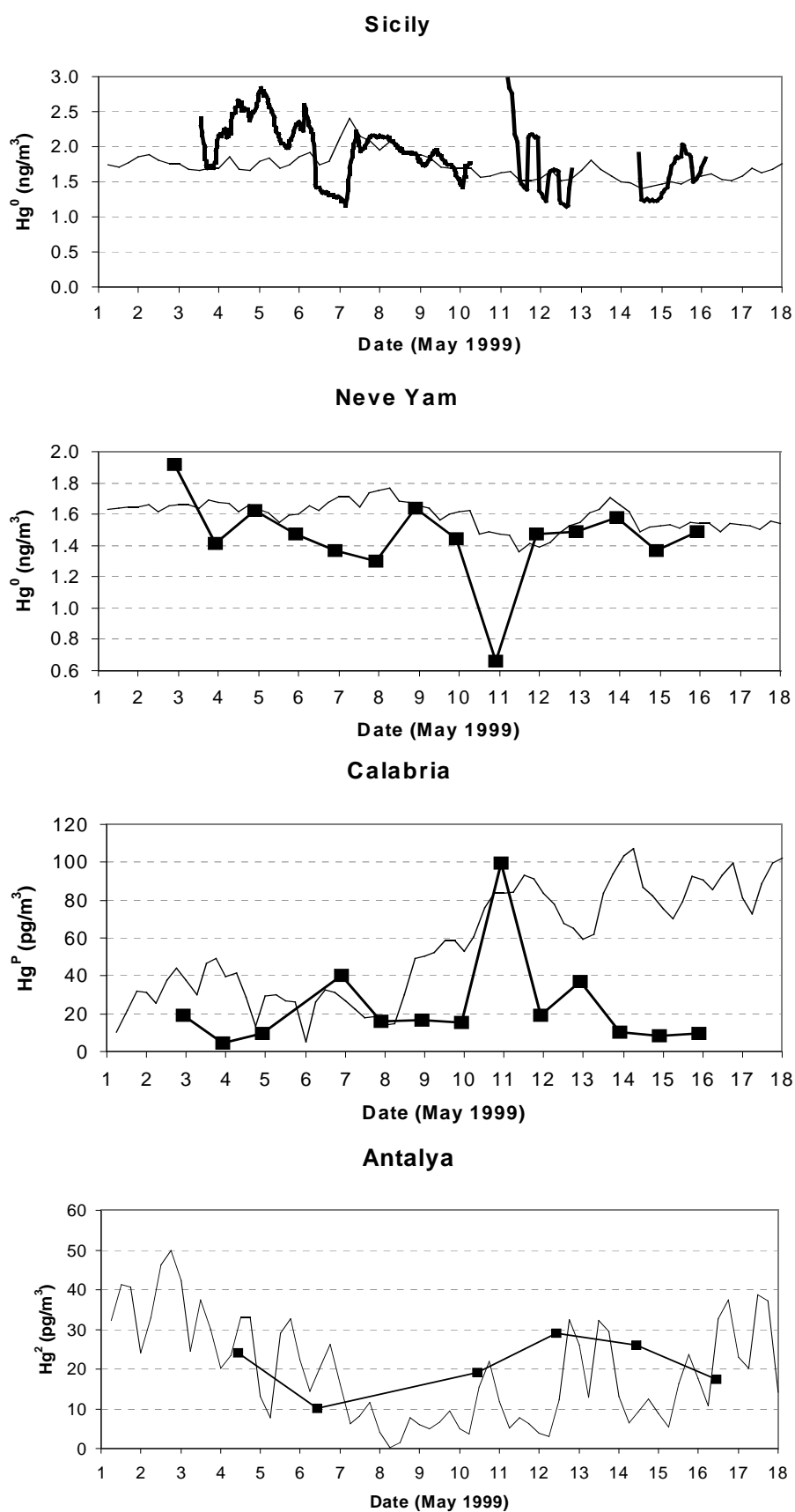
Figure 3.11 - cont'd.



**Figure 3.12** -Total deposition of Hg species for the Summer period (17 July - 3 Aug. 1999. **a**) Dry deposition of adsorbed  $Hg^0$  (pg/m<sup>2</sup>), **b**) wet deposition of adsorbed  $Hg^0$  (pg/m<sup>2</sup>), **c**) dry deposition of  $Hg^{II}$  (ng/m<sup>2</sup>), **d**) wet deposition of  $Hg^{II}$  (ng/m<sup>2</sup>), **e**) dry deposition of  $Hg^P$  (ng/m<sup>2</sup>), and **f**) wet deposition of  $Hg^P$  (ng/m<sup>2</sup>) (from the MAMCS systems based SKIRON/Eta meteorological model) (Pirrone et al. 2000a).



**Figure 3.13** -Total annual deposition of Hg species **a)** Dry deposition of adsorbed  $\text{Hg}^0$  ( $\text{ng/m}^2$ ), **b)** wet deposition of adsorbed  $\text{Hg}^0$  ( $\text{ng/m}^2$ ), **c)** dry deposition of  $\text{Hg}^{\text{II}}$  ( $\text{ng/m}^2$ ), **d)** wet deposition of  $\text{Hg}^{\text{II}}$  ( $\text{ng/m}^2$ ), **e)** dry deposition of  $\text{Hg}^{\text{P}}$  ( $\text{ng/m}^2$ ), and **f)** wet deposition of  $\text{Hg}^{\text{P}}$  ( $\text{ng/m}^2$ ) (from the MAMCS systems based on the SKIRON/Eta meteorological model) (see for details Pirrone et al.2001a) (Pirrone et al. 2000a).



**Figure 3.14** - Modelled vs. measured ambient concentrations of TGM,  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^{\text{P}}$  at five MAMCS sites. (Pirrone et al. 2000a).

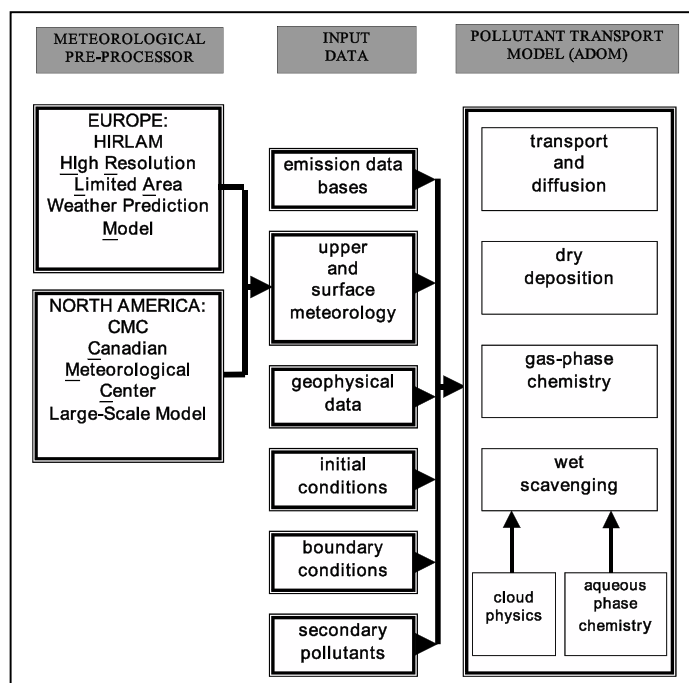


Figure 3.15 - ADOM modules and input parameters.

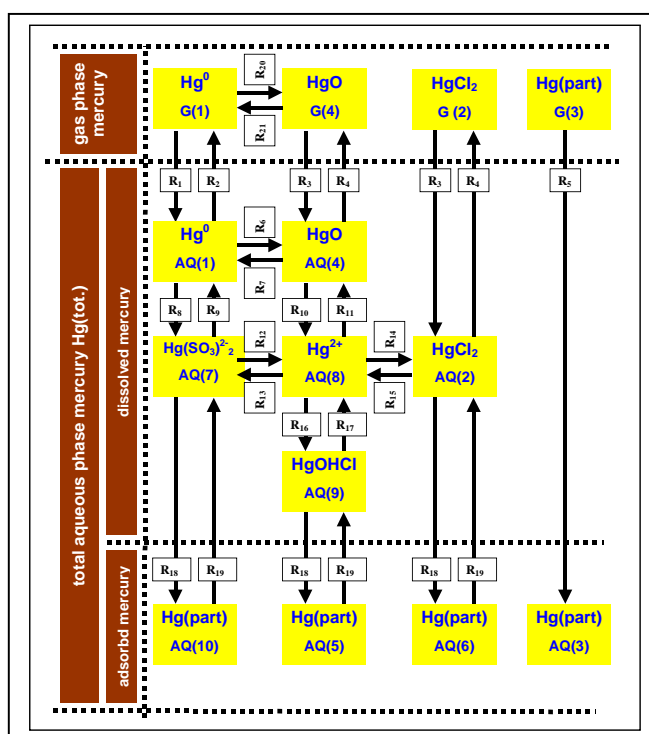
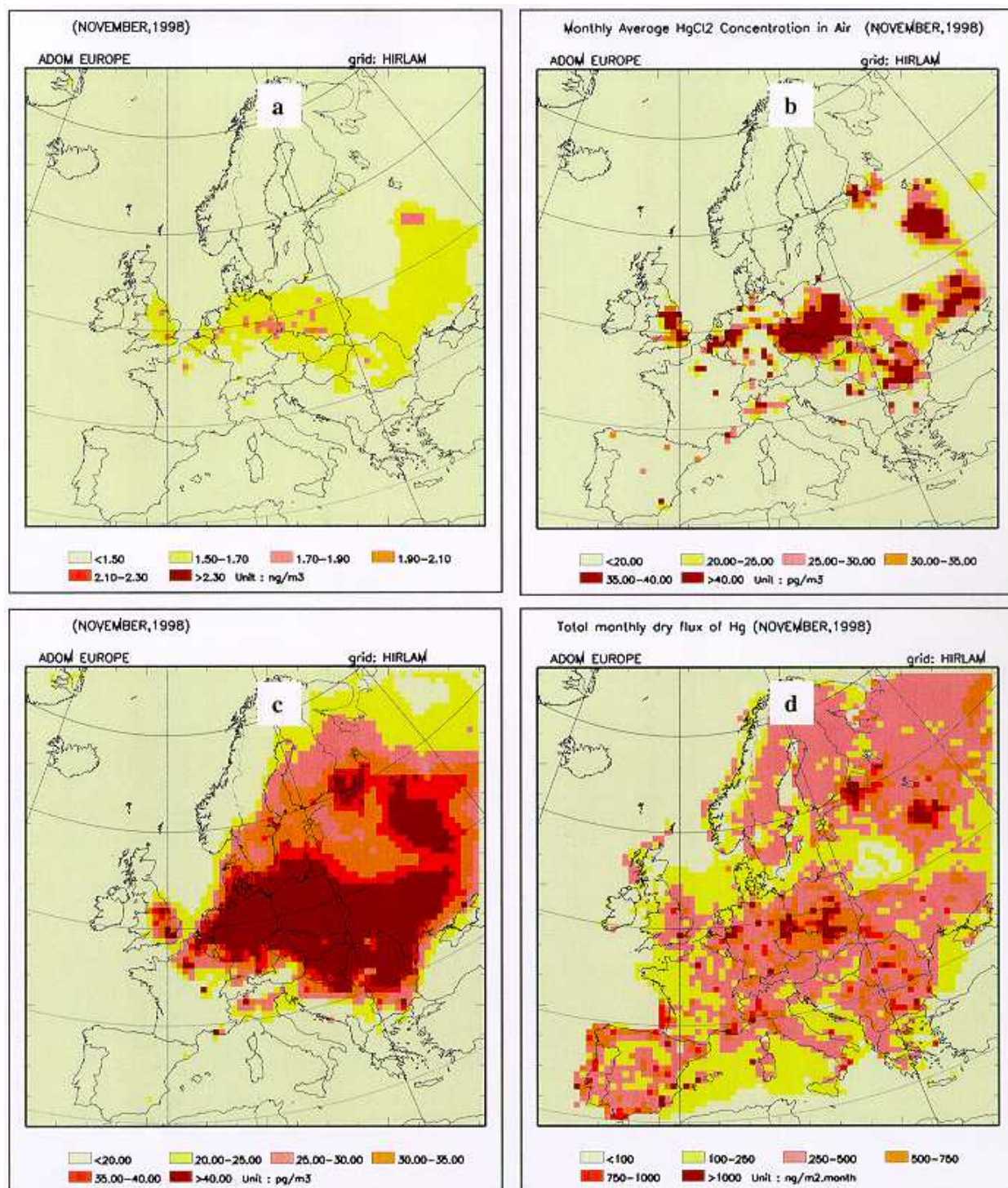


Figure 3.16 - The chemistry scheme used with the ADOM model.



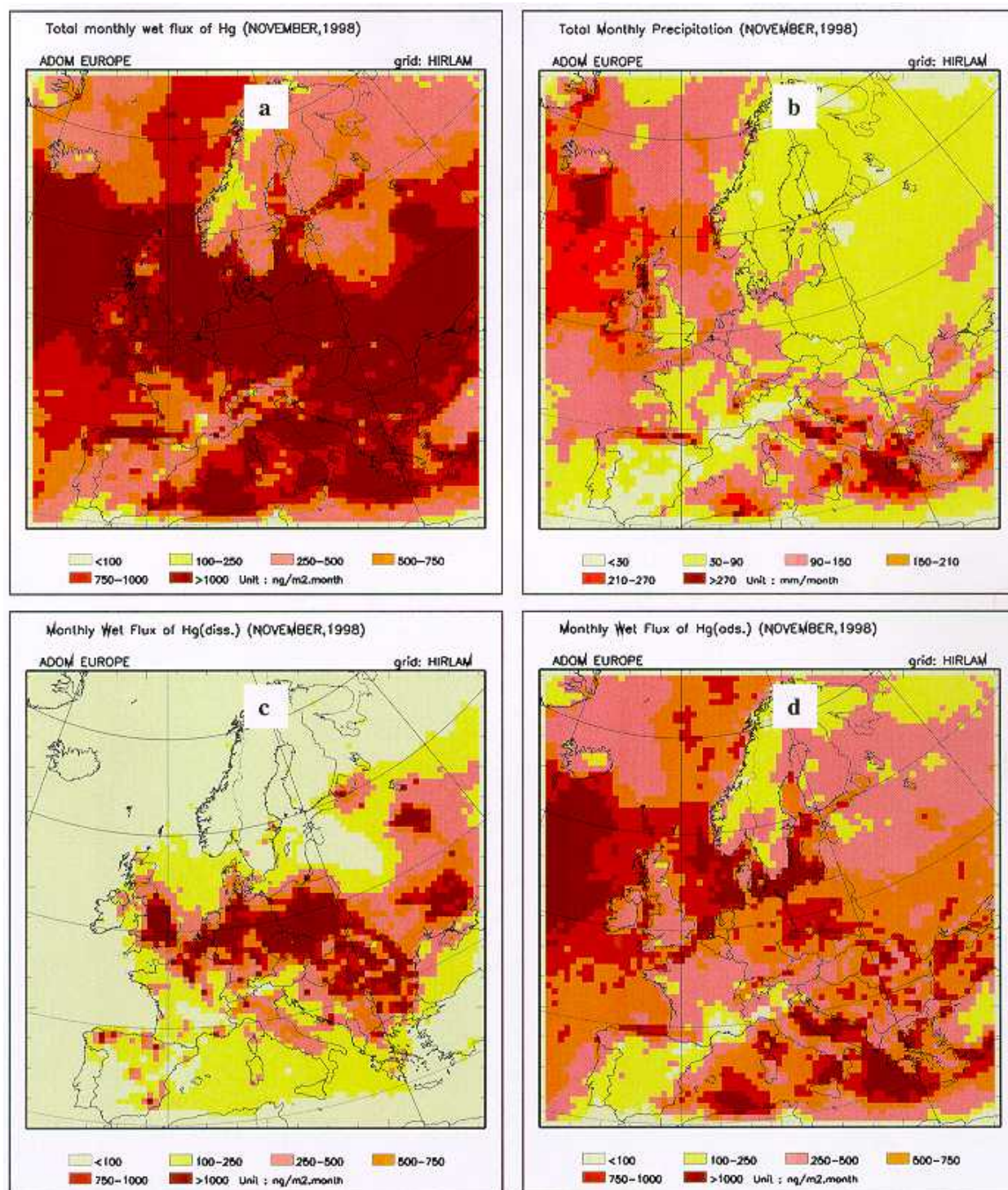


**Figure 3.17 - Monthly average concentration in ambient air and dry deposition flux predicted by ADOM (November 1998).**

(a) elemental mercury  
(c) particulate mercury

(b) mercury chloride  
(d) total dry deposition flux

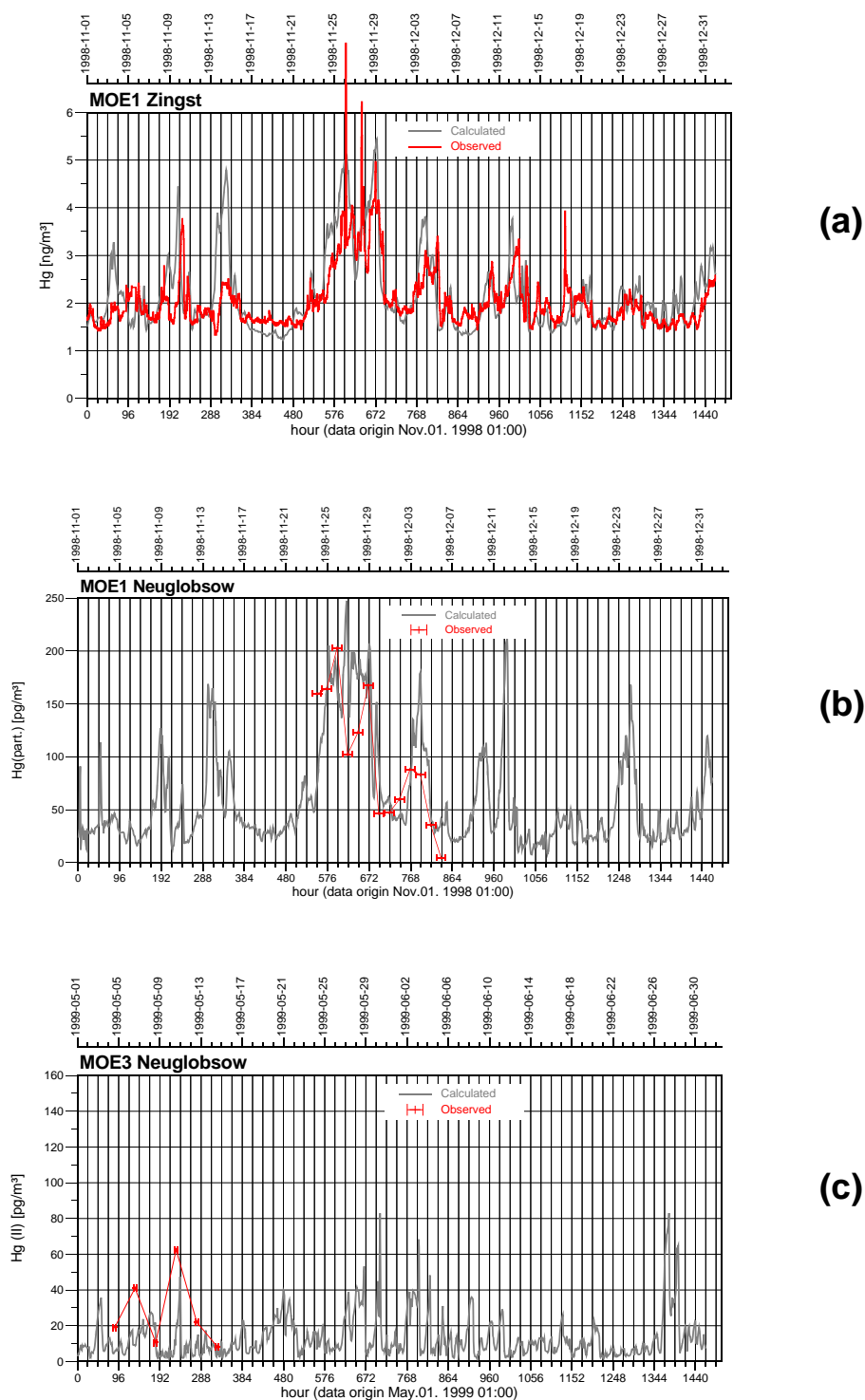




**Figure 3.18** - Monthly wet deposition fluxes and precipitation predicted by ADOM (November 1998).

(a) total wet deposition flux  
(c) wet deposition flux of dissolved species

(b) precipitation  
(d) wet deposition flux of adsorbed species



**Figure 3.19** - Time series of model predicted and observed mercury concentrations in ambient air. **(a)** hourly averages of  $\text{Hg}^0$  November 1 –December 31, 1998; **(b)** model predicted hourly averages and observed daily averages of  $\text{Hg}(\text{part.})$  November 1 –December 31, 1998; **(c)** model predicted hourly averages and observed 7 hour averages of  $\text{HgCl}_2$  (May 1 –June 30, 1999).



## **CHAPTER-4. MERCURY IN THE AMBIENT AIR**

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### **4.4 ANALYTICAL AND SAMPLING METHODS**

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## 4.1 INTRODUCTION

A particular characteristic of mercury is that it exists in the environment in a number of different chemical and physical forms (see Table 4.1) each with different behaviour in terms of transport and environmental effects (Schroeder and Munthe, 1998). Extensive research efforts have been put into the identification and quantification of these species over the last decades (Brosset, 1982; Brosset 1987; Iverfeldt, 1991; Stratton and Lindberg, 1999; Brosset and Lord, 1995).

**Table 4.1** - Physical and chemical properties of mercury and its major compounds

Property	Hg <sup>0</sup>	HgCl <sub>2</sub>	Hg <sup>0</sup>	HgS	CH <sub>3</sub> HgCl	(CH <sub>3</sub> ) <sub>2</sub> Hg
<b>Melting point (°C)</b>	-39	277	Decomp. at +500°C	584 (sublim.)	167 (sublim)	-
<b>Boiling point (°C)</b>	357 at 1 atm	303 at 1 atm	-	-	-	96 at 1 atm
<b>Vapour Pressure (Pa)</b>	0.180 at 20°C	899 x 10 <sup>-3</sup> at 20°C	9.20x10 <sup>-12</sup> at 25°C	n.d.	1.76 at 25°C	8.30 x 10 <sup>3</sup> at 25°C
<b>Water Solubility (g/l)</b>	49.4 x 10 <sup>-6</sup> at 20°C	66 at 20°C	5.3 x10 <sup>-2</sup> at 25°C	~2 x 10 <sup>-24</sup> at 25°C	~5-6 at 25°C	2.95 at 24°C
<b>Henry's Law Coefficient</b>	729 at 20°C	3.69 x 10 <sup>-5</sup>	3.76 x 10 <sup>-11</sup>	n.d.	1.6 x 10 <sup>-5 a</sup>	646 at 25°C
[Pa m <sup>3</sup> mol <sup>-1</sup> ]	0.32 <sup>a</sup>	at 20°C	at 25°C		at 15°C	0.31 <sup>a</sup>
	at 25°C				And	at 25°C
	0.18 <sup>a</sup>				pH=5.2	0.15 <sup>a</sup>
	at 5°C					at 0°C
<b>Oct.-water part. coef.</b>	4.2 <sup>a</sup>	0.5 <sup>a</sup>	-	n.d.	2.5 <sup>a</sup>	180 <sup>a</sup>

Sources: Schroeder et al. (1991) and references cited therein. <sup>a</sup> Dimensionless units.

In the atmosphere, the main three forms of Hg are: elemental Hg vapour (Hg<sup>0</sup>), Reactive Gaseous Mercury (RGM) and Total Particulate Mercury (TPM). Of these three forms, only Hg<sup>0</sup> has been tentatively identified with spectroscopic methods (Edner et al., 1989) while the other two are operationally defined species, i.e. their chemical and physical structure cannot be exactly identified by experimental methods but are instead characterised by their properties and capability to be collected by different sampling equipment. RGM is defined as water-soluble mercury species with sufficiently high vapour pressure to exist in the gas phase. The reactive term refers to the capability of stannous chloride to reduce these species in aqueous solutions without pre-treatment. The most likely candidate for RGM species is HgCl<sub>2</sub> with the possibility of other divalent mercury species being present (Schroeder and Munthe, 1998; Munthe et al. 2001).

TPM consists of mercury bound or strongly adsorbed to atmospheric particulate matter. Several different components are possible; Hg<sup>0</sup> or RGM adsorbed to the particle surface, divalent mercury species chemically bound to the particle or integrated into the particle itself (Brosset, 1987). Another species of particular interest is methylmercury (MeHg) due to the

high capacity of this species to bioaccumulate in aquatic foodchains and to its high toxicity. The presence of MeHg in the atmosphere and its importance in the overall loading of aquatic ecosystems has been demonstrated in a number of publications (Bloom and Watras, 1989; Brosset and Lord, 1995; Hultberg et al., 1994). Since MeHg is only present at low concentrations in ambient air (few  $\text{pg m}^{-3}$ ) it is not an important species for the overall atmospheric cycling of Hg (in the global mass balance), but remains an important mercury compounds to be considered in the risk assessment due to its toxicity and high capacity for bioaccumulation.

Typical concentrations of mercury and its compounds in ambient air and precipitation in Europe are reported in Table 4.2. Ambient concentrations of mercury in air may range between 1.0 to 3.6  $\text{ng m}^{-3}$  for elemental mercury, from 1 to 50  $\text{pg m}^{-3}$  for RGM and TPM whereas MeHg has been found in the range of 1 to 20  $\text{pg m}^{-3}$ . Mercury concentrations in precipitation samples depends on a number of factors primarily related to emission sources type, location of the monitoring station and meteorological conditions (i.e., frequency and intensity of precipitation events), however, typical concentrations observed at European sites were in the range of 5 to 80  $\text{ng L}^{-1}$  for total mercury, 5 to 50  $\text{pg m}^{-3}$  for RGM and TPM, whereas MeHg levels were between 0.005 and 0.5  $\text{ng L}^{-1}$ .

**Table 4.2** - Typical concentrations of mercury species in air and precipitation (\*)

Mercury species	In Air	In Precipitation ( $\text{ng L}^{-1}$ )
Total Mercury	1.2 - 3.7 ( $\text{ng m}^{-3}$ )	5 - 80
Elemental Mercury Hg(0)	1.0 - 3.6 ( $\text{ng m}^{-3}$ )	< 0.005
Reactive Gaseous Mercury (RGM)	1 - 50 ( $\text{pg m}^{-3}$ )	5 - 50
Total Particulate Mercury, TPM	1 - 50 ( $\text{pg m}^{-3}$ )	5 - 50
Methyl Mercury, MeHg	1 - 20 ( $\text{pg m}^{-3}$ )	0.005 - 0.5

(\*) Refer for details to § 4.6

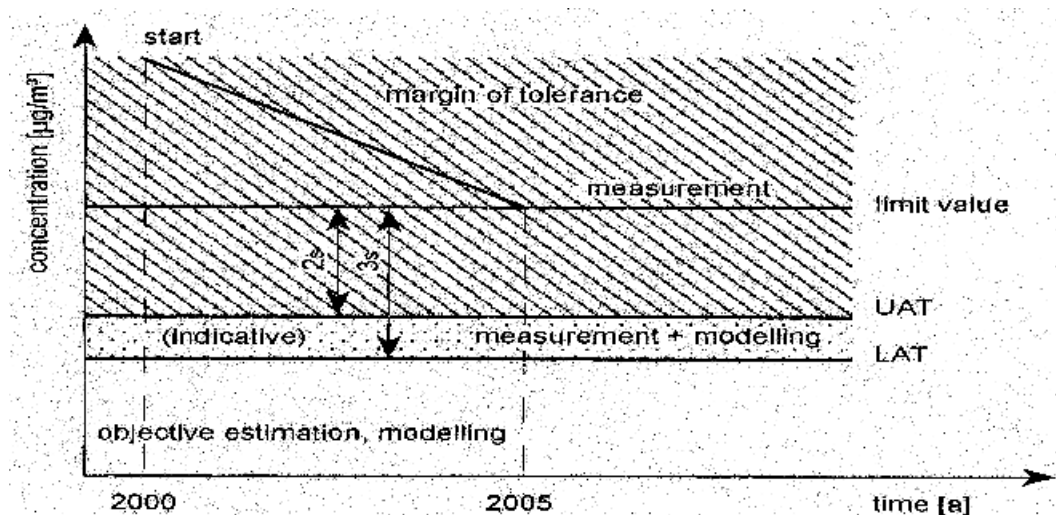
## 4.2 REQUIREMENTS OF THE FRAMEWORK DIRECTIVE

The Council Directive 96/62/EC on Ambient Air Quality Assessment and Management states in the Art. 1 that:

- the assessment of ambient air quality in member states on the basis of common methods and criteria, and
- the adequate and comprehensive information of the public, rank under important objectives of this directive.

The general strategy for the assessment of ambient air quality is mainly described in Art. 6 of the Framework Directive (FD), specific requirements have to be laid down in daughter directives. For the components SO<sub>2</sub>, NO<sub>x</sub>, PM<sub>10</sub> and Pb, this has been done in the first daughter directive, and for benzene and CO the Commission has approved the second daughter directive. In order to establish an assessment system where the subsystems for different pollutants fit as much as possible together, and in order to save costs by collocation of stations whenever possible, the requirements laid down in the first and second daughter directives present important guidance also for the daughter directive on mercury and its compounds. Deviations from this scheme should be kept to a minimum and should be introduced only if they are justified by specific properties of the other pollutants. Consequently, the requirements of the framework directive are discussed in combination with the already existing daughter legislation.

The assessment of air quality in Member States is not based on measurements alone, but explicitly includes model calculations, emission inventories, objective estimation and monitoring as parts of an integrated system. Notwithstanding this general principle, measurements can be regarded as “backbones” of this system, especially for compliance checking. The monitoring efforts are reasonably differentiated according to the pollution burden within three regimes (Figure 4.1).



**Figure 4.1** - The monitoring regimes of the EU framework directive.

In the regime above and close to the limit values (above the upper assessment threshold UAT) measurements are mandatory. The UAT was introduced to safeguard measurements also in those cases where the pollution burden is scarcely below the limit value, but may exceed the limit value in the near future, *e.g.* due to meteorological circumstances. Therefore the UAT can be defined as the limit value minus approximately twice the standard deviation of annual variations of the pollution burden. The role of the model calculations within this regime is to supplement measurements and to plan reduction measures (action plans). The margins of tolerances also contained in Figure 4.1 are important for the setting up of action plans, but do not have direct significance for the assessment.

In the second regime between the UAT and the lower assessment threshold (LAT), the monitoring efforts may be reduced (*e.g.* by using indicative measurements), and the measurements may be combined with and partly substituted by model calculations. The LAT can be defined as the limit value minus approximately three times the standard deviation of the inter-annual variability of the pollution burden. Below the LAT, attainment with the limit values can be taken for granted. Therefore, measurements are no longer mandatory (with the exception of agglomerations) and can be fully substituted by model calculations and objective estimates. The three monitoring regimes are also important for the quality assurance.

The overriding principle for measurement planning is the assessment of exposure to mercury. Therefore, deposition flux and ambient concentration measurements have to be performed at places which are representative for the exposure of the general population and environment. The measurement planning thus follows an overall strategy that should generally be directed towards spatial representativeness and should allow to quantify the levels of mercury and its compounds in air and precipitation samples and ultimately to assess the flux of mercury entering to the aquatic and terrestrial ecosystems.

Based on this driving principle, the upper and lower limits (UAT and LAT) in terms of ambient concentrations will be linked to dry and wet deposition fluxes of mercury (and its compounds) entering to sensitive ecosystems by considering the average meteorological conditions prevailing in a given region (see Chapter-3). Therefore, the task of this working group is thus to propose the micro-environments which should be monitored (dependent on routes of exposure, sources for mercury and its compounds, etc.), and to describe (and possibly suggest) those parts of the monitoring strategy which are particularly important for mercury and its compounds (see § 4.3).

Quality assurance is of paramount importance, if comparable assessment results with known and retraceable uncertainties are called for. The framework directive and the daughter legislation therefore give special attention to this subject. Important elements are data quality objectives for the required accuracy of assessment methods as well as minimum requirements for data capture and the time coverage of the measurements.

Finally, the use of reference methods is an important means to safeguard the comparability of monitoring results. Analytical and sampling methods for mercury and its compounds are discussed in the Chapter-4 (see § 4.4). An *ad-hoc* working group in the framework of CEN-TC/264 has been formed to develop, test and validate methods for the assessment of the levels of mercury and its compounds in different physical and chemical forms (§ 4.5).

### 4.3 SPECIFIC MONITORING REQUIREMENTS FOR MERCURY AND ITS COMPOUNDS

Based on the exposure and risk assessment (Chapters 5 and 6), modeling (Chapter 3) and emission inventory (Chapter 2) the following important conclusions can be drawn.

1. Adverse human health effects caused by mercury and its compounds can be expected to occur in Europe in a long-term perspective.
2. Atmospheric deposition is the main source of mercury to aquatic and terrestrial ecosystems via dry and wet deposition mechanisms. Anthropogenic emissions to the atmosphere from energy production and industrial sources is the main cause of increased atmospheric concentrations and enhanced deposition fluxes.
3. Atmospheric transport models describing emissions, transport, transformations and deposition are necessary tools for the assessment of source-receptor relationships and for the development of relevant and cost-effective control strategies.
4. The major route of exposure to mercury and its compounds is primarily contaminated food (i.e., fish, seafood), therefore measurements of ambient air concentrations should be coupled with measurements of deposition fluxes.
5. Atmospheric mercury deposition has led to accumulation in forest soils in Europe. This mercury can leach out and act as a source to aquatic ecosystems for long time periods. A potential for negative effects on soil micro-organisms is also evident.

Monitoring of atmospheric mercury is generally carried out with the objective to provide information on temporal trends and spatial variations. Within the EMEP framework, monitoring is also performed to provide data for the development and testing of long-range transport models. With these objectives in mind, manuals for site location (EMEP, 1995) have been prepared and manuals for sampling and analytical techniques for heavy metals including mercury are currently being prepared. The main criteria for location of sampling stations are to avoid any significant local sources of mercury and to ensure that meteorological patterns at the site are representative. From an air-quality perspective, if direct harmful exposure of the species is expected, monitoring should be carried out in areas of high population density and near sources where maximum concentrations are expected. For mercury, for which the main health risk is consumption of contaminated fish and seafood, monitoring sites should be located so that they represent atmospheric conditions at sensitive ecosystems. Location of monitoring sites in other areas (near sources, in areas of high population density, urban/industrialised areas) may also be warranted if extreme concentration events are expected and to provide a basis for identification of emission source areas and source-receptor assessments.

The frequency of measurements is generally a compromise between costs and needs. For model development and testing, high time resolution (hourly measurements) is often requested. This can only be achieved by the use of automated instruments for TGM. If manual methods are employed, 24 hour integrated measurements are feasible. Due to the high costs and relative complex techniques involved for measurements of TGM and RGM, at lower frequency may also be realistic. Wet deposition can be sampled on event or integrated basis. Present monitoring networks use sampling periods ranging from one week to one month. Table 4.3 reports on the type of micro-environment and characteristics of areas/sites where

the measurements of mercury and its compounds have to be performed for ambient air and precipitation events to assure the correct implementation and verification of the mercury directive in Europe.

**Table 4.3** - Characterisation of the micro-environments relevant for the monitoring of ambient concentration and deposition flux of mercury and its compounds.

Site	Characteristics
Rural background and remote areas (also covered by EMEP network)	Sites located in rural areas and very far away from major emission sources. It must have a spatial representativeness of few hundred to few thousands squared kilometres (EMEP siting criteria are valid for these sites).
Industrial (hot spots)	Residential areas with high population density directly influenced by large industrial facilities or other sources of mercury.
Sensitive ecosystems	Areas where accumulation of mercury in ecosystems (freshwater fish, seafood forest soils) are of already above or near maximum acceptable levels.

## 4.4 ANALYTICAL AND SAMPLING METHODS

### 4.4.1 Ambient Concentration Measurements

Sampling and analysis of atmospheric Hg is often made as Total Gaseous Mercury (TGM) which is an operationally defined fraction that includes species passing through a 0.45 µm filter or some other simple filtration device such as quartz wool plugs and which are collected on gold. TGM is mainly composed of elemental Hg vapour with minor fractions of other volatile species such as HgCl<sub>2</sub>, CH<sub>3</sub>HgCl or (CH<sub>3</sub>)<sub>2</sub>Hg. At remote locations, where particulate mercury concentrations are usually low, TGM makes up the main part (>99%) of the total mercury concentration in air.

In the last few years, new automated and manual methods have been developed to measure TGM (Tekran, Inc.; Urba *et al.*, 1999) (see Table 4.4), RGM (Tekran, Inc.; Stratton and Lindberg, 1998; Sommar *et al.*, 2000) (see Table 4.5) and particulate mercury (PM) (Keeler, *et al.* 1995; Lu *et al.*, 1999) (see Table 4.6). These developments make it possible to determine both urban and background concentrations of RGM, PM and TGM. Accurate determinations of emissions and ambient air concentrations of different Hg species will lead to an increased understanding of the atmospheric behaviour of Hg and to more precise determinations of source-receptor relationships. This information linked with other data can be used to assess the various pathways of human exposure to mercury (EPA report to Congress, 1998; Xiao *et al.*, 1996)

Denuders have been used in a variety of air pollution studies to collect reactive gases for subsequent analysis, such as ammonia, nitric acid and sulphur oxides (Ferm *et al.*, 1979; Possanzini, *et al.*, 1983). Denuders were also used to remove reactive gases to prevent sampling artefacts associated with aerosol collection (Stevens *et al.*, 1978). Gold-coated denuders were developed for removal of Hg vapour from air but were not applied to air sampling (Munthe *et al.*, 1991). Potassium chloride (KCl) coated tubular denuders followed

by silver coated denuders were used by Larjava et al. (1992) to collect  $\text{HgCl}_2$  (RGM) and elemental Hg emissions from incinerators.

For particulate Hg, a variety of different filter methods have been applied such as Teflon or Quartz Fibre filters (Keeler, et al. 1995). Before analysis, these filters undergo a wet chemical digestion usually followed by reduction-volatilisation of the mercury to  $\text{Hg}(0)$  and analysis using Cold Vapour Atomic Absorbance Spectrometry (CVAAS) or Cold Vapour Atomic Fluorescence Spectrometry (CVAFS). Recently, a collection device based on small quartz fibre filters mounted in a quartz tube was designed. The mercury collected on the filter can be released thermally, followed by gold trap amalgamation and CVAFS detection (Lu et al, 1998). A number of different sampling techniques were employed for different mercury species. In this section is reported an outline of sampling and analytical methods available for determining the ambient concentration of mercury species in the gas and particle phases (i.e.  $\text{Hg}(0)$ , RGM, TPM,  $\text{CH}_3\text{HgCl}$ ,  $\text{Hg}(\text{CH}_3)_2$ ). Some of these analytical methods are described below, however, more details on these techniques can be found in the cited literature.

In order to compare different methods used to determine the level of mercury and its compounds in air a number of field intercomparison exercises have been performed in recent years (*e.g.* Ebinghaus et al., 1998; Munthe et al., 2001). A major conclusion from these exercises is that ambient levels of TGM can be measured with relatively high accuracy whereas TPM and especially RGM are more complex. Although the basic techniques available for measurements of TPM and RGM have proven to be reliable in research projects, further work on standardisation is clearly warranted before they can be applied to routine measurements or monitoring.

#### **4.4.2 TGM Measurements**

##### **4.4.2.1 Automated Methods**

The Table 4.4 reports on major automated methods/instruments currently available to quantify the level of TGM in ambient air.

##### PSA - Sir Galahad II System

The Sir Galahad II System is used to determine the mercury concentrations as TGM. The Sir Galahad II is based on the Millennium Merlin fluorescence detector. The air sample is pumped at a known flow rate through a filter and over the Amasil ® trap. Any mercury ( $\text{Hg}^0$ ) or mercury compound present forms an amalgam with the gold, thereby becoming trapped. The mercury can be reliably trapped even at elevated temperatures. On completion of the sampling phase the trap is flushed with argon. This removes any trace of the sample gas which could cause quenching and replaces it with argon which allows maximum sensitivity. A rapid heating cycle is then activated converting all forms of mercury to the vapour which enters into the detector where it produces a transient peak. An absolute calibration procedure, based on the work by Dumarey et al. (1985), is simple, effective and can be computer controlled. The detection level is below 0.1 picograms (PSAnalytical, personal communication). The Sir Galahad is normally operated in the continuous mode where the sample line is linked directly for repeat analysis on a cyclic basis. Remotely collected samples can also be analysed using the static approach.



### Tekran Gas Phase Mercury Analyser

The Tekran Gas Phase Mercury Analysers (Model 2537A) is suitable for TGM measurements. The pre-filtered sample air stream is passed through gold cartridges where the mercury is collected. The mercury is then thermally desorbed and detected in an integrated Atomic Fluorescence Spectrophotometry (AFS) (Tekran, 1998). The instrument utilises two gold cartridges in parallel, with alternating operation modes (sampling and desorbing/analysing) on a predefined time base of 10 min. With a sampling flow rate of 1.5 L min<sup>-1</sup> a detection limit of 0.15 ng m<sup>-3</sup> is achieved. A 47-mm diameter Teflon pre-filter protects the sampling cartridges against contamination by particulate matter. The accuracy and precision of this instrument has recently been assessed in intercomparison measurement exercises performed at an urban/industrial site in Windsor, Ontario, Canada (Schroeder et al., 1995a), at a remote site in north-central Wisconsin, USA (Schroeder et al., 1995b), at a remote marine background station in Ireland (Ebinghaus et al., 1999), and at a rural-background site in Tuscany, Italy (Munthe et al. 2001). The instrument and the internal permeation source are calibrated prior to the field campaign by manual calibration (Dumarey et al. 1985).

### Gardis Mercury Analyser

The Gardis instrument is based on gold amalgamation and Atomic Absorption Spectrometry (AAS) detection (Urba *et al.*, 1995). The Gardis instrument operates with ambient air as carrier gas and does not require Argon or Helium for detection. The sampling is run at about 1 L min<sup>-1</sup>, with sampling times of 10 minutes. Under these conditions, a detection limit of about 0.1 ng m<sup>-3</sup> is achieved. A 25 mm diameter PTFE membrane is used to protect the analyser gas inlet from contamination caused by aerosol particles. This instrument has been part of previous intercomparison exercises (Urba et al., 1999; Ebinghaus et al., 1999; Munthe et al. 2001).

#### **4.4.2.2 Manual Methods**

The manual methods (see Table 4.4) are based on gold (or silver) trap amalgamation. The samples are manually analysed using thermal desorption and CVAFS detection (Brosset, 1987; Bloom and Fitzgerald, 1988). Samples are collected on 10-cm long traps consisting of a 6-mm diameter quartz glass tube containing a mixture of small pieces (1-2 mm) of gold wire and quartz glass grains. Alternatively, the adsorbing material may consist of gold-coated quartz glass grains. The airflow is normally > 0.5 l min<sup>-1</sup>. With 24 h sampling time the detection limit is typically 0.01 ng m<sup>-3</sup>.

**Table 4.4** - Overview of selected sampling and analytical methods to measure the levels of total vapour phase mercury (TGM) in air.

Mercury species	Sampling Techniques	Equipment/ Device	Analytical Techniques	Bibliography
<b>TGM</b>	<b>Automated Methods</b>	Tekran 2537A Analyser  PSA – Sir Galahad II System  Gardis Analyser	Atomic Fluorescence spectrometry (AFS)  Atomic Fluorescence spectrometry (AFS)  Atomic absorption spectrophotometry (AAS)	Fitzgerald and co-workers Schroder and co-workers Corn and co-workers Stockwell and co-workers Munthe and co-workers Dumarey and co-workers
<b>TGM</b>	<b>Manual Methods</b> With Amalgamation on a metal surface	<b>Gold Traps</b> (foil, wire, chips, thin film/coating on a substrate having a large surface area).  <b>Silver</b> (gauze, wool, wire, thin film/coating on a substrate having a large surface area).	UV absorption spectrophotometry  Atomic absorption spectrophotometry (AAS)  Cold-Vapor Techniques; Atomic Fluorescence spectrometry (AFS)  Atomic Emission Spectrometry (AES)	Keeler et al. (1995) Munthe et al. (2001) Wngberg et al. (2001) Schroeder and Munthe (1998) Ebinghaus et al. (1999) Pirrone et al. (2000a)

#### 4.4.3 RGM Measurements

Table 4.5 reports on several methods today available to quantify the level of RGM in air. In the following a brief overview of these methods is given.

##### Mist Chamber

The mist chamber technique has been developed by Lindberg and Stratton (1995). Air is drawn through a Pyrex glass chamber of 100 ml total volume containing 30 ml diluted HCl solution. Part of the MC-solution is dispersed as a fine aerosol, by a nebulizer inside the chamber. A hydrophobic filter at the top of the MC separates the droplets from the air and allows the liquid to drain back into the chamber. Mercury(II) species adsorbed in the MC-solution are analysed after reduction to elemental mercury by  $\text{SnCl}_2$  and CVAFS detection. The air sampling flow rate is  $10\text{--}15 \text{ L min}^{-1}$  and the detection limit for a 6 h sample is  $1 \text{ pg m}^{-3}$ .

### Tubular Denuder

Tubular denuders consist of 6 mm quartz tubes coated with KCl. The method is described in Sommar *et al.* (1998). During sampling, the denuders are electrically heated to approximately 45 °C to avoid water vapour condensation. The sampling flow rate is of 1 L min<sup>-1</sup>. Analysis is made using thermal desorption and CVAFS detection. The denuders is heated to 450 °C and purged with N<sub>2</sub>. Mercury released from the denuder is collected on a gold trap which then is analysed using CVAFS. The detection limit is of 5 pg m<sup>-3</sup> for a 24 h-integrated sample.

### Annular Denuder

Annular denuders for sampling of RGM consist of a 15 mm outer diameter quartz tube with an inner, enclosed 8 mm tube. Air is pulled through the space between the two tubes. Both the inner surface of the outer tube and the outer surface of the inner tube are coated with KCl. The RGM is quantitatively collected in the annular denuder at a sampling flow rate of 5-10 L/min. In the analysis step the denuder is heated to 500 °C which converts the adsorbed RGM to elemental mercury vapour which is pre-concentrated on a gold trap. The gold trap is then analysed using the normal desorption and CVAFS detection procedure. The detection limit for a measurement with 2 h sampling time is under 2-3 pg m<sup>-3</sup>. The annular denuders are suitable for automated applications. In the Table 4.5 is reported a summary of the methods currently available and in use for the determination of RGM in air. More details on analytical and sampling procedure can be found in the cited literature.

**Table 4.5** - Overview of sampling and analytical methods available to measure the levels of Reactive Gas phase Mercury (RGM) in ambient air.

Mercury species	Sampling Techniques	Analytical Techniques	Bibliography
	<b>Collection by a Solid Sorbent</b>		
<b>RGM</b> + Organomercury Compounds: $\text{CH}_3\text{HgCl}$ + $(\text{CH}_3)_2\text{Hg}$	Activated carbon/charcoal  Activated carbon/charcoal treated with acid or base  Activated charcoal/mineral wool impregnated with: iodine, ferric chloride, palladium chloride.  Silica gel or alumina-coated with gold chloride.  Indicating papers impregnated with solutions of: KI, $\text{CuI}_2$ , Se, selenium sulfide.  KCl-coated annular denuders  KCl-coated tabular denuders	Electrochemical methods;  Radiochemical Techniques;      $\text{SnCl}_2$ -reduction;  CVAFS; AFS	Matsumura, 1974 Trujillo & Campbell, 1975 Makris et al., 1977  Braman & Johnson, 1974 Soldano et al., 1975  Belozovskii et al., 1972 Corte & Dubois, 1973  Campbell et al., 1973  McCullen & Michaud, 1978  Hemeon & Haines, 1961 Demidov & Mokhov, 1962  Xiao Z. et al., 1997 Kvietkus K. et al., 1995  Sommar et al., 1998
	<b>Absorption into a Liquid</b>		
<b>Organomercury Compounds:</b> $\text{CH}_3\text{HgCl}$ $(\text{CH}_3)_2\text{Hg}$	Acid permanganate solution $\text{KMnO}_4\text{-H}_2\text{SO}_4$ $\text{KMnO}_4\text{-HNO}_3$  Iodine monochloride solution  Iodine/potassium iodide solutions  Bromine or chlorine solutions  Sodium borohydride solutions.  Mist-Chamber (MC) filled with an aqueous solution containing 0.05M HCl.	Gas Chromatography (GC);  $\text{SnCl}_2$ -reduction; Cold-Vapor Techniques; Atomic Fluorescence spectrometry (AFS);  Aq. Ethyl.-Gas Chromatography-CVAFS	Henriques et al., 1973  Makris et al., 1977  Federal register, 1971  ACGI, 1957  AIHA, 1969  Asperger & Murati, 1954  Kimura & Miller, 1960  Miller et al., 1975  Stratton and Lindeberg, 1995

#### 4.4.4 Particulate Mercury Measurements

##### Total Particulate Mercury

The total mercury content of airborne particles (TPM) in ambient air is in the range of less than  $1 \text{ pg m}^{-3}$  to some hundreds of  $\text{pg m}^{-3}$ . The low concentrations level makes adequate quantification difficult. The traditional procedure is to sample particles on fibre or membrane filters (Keeler et al. 1995). About  $10 \text{ m}^{-3}$  of ambient air is sampled with a sampling rate of  $10 \text{ L min}^{-1}$ . The filters are analysed via acid digestion where the mercury is dissolved as  $\text{Hg(II)}$ . The mercury content of the digestion solution is determined by standard methods, *i.e.*  $\text{Sn(II)}$  reduction and pre-concentration via Au-amalgamation followed by CVAFS or CVAAS detection. The method allows large air volumes to be sampled in a relatively short time thereby collecting enough mercury to improve analysis accuracy. A disadvantage is the risk of contamination in conjunction with sample handling. The analysis procedure is time consuming and involves treatment with chemicals that are not totally free of mercury, hence limiting the detection limit of the method.

Miniaturised TPM-traps, which serves as both particulate trap and pyrolyzer, constitute an alternative method (*i.e.*, Wangberg et al. 2001; Munthe et al. 2001). The trap consists of a small quartz glass fibre filter supported in a small quartz glass tube. After sampling the device is analysed by pyrolysis followed by an amalgamation/ thermal desorption/CVAFS-detection step, very similar to Au-traps for elemental mercury. Contrary to traditionally methods this new technique does not require treatment with chemicals, no manual sample transfer or sample handling. Hence, the risk of contamination is low. The sampling flow-rate is limited to  $4\text{-}5 \text{ L min}^{-1}$ , but is well compensated for due to low blanks. The low total cost per sample and the safe handling performance makes the miniaturised TPM-traps a conceivable candidate for a standard method. This technique has been tested during intercomparison exercises and also used in environmental field studies. The detection limit for a 24 h measurements is close to  $1 \text{ pg m}^{-3}$ .

Standardisation needs extensive intercomparison and reproducibility exercises and if possible comparison with an independent method. The inlet characteristics of the sampler in terms of the particle size distribution also needs to be studied and optimised.

##### Size-Fractionated Particulate Mercury

Information on size fractional particulate mercury (SFPM) is of interest in order to determine source receptor relations. SFPM can be obtained using multistage micro-orifice cascade impactors (MOUDI) (Keeler *et al.*, 1995). The impactor can be operated to collect mercury fractions in up to 8 classes. In this context aerosol separation into 2 or 3 size classes may, however, be sufficient. The aerosols are collected on quartz glass fibre filters, which in turn are analysed by acid digestion followed by  $\text{Sn(II)}$  reduction and pre-concentration via Au-amalgamation followed by CVAAS detection.

**Table 4.6** - Sampling and analytical methods available to measure the levels of particulate mercury as Total (TPM) and as Size-Fractionated (SFPM) in air.

Mercury Species	Sampling Techniques	Analytical Techniques	Bibliography
<b>TPM</b>	AES-Mini-Traps-quartz filters; Cellulose acetate filters	Therm.desorb/ Pyrolysis/ amalgamation/ AFS or AAS or CVAAS	Lu et al., 1998;
<b>SFPM</b> (PM <sub>2.5</sub> / PM <sub>10</sub> , multi-stage MOUDI)	Glass Fibre Filters  quartz/Teflon filters	Acid digest, SnCl <sub>2</sub> -CVAFS;  Acid digest, SnCl <sub>2</sub> -CVAFS  Instrumental neutron activation analysis (NAA)/gamma-ray spectrometry;  X-ray fluorescence spectrometry;  Proton induced X-ray emission spectrometry (PIXE).	Landis and Keeler, 1997;  Keeler et al., 1995;  Chilov, 1975  Reimers et al, 1973

#### 4.4.5 Deposition Measurement Methods

Rainwater represents an important source of reactive Hg (Hg<sub>R</sub>) and MeHg, which undergo fast transformation processes in the seawater including decomposition of MeHg and subsequent reduction of Hg<sub>R</sub> to elemental Hg. Therefore speciation of mercury in rain water represents an important input data for a better understanding of mercury exchange at the water-air interface.

A summary of sampling techniques used in different monitoring networks is presented in the Table 4.7. Two alternative materials for funnels and collection bottles are adequate for sampling of precipitation; borosilicate glass and halocarbon such as Teflon. In both cases, extensive cleaning and careful handling is necessary to ensure high quality results. Borosilicate glass is often preferred due to lower cost and general availability. Quartz glass may also be used but is generally avoided due to high costs.

Precipitation can be sampled using wide mouth jars or funnels and bottles. The sampling vessels can either be bulk samplers, which are open at all times, or placed in a wet-only sampling device which is only open during precipitation events. For monitoring purposes, bulk sampling using funnels and bottles is normally adequate (Iverfeldt, 1991a,b; Jensen and Iverfeldt, 1994). Wet-only samplers are used by the Umweltbundesamt in the German national monitoring program as well as by research groups working in the Great Lakes area (Landis and Keeler, 1996) and in the National Atmospheric Deposition Program (Vermette *et al*, 1995) in the USA. The wet-only samplers have the advantage of avoiding particle dry deposition although the contribution to the measured wet deposition fluxes from gaseous or particulate mercury species is probably not large in non-industrialised or non-urban areas (Iverfeldt and Sjöberg, 1992; Iverfeldt and Munthe, 1993).

For extended sampling periods it is also necessary to prevent significant gas phase diffusion of  $\text{Hg}^0$  to the surface of the collected sample where it could contribute to the mercury content of the sample via oxidation to water-soluble forms. This can be easily done using a capillary tube between the funnel and the bottle. Shielding of the sample bottles from light is also necessary to avoid photo-induced reduction of the mercury in the precipitation sample.

Samplers should be designed for sampling during all seasons and climatic conditions. Thus a heating device should be included for melting of snow and prevent formation of ice in the funnel and bottles. Depending on climatic conditions, cooling of the samples may be an improvement in locations where high temperatures can be expected during summer. Funnel area and bottle sizes must be modified to suit the sampling period used.

**Table 4.7** - Overview of samplers for precipitation used in different networks.

Type of Sampler	Characteristics	References
<b>Bulk-Samplers</b>		
IVL/Sweden	Borosilicate glass funnel (Ø 8,2 cm) 52,8 cm <sup>2</sup> with glass filter, capillary tube Ø 4 mm with length of 0,5 cm, glass bottle	Jensen and Iverfeldt, 1994; Iverfeldt, 1991b
WDNR modified IVL/USA	glass funnel (Ø 9,7 cm), 500 mL glass bottles, heating system to prevent wintertime freeze-ups	Chazin et al., 1995
GKSS/Germany	Teflon funnel Ø 35 cm, brown-glass bottles	Ebinghaus et al., 1995
<b>Wet only Samplers</b>		
NSA 181 KD/Germany	Quartz glass funnel Ø 25 cm - 490 cm <sup>2</sup> , Teflon tube 25 cm, Teflon bottles (1l), heating of funnel in wintertime, thermostatic system for samples (4°C)	Kreutzmann et al., 1995
ARS 721/Germany	Borosilicate glass funnel Ø 25,6 cm, 500 cm <sup>2</sup> PFA bottle (2l), heating system	Bieber, 1995
MDN 1 sampler modified Aerochem Metric Sampler/USA-NADP	double system - glass funnel, glass capillary and bottle (1l) for Hg-sampling the other PE or Teflon funnel and PE or Teflon bottle for trace metals	Vermette et al., 1995

## 4.5 STANDARDISATION AND HARMONISATION ACTIVITIES

A number of different methods for sampling and measurements of atmospheric mercury have been employed in monitoring and research activities. In recent years, some efforts have been made to standardise or give recommendations for proven methods for several mercury species (Keeler et al. 1995; Pirrone et al. 2000a; Munthe et al. 2001; Waengberg et al. 2001). Guidelines for sampling and analysis of atmospheric mercury species have been prepared for the Oslo and Paris Convention for the protection of the North Sea (OSPAR) (Munthe, 1996). Manuals for atmospheric mercury measurements have been prepared by the Chemical Co-ordination Centre (CCC) of the EMEP (EMEP CCC Note).

Recently, an *ad-hoc* expert group has been established within the CEN-TC/264 aiming to the development of European standard methods for assessing the levels of mercury and its compounds in the ambient air and precipitation samples. The proposed standard methods will describe alternative approaches for sampling and sample treatment for:

- ❑ Urban areas
- ❑ Near sources
- ❑ Rural and remote areas
- ❑ Dry regions

The alternatives require different methods for sampling and sample treatment which will be described separately in the standard. The Atomic Fluorescence Spectrophotometry (AFS) and the Atomic Absorption Spectrometry (AAS) methods will be adopted as analytical techniques that assure appropriate detection limits for the specific analytes.

The *ad-hoc* group will give priority to atmospheric mercury in the gas and particulate phases. Gaseous and particulate phase target analytes are:

- ❑ Elemental mercury (Hg(0)).
- ❑ Reactive gaseous mercury (RGM; mainly present in the +2 oxidation state).
- ❑ Total particulate phase mercury (TPM; sum of all particle associated Hg species).

In addition to the airborne species, the *ad-hoc* group also recognised the need for monitoring of deposition fluxes. For precipitation priority will be given to the sampling procedure, whereas for the analytical technique will refer to the standard method developed by CEN-TC 230/SC2/TG7 Mercury in Water EN 13506 (currently subject to final vote).

In order to minimise the uncertainty associated to the standard method and assure the reproducibility of results (following also the suggestion of the CEN/TC264 WG on Uncertainty for Ambient Air Reference Measurement Methods), the *ad-hoc* group came to the conclusion (see resolution of the *ad-hoc* group meeting of October 15-16, 2000) that the development of the standard method for assessing the levels of mercury in the ambient air must be carried out for all the three major forms of mercury (namely TGM, RGM and TPM) at the same time and in parallel.



## 4.6 AMBIENT MEASUREMENT DATA

### 4.6.1 Mercury concentrations in ambient air at background and at heavily impacted locations

The different mercury species are ubiquitous in the atmosphere with ambient TGM concentrations averaging about  $1.5 \text{ ng m}^{-3}$  in background air throughout the world (Slemr and Langer, 1982; Iverfeldt, 1991; Wangberg et al. 2001). Higher concentrations are found in industrialised regions and close to emission sources. RGM and TPM vary substantially in concentration typically from 1 to  $600 \text{ pg m}^{-3}$  depending on the location (Keeler et al. 1995; Stratton and Lindberg, 1998; Sprovieri and Pirrone, 2000; Pirrone et al. 2000a; Wangberg et al. 2001). Because RGM compounds are very water-soluble, they are efficiently removed from the atmosphere during rain events and have an atmospheric lifetime on the order of days or a few weeks (Schroeder and Munthe, 1998). Elemental Hg on the other hand has a relatively long lifetime of 0.5 to 2 years due to its low solubility in water and slow removal rate from the atmosphere via deposition and transformation to water soluble species (Lindqvist et al. 1991). In the following tables (see Tables 4.8-4.15), concentrations of mercury species in air at European locations are presented. Each data set will report on mercury measurements performed in Europe at background and/or urban-industrial sites and in heavily polluted areas (*i.e.* near known mercury sources).

**Table 4.8** - Concentrations of TGM ( $\text{ng m}^{-3}$ ) at European background and urban/industrial locations.

Location	Period	Median	Max.	Min.	Reference
Neuglobsow, D	1995-1997	2.10	4.77	1.36	Schmolke et al., 1999
Zingst, D	1995-1997	1.83	5.02	1.45	Schmolke et al., 1999
Rörvik, SE	1995-1997	1.54	1.97	1.18	Schmolke et al., 1999
Aspvreten, SE	1995-1997	1.51	1.73	1.03	Schmolke et al., 1999
Aspvreten, SE	1998-1999	1.41	2.05	1.05	Wangberg et al., 2001
Rörvik, SE	1998-1999	1.45	3.50	1.15	Wangberg et al., 2001
Zingst, DE	1998-1999	1.57	4.09	1.21	Wangberg et al., 2001
Neuglobsow, DE	1998-1999	1.94	3.17	1.15	Wangberg et al., 2001
Mace Head, IR	1998-1999	1.77	2.14	1.06	Wangberg et al., 2001;
Calabria, IT	1998-1999	1.35	2.29	0.93	Wangberg et al., 2001; Pirrone et al., 2000a
Sicily, IT	1998-1999	1.87	3.24	1.06	Wangberg et al., 2001; Pirrone et al., 2000a
Mallorca, ES	1998-1999	3.57	6.20	2.48	Wangberg et al., 2001; Pirrone et al., 2000a
Antalya, TU	1998-1999	1.62	2.14	0.87	Wangberg et al., 2001; Pirrone et al., 2000a
Neve Yam, IS	1998-1999	1.60	2.36	0.66	Wangberg et al., 2001; Pirrone et al., 2000a
Rörvik, SE	1979 to 1992	3.14	13.0	1.10	Iverfeldt et al., 1995
Rörvik, SE	1995 to 1999	1.40	3.50	1.0	Wangberg, Munthe 2001
Pallas, FI	1996 to 1999	1.37	2.16	0.85	Wangberg, Munthe 2001
Deuselbach, DE	1978	2.6 – 4.4			Erlich, 2001
Borken, DE	1990	5.3			Erlich, 2001
Neuglobsow, DE	1977	8.6			Erlich, 2001

The lack of continuous and systematic mercury measurements in Europe does not allow to assess a spatial distribution of ambient concentrations of mercury and its compounds in air for different type of locations (rural-urban-industrial). However, in the framework of the MAMCS and MOE projects funded by European Commission for the first time airborne mercury species have simultaneously been measured at 10 sites in the Mediterranean area and in Northwest Europe. In order to assure measured data comparability a protocol for monitoring and sample treatment was adopted at all MAMCS and MOE sites. The result indicates that average concentrations of airborne mercury species are higher in the Mediterranean area than in Northwest Europe. Ambient concentrations of Total Gaseous Mercury (TGM) at European background locations (see Table 4.8) are in the range of 1.3 to 2.1 ng m<sup>-3</sup> with higher values up to 10-12 ng m<sup>-3</sup> near urban locations affected by near source emissions. TPM concentrations at background locations in Europe are reported in Table 4.9, whereas RGM concentrations have been made only recently at background-rural locations in the framework of the MAMCS and MOE projects (Table 4.10). TPM and RGM concentrations show higher values in the South Europe primarily driven by higher seasonal temperatures, air mass transport patterns and solar irradiation which may speed up photochemical processes in the marine boundary layer (MBL) and thus may lead to enhanced oxidation of elemental mercury vapour yielding to an increase concentration of RGM and possibly TPM, via gas-particle interactions. Another aspect influencing the atmospheric content of TPM and RGM is precipitation. The lower values in Northern Europe may be due to washout being a more efficient removal process in the north in comparison to the south.

**Table 4.9** - Concentrations (pg m<sup>-3</sup>) of TPM at European background locations.  
Data collected in the MOE and MAMCS projects (Pirrone et al., 2000a;  
Wangberg et al., 2001).

Location	Period	Median	Max.	Min.
Aspvreten, SE	1998-1999	7.4	58	0.5
Rörvik, SE	1998-1999	6.2	40	0.6
Zingst, DE	1998-1999	24	74	7.1
Neuglobsow, DE	1998-1999	27	150	4.6
Mace Head, IR	1998-1999	2.9	42	< 0.5
Calabria, IT	1998-1999	18	210	< 0.5
Sicily, IT	1998-1999	6.4	33	< 0.5
Mallorca, ES	1998-1999	40	200	3.6
Antalya, TU	1998-1999	20	100	4.4
Neve Yam, IS	1998-1999	33	170	1.0

Ambient concentrations of TGM and TPM have been measured at heavily impacted locations near emission anthropogenic sources (see Tables 4.11 and 4.12) with TGM levels in the range of few ng m<sup>-3</sup> to several hundred of ng m<sup>-3</sup>. TPM levels follows a similar behaviour with high values of up to 20 ng m<sup>-3</sup> at downwind of industrial locations.

**Table 4.10** - Concentrations of RGM ( $\text{pg m}^{-3}$ ) at European background stations.  
Data collected in the MOE and MAMCS projects  
(Pirrone et al., 2000a; Wangberg et al., 2001).

Location	Period	Mean	Min.	Max.
Rörvik, SE	1998-1999	9.1	0.93	29
Zingst, DE	1998-1999	14.4	0.23	46
Neuglobsow, DE	1998-1999	26.3	0.14	100
Mace Head, IR	1998-1999	19.1	2.0	62
Calabria, IT	1998-1999	23.2	2.2	69
Sicily, IT	1998-1999	7.5	1.2	57
Mallorca, ES	1998-1999	48.2	11.1	140

**Table 4.11** - Concentrations of TGM ( $\text{ng m}^{-3}$ ) at European heavily impacted locations.

Location	Period	Mean	Max.	Min.	Reference
Tessenderlo Dennerhof, BE	1998	19.6	126	0.02	Desmedt (2000) De Temmerman (1999)
Tessenderlo Dennerhof, BE	1999	24.9	144	1.25	Desmedt (2000) De Temmerman (1999)
Brussel Meudonpark	1999	3.13			Desmedt, (2000)
Buna, DE	1995		530	10	Desmedt, (2000)
Magdeburg, DE	1977	85			Desmedt, (2000)
Terveuren, BE	1998	1.96	13.9	0.17	Desmedt, (2000)
Terveuren, BE	1999	2.19	5.02	0.72	Desmedt, (2000)
Altenweddingen, DE		33.8			Desmedt, (2000)
Tessenderlo Rodeheide, BE	1998	6.46	35.1	0.11	Desmedt (2000) De Temmerman (1999)
Tessenderlo Rodeheide, BE	1999	6.31	28.7	0.39	Desmedt (2000) De Temmerman (1999)
Brussel Meudonpark, BE	1999	3.13			Desmedt, (2000)
Halla, Leipzig/Bitterfeldt, DE	1988	4-6			Erlich, 2001
Mainz, DE	1987	9			Erlich, 2001
Karlsruhe, DE	1991	3-6			Erlich, 2001
Duisburg, DE	1990	6.1-6.7			Erlich, 2001

**Table 4.12** - Ambient concentrations of TPM ( $\text{pg m}^{-3}$ ) at European heavily impacted locations.

Location	Period	Mean	Min.	Max.	Reference
Tessenderlo Dennerhof, BE	1998	830	30	19600	Desmedt (2000) De Temmerman (1999)
Tessenderlo Dennerhof, BE	1999	770	10	11100	Desmedt (2000) De Temmerman (1999)
Tessenderlo Rodeheide	1998	450	70	4300	Desmedt (2000) De Temmerman (1999)
Tessenderlo Rodeheide	1999	350	10	5100	Desmedt (2000) De Temmerman (1999)
Tervueren	1998	230	40	6900	Desmedt, (2000)
Tervueren	1999	90	10	1200	Desmedt, (2000)

Simultaneous measurements have been performed recently along 6000 km cruise path over the Mediterranean Sea in the framework of the MED-OCEANOR project (Pirrone et al. 2001). Concentrations of mercury and its compounds along with other environmental parameters have been determined in air as well as in surface and deep seawater. A summary of concentrations of mercury species in air at open sea and coastal zone locations is reported in Table 4.13. TGM concentrations averaged from  $1.7\text{--}1.9 \text{ ng m}^{-3}$  in open sea atmosphere to  $3 \text{ ng m}^{-3}$  in coastal-urban environment (i.e., Naples-near shore area), RGM was from few  $\text{pg m}^{-3}$  in open sea to up about  $30 \text{ pg m}^{-3}$  at coastal sea locations, whereas TPM levels were quite uniform over the sea.

**Table 4.13** - Ambient concentrations of TGM ( $\text{ng m}^{-3}$ ), RGM ( $\text{pg m}^{-3}$ ) and TPM( $\text{pg m}^{-3}$ ) over the Mediterranean Sea in coastal and open sea during the MED-OCEANOR project (July-August 2000) (Pirrone et al. 2001).

	Location	Mean	St. Dev.	Min.	Max.
<b>TGM</b>	Open Sea - South East	2.1	0.63	1.3	3.8
	Open Sea - South	1.7	0.18	1.4	2.8
	Open Sea - North West	1.7	0.44	0.13	2.9
	Coastal area - Sicily	1.8	0.65	0.37	9.9
	Coastal area - Sardinia	1.8	0.59	0.11	7.2
	Coastal area - Naples	2.9	2.2	0.13	23.9
<b>RGM</b>	Open Sea - South East	2.6	1.3	1.13	5.5
	Open Sea - South	4.2	1.4	2.5	5.7
	Open Sea - North West	19.1	10.6	9.1	34.0
	Coastal area - Sicily	7.7	2.1	4.4	9.9
	Coastal area - Sardinia	10.5	10.4	0.2	30.1
	Coastal area - Naples	7.3	3.7	2.5	12.6
<b>TPM</b>	Open Sea - South East	9.3	2.2	7.7	10.9
	Open Sea - South	10.1	8.9	3.8	16.4
	Open Sea - North West	14.1	4.1	11.3	17.0
	Coastal area - Sicily	11.0	5.9	4.6	12.1
	Coastal area - Sardinia	10.4	1.2	9.6	11.2
	Coastal area - Naples	-	-	-	-

#### 4.6.2 Mercury Concentrations in Precipitation and Deposition Fluxes

Mercury in precipitation is monitored in a few countries in Northern Europe and reported to the EMEP database. Annual volume weighted concentrations from 4 stations in the Swedish National Monitoring Network from 1995 to 1999 are presented in Table 4.14.

**Table 4.14** - Annual volume-weighted concentrations ( $\text{ng L}^{-1}$ ) of total mercury in precipitation.

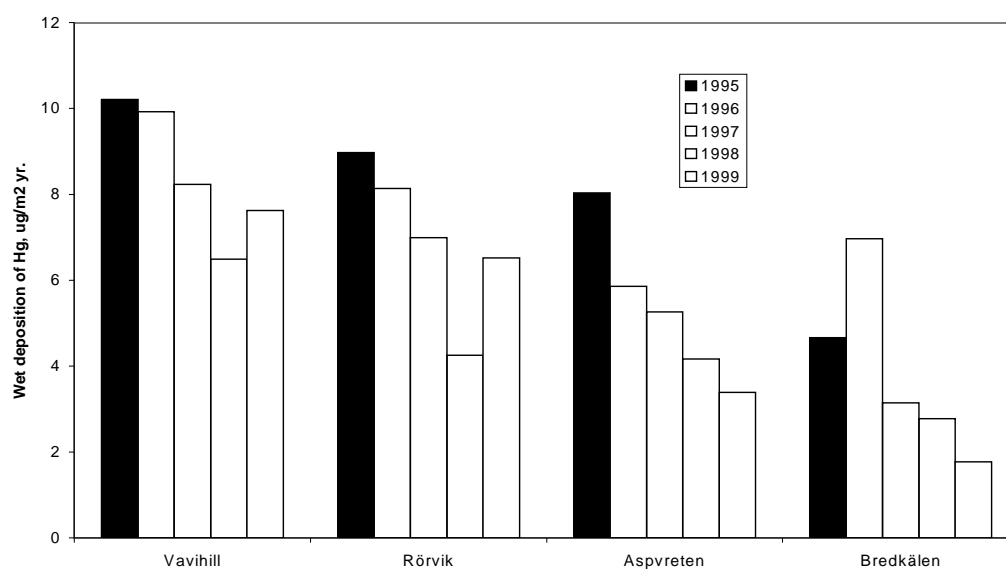
Location	1995	1996	1997	1998	1999
Vavihill	17.0	19.8	12.6	8.29	10.4
Rörvik	16.8	17.5	14.5	6.80	9.44
Aspvreten	17.9	13.9	12.5	8.25	8.77
Bredkälen	13.0	15.8	7.00	4.27	4.17

In the MOE and MAMCS projects, mercury in precipitation was sampled on an event basis during 4 simultaneous campaigns in 1998 and 1999. This data set also includes 5 stations in the Mediterranean area and represents the first data collected in this region. Median, maximum and minimum concentrations are presented in Table 4.15.

**Table 4.15** - Total mercury concentrations in precipitation. Data collected within the MOE and MAMCS projects from November 1998 to September 1999. (Pirrone et al., 2000a; Wangberg et al., 2001).

Location	Period	Median	Min.	Max.
Aspvreten, SE	1998-1999	12.3	3.7	80
Rörvik, SE	1998-1999	9.5	4.2	49.2
Zingst, DE	1998-1999	15.1	1.2	109
Neuglobsow, DE	1998-1999	15.8	4.7	23.3
Mace Head, IR	1998-1999	3.8	1.2	42.5
Sicily, IT	1998-1999	5.2	--	--
Calabria, IT	1998-1999	27.39	30	8.5
Neve Yam, IS	1998-1999	26.9	37	17
Antalya, TU	1998-1999	38.23	53	5.7
Mallorca, ES	1998-1999	17.2	75	4.6

Mercury wet depositions from the Swedish National Monitoring Network is presented in Figure 4.2. The deposition decreases from south to north (from Vavihill to Bredkålen) and also exhibits a decreasing trend with time.



**Figure 4.2** - Annual wet deposition of total mercury at Swedish monitoring sites.

### 4.6.3 Mercury evasion from surface waters and top soils

Evasion of mercury from natural surfaces is an important process which needs to be taken into account when considering the impact of atmospheric mercury on the environment. Evasion of mercury can occur from two major processes:

- De-gassing from mercury-rich minerals, and
- Re-emission of previously deposited mercury.

Data on re-emissions and de-gassing of mercury in Europe is scarce and limited to measurement results from Sweden (soils, freshwater and coastal waters) and Italy (seawater, mercury rich mineral soils). In Table 4.16 measured mercury fluxes from various surfaces are presented.

The de-gassing is primarily important in areas that extend from southern Spain to northern Italy crossing Slovenia and parts of the former Yugoslavia. In this area, mercury mining has been extensive and is still in operation in Almaden (Spain). Emission fluxes over water are generally higher than those over soils, and mercury fluxes from freshwater have been found higher than that observed over seawater. The role of vegetation (forest canopies, grass etc) on the global/hemispheric mercury budget is somewhat unclear.

Several studies suggest that the evasion of elemental mercury from surface water is primarily driven by (1) the concentration of mercury in the surface water, (2) solar irradiation which is responsible for the photo-reduction of oxidised mercury available in the top-water microlayer, and (3) the wind speed. Mercury emission rates from surface water have been measured in different areas of Europe and in different seasons using the floating chamber technique (Schroeder *et al.* 1989; Xiao *et al.* 1991; Cossa *et al.*, 1996; Ferrara *et al.* 2000). The evasion of mercury from lake surfaces is generally higher than that observed over the sea. Average emission rates in the North Sea were in the range  $1.6$  to  $2.5 \text{ ng m}^{-2} \text{ h}^{-1}$  (Cossa *et al.*, 1996 and ref. therein), whereas higher values ( $5.8 \text{ ng m}^{-2} \text{ h}^{-1}$ ) have been observed in the Scheldt outer estuary (Belgium) and over lakes in Sweden (up to  $20.5 \text{ ng m}^{-2} \text{ h}^{-1}$ ). In the Mediterranean Sea mercury emission rates were in the range  $0.7$  to  $10.1 \text{ ng m}^{-2} \text{ h}^{-1}$  in unpolluted areas (dissolved mercury concentration in the top water  $30 \text{ ng m}^{-3}$ ) and between  $2.4$  and  $11.25 \text{ ng m}^{-2} \text{ h}^{-1}$  in polluted coastal areas (dissolved mercury concentration in the top water microlayer was  $15 \text{ ng L}^{-1}$ ) close to a chlor-alkali plant (Ferrara *et al.* 2000). In open sea, mercury emission rates were much lower ( $1.16$ - $2.5 \text{ ng m}^{-2} \text{ h}^{-1}$ ) and less variable between day and night, though the dissolved mercury concentration in the top water microlayer ( $30 \text{ ng m}^{-3}$ ) was very similar to that observed in unpolluted coastal areas. Higher fluxes have been observed at contaminated industrial sites, floodplains and coastal areas with contaminated sediments.

**Table 4.16** - Degassing rates of mercury ( $\text{ng m}^{-2} \text{h}^{-1}$ ) from volcanoes, surface waters and top soil in Europe and in the Mediterranean region (Pirrone et al. 2001 and references therein).

Country	Method	Surface type	Period		Emission rate
North-Western Mediterranean	N.A.	Sea surface	N.A.		$1.16 \text{ ng m}^{-2} \text{h}^{-1}$
Scheldt outer estuary (Belgium)	N.A.	Sea surface	N.A.		$5.8 \text{ ng m}^{-2} \text{h}^{-1}$
Grand Estuaire de la Loire (France)	N.A.	Sea surface	N.A.		$0.4\text{-}2.5 \text{ ng m}^{-2} \text{h}^{-1}$
Baie de la Seine (France)	N.A.	Sea surface	N.A.		$1.7\text{-}3.3 \text{ ng m}^{-2} \text{h}^{-1}$
Northern-Tyrrhenian Sea (Poll. Coastal zone)	FC	Sea surface	Summer	Day	$11.25 \text{ ng m}^{-2} \text{h}^{-1}$
				Night	$2.4 \text{ ng m}^{-2} \text{h}^{-1}$
Northern-Tyrrhenian Sea (Off-shore)	FC	Sea surface	Summer	Day	$2.5 \text{ ng m}^{-2} \text{h}^{-1}$
				Night	$1.16 \text{ ng m}^{-2} \text{h}^{-1}$
Northern-Tyrrhenian Sea (Unpoll. Coastal zone)	FC	Sea surface	Summer	Day	Up to $10.1 \text{ ng m}^{-2} \text{h}^{-1}$
				Night	$1 \text{ ng m}^{-2} \text{h}^{-1}$
			Winter	Day	$0.7\text{-}2.0 \text{ ng m}^{-2} \text{h}^{-1}$
Sweden	FC	Lake surface	N.A.		$2.05\text{-}20.5 \text{ ng m}^{-2} \text{h}^{-1}$
North Sea, Sweden	N.A.	Coastal waters			$-1 \text{ to } 9 \text{ ng m}^{-2} \text{hr}^{-1}$
North Sea	N.A.	Sea surface	N.A.		$1.6\text{-}2.5 \text{ ng m}^{-2} \text{h}^{-1}$
Etna, Stromboli, Vulcano (Med. Sea, IT)	MN/ Gardis		Fall/Spring		$0.6\text{-}1.3 \text{ t y}^{-1}$
Forest, Sweden	N.A.	Top soil	Summer		$0.1 \text{ to } 1.4 \text{ ng m}^{-2} \text{hr}^{-1}$
Forest, Sweden	N.A.	Top soil	Winter *		$-1.1 \text{ to } 1.0 \text{ ng m}^{-2} \text{hr}^{-1}$
Mt Amiata, Italy	FC	Mercury rich mineral soils			$26 \text{ to } 10000 \text{ ng m}^{-2} \text{hr}^{-1}$

N.A.= not available, FC = Flux Chamber, LD=LIDAR Technique, MN = Manual Technique, (\*) Negative values indicate dry deposition



## 4.7 RECOMMENDATIONS

Based on the compilation of available information on emissions, atmospheric behaviour, exposure routes and health effects of mercury described in this Position Paper, the following preliminary monitoring plan is proposed to the members states for assessing the level of mercury and its compounds in air and precipitation at different locations.

1. Each member state should set up and operate *at least* one monitoring station for atmospheric mercury species (TGM, RGM, TPM and wet deposition).
2. Member states with large emissions of mercury (*e.g.* > 10% of total EU emissions) should set up and operate 3-4 monitoring stations.
3. Member states with significantly elevated mercury levels in soils or aquatic food chains should set up and operate 3-4 monitoring stations.
4. Three different categories of monitoring stations should be considered: **A** Near source areas and areas with high population density; **B** Remote areas representing a large geographical areas; and **C** Areas with sensitive ecosystems and high accumulation levels.
5. Member states required to set up and operate one monitoring station should select a category that is relevant to their own conditions. Member states required to set up and operate 3-4 monitoring stations should do so in different categories as reported in above (see 4).
6. Monitoring stations of category **A** and in some cases of category **C** should be co-located with current and planned EMEP stations.
7. Monitoring stations of category **B** could be co-located with stations where measurement activities linked to the Air Quality directive for other pollutants are on-going.
8. Standard measurement methods and quality assurance/quality control (QA/QC) procedures should be developed within the framework of CEN and clear guidelines/instructions should be distributed to member states.
9. Intercomparison exercises for performing laboratories in member states should be arranged.
10. The Working Group recommend to include the proposed measurement plan in the framework of the Clean Air For Europe (CAFE) program.
11. Measurement data should be compiled and stored in a joint database. This data should be openly available for assessment and application to *e.g.* model development and evaluation.

## 4.8 REFERENCES

- Berg, T., Bartnicki, J., Munthe, J., Lattila, H., Hrehoruk, J. and Mazur, A. 2000. Atmospheric mercury species in the European Arctic: measurements and modelling. *Atmospheric Environment*, in press.
- Bloom, N.S. and Fitzgerald, W.F. 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapor atomic fluorescence detection. *Analytica Chimica Acta* **209**, 151-161.
- Bloom, N.S. and Watras, C.J. 1989. Observations of methylmercury in precipitation. *Sci. Total Environ* **87/88**, 199.
- Braman, R.S. and Johnson, D.L. 1974 Selective absorption tubes and emission technique for determination of ambient forms of mercury in air. *Env. Sci. Technol.* **8**, 996-1004.
- Brosset, C. 1982. Total airborne mercury and its origin. *Water, air, Soil Pollut.* **17**, 37-50.
- Brosset, C. 1987. The behaviour of mercury in the physical environment. *Water, Air, Soil Pollut.* **34**, 145-166.
- Brosset, C. and Lord, E. 1995. Brosset, C. and Lord, E. 1995. Methylmercury in ambient air. Method of determination and some measurement results. *Water, Air Soil Pollut.* **82**, 739-750.
- Desmedt (2000) Marjory, Vlaamse Milieumaatschappij, Kronenburgstraat 45 bus 3, 2000 Antwerpen, personal communication.
- Dumarey, R., Temmerman, E., Dams, R., & Hoste, J. 1985. The Accuracy of the Vapour-Injection Calibration Method for the Determination of Mercury by Amalgamation/Cold-Vapour Atomic Adsorption Spectrometry. *Analytica Chimica Acta*, **170**, 337-340.
- De Temmerman, L. (1999) CODA, Biologisch onderzoek van de verontreiniging van het milieu door zware metalen te Hoboken en Tessenderlo, groeiseizoen 1998 resp., (report in Dutch).
- Ebinghaus, R., S.G. Jennings, W.H. Schroeder, T. Berg, T. Donaghy, J. Guentzel, C. Kenny, H.H. Kock, K. Kvietkus, W. Landing, J. Munthe, E.M. Prestbo, D. Schneeberger, F. Slemr, J. Sommar, A. Urba, D. Wallschläger, Z. Xiao 1999. International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, *Atmospheric Environment* **33**, 3063-3073
- Edner, H., Faris, G.W., Sunesson, A. and Svanberg, S. 1989. Atmospheric atomic mercury monitoring using differential absorption LIDAR technique. *Appl. Opt.* **28**, 921.
- Erlich, H.C. (2001) Data extracted from: Immissionswerte für Quecksilber, Quecksilberverbindungen Bericht des Unterausschusses "Wirkungsfragen" des LAI; Berlin: Erich Schmidt Verlag 1996, ISBN 3-503-03964-3
- Feng, X., Sommar, J., Gårdfeldt, K. and Lindqvist, O. 2000. Improved determination of gaseous divalent mercury in ambient air using KCl coated denuders. *Fres. J. Anal. Chem.* **366**, 423-428.
- Ferm, M. 1979. Method for determination of atmospheric ammonia. *Atmospheric Environment* **13**, 1385-1393.
- Ferm, M. 1986. A Na<sub>2</sub>CO<sub>3</sub> coated denuder and filter for determination of gaseous HNO<sub>3</sub> and particulate NO<sub>3</sub>- in the atmosphere. *Atmos. Environ.* **20**, 1193-1201.
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N. (2000) Temporal trends in gaseous mercury evasion from the Mediterranean Seawaters. *Sci. Tot. Environ.* **259**, 183-190.

- Fitzgerald, W.F. and Gill, G.A. 1979. Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Analytical Chemistry* **51**, 1714–1720.
- Hultberg, H., Iverfeldt, Å. and Lee, Y.-H. 1995. Methylmercury input/output and accumulation in forested catchments and critical loads for lakes in southwestern Sweden. In: Mercury Pollution - Integration and Synthesis. Watras, C.J. and Huckabee, J.W. (Eds.), CRC Press Inc., Lewis Publishers, Boca Raton Florida, USA.
- Iverfeldt, Å. 1991a. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water, Air, Soil Pollut.* **56**, 251-265.
- Iverfeldt, Å. 1991b. Mercury in canopy throughfall water and its relation to atmospheric deposition. *Water, Air, Soil Pollut.* **56**, 553-542.
- Iverfeldt, Å. and Munthe, J. (1993) In: Proceedings from the EPA/A&WMA Symposium Measurement of Toxic and Related Air Pollutants., Durham, NC, May 3-7, 1995.
- Iverfeldt, Å. and Sjöberg, K. 1992. Intercomparison of methods for the determination of mercury deposition to convention waters. IVL Report B 1082, Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-402 58 Göteborg, Sweden.
- Iverfeldt, Å., Munthe, J., Brosset, C. and Pacyna, J. (1995) Long-term changes in concentrations and deposition of atmospheric mercury over Scandinavia. *Water, Air, Soil Pollution* **80**, 227-233.
- Jensen, A. and Iverfeldt, Å. 1993. Atmospheric bulk deposition of mercury to the southern Baltic sea area. In: Mercury as a global pollutant. Huckabee, J. and Watras, C. (Eds) Cleveland, CRC Press.
- Landis, M.S. and Keeler, G.J. 1996 A critical evaluation of a wet only precipitation collector designed for network operation for mercury and trace elements. Presented at the Fourth International Conference on mercury as a global pollutant, Hamburg, august 1996.
- Vermette, S., Lindberg, S. and Bloom, N. 1995. Field tests for a regional mercury deposition network - sampling design and preliminary test results. *Atmospheric Environment* **29**, 1247-1251.
- Keeler, G., Glinsorn, G. and Pirrone, N. 1995. Particulate mercury in the atmosphere: Its significance, transport, transformation and sources. *Water, Air, Soil Pollut.* **80**, 159-168.
- Landis, M.S. and Keeler, G.J. 1997. Critical Evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations. *Environ. Sci. Technol* **29**, 2123-2132.
- Larjava, K., Laitinen, T., Vahlman, T., Artmann, S., Siemens, V., Broekaert, J.A.C. and Klockow, D. Measurements and control of mercury species in flue gases from liquid waste incineration. *Int. J. Anal. Chem.* **149**, 73-85.
- Lindqvist O., Johansson K., Aastrup M., Andersson A., Bringmark L, Hovsenius G., Hakanson L., Iverfeldt Å, Meili, M. and Timm B. 1991. Mercury in the Swedish environment – Recent research on causes, consequences and corrective methods. *Water Air Soil Pollut.* **55**, 23-32.
- Lu, J. Y., Schroeder, W. H., Berg, T. Munthe, J., Schneeberger, D., Schaedlich, F., 1998. A Device for Sampling and Determination of Total Particulate Mercury in Ambient Air. *Analytical Chemistry* **70**, 2403-2408.

- Mason, R.P., Fitzgerald, W.F. and Morel, F.M.M. 1995. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim Acta* **58**, 3191 – 3198.
- Munthe, J., Xiao, Z., Schroeder, W.H. and Lindqvist, O. 1991. Removal of gaseous mercury from air using a gold coated denuder. *Atmos. Environ.* **24A**, 2271-2274.
- Munthe, J. 1998. JAMP Guidelines for the sampling and analysis of mercury in air and precipitation. Oslo Paris Commission - Joint Assessment and Monitoring (JAMP) programme 23/02/98.
- Munthe, J., Waengberg, I., Pirrone, N., Iverfeldt, Å., Ferrara, R., Ebinghaus, R., Feng, X., Gårdfeldt, K., Keeler, G., Lanzillotta, E., Lindberg, S.E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroeder, W.H., Sommar, J., Sprovieri, F., Stevens, R.K., Stratton, W., Tuncel, G., Urba, A. (2001) Intercomparison of methods for sampling and analysis of atmospheric mercury species. *Atmos. Environ.* **35**, 3007-3017.
- Petersen, G., Iverfeldt, Å., Munthe, J., 1995. Atmospheric Mercury Species over Central and Northern Europe; Model Calculations and Comparison with Observations from the Nordic Air and precipitation Network for 1987 and 1988. *Atmospheric Environment* **29**, 47-67.
- Pirrone, N. (Coordinator), Pacyna, J. Munthe, J., Kallos, G., Ferrara, R., Mamane, Y. (2000a) Mediterranean Atmospheric Mercury Cycle System (MAMCS)-Final Technical Report (Contr. No. ENV4-CT97-0593). EU-DG Research-Environment and Climate Programme, Brussels, Belgium.
- Pirrone, N., Sprovieri, F., Pesenti, E. (2001) MED-OCEANOR Project-Technical Report. Workshop on Data Analysis of the URANIA Oceanographic Mediterranean Campaign-Summer 2000. 26-27 Febbraio 2001, Pisa, Italy.
- Possanzini, M., Febo, A., and Liberti, A. 1983. New design of a high-performance denuder for the sampling of atmospheric pollutants. *Atmospheric Environment* **17**, 2605-2610.
- Schmolke, S., Schroeder, W. H., Munthe, J., Kock, H. H., Schneeberger, D and Ebinghaus, R., 1999. Simultaneous measurements of total gaseous mercury at four sites on a 800 km transect: spartial distribution and short time variability of total gaseous mercury over Central Europe. *Atmospheric Environment* **33**, 1725-1733.
- Schroeder, W. H., Keeler, G., Kock, H., Roussel, P., Schneeberger, D., & Schaedlich, F. 1995a. International field intercomparison of atmospheric mercury measurement methods. *Water Air and Soil Pollution* **80**, 611-620.
- Schroeder, W. H., Lamborg, C., Schneeberger, D., Fitzgerald, W.F., Srivastava, B., 1995b. Comparison of a manual method and an automated analyser for determining total gaseous mercury in ambient air. Proceedings of 10th International Conference on Heavy Metals in the Environment, R.-D. Wilken, U. Förstner, & A.Knöchel (Eds.) CEP Consultants Ltd., Publisher, Edinburgh, U.K., 2, 57-60.
- Schroeder, W. H.; Munthe, J., 1998) Atmospheric Mercury – An Overview. *Atmospheric Environment* **29**, 809-822.
- Schroeder, W.H., Lamborg, C., Schneeberger, D., Fitzgerald, W.F., Srivastava, B. (1995b). Comparison of a manual method and an automated analyser for determining total gaseous mercury in ambient air. Proceedings 10th International Conference on Heavy Metals in the Environment, R.-D. Wilken, U. Förstner, & A.Knöchel (Eds.) CEP Consultants Ltd., Publisher, Edinburgh, U.K., 2, 57-60.
- Slemr, F. and Langer, E. 1992. Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature* **355**, 434-437.

- Sprovieri, F. and Pirrone, N. (2000) A Preliminary Assessment of Mercury Levels in the Antarctic and Arctic Troposphere. *J. Aeros. Sci.* **31**, 757-758.
- Sommar, J., Feng, X., Gårdfeldt, K. and Lindqvist, O. 1999. Measurements of fractionated gaseous mercury concentrations in Northwestern and Central Europe, 1995-1999. *J. Environ. Monitor.* **1**, 435-439.
- Stevens, R. K. 2000. Automated Mercury Speciation Methods and Demonstrations. Proceedings from *Workshop on Source Emissions and Ambient Air Monitoring of Mercury, September 13-14, Bloomington, MN*, EPA /625/R-00/002 pp 82-83.
- Stevens, R.K., Dzubay, T.G., Russwurm, G.M. and Rickel, D. 1978. Sampling and Analysis of Atmospheric Sulfates and Related Species. *Atmospheric Environment* **12**, 55-68.
- Stratton, W. J., Lindberg, S. E., 1995. Use of A Refluxing Mist Chamber for Measurement of Gas-Phase Mercury(II) Species In The Atmosphere. *Water, Air and Soil Pollution* **80**, 1269-1278.
- TEKRAN, 1998. Model 2357A-Principles of Operation. Tekran Inc., Ontario, Canada.
- U.S. EPA (1996) Mercury Stucy Report to Congress: SAB Review Draft. Report No. EPA-452R-96-001, U.S: Environmental Protection Agency, Research Triangle Park, North Carolina, U.S.A.
- UN ECE 1998 Protocol on Heavy Metals. Convention on Long-range Transboundary Air Pollution, United nations Economic Commission for Europe.
- Urba A., K.Kvietkus, S.Schmolke and J.Munthe. International field intercomparison and other measurements of total gaseous mercury at Preila, Lithuania, during 1996-1997 // Proceedings of EUROTRAC Symposium '98. Editors: P.M. Borrel and P. Borrel. 1999, WIT press, Southampton, p. 364-368 (1999).
- Urba, A., Kvietkus, K., Sakalys, J., Xiao, Z. and Lindqvist O., 1995. A new sensitive and portable mercury vapor analyzer GARDIS-1A. *Water, Air and Soil Pollut.* **80** 1305-1309.
- Wangberg, I., Munthe, J. 2001. Atmospheric Mercury in Sweden, Northern Finland and Northern Europe; Results from National Monitoring and European Research. IVL-Report B1399, Göteborg, January 2001.
- Wangberg, I., Munthe, J., Pirrone, N., Iverfeldt, Å., Bahlman, E., Costa, P., Ebinghaus, R., Feng, X., Ferrara, R., Gårdfeldt, K., Kock, H., Lanzillotta, E., Mamane, Y., Mas, F., Melamed, E., Osnat, Y. , Prestbo E., Sommar, J., Spain, G., Sprovieri, F., Tuncel, G. 2001, Atmospheric Mercury Distribution In Northern Europe and in the Mediterranean Region. *Atmos. Environ.* **35**, 3019-3025.
- Xiao, Z., Sommar, J. Wei, S. and Lindqvist, O. 1997. Sampling and determination of divalent mercury in air usinf KCl coated denuders. *Fres. J. Anal. Chem.* **358**, 386-391.

## **CHAPTER-5. EXPOSURE TO MERCURY IN EUROPE**

### **5.1 INTRODUCTION**

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## 5.1 INTRODUCTION

Although the question on what is the acceptable level of exposure to MeHg and other chemical forms of mercury is not new to the scientific community, there are still a lot of controversies in this subject, which become even more evident in recent studies. Although it was believed for a long time that hair and blood are appropriate biomarkers or measurements of exposure, there are controversies in recent studies whether a measured biomarker value truly corresponds to Hg exposure levels. This chapter provides a short overview on the subject and provides suggestions for further studies to improve uncertainties in model predictions of individual and population exposures to mercury. In the limited scope of the position paper only a very brief summary is provided based on recent reviews (NRC 2000, US EPA 1997) as well as environmental health criteria provided by the WHO (IPCS, 1990, 1991).

## 5.2 SOURCES AND PATTERNS OF EXPOSURE

There is a considerable variation of mercury levels in those media that are the sources of human exposure, and, consequently, in their contribution to the toxicity risk. Main mercury absorption routes in humans are through respiratory and dietary routes. Non-occupational groups are primarily exposed through the diet and dental amalgam.

### 5.2.1. Ambient Air

In Europe the highest background concentration of TGM is measured in central Europe (e.g. Germany and Poland), where the concentrations may reach up to  $2.5 \text{ ng/m}^3$  (EMEP; 1999). The concentrations in rural areas are normally very low, close to the mean global values (EMEP, 1999). The values in urban areas are usually higher and vary between 5 to  $15 \text{ ng/m}^3$  (IPCS, 1991) and in some contaminated places even higher (Dizdarevic, 2001). The reference concentrations (RfC) recommended by the US EPA amounts to  $0.3 \text{ } \mu\text{g/m}^3$  (IRIS, 1995), which means that in general mercury concentrations in air do not represent a considerable intake of Hg for humans. The WHO has estimated the daily intake of each form of Hg on the assumption that 75% of Hg is in elemental Hg from, 5% as inorganic Hg and 20% of MeHg. By assuming a daily ventilation of  $20 \text{ m}^3$ , and the amount absorbed across the pulmonary membranes (80% of elemental Hg, 50% of inorganic Hg, and 80% of MeHg) daily intakes were calculated and given in Table 5.1.

### 5.2.2. Dental Amalgam

Dental mercury fillings are reported to release Hg vapour into the oral cavity (Clarkson et al., 1988 a, 1988b, Skerfving, 1991). The resulting concentrations in intra-oral air can substantially exceed those found in the ambient atmosphere, especially after a period of chewing. It is estimated that average daily amounts of Hg entering the pulmonary system ranges from 3 –  $17 \text{ } \mu\text{g}$  of Hg (IPCS, 1991, Berglund 1990, Lorscheider 1995, Sandborgh 1998, Barregard et al. 1995, Sallsten et al., 1996), but there is variability among populations, and intakes in the order of  $100 \text{ } \mu\text{g/day}$  may occur.

**Table 5.1** - Estimated average daily intakes and retention in ( $\mu\text{g/day}$ ) of different mercury forms in the general population not occupationally exposed (IPCS, 1991).

Exposure	Elemental Hg vapour	Inorganic Hg compounds	Methylmercury
Air	0.03(0.024)*	0.002(0.001)	0.008(0.0069)
Dental amalgams	3.8-21 (3-17)	0	0
Food			
- fish	0	0.60 (0.042)	2.4 (2.3)**
- non-fish	0	3.6 (0.25)	0
Drinking water	0	0.050 (0.0035)	0
Total	3.9-21 (3-1-17)	4.3 (0.3)	2.41 (2.31)

The data in parenthesis represent retained Hg in the body of an adult.

\* If the concentration is assumed to be  $15 \text{ ng/m}^3$  in an urban area the figure would be  $0.3(0.24) \mu\text{g/day}$

\*\* 100 g of fish per week with the Hg concentration of  $0.2 \text{ mg/kg}$ .

### 5.2.3 Water

Concentration of mercury in drinking water is normally very low (below  $1 \text{ ng/l}$ ). Values of up to  $25 \text{ ng/l}$  are reported (IPCS, 1991). Based on the assumption that an adult consumes about 2 l of water per day, the daily intakes of Hg from drinking water is insignificant. The WHO guidelines and many national legislation set the values of  $1000 \text{ ng/l}$  (WHO-FAO, 1993).

### 5.2.4 Soil

The average mercury concentration in surface soil is reported to be from 20 to  $625 \mu\text{g/kg}$  (Reiman and de Caritat, 1998). Higher concentrations are reported in soils from urban locations and close to sources of Hg pollution (smelting, mining, coal burning facilities, chlor-alkali industry, etc). In Europe very little knowledge is available for vitalization of Hg from soil and consequently on the direct exposure of humans to Hg in soils.

### 5.2.5 Diet

Daily intakes and retention of mercury from food is difficult to estimate accurately. In most food stuff Hg concentration is below  $20 \mu\text{g/kg}$ . Mercury is known to bioconcentrate in aquatic organisms and it is biomagnified in aquatic food webs. For example, the concentration of Hg in small fish at low food web level (such as anchovies) is below  $0.085 \text{ mg/kg}$ , while in sword fish, shark and tuna values above  $1.2 \text{ mg/kg}$  are frequently reported (IPCS, 1991). In Scandinavian predatory fresh-water fish (perch and pike) average levels are about  $0.5 \text{ mg/kg}$ .



The use of fish meal as the feed for poultry and other animals used for human consumption may results in increased levels of Hg. In Germany, the poultry contains 0.03 - 0.04 mg/kg. Cattle are able to demethylate Hg in the rumen, and therefore, beef meet and milk contain very low concentrations of Hg.

**Table 5.2-** Current data on the daily dietary intake of mercury.

Country	Intake ( $\mu\text{g day}^{-1}$ )	References
Belgium	All food: <b>13</b> of which <b>2.9</b> is from fish All foodstuff: <b>6.5</b>	Fouassin and Fondu, 1978 Buchet et al. 1983
Poland	<b>5.08</b> ( age group 1-6 years) <b>5.43</b> (age group 6-18 years) <b>15.8</b> in adults From fish: 7% of total dietary intake	Szprengier-Juszkiewicz, 1988 Nabrzyski and Gajewska, 1984
Germany	<b>0.8</b> from fish <b>0.2</b> from food (except fish and vegetables)	LAI, 1996
Croatia	From fish: <b>27.7</b> (total Hg) <b>20.8</b> ( MeHg form)	Buzina et al., 1995
Spain	<b>4-8</b> (60-90 % from seafood) in Velencia only 27% is from the seafood <b>18</b> of which about <b>10</b> is from fish (Bask country)	Moreiras et al. 1996 Urieta et al., 1996
Sweden	<b>1.8</b> (market-basket)	Becker and Kumpulainen, 1991
United Kingdom	<b>2</b>	MAFF, 1994
Finland	<b>2</b>	Kumpulainen and Tahvonen, 1989
The Netherlands	<b>0.7</b>	Van Dokkum et al., 1989
Czech Rep.	<b>0.7</b>	Ruprich, 1995
Brazil	<b>315 - 448</b> (Amazon, Medeira river)	Boishio and Henshel, 1996
Japan	<b>10</b> <b>6.9 –11.0</b> <b>24 (18 as MeHg)</b>	Tsuda et al., 1996 Ikerashi et al., 1996 Nakagawa et al., 1997

The main problem to accurately estimate daily intakes of various Hg forms from diet is that national survey programmes mainly report total Hg concentrations and the percentage of Hg as MeHg is not known. Total mercury daily intakes reported in various countries are given in Table 5.2. In some national survey the percentage of Hg originating from fish is provided. It is assumed that in this foodstuff the percentage of as MeHg is from 60 to 90 %. Therefore fish and fish products represent the major source of methylmercury.

The US EPA reference dose (RfD) for MeHg is 0.1  $\mu\text{g/kg}$  body weight/day (IRIS, 1995a). This would be 42  $\mu\text{g/week}$  for a 60 kg adult. The equivalent amount of fish consumed would be 420 g of fish per week with 0.1 mg Hg/kg or 105 g of fish per week with 0.4 mg Hg /kg. WHO-FAO provisional tolerable weekly intake (PTWI) amounts to 5  $\mu\text{g/kg}$  body weight (0.7  $\mu\text{g/kg}$  body weight/day), but a revision is currently in progress. The PTWI set by the Welfare Ministry of Japan is 0.17 mg of methylmercury (0.4  $\mu\text{g/kg}$  body weight/day) (Nakagawa et al., 1997). In Europe the recommended limits for mercury vary. In Scandinavian countries Hg in fish should not exceed 0.5 mgHg/kg. The Swedish Food and Health Administration is at present evaluating the relevance of a new limit at 0.3 mgHg/kg, while Japan has already

adopted a 0.3 mg/kg guideline (Dickman and Leung, 1998). In Sweden pregnant women are advised not to eat perch or pike at all during pregnancy.

It may be concluded that in those areas in Europe where fish consumption represents a considerable part of diet, the value the US EPA RfD could be considerably exceeded.

### 5.3 BIOMONITORING OF MERCURY EXPOSURE IN HUMANS

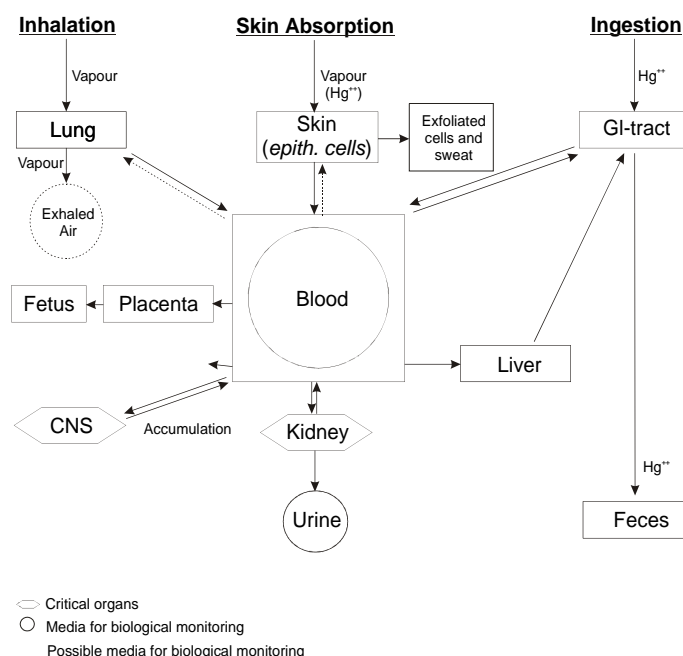
This chapter deals with biological samples that are used to assess mercury exposure in humans. The selection of biological media depends on mercury compounds, exposure pattern (e.g. chronic, acute) and time of sampling after exposure.

#### 5.3.1 Elemental and Inorganic Mercury

In case of exposure to elemental mercury blood and urinary mercury are commonly used to assess occupational exposure. Elemental  $\text{Hg}^0$  in exhaled air and urine has also been used to assess the level of recent exposure to elemental Hg. Kinetics of elemental Hg and biological samples for biomonitoring are presented in Figure 5.1. One should note that inhaled vapour of Hg is oxidised to Hg (II) and both species are present (elemental and divalent Hg). The elemental Hg is highly mobile, readily crosses the placenta, cell membranes, and the blood-brain barrier. The Hg (II) ions are much less mobile, crossing the above barriers at a much slower rate.

The usefulness of blood as a bioindicator of exposure to elemental Hg depends on time elapsed since exposure and the level of exposure. The whole blood analysis may be used to assess the exposure. Mercury in blood increases rapidly with the exposure, and decreases with an initial half-life of approximately two to four days, and a slower phase of a couple of weeks (Barregård et al. 1992, Sallsten et al. 1993). This means, that the usefulness of the blood is of limited value, in particular, if it is taken several weeks after exposure. It is, however, valuable for assessment of peak exposures (Barregård 1993).

At low levels of elemental Hg exposure, individual differences in total Hg in blood could be explained by current exposure to Hg due to the number of amalgams fillings, fish consumption and other possible exposure routes (e.g. living environment in Hg mining area). At low-level elemental Hg exposure, blood Hg poorly represents information on current and past  $\text{Hg}^0$  exposure. A separation of whole blood into its plasma and erythrocytes fractions permits better discrimination between exposure to  $\text{Hg}^0$  and methyl mercury. Such discrimination will, of course, be more correct using speciation of mercury in blood.



**Figure 5.1 - Metabolism and media for biological monitoring**  
 (Elinder et al. 1988).

Urinary Hg indicates mercury levels present in kidneys (Clarkson et al. 1988a,b). In the case of occupational exposure, urinary Hg has been used to estimate exposure. In urine, mercury levels decrease at a much slower rate as compared to blood. The half life of exposure varies between 40 and 90 days (Barregård et al. 1992, Roels et al. 1991, Sallsten et al. 1994). After exposure to higher levels of mercury, urinary Hg levels stay elevated over a longer period of time, which means that urine is a much better indicator for longer periods of exposure than blood samples. Internal dose of mercury is normally assessed using determination of mercury in first morning urine, corrected for varying dilution using creatinine determination. Urinary methylmercury levels are normal very low, which means that very little dietary Hg is excreted by urine. It is important to note that good correlation between urinary Hg values and concentration of Hg in air has only been demonstrated after stable exposure and correction of the urinary Hg values with the urinary excretion rate and normalization to the time elapsed after exposure (Roels et al. 1987). However, intra-individual differences still remain high. It is interesting to note that Hg levels in former Hg miners and active miners currently not exposed, Hg levels in urine are comparable to those of occupationally non-exposed population (Kobal et al., 2001, Kobal and Dizdarevic, 1997).

The concentration of Hg in urine is a good indicator of a long-term integrated exposure, while total Hg in blood is a good indicator of recent exposure (Gompertz, 1982, Barregård 1993). After inhalation mercury is rapidly oxidized, bound to organic molecules, and is then excreted in the bound form through urine. At a higher rate of absorption, a small part of the Hg circulates in the blood and kidney in elemental Hg form, and is partially excreted as dissolved elemental Hg in urine (Yamamura, 1991).

An attempt has been made to use the exhaled air as a possible bioindicators of exposure to elemental Hg (Sallsten et al. 1998, 2000). A portion of absorbed Hg is excreted via the lungs. Excretion half-life is approximately 18 hours (Hursh et al. 1976). At a lower levels of

exposure, the usefulness of this biomarker is limited due to numerous confounding factors, such as Hg released from the amalgam filling, drinking of alcohol, etc..

The kinetics of uptake and release in blood and urine are fairly rapid, while Hg levels in target organs may change far more slowly (Clarkson, 1988). Mercury levels in blood and urine may not reflect the accumulation of Hg in the brain, while urinary Hg mainly reflects kidney Hg (Clarkson 1988 a,b, Borjesson et al. 1995). The mobilisation tests with 2,3-dimercaptopropane-1-sulfonate (DMPS) or meso-2,3-dimercaptosuccinic acid (DMSA) increases the amount of Hg excreted, but does not yield any additional information to pre-chelation excretion (Sallsten et al. 1994).

As the elemental Hg vapour is readily oxidized to inorganic Hg after absorption, similar biomarkers (blood and urine) could be used to assess exposure to inorganic Hg.

### 5.3.2. Methylmercury

In case of exposure to methylmercury two bioindicators are normally used: blood and hair samples. In the blood MeHg accumulates mainly in the red blood cells, therefore Hg in red blood cells is frequently used as an index to MeHg exposure. Exposure to elemental Hg will lead to an increased value of Hg in plasma, therefore through the analysis of total Hg in these samples it is possible to differentiate between exposure to elemental Hg and MeHg. However, it is recommended to measure total Hg and MeHg in order to take into account possible co-exposure to elemental/inorganic Hg. This is not difficult as a number of methods have been developed in recent years to facilitate accurate analysis of total and MeHg in biological materials. The kinetics of MeHg in humans and corresponding tissues suitable for biomonitoring are presented in Figure 5.2.

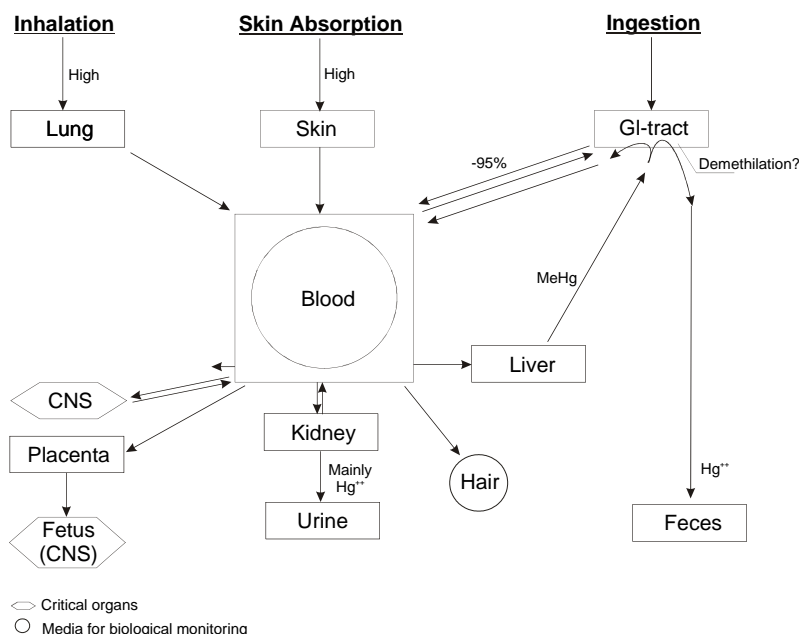
Scalp hair has widely been used as a good indicator of exposure to MeHg in the diet. MeHg is incorporated into hair follicle in proportion to its content in blood.

The hair-to-blood ratio in humans has been estimated as approximately 250:1 expressed as µg/g hair to mgHg/L blood. Once MeHg is incorporated into hair, MeHg is stable, and therefore provides a longitudinal history of blood MeHg. Hair grows with an approximate rate of about 1 cm/month, recapitulation over a long period is possible, dependent on the length of the hair. In population constantly exposed to MeHg, the percentage of Hg as MeHg is close to 100%. However, due to possible co-exposure to elemental Hg or possible external contamination of hair samples with inorganic Hg, it is recommended that both total Hg and MeHg are measured, in cases when high levels of Hg are found.

Concentrations of MeHg in body and/or pubic hair were as well proven to be good indicators of MeHg burden (Horvat et al., 1988).

It is well understood that pregnant women and their foetus are the most critical population group as regards the exposure to MeHg through food consumption. Some recent studies carried out in Faroe islands (Grandjean et al., 1997, Sorensen et al. 1999, Budtz-Jorgensen et al. 2000, Steuerwald et al. 2000) indicated the usefulness of umbilical cord blood as good exposure indicator during pregnancy. There is a good correlation between MeHg in maternal and umbilical cord blood, with higher values found in cord blood, indicating efficient

transport of MeHg through the placental barrier to the foetus. At more elevated levels of MeHg in maternal blood (about 7 ng/ml), the umbilical: maternal blood ratio is about 3. The usefulness of placenta as an indicator of exposure is still not clear, although most studies show very good correlation between MeHg in blood, hair and placenta. The percentage of Hg and MeHg in placenta is much lower than in blood samples, most probably reflecting removal of inorganic Hg before it can be transferred to the foetus (Horvat et al. 1988).



**Figure 5.2 - Metabolism and media for biological monitoring of methylmercury** (Elinder et al. 1988).

The poisoning nature of mercury is well acknowledged (IPCS 1991; Ishihara and Urushiyama, 1994). But less known are the effects of mercury on humans as a consequence of long term exposure to low concentrations. In many cases the use of biomarkers, such as Hg concentrations blood and urine, are not sufficient to assess the internal doses and potential effects on the central nervous system, kidney, the immune system, and other possible effects. Therefore, better scientific understanding of risks to human health, especially to those citizens living close to potentially dangerous sites, is needed. Therefore other biomarkers than mercury measurements alone should be used. An example is N-acetyl-glucose-aminidase (NAG) and other low molecular weight proteins in urine, that seem to reflect effects at low level exposure to Hg<sup>0</sup>. There is a need for continuous research, and for example, markers of oxidative damage could be tested.

## 5.4 ANALYTICAL METHODS FOR BIOLOGICAL MONITORING

Methods for the determination of total and major species of mercury are classified according to the isolation techniques and detection systems. They are selected depending on the nature of the sample and in particular the concentration levels of mercury. The key elements for obtaining accurate measurements are connected with contamination-free sampling, sample storage and handling. The analytical methods for determination of total mercury and its species in various biological and environmental samples and the needs for future development are reviewed (Horvat, 1996; Horvat and Schroeder, 1995; Schroeder, 1995).

Relatively little is known about the effects of storage on the stability of total Hg and monomethylmercury compounds (MeHg) in biological samples. Fresh samples are usually stored (deep frozen or lyophilised) in darkness (Horvat and Byne, 1992). Sometimes samples are sterilized ( $\gamma$ -irradiation or autoclaving) in order to prevent further transformation of mercury species by bacteriological activity. Sample preparation must be carried out under clean mercury-free conditions. Significant external contamination of samples with methylmercury is unlikely to occur, however extreme cautions are necessary to avoid contamination by inorganic mercury.

### 5.4.1 Determination of Total Mercury

Most of the methods for the determination of total mercury in biological samples require preliminary digestion of the sample. They are classified as wet oxidizing digestion, for example see Liang and Bloom (1993) and dry combustion/pyrolysis decomposition methods, for examples see (Byrne and Kosta, 1974; LECO, 1999).

### 5.4.2 Instrumental Methods

Frequently applied detection techniques are cold vapour atomic absorption spectrometry (CV AAS), more sensitive atomic fluorescence spectrometry (CV AFS), and various types of emission spectrometry. Their relative detection limits are presented in Table 5.3.

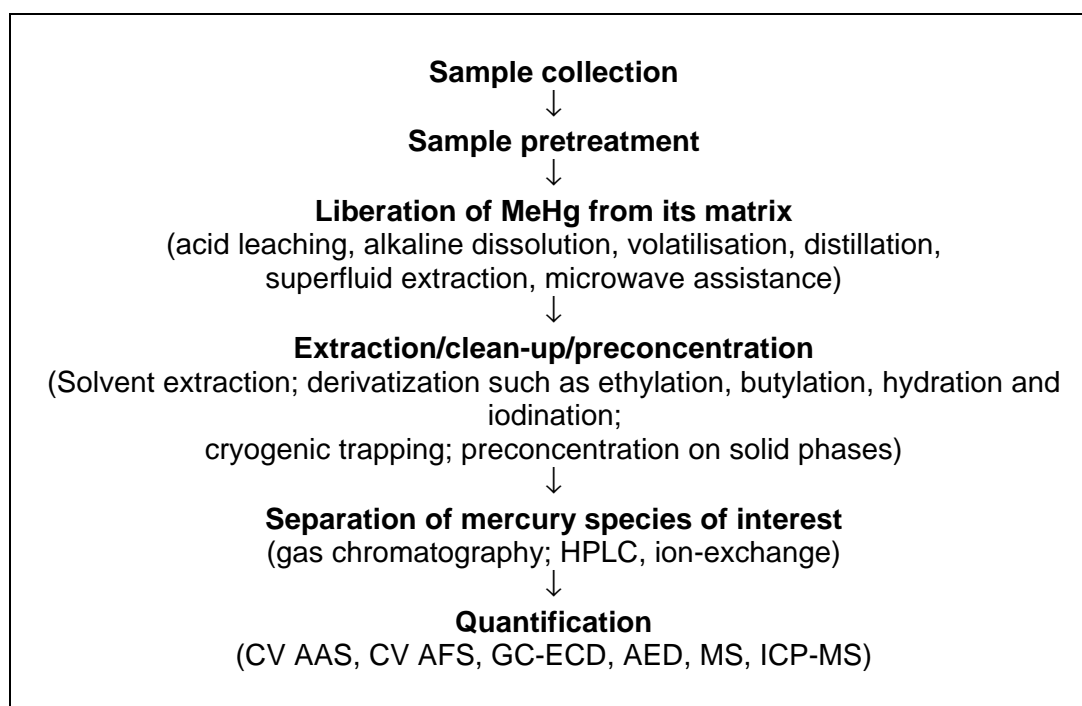
**Table 5.3** - Most frequently used methods for quantification of mercury and their relative detection limits (Horvat, 1996).

Method	Reported Detection Limits
Colorimetric methods	0.01 - 0.1 µg/g
AAS graphite furnace (GF AAS)	1 ng/g
cold vapour (CV AAS)	0.01 - 1 ng/g
AFS cold vapour (CV AFS)	0.001 - 0.01 ng/g
NAA instrumental (INAA)	1-10 ng/g
radiochemical (RNAA)	0.01 - 1 ng/g
GC Electron Capture Detector	0.01 - 0.05 ng/g
Atomic Emission Detector	~ 0.05 ng/g
Mass Spectrometer	0.1 ng/g
CV AAS/AFS	0.01- 0.05 ng/g
HPLC UV	1 ng/ml
CV AAS	0.5 ng/ml
CV AFS	0.08 ng/ml
Electrochemical detectors	0.1-1 ng/ml
ICP-MS	0.01 ng/ml
ICP-AES	2 ng/ml
Photo-acoustic spectroscopy	0.05 ng
X ray fluorescence	5 ng/g - 1 µg/g
Electrochemical methods	0.1 - 1 ng/g
Gold-film analyzer	0.05 µg/g

### 5.4.3 Determination of Organomercury Compounds

Hundreds of papers on the analyses of organomercury compounds in environmental samples have appeared during the past twenty years. They are systematically reviewed in several articles and monographs (Rodriquez-Vazquez, 1978, Craig, 1982, Horvat and Schroeder, 1995, Horvat, 1996). In general, methods are classified according to the isolation technique and the detection system. Most common steps for determination of MeHg are reviewed and schematically presented in Figure 5.3.

There are also a few methods that are based on differential reduction, which is frequently used in clinical laboratories. In the method developed by Magos (Magos, 1971) the inorganic mercury in an alkaline digested sample is selectively reduced by stannous chloride while organomercury compounds are reduced to elemental mercury by a stannous chloride-cadmium chloride combination. CV AAS can measure elemental mercury released.



CVAAS – cold vapour atomic absorption spectrometry  
 CVAFS – cold vapour atomic fluorescence spectrometry  
 GC-ECD – gas chromatography coupled with the electron capture detector  
 AED – atomic emission spectrometry  
 ICP-MS – inductively coupled mass spectrometry  
 HPLC – high performance liquid chromatography

**Figure 5.3** - Steps for determination of MeHg.

#### 5.4.4 Quality Control and Quality Assurance

There are various means to achieve good quality data in analytical laboratories. Representative samples need to be properly collected and stored, prior to analysis, and all laboratory work conducted under a good QA programme. This can efficiently be achieved through skilled, well-trained, experienced and motivated staff. Protocols for sampling and sample storage should be well developed in order to prevent contamination and /or losses of Hg. In addition, interconversion of various Hg species during sample handling should also be prevented. Samples should be processed under very clean laboratory conditions and the appropriate quality labware and reagents (Hg-free) should be employed. The analysts should only use an analytical procedure on a routine basis after it has been validated for the range of concentrations and matrices to be dealt with the measurement programme using the relevant reference materials (RMs) and certified reference materials (CRMs). Other important measures include the quality assurance manual, training of personnel, a good managerial structure of the laboratory, the use of validated methods, the application of statistical control principles (e.g. control charts), and the external quality control measures (e.g. interlaboratory tests).

There are a number of CRMs available for total mercury in biological, sediment, and water samples (IAEA, 1995, 1996). In addition, the COMAR database ([http://www.bam.de/a\\_i/comar/scr/titel.htm](http://www.bam.de/a_i/comar/scr/titel.htm)) is one of the most extensive data base on the



availability of certified reference materials on a global scale and it is continuously updated. However, only human hair CRMs are available for determination of both, total Hg and MeHg in samples of human exposure (Horvat, 1999).

Currently available CRMs are not sufficient to cover the needs in terms of various origin (urine, blood, hair) and concentration ranges. Human hair CRMs will soon become obsolete and to our knowledge no new CRMs are in preparation. In the absence of proper CRMs an alternative way to control the accuracy of analytical data is regular participation in intercomparison exercises.

## 5.5 MEASURED AND MODELED LEVELS OF MERCURY IN BIOMARKERS

### 5.5.1 Modeling Human Exposure

Humans are exposed to mercury of natural and anthropogenic sources. Models were developed to calculate exposure of individual and population exposures. In Europe such large-scale studies are practically non-existence, however in the USA various scenarios were modelled (US EPA, 1996), although large uncertainties exist from one to another geographical locations.

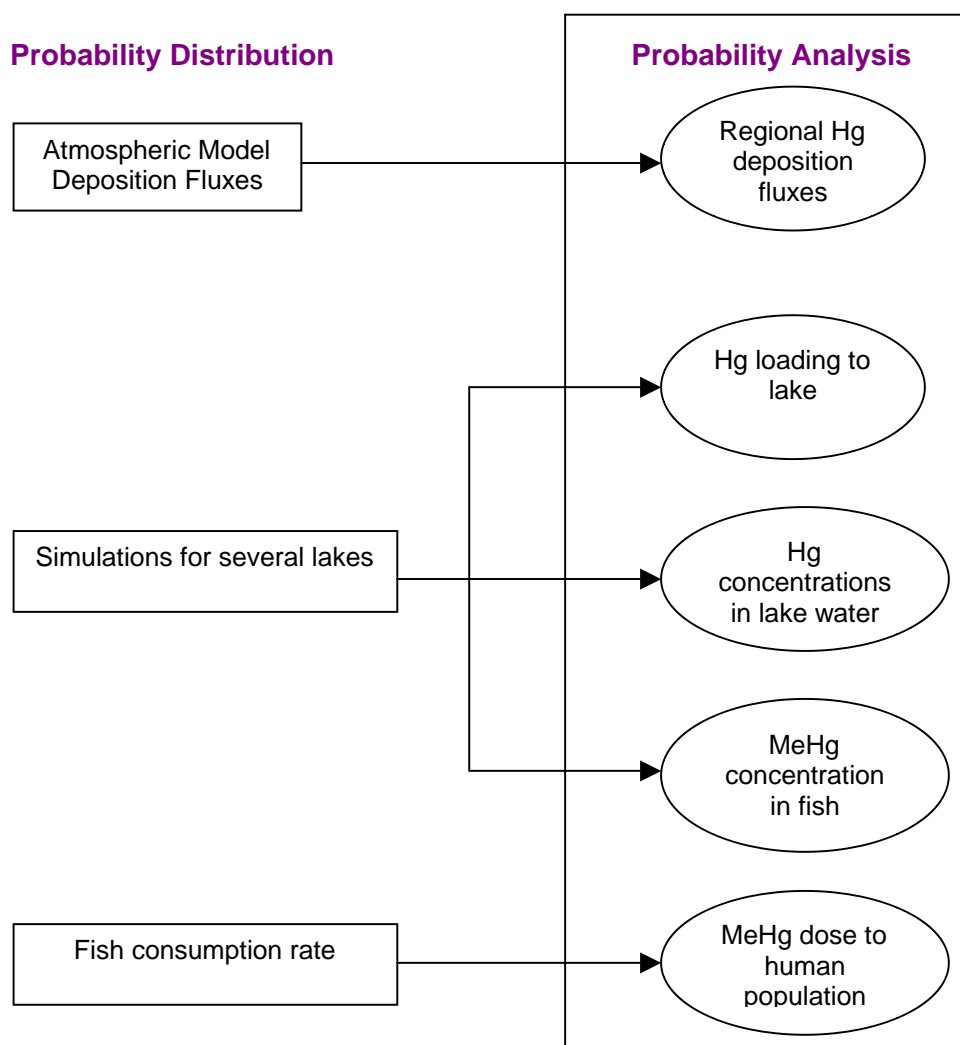
Models consist of various sub-models mainly dealing with simulation of environmental fate of mercury (Table 5.4.).

**Table 5.4** - Models used in US to predict mercury air concentrations, deposition fluxes and environmental concentrations (US EPA, 1997).

Atmospheric model	Predicts average annual atmospheric mercury concentration and wet and dry deposition flux for selected grid, due to all anthropogenic sources of mercury and a natural background atmospheric Hg concentrations. It also accounts for the long-range transport of mercury emitted from anthropogenic sources.
Local air transport model (GAS -ISC3)	Calculates average concentrations and deposition fluxes within a selected grid from emission source (categorised in four major groups scenarios)
Modelling environmental concentrations (IEM-2M)	Predicts environmental concentrations of three chemical forms of Hg (elemental, divalent and monomethylmercury compounds) in soil, water and biota. It is based on local-scale estimates of air concentrations and deposition rates to watersheds and water bodies.

Model for human exposure through inhalation and ingestion of other contaminated food were also evaluated. Atmospheric concentrations are predicted by atmospheric models and soil concentrations from the IEM-2M model. Concentrations in plants are calculated from soil-to plant and air-to plant transfer factors. Concentrations in animal tissue are then calculated from predicted concentration in plants, animal consumption rates, and specific biotransfer factors. Mercury concentrations in fish are calculated from simplified assumptions that aquatic food chains can be adequately represented using four trophic levels: phytoplankton (algal

producers), zooplankton (primary herbivorous consumers), small forage fish (secondary consumers) and larger, piscivorous fish (tertiary consumers), which are consumed by humans. It is well documented that food chain structures vary considerably among different aquatic systems with large variability in bioaccumulation factors. Another important simplification in these models is that the concentration of MeHg in fish is directly proportional to dissolved MeHg concentrations in the water. It is also well documented that this relationship may vary considerably from one to another water body.



**Figure 5.4** - Schematic description of the methodology for the probabilistic assessment of regional Hg exposure (Seigneur et al., 1997).

The bioaccumulation factor (BAF) for the piscivorous fish is calculated to be  $1.6 \cdot 10^6$ , calculated on the assumption that the percentage of Hg as MeHg is about 7.8% of total dissolved Hg in water, and 65% of these is freely dissolved.

Exposure scenarios are defined by the source of contamination, the potential receptor population, the potential pathways of exposure and the variables that affect the exposure pathways. The fate of deposited mercury should be examined for each situation separately. This is of particular importance in case of expected elevated mercury concentration close to

emission sources. The exposure scenarios must then include the total amount of food derived from the affected area and the extent of mercury contamination of these food sources. Each situation should be examined separately in order to identify the most important factors that should be taken into account in the modelling, and by this to reduce uncertainties of simulated results.

A probabilistic assessment of regional mercury exposure was developed by Seigneur et al. (1997). The methodology is based on a multimedia model of the atmospheric fate and transport of mercury over a continental scale and the aquatic simulation of the transformation and bioaccumulation of mercury in lakes in the region of interest. The model, however, addresses only the variabilities of key input variables and does not include a treatment of input data uncertainties or model formulation uncertainties. The methodology is schematically presented in Figure 5.4 and was practically applied in the Great Lakes region of the USA as an example.

### 5.5.2 Measured Biomarkers of Exposure

Reference values for total mercury concentrations in biological media for the general population were discussed by the WHO (IPCS, 1990), in this context referred to as 'normal levels'. The mean concentration for whole blood was considered to be about 8 µg/l. This level seems to be too high as an average for the European populations of today. As the exposure to methyl mercury predominantly is related to fish consumption the whole blood reference values will differ according to dietary habits, mainly fish consumption. In subjects with dental amalgams and low exposure to methyl mercury, the amalgams will, however, also contribute to whole blood mercury levels (Clarkson et al. 1988b, Barregård 1993). In rare cases the blood mercury levels due to dental amalgam may be as high as 20 µg/l (Barregård et al. 1995).

Scandinavian studies in the 1980-1990 showed average mercury levels in whole blood of 3-5 µg/l in occupationally unexposed adults, used as referents in occupational epidemiology studies (Akesson 1991, Langworth et al. 1991, Svensson et al. 1992, Barregård et al. 1994, Ellingsen 1993). Nearly all of them had amalgam fillings, and the average consumption of (salt water) fish was 1/week. In subjects born in the 1970s and later, the levels are lower, mean 1-2 µg/l owing to less dental amalgam and lower fish consumption (Sandborgh-Englund et al. 1996, 1998, Vahter et al. 2000). German adults have mean blood mercury levels of only about 0.5 µg/l (Schweinsburg and Kroiher 1994, Drexler et al. 1998, Seifert et al. 2000).

Mean urine mercury levels in occupationally unexposed adults in Scandinavia were 2-3 µg/g creatinine (2-4 µg/l in 24h urine) in the 1980s (Barregård 1993). In younger subjects, the levels are lower, mean 1-2 µg/g creatinine, owing to less dental amalgam (Herrstrom et al. 1995, Vahter et al. 2000). In Germany the levels are lower, about 0.5 µg/l (Zander et al. 1990, Drexler et al. 1998, Ganss et al. 2000, Seifert et al. 2000).

For scalp hair the mean concentration was considered to be about 2 µg/g by the WHO. This level too seems to be too high as an average for the European populations of today. In Sweden and Germany average hair mercury levels in adults are about 0.5 µg/g (Oscarsson 1994, 1996, Bratel 1997, Schweinsburg and Kroiher 1994).

In order to derive the reference doses for humans, it is necessary to determine the ingested dose that resulted in the Hg concentration in the biomarker. In order to do such calculations it is necessary to use toxicokinetics models. There are several toxicokinetic parameters that determine the tissue (or biomarker) MeHg concentration after ingestion of a given dose of MeHg. For example in case of MeHg ingestion through food, those parameters include the uptake of MeHg from the gastrointestinal tract, the distribution of MeHg to the various body tissues, and the elimination of MeHg or Hg from those tissues (Figures 2 and 3). Two models are used for this purpose. (1) physiologically based pharmacokinetic model - PBPK (Clewett et al. 1999) and (2) a single compartmental pharmacokinetic model (IPCS 1990; US EPA 1997). The PBPK model attempts to characterise the distribution and redistribution of MeHg among several body compartments, including maternal hair and foetal cord blood. This model is conceptual more accurate and flexible compared to one-compartmental model; it is very complex and more difficult to evaluate.

The accumulation and excretion of MeHg in humans, measured in terms of hair and blood levels, can well be represented by single-compartment model. This is a useful working model for comparing blood and hair levels to daily intakes of methylmercury. This model collapses the maternal-body compartments into a single maternal blood compartment. Toxicokinetic compartments that are not directly considered in the model include MeHg in cord blood and other foetal tissues, net absorption of MeHg and MeHg in maternal hair.

In adult humans the whole body concentration would assume steady state in about one year. The comparison of predicted relationship with those observed in field studies on population believed to have attained the steady state from long-term dietary exposure to MeHg in fish shows that field studies always show lower values. One reason may be that the populations under investigation were not in true steady state, since intake is frequently seasonal in fish-eating population. This model is referred to the average adult human of a body weight of 70 kg. It is assumed that children and teenagers are more vulnerable to high intakes of MeHg due to higher energy intake.

At a steady state the accumulated amount (A) is given by:

$$A = \frac{a}{b}$$

Where:

A = the accumulated amount

a = the amount taken up by the body (or organ) daily

b = the elimination constant (related to the biological half-time)

The steady state concentration in blood may be related to the following equation (IPCS,

$$C = \frac{0.95 \times 0.05 \times d}{0.01 \text{ days}^{-1} \times 5 \text{ litres}}$$

1990):

Where:

C = Concentration in blood (µg/litre)

0.95 = Fraction of the daily intake absorbed

0.05 = part of absorbed amount that goes to the blood compartment

d = average daily dietary intake (µg of Hg)

5 litres = blood volume

0.01 days<sup>-1</sup> = elimination constant

Both models suffer from interindividual variability in physiology and kinetics, for which no correct value exist. Each of the model parameters is a random variable whose possible values in a population can be described by probability distribution. Failure to consider interindividual toxicokinetic variabilities can result in an RfD that is not protective of a substantial portion of the population. Interindividual toxicokinetic variability can be addressed in the derivation of RfD by application of uncertainty factors to a central-tendency estimate of the ingested dose. It is still not certain which values are most appropriate for the model parameters used to derive the central tendency estimates. The choices for each case should be carefully considered with reference to discussions presented in the known and published analysis of toxicokinetic variability (NRC, 2000).

Concentration of MeHg in hair is proportional to blood concentration at the time of formation of the hair strand. In general, the concentration in hair is 250 times the simultaneous concentration in blood. Once MeHg is incorporated in hair mercury concentration remains unchanged. The mean mercury concentrations in hair and consumption of fish are presented in Table 5.4.

An interesting example in the Mediterranean was conducted by the WHO and FAO where over 4000 people were screened through a dietary survey, and a total of 1098 hair samples were analysed (659 from Greece, 241 from Italy, and 198 from Croatia) (WHO, 1988). The results confirmed a positive correlation between seafood consumption and the levels of MeHg in hair.

Based on the WHO criteria for identifying population possible at risk (25 µg/kg of Hg in hair of adults and 6 µg/kg in hair of pregnant women) none was identified in Croatia. In Greek population only the residents of remote fishing communities, exceeded the criteria. Most of the Italian individuals have also been considered free from risk, except population of fisherman spending considerable time at sea, and babies that had high intrauterine exposure from the high seafood consumption of their mothers.

Until recently, complete metabolic model for inhaled mercury vapour in humans was not available, despite the fact that the continuous occupational exposure of thousands of workers annually and the long history of mans exposure to this form of mercury. A few studies have presented toxicokinetics of Hg in experimental animals (Falnoga et al., 1994, Thomas et al. 1988). Recently, a four-compartmental model, including two depot compartments to account

for retention in lungs and kidneys, respectively, gave very good fit of the model output with the measurement data (Jonsson et al. 1999). The fraction of dose excreted from the central compartment directly into urine was found to be positively correlated with the pre-exposure excretion rate of Hg via urine. All studies concluded that the true uptake of Hg from amalgam fillings is very difficult to measure due to a number of uncertainties including estimates on either intraoral measurements, blood or urinary Hg levels. This would of course cause difficulties in modelling exposure of population to Hg in amalgams (Sandborgh, 1998).

**Table 5.5** - Mercury concentration in hair in relation to exposure data.

Country	Total Hg in Hair	Reference
Faroe Islands (Denmark)	> 10 µg/g max. 39.1 µg/g (consumption of pilot whale with 3.3. mg/kg of Hg)	Weihe et al. 1996
Faroe Island	No fish: 0.8 µg/g 1 fish meal/week: 1.6 µg/g 2 fish meal/week: 2.5 µg/g 3 fish meal/week: 2.1 µg/g 4 fish meal/week: 5.2 µg/g	Grandjean et al. 1992
13 countries – a review	Once/month: 1.4 µg/g; once/two weeks: 1.9 µg/g; once/week: 2.5 µg/g; once /day: 11.6 µg/g.	Airey et al. 1983
North Sweden	0.28 µg/g	Oskarsson et al. 1996
Germany	0.25 µg/g	Drasch et al. 1997
Spain, Madeira	Fisherman and their families 38.9 µg/g (men) and 10.4 µg/g (women)	Renzoni 1998
Sweden	1-3 fresh water fish meals/week: 2.5µg/g >3 fresh water fish meals/week: 3.8µg/g 1 meal of salt water fish/week: 0.6µg/g	Oskarsson et al. 1990 Bratel et al. 1997
Croatia		
USA	1.5 µg/g	Dickman and Leung 1998
Brasil  Rio Tapajos	8.76 µg/g (110 g of fish/day with the concentration of MeHg from 0.1 to 0.5 µg/g) 26% of fish consumed contain Hg above 0.5 mg/kg: High fish diet 16.1 µg/g Mixed fish diet: 14.8 µg/g Low fish diet: 7.8 µg/g	Kehrig et al. 1998  Lebel et al. 1997

One may conclude that we still do not have sufficient information to relate mercury levels in air to accumulated body burden and to identify the most appropriate indicator media for levels of mercury vapour in the target organ (the brain). One study also addressed the pharmacokinetics of Hg released from dental amalgams. Inhaled mercury may also cross the placenta, but no information is available on human subjects concerning this important question.

## 5.6 CONCLUSIONS AND RECOMMENDATIONS

In order to understand environmental Hg exposures it is necessary to have the information on all sources of Hg exposures.

Quantitative dietary intake data on intakes of all fish and related products should be collected in any serious study of this contaminant. Such data are necessary to quantify exposures, separating the effect modifiers that account for the differences between exposures and target tissue concentrations. Such data are also essential for identification of possible confounding factor such as other contaminant or nutrient that are abundant in this food sources and not in others.

Mercury in urine is an established marker of long-term exposure to inorganic Hg. Blood and hair analysis provide good estimate of exposure to MeHg through food consumption. In most sensitive population (e.g. pregnant women and newborn) cord blood Hg concentrations may be the best surrogate biomarker for Hg in foetal brain compartment.

Exposure assessment in European population, in particular those with high fish consumption, is urgently needed to provide a full picture of the distribution of MeHg and Hg exposures nationally and regionally. Exposure to elemental Hg from dental amalgams represent a considerable daily intake of Hg and should be also considered in risk assessment of MeHg.

Further studies of MeHg exposures in humans should include a thorough assessment of the diet during the period of vulnerability and exposure. Dietary assessments should be conducted concurrently with the exposure, because retrospective assessment is influenced by many factors, including memory, changes in eating behaviour, use of vitamins and mineral supplementation. In all studies, the estimates should be used with information on MeHg concentrations in the food to estimate possible MeHg intake by pregnant women, young children and adults. Attempts should be made to validate estimates on the relationship between hair concentration and diet intake. Information on dose from breast-feeding should as well be improved.

Any biomarker based RfD for MeHg should specifically address interindividual toxicokinetic variability in the estimation of dose corresponding to a given biomarker concentration.

Modelling predictions of individual and population exposure are virtually nonexistent in Europe and should be developed and tested in various environmental conditions and different source terms of mercury contamination. To achieve this goal a multidisciplinary approach is needed linking environmental and health related expertise.

## 5.7 REFERENCES

- Airey, D. (1983) Total mercury concentrations in human hair from 13 countries in relation to fish consumption and location. *Sci. Total. Env.* 31: 157-180.
- Barregård L, Sällsten G, Järnholm B. (1995) People with high mercury uptake from their own dental amalgam fillings. *Occup Environ Med.* ;52:124-128.
- Barregård L. (1993) Biological monitoring of exposure to mercury vapor. *Scand. J. Work Environ. Health* 19 suppl 1:45-9.
- Barregård L. (1999) Uptake of mercury from dental amalgams - looking beyond the average. In: Novakova V. (ed) *Amalgam and Health - New perspectives on risks*. Swedish Council for Planning Coordination of Research. Stockholm, 1999.
- Becker W, Kumpulainen J. Contents of essential and toxic mineral elements in Swedish market-basket diets in 1987. *Br. J. Nutr.* 66:151-60.
- Berglund A.(1990) Estimation by a 24-hour study of the daily dose of intra-oral mercury vapour inhaled after release from dental amalgam. *J. Dent. Res.* 69:1646-1651.
- Bioschio A.A., Hensel, D.S. (1996) Risk assessment of mercury exposure through fish consumption by the riverside people in the Madeira Basin, Amazon, 1991. *Neurotox.*, 17: 169-175.
- Borjesson J, Barregård L, Sällsten G, Schütz A, Jonson R, Alpsten M, Mattsson S. (1995) In vivo XRF analysis of mercury: the relation between concentrations in the kidney and the urine. *Phys. Med. Biol.* 40:413-426.
- Buchet, J.P., Lauwerys, R., Vandevoorde, A., Pycke, J.M. (1983) Oral dietary intake of cadmium, lead, manganese, chromium, mercury, calcium, zinc, and arsenic in Belgium. A duplicate meal study, *Food Chem. Toxicol.*, 21: 19-24.
- Budtz-Jorgensen E, Grandjean P, Keiding N, White RF, Weihe P. (2000) Benchmark dose calculations of methylmercury-associated neurobehavioural deficits. *Toxicol Lett.* 112-113:193-9.
- Buzina R., Stegnar P., Buzina-Suboticane K., Horvat M., Petric I., Farley T.M.M. (1995) Dietray mercury intake and human exposure in an Adriatic population, *Sci. Tot. Environ.* 170: 199-208.
- Byrne, A.R. and Kosta, L. (1974) Simultaneous neutron activation determination of selenium and mercury in biological samples by volatilisation, *Talanta* 21: 1083.
- Clarkson T.W., Friberg, L., Hursh, J.B., Nylander, M. (1988 a) The prediction of intake of mercury vapour from amalgams. In: Clarkson, T.W., Friberg, L., Nordberg, G.F., Sager, P.R., eds. *Biological monitoring of toxic metals*, New York, London, Plenum Press,. pp. 247-264.
- Clarkson, T.W., Hursh, J.B., Sager, P.R., Syversen, T.L.M. (1988b). Mercury, In: *Biological monitoring of Biological metals*. Eds. T.W. Clarkson, L. Friberg, G.F. Nordberg, P.R. Sager, Plenum Press, New York, pp. 199-246.
- Clewell H.J., Gearhard J.M., Gentry P.R., Covington T.R., VanLandingham C.B., Crump K.S., Shipp A.M. (1999) Evaluation of the uncertainty in an oral reference dose for methylmercury due to inter-individual variability in pharmacokinetics. *Risk. Anal.* 19(4): 547-558.



- Craig, P.J. (1986) *Organometallic Compounds in the Environment - Principles and Reactions*, Longman Group Limited, England.
- Dickman, M.D., Leung K.M. (1998) Mercury and organochlorine exposure from fish consumption in Hong Kong. *Chemosphere*, 37: 991-1015.
- Dizdarevic T, (2001) The influence of mercury production in Idrija mine on the environment in the Idrija region and over a broad area, *Mat. and Geoenviron.*, 48:, 56-64.
- Drasch G., Wanghofer E., Roeder G. (1997) Are blood, urine, hair and muscle valid biomarkers for the internal burden of men with heavy metals: mercury, lead and cadmium? *Trace elements and Electrolytes*, 14: 116-123.
- Elinder C.G., Gerhardsson L., Oberdorster (1988) Biological monitoring of toxic metals – Overview. Pp 1-71. In *Biological Monitoring of Toxic Metals*, T.W. Clarkson, L. Friberg, G.F. Nordberg and P.R. Sager, eds. New York, Plenum press.
- EMEP (1999) Monitoring and modelling of lead, cadmium and mercury transboundary transport in the atmosphere of Europe. Joint report of EMEP Centers: MSC-E and CCC. EMEP report 3/99, July 1999.
- EPA Mercury Study Report to the Congress, EPA 452/R-97-0003, EPA, USA, December 1997.
- Ewers U, Krause C, Schulz C, Wilhelm M. (1999) Reference values and human biological monitoring values for environmental toxins. *Int Arch Occup Environ Health* 72:255-260.
- Falnoga I., Mrhar A., Karba R., Stegnar P., Škreblić M., Tušek-Žnidarič M. (1994) Mercury toxicokinetics in Wistar rats exposed to elemental mercury vapour: modeling and computer simulations. *Arch. Toxicol.* 68: 406-415.
- Fouassin A and Fondu M. (1978) Evaluation de la teneur moyenne en mercure de la ration alimentaire en Belgique. *Arch. Belg. Med. Soc. Hyg. Med. Trav. Med. Leg.* 36: 481-490.
- Gompertz, D. (1982) Biological monitoring of workers exposed to mercury vapour. *J. Soc. Occup. Med.* 32: 141-145.
- Grandjean P., P. Weihe, R.F. White, F. Deves, S. Araki, K. Yokoyama, K. Murata, N. Sorensen, R. Dahl, P.J. Jorgensen (1997), *Neurotoxicol. and Teratol.*, 1997, **20**, 1.
- Halbach S.(1994) Amalgam tooth fillings and man's mercury burden. *Human. Exp. Toxicol.* 13:496-501.
- Horvat M. and A.R. Byrne (1992) Preliminary study of the effects of some physical parameters on the stability of methylmercury in biological samples, *Analyst*, 117: 665-668.
- Horvat M. (1996) Mercury analyses and speciation. In "Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances" (Edited by W. Baeyens et al.), pp 1-31. Kluwer Academic Publishers, The Netherlands (1996).
- Horvat, M, Stegnar, P., Byrne, A.R., Dermelj, M., Branica, Z. (1988) A study of trace elements in human placenta, blood, and hair from the Yugoslav Central Adriatic, *Trace Element Analytical Chemistry in Medicine and Biology*, Proc. 5th Int. Workshop, 1988, eds. P. Bratter, P. Schramel, Walter de Gruyter, Berlin, New York, 1988. pp- 243-250.
- Horvat, M. and Schroeder, W.H. (1995) Mercury (a) Determination of organomercurials. *Encyclopaedia of Analytical Science*, Harcourt Brace & Company Limited, London.

- Horvat, M. (1999) Current status and future needs for biological and environmental reference materials certified for methylmercury compounds. *Chemosphere (Oxford)* 39: 1167-1179.
- Huang YL., Cheng SL. and Lin TH. (1996) Lipid peroxidation in rats administrated with mercuric chloride. *Biol. Trace Elem. Res.* 52:193-206.
- Hursh J.B., Cherian M.G., Clarkson, T.W., Vostal J.J., Mallie P.V. (1976) Clearance of mercury /Hg-197), Hg-203) vapor inhaled by human subjects. *Arch. Environ. Health.* 31(6), 302-309.
- IAEA-TECDOC-854, Survey of reference materials, Volume 1: Biological and environmental reference materials for trace elements, nuclides and micro-contaminants, A report prepared by the IAEA and UNEP, December 1995, Vienna.
- IAEA-TECDOC-880, Survey of reference materials, Volume 2: Biological and environmental reference materials for trace elements, nuclides and micro-contaminants, A report prepared by the IAEA and UNEP, May 1996, Vienna.
- Ikarashi M., Sasaki K., Toyoda M., Saito Y (1996) Annual daily intakes of Hg, PCB, and arsenic from fish and shellfish and comparative survey of their residue levels in fish by body weight, *Esei Shikenjo Hokoku*, 114: 43-47.
- IPCS/WHO (1990) Environmental health Criteria 101. Methylmercury. World Health Organisation, Geneva, 1990.
- IPCS/WHO (1991) Environmental Health Criteria 118. Inorganic mercury, World Health Organisation, Geneva, 1991.
- IRIS (1995) Mercury, elemental.
- IRIS (1995a) Methylmercury.
- Ishihara N. and Urushiyama K. (1994) Longitudinal study of workers exposed to mercury vapour at low concentrations: time course of inorganic and organic mercury concentration in urine, blood and hair. *Occup Environ. Med.* 51: 660-662.
- Jonsson F., Sandborgh-Englund G., Johansson G. (1999) A compartmental model for the kinetics of mercury vapor in humans. *Toxicol. Appl. Pharmacol.* 155: 161-168.
- Kehrig H.A., Malm O., Akagi H. (1998) Methylmercury in fish and hair samples from the Balbina reservoir, Brazilian Amazon, *Environ., Res.* 77: 84-90.
- Kobal A. and Dizdarevic T. (1997) The health safety programme for workers exposed to elemental mercury at the mercury mines in Idrija. *Water Air Soil Pollut.* 97 : 169-184.
- Kobal, A.B., Osredkar J., Horvat, M., Prezelj, M., Sesek-Briski, A., Kersnik, M., Dizdarevic, T., Falnoga I., Stibilj, (2001) V. The impact of long-term past exposure to elemental mercury on antioxidative capacity and lipid peroxidation in mercury miners, in preparation.
- Kosta, L. and Byrne, A.R. (1969) Activation analyses for mercury in biological samples at nanogram levels *Talanta* 16: 1297.
- Kosta, L., Byrne, A.R., Zelenko, V. 1975. Correlation between selenium and mercury in man following exposure to inorganic mercury, *Nature*, 254: 238-239.
- Kumpulainen J and Tahvonen, R. (1989) Report on the activities of the sub-network on trace elements status in food. *FAO Report of the 1989 Consultation of the European Cooperative Research Network on trace elements*, Lousanne, september, 1989 Amazonian population

- LAI, Emissionswerte für Quecksilber, Quecksilberverbindungen, Bericht des Unterausschusses "Wirkungsfragen", Berlin: Erich Schmidt Verlag 1996, ISBN 3-503-09364-3.
- Lebel, J., Roulet, M., Mergler, D., Lucotte, M., Larribe, F. (1997) Fish diet and mercury exposure in a riparian area, *Water, Air, Soil Pollut.* 97: 31-44.
- LECO, AMA 254, Determination of Mercury in Animal Tissues, Organic Application Note, 1999. LECO Corporation.
- Liang L., and Bloom N. (1993) Determination of total mercury by single amalgamation cold vapor atomic absorption spectrometry. *Analyst*, 16, 1297-1301.
- Lorscheider FL, Vimy MJ, Summers AO. Mercury exposure from "silver" tooth fillings: emerging evidence questions a traditional dental paradigm. *FASEB J* 9:504-508.
- MAFF, 1994. 1991 Total Diet Study. Food Surveillance Information Sheet 34, July 1994.
- Magos, L., (1971) Selective Atomic-absorption determination of inorganic mercury and methylmercury in undigested biological samples, *Analyst* 96: 847-852.
- Malm O., Calasans C.F., Fernandes A.P., Bastos W.R. and Pfeiffer W.C. Exposure to metallic mercury in workers in a tropical chloralkali plant evaluated through urine analysis, Rio de Janeiro, Brazil. *Water Air Soil Poll.* 97: 185-191.
- Moreiras O., Cuadrado C., Kumpulainen J.T., Carbajal A., Ruiz-Roso B. (1996) Intake of contaminants, heavy metals and nutrients with potential toxicity via total diet in four geographical areas of Spain. FAO Regional office for Europe, REU Technical series 49. Trace elements, natural antioxidants and contaminants in European foods and diets. FAO, Rome, 1996: 59-92.
- Nabrzyski, M. and Gajewska, R. (1984) determination of mercury, cadmium, and lead in food. *Rocz. PZH*, 35(1): 1-11 (in Polish).
- Nakagawa R., Yumita Y., Hiromoto M. (1997) Total mercury intake from fish and shellfish by Japanese people, *Chemosphere*, 35: 2909-2913.
- Nordberg G., Skerfving (1972) Metabolism. In: mercury in the environment. A toxicological and epidemiological appraisal. L. Friberg and J. Vostal, eds. Chemical Rubber Co., Cleveland, Ohio. 29-91.
- NRC (2000) Toxicological effects of methylmercury Committee on the Toxicological Effects of methylmercury, Board on Environmental Studies and Toxicology, Commission of Life Sciences, National Research Council, National Academy Press, Washington, DC.
- Oskarsson A., Ohlin B., Ohlander EM, Albanus L. (1990) Mercury levels in hair from people eating large quantities of Swedish freshwater fish. *Food Addit Contam.* 7:555-62.
- Bratel J., Haraldson T., Meding B., Yontchev E., Ohman SC, Ottosson JO. (1997) Potential side effects of dental amalgam restorations. (I). An oral and medical investigation. *Eur. J. Oral. Sci.* 105:234-43.
- Oskarsson A., Schultz A., Skerfving S et al. (1996) Total and inorganic mercury in breast milk in relation to fish consumption and amalgam in lactating women. *Arch. Environ. Health* 51: 234-241.
- Reimann C. and de Caritat P. (1998) Chemical elements in the environment. Factsheets for the geochemist and environmental scientist. Springer. 1998.

- Renzoni A., Zino F, Franchi E (1998) Mercury levels along the food chain and risk for exposed populations. *Environ. Res.* 77: 68-72.
- Rodriguez-Vazquez, J.A. (1978) Gas-Chromatographic determination of organomercury(II) Compounds, *Talanta* 25: 299-310.
- Roels H., Abdeladim, S., Ceulemans E. Lauwerys R. (1987) Relationship between the concentrations of mercury in air and in blood and urine in workers exposed to mercury vapour. *Ann. Occup. Hyg.* 31: 135-145.
- Ruprich j. 1995. Health risk assessemnt of dietary exposure to the selected chemical substances in the Czech Republic: Alimentary diseases (1993) and total diet study (1994), pp. 274.
- Sällsten G, Barregard L, Schütz A. Clearance half life of mercury in urine after the cessation of long term occupational exposure: influence of a chelating agent (DMPS) on excretion of mercury in urine. *Occup Environ Med* 1994;51:337-342.
- Sällsten G, Barregard L, Schütz A. Decrease of mercury concentration in blood after long-term exposure - a kinetic study of chloralkali workers. *Br J Ind Med* 1993;50:814-821
- Sällsten G, Kreku S, Unosson H. (2000) A small dose of ethanol increases the exhalation of mercury in low exposed humans. *J Tox Environ Health.* 60:89-100.
- Sällsten G, Nolkrantz K. (1998) Determination of trace amounts of mercury vapour in humid air: performance of gold traps in an atomic fluorescence system. *Analyst.* 123:665-68.
- Sällsten G, Thorén J, Barregård L, Schütz A, Skarping G. Long term use of nicotine chewing gum and mercury exposure from dental amalgam fillings. *J Dent Res* 75:594-598.
- Sandborgh Englund G. Pharmacokinetics of mercury from dental amalgam. Thesis. Faculty of Dentistry. Karolinska Institute, Huddinge, Sweden, 1998.
- Schroeder W.H. Mercury: Inorganic (and total) determination. In "Encyclopedia of Analytical Science", pp. 3050-3059. Academic Press Limited (1995).
- Seigneur C. Pai P., Gerath M., Mitchell D., Hamby G., Gong G., Whipple C., Levin L. (1997) Probabilistic assessment of regional mercury exposure. *Wat. Air. Soil Pollut.* 97: 159-168.
- Skerfving S. (1991) Exposure to mercury in the population. In *Advances in Mercury Toxicology*. Ed. T. Suzuki N. Imura, T.W. Clarkson, , Plenum Press, New York., 1991. 411-425.
- Sorensen N, Murata K, Budtz-Jorgensen E, Weihe P, Grandjean P. (1999) Prenatal methylmercury exposure as a cardiovascular risk factor at seven years of age. *Epidemiology*, 10:370-5.
- Stern, A.H., Korn L.R., Ruppel B.E. (1996) Estimation of fish consumption and methylmercury intake in the new jersey population. *J. Expo. Anal. Environ. Epidemiol.* 6: 503-525.
- Steuerwald U, Weihe P, Jorgensen PJ, Bjerve K, Brock J, Heinzow B, Budtz-Jorgensen E, Grandjean P. (2000) Maternal seafood diet, methylmercury exposure, and neonatal neurologic function. *J Pediatr.* 136:599-605.
- Szprengier-Juszkiewicz T. (1988) Evaluation of daily intake of mercury with food stuff in Poland. *Bromatol. Chem. Tokykol.* 21: 228-232 (in Polish).
- Thomas D.J., Fisher H.I., Sumler M.R., Hall L.L., Mushak P (1988) Distribution and retention of organic and inorganic Hg in methylmercury treated noenatal rats. *Env. Res.* 47: 59-71.

- Tsuda T., Inoue T., Kojima M., Aoki S. (1995) Market basket and duplicate portion estimation of dietary intakes of cadmium, mercury, arsenic, copper, manganese, and zinc by Japanese adults, *J. AOAC Int.* 78: 1363-1368.
- Urieta I., Jalon M., Equilero I. (1996) Food surveillance in Basque country (Spain) *Food Addit. Contam.* 13: 289-52.
- Van Dokkum W., de Vos. R.H., Muys T.H., Westra, J.A. 1989. Minerals and trace elements in total diets in the Netherlands, *British Journal of Nutrition*, 61, 7-15.
- Weihe P.D., Grandjean P., Debes F., White R. (1996) Health implications for Feroe islanders of heavy metals and PCBs from pilot whales. *Sci. Tot. Env.* 186: 141-148.
- WHO-FAO (1993) Toxicological evaluation of certain food additives and contaminants. WHO Technical report series No. 837.
- WHO (1988) Consultation meeting on the Mediterranean Health-Related Environmental Quality Criteria (WHO/FAO/UNEP Joint Project, MED POL Phase II). EUR/ICP/CEH 059(S), Bled, Slovenia, 12-16. September, 1988.
- Woods JS. (1996) Altered porphyrin metabolism as a biomarker of mercury exposure and toxicity. *Can. J. Physiol. Pharmacol.* 74(2):210-5.
- Yamamura, Y. (1985) Inorganic mercury in blood, urine, and expired air in workers exposed to elemental mercury vapour (in Japanese). *Assoc. Ind. Hyg. Jap.* 24: 46-51.
- Yamamura, Y., Yoshida, M., Yamamura, S., (1991) Blood and urinary mercury levels as indicators of exposure to mercury vapour. In *Advances in Mercury Toxicology*. Ed. T. Suzuki N. Imura, T.W. Clarkson, Plenum press, New York., 1991. 427-437.
- Yoshida, M. (1985) Relation of mercury exposure to elementary mercury levels in urine and blood. *Scand. J., Work. Environ. Health* 11: 33-37.

## CHAPTER-6 HEALTH EFFECTS AND RISK ASSESSMENT

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## 6.8.1 ELEMENTAL MERCURY

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## 6.1 INTRODUCTION

The present chapter reviews health effects and risk assessment from elemental mercury vapour and methylmercury at the exposure conditions commonly experienced by the general population. It was largely based on previous reviews by the World Health Organization (WHO 1990, 1991), the International Agency for Research on Cancer (IARC 1993), the US Environmental Protection Agency (EPA 1997, 2001), and the US National Research Council (NCR 2000).

Mercury exists in various physical and chemical forms. The most important from a toxicological point of view are the metallic form, also called the elemental form, and methylmercury. In this review only the two most important forms of mercury in relation to human exposure, i.e. elemental mercury vapour and methylmercury, will be dealt with in detail.

## 6.2 TOXICOKINETICS DATA

### 6.2.1 Elemental Mercury

Vapour of elemental mercury is rapidly absorbed via the lungs. In humans 75-85% of an inhaled dose is absorbed (Hursh et al., 1985, WHO 1991). Elemental mercury in liquid or vapour form is not well absorbed from the gastro-intestinal tract (possibly less than 0.01%) (Bornmann et al. 1970).

Elemental mercury is lipid soluble and its diffusion into the lungs and dissolution in blood lipids is rapid (Berlin 1986, WHO 1991). It is distributed throughout the body, and readily crosses the placental barrier and the blood-brain barrier (Vimy et al. 1990, Drasch et al. 1994).

Elemental mercury is oxidised to mercuric mercury in the erythrocytes and other tissue by a peroxidatic reaction with catalase- complex I; the formation of  $H_2O_2$  is rate limiting for the process. Glutathione peroxidase inhibits the reaction by competing with catalase for hydrogen peroxide. (Halbach and Clarkson 1978). Mercuric mercury only slowly crosses the blood brain barrier and the placental barrier. Ethanol inhibits catalase and therefore inhibits the oxidation of elemental mercury as has been demonstrated in both experimental animals and in humans (Hursh et al. 1980). Likewise, alcohol intake increases the amount of vapour lost by expiration (Sallsten et al. 2000), and consequently reduces the retention. On the other hand an extended retention-time in the blood will allow more mercury to pass the blood-brain barrier and placenta. Yoshida et al. (1997) found that pre-treatment of pregnant guinea pigs with ethanol increased the fetal exposure to elemental mercury compared to non ethanol pre-treated animals.

After uptake of elemental Hg, mercury is distributed to all kinds of tissue, but accumulates more in certain organs, including in particular the kidneys.

Elemental mercury is, after oxidation, excreted through the feces, urine, and to some extent also by exhalation and sweat. At occupational exposure, about 50 % is believed to be excreted by urine and feces respectively. The rate of urinary excretion is probably dose-dependent (Barregard et al., 1996), and a considerable species difference has been observed.



Mercury concentrations in the blood decrease rapidly with an initial half-life of approximately two to four days, and a slower phase of a couple of weeks (Cherian et al. 1978, Barregard et al. 1992, Sallsten et al. 1993). In urine the half-life is 40-90 days (Roels et al. 1991, Barregard et al. 1992, Sallsten et al. 1994). These results therefore reflect the existence of compartments with elimination half-lives of about 2 months, presumably in the kidney.

In workers chronically exposed to mercury vapour, a good correlation has been observed between the current intensity of exposure and blood and urine mercury concentrations at the end of a work shift (Roels et al. 1987). Occupational exposure limits in Europe are given in the table below. For biomonitoring, blood and urine Hg levels may be used, see Chapter 5.

**Table 6.1** - Occupational exposure limits ( $\text{mg m}^{-3}$ ).

	Countries	Exposure Limit
<b>In Europe</b>	Austria, Denmark, Finland, Switzerland	0.05
	Belgium	0.1
	Hungary	0.02
	Poland	0.025
	Sweden	0.030
<b>Outside Europe</b>	U.S.A, Japan	0.025

### 6.2.2 Methylmercury

As a lipophilic substance methylmercury easily passes biological membranes. About 95% of the methylmercury in fish ingested by humans was found to be absorbed from the gastrointestinal tract (Åberg et al., 1969, WHO 1990). Although the oral exposure route is most important for humans, it should be noted that methylmercury is also readily absorbed through the skin and the lungs.

Once absorbed into the blood stream, methylmercury enters the red blood cells bound to haemoglobin. A smaller fraction is found in the plasma. The cell to plasma ratio is 10-20 (Åberg et al., 1969, Kershaw et al., 1980, WHO 1990).

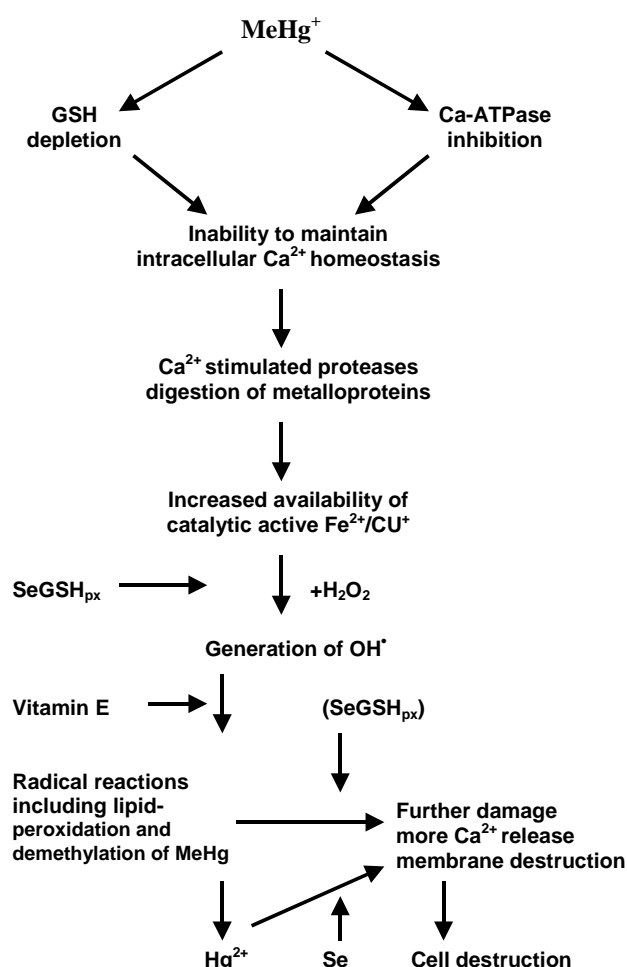
Less than 1% of the blood mercury is diffusible, and this fraction is believed to play an important role for the organ distribution of methylmercury. Experimental data suggest that the reduced glutathione (GSH) molecule is important for binding of mercury, as a reduction of available GSH decreases the concentration of mercury in the brain and kidneys (Richardson and Murphy 1975), and intracellular GSH seems to play a significant role in the metabolism of mercury.

The essential element selenium also is associated with the binding and transport of mercury, see below. However, it is still uncertain to which degree normal dietary intake of selenium affects the mercury toxicokinetics in humans.

The demethylation of methylmercury takes place in many organs including the brain (WHO 1990). The latter has been shown in humans (Tsubaki and Takahashi 1986, Pedersen et al. 1999), in monkeys (Lind et al. 1988), and in dogs (Hansen et al. 1989, Hansen and Danscher 1995). In skeletal muscles little or no demethylation activity has been observed in dogs (Hansen et al. 1989, Hansen and Danscher 1995), marine mammals and birds (Dietz et al.

1990), fish (AMAP 1998). Therefore fish muscle is a major source for dietary methylmercury exposure.

Demethylation is thought to occur via reactive oxygen intermediates (Suda et al. 1991). Macrophages may be important for demethylation of organic mercury (Suda and Tagahashi 1986). The liver, spleen, and lymph nodes are the most important organs for transforming methylmercury (Suda and Tagahashi 1990, Hansen et al. 1989, Hansen and Danscher 1995). The hypothetical, mechanistic model is presented in Figure 6.1



**Figure 6.1** - Theoretical model for biochemical reactions of methylmercury (Hansen and Danscher 1997).

Methylmercury is mainly excreted via faeces. In humans, approximately 90% of the absorbed dose of methylmercury is excreted in the feces as mercuric mercury. Excretion via the urine is minor but slowly increases with time; at 100 days after dosing, urinary excretion of mercury accounted for 20% of the daily amount excreted. Methylmercury is also excreted in breast milk. The ratio of mercury in breast milk to mercury in whole blood was approximately 1:20 in women exposed to methylmercury via contaminated grain in Iraq between 1971 and 1972 (Bakir et al. 1973), and about 1:6 in Swedish women having a normal diet (Oskarsson et al. 1996).

Methylmercury bound to cysteine is excreted into the bile. Subsequent gastrointestinal absorption leads to an enterohepatic circulation. However, some of the methylmercury may get demethylated by gut bacteria and is then poorly absorbed and therefore eliminated via the faeces. Breast-fed infants may not harbour the demethylating bacteria in the gut, and faecal elimination may therefore be less efficient.

Biological half-lives published in four studies of controlled exposures to methylmercury range from 32 to 70 days (Miettinen et al. 1971, Sherlock et al. 1984, Smith et al. 1994, Kershaw et al. 1980) with a pooled mean of approximate 49 days (SD 7.5) (Clewell et al. 1999). Half-lives obtained from patients during the Iraqi grain poisoning incident averaged 72 days (Al-Sharistani and Shihab 1974).

For biomonitoring, scalp hair or blood is often used to assess methylmercury exposure, see Chapter 5.

## **6.3 BIOLOGICAL EFFECTS OF MERCURY IN DIFFERENT PHYSICAL AND CHEMICAL FORMS**

### **6.3.1 Elemental Mercury**

Signs and symptoms observed in mercury vapour poisoning differ depending on the level and duration of exposure. Most studies have been performed in occupationally exposed subjects, but there are also some data from accidents in the general population, and on low level exposure from dental amalgams. The latter subject has been widely discussed and reviewed (US Public Health Service 1993).

In the following, information is given first on neoplastic effects and then on non-neoplastic effects from various organs/systems.

#### **6.3.1.1 Neoplastic Effects**

Data on the carcinogenicity of metallic mercury and its inorganic compounds mainly come from studies on cancer occurrence in occupational populations, including dentists, nuclear weapon manufacturers, chloralkali workers and miners. Previous data are summarized in reviews (IARC 1993, Boffetta 1993).

Cohorts of 3454 male and 1125 female dentists and 4662 dental nurses identified from the Swedish census in 1960 were followed for cancer development in the period 1961-79 by linkage with cancer register data (Ahlbom *et al.*, 1986). The overall standardized incidence ratio (SIR) was 2.1 (95% CI, 1.3-3.4) for glioblastoma (astrocytoma III-IV) in comparison with national incidence rates. The SIR of glioma (astrocytoma I-II) was 1.8 (95% CI, 0.5-4.7), that of meningioma was 1.3 (95% CI, 0.5-2.8). For comparison, physicians and female nurses were also studied; no indication was found of an excess of glioblastomas. In another analysis of intracranial gliomas from the same population, the increased incidence among dentists was confirmed, and an increased incidence was reported also among other medical professions (McLaughlin *et al.*, 1987).

A cohort of 2133 white men from Oak Ridge, TN, USA, who were exposed to metallic mercury was studied with regard to mortality in comparison with national rates for white men (Cragle *et al.*, 1984). Exposure to mercury occurred in the context of lithium production in a nuclear weapons plant. The cohorts were followed-up from 1953 until 1979. There was an excess of lung cancer (SMR, 1.34; 95% CI 0.97-1.81). A similar excess, however, was present in a group of workers from the same plant but unexposed to mercury. The SMR was 1.22 for cancers of the brain and central nervous system (95% CI 0.33-3.12) and 1.65 for kidney cancer (95% CI 0.45-4.23). It was, however, recently reported that these workers were exposed to high levels of radiation through routine chest X-ray, also with high-dose techniques, some of them as often as once a month (Cardarelli 2001).

Mortality and cancer incidence were reported for a group of 1190 male Swedish chloralkali workers in whom mercury had been measured in the blood or urine for at least one year between 1946 and 1984 (Barregard *et al.*, 1990). Their mortality and cancer incidence were compared with those of the general male population. The mean level of mercury excreted in the urine had been about 200 µg/L in the 1950s, 150 µg/L in the 1960s and less than 50 µg/L in the 1980s. Lung cancer was the only type of tumour in clear excess (SIR with a latency of 10 years 2.0; 95% CI, 1.0-3.8). There were slight excesses of some other cancers with a latency of 10 years or more, namely brain tumours (SIR, 2.7; 95% CI, 0.5-7.7), kidney cancer (1.6; 0.3-4.7). One case of mesothelioma was observed, suggesting exposure to asbestos.

A cohort study included 674 male Norwegian chloralkali workers exposed to inorganic mercury for more than one year prior to 1980, who had a mean cumulative urinary concentration of 740 µg/L (Ellingsen *et al.*, 1993). During the follow-up period, there were 19 incident cases of lung cancer, with 11.5 expected (SIR, 1.66; 95% CI, 1.00-2.59) on the basis of national rates. There was no correlation with cumulative mercury dose, employment or latency; a somewhat increased frequency of smoking and exposure to asbestos (one mesothelioma was found) were considered to explain the excess of lung cancer. Three kidney cancers and two brain tumours were observed *versus* 3.2 and 2.5 expected, respectively.

A multicentric study included 6784 male and 265 female workers of four mercury mines and mills in Spain, Slovenia, Italy and the Ukraine (Boffetta *et al.*, 1998). Workers were employed between the beginning of the century and 1990; the follow-up period lasted from the 1950s to the 1990s. An increase was observed in mortality from lung cancer (SMR 1.19, 95% CI 1.03-1.38) and liver cancer (SMR 1.64, 95% CI 1.18-2.22). There was no relationship between lung cancer and employment or estimated mercury exposure. For liver cancer, there was a trend with estimated cumulative exposure but not with duration of employment, however the excess was not present in a parallel analysis of cancer incidence among workers from Slovenia. No increase was observed for other types of cancer, including brain and kidney tumours.

A cohort study included 326 men and 820 women compensated since 1974 for mercury intoxication in an area of Italy in which felt hat manufacture was the main source of occupational exposure to mercury, who were followed up for mortality during 1950-1992 (Merler *et al.*, 1994). Lung cancer mortality was increased among women (SMR 2.10, 95% CI 1.05-3.76), but not among men (SMR 1.16, 95% CI 0.68-1.86). Heavy exposure to mercury but also to arsenic and other chemicals occurred in the Italian hat-making industry.

Lung cancer is the only neoplasm, which seems to be consistently increased among various groups of workers exposed to metallic and inorganic mercury. The main difficulty in the

interpretation of the data on lung cancer is the possible co-exposure to other lung carcinogens, in particular arsenic (in the fur industry), radon and silica (among miners). An additional limitation is the almost universal lack of data on tobacco smoking. The fact that no increase was found in a large group of European mercury miners not exposed to quartz (Boffetta et al. 1998) argues against the hypothesis that mercury vapour should cause lung cancer. There is no suggestion of a consistent increase of any other neoplasm, including brain and kidney cancers, in these populations.

The International Agency for Research on Cancer (IARC, 1993) evaluated metallic mercury and inorganic mercury compounds and found them not classifiable (group 3) with respect to carcinogenicity in humans.

### 6.3.1.2 Neurological Effects

As reviewed by the US EPA (1997), the reports from accidental exposures to high concentrations of mercury vapors (Aronow et al. 1990; Fagala and Wigg 1992; Taueg et al. 1992), as well as studies of populations chronically exposed to potentially high concentrations (Ehrenberg et al. 1991; Roels et al. 1982; Sexton et al. 1978) have shown effects on a wide variety of cognitive, sensory, personality and motor functions. In general, symptoms have been observed to subside after removal from exposure. However, persistent effects (tremor, cognitive deficits) have been observed in occupationally exposed subjects 10-30 years after cessation of exposure (Albers et al. 1988, Kishi et al. 1993, Mathiesen et al. 1999, Letz et al. 2000). Studies of workers exposed to elemental mercury vapor have reported a clear increase in symptoms from the CNS at exposure levels greater than  $0.1 \text{ mg/m}^3$  (Smith et al. 1970) and clear symptoms of mercury poisoning at levels resulting in urinary mercury greater than  $300 \text{ } \mu\text{g}$  in a 24-hour urine sample (Bidstrup et al. 1951). Several studies, however, have shown evidence of neurotoxicity at approximately 2- to 4-fold lower concentrations. Self-reported memory disturbances, sleep disorders, anger, fatigue, and/or hand tremors were increased in workers chronically exposed to an estimated  $0.025 \text{ mg/m}^3$  (urinary and blood Hg levels of about  $25 \text{ } \mu\text{g/g}$  and  $10 \text{ } \mu\text{g/L}$ ) (Langworth et al. 1992), but not in a recent study with somewhat lower exposure levels, U-Hg  $10\text{-}15 \text{ } \mu\text{g/g}$  (Ellingsen et al. 2001). Also, objective measures of cognitive and/or motor function in exposed populations have shown significant differences from unexposed controls (Ehrenberg et al. 1991; Liang et al. 1993; Roels et al. 1982). In the study by Langworth et al. (1992), there were, however, no objective findings in neuropsychological tests or tremor recordings. This was also mainly the case in the study by Ellingsen et al. (2001), although there were possibly some exposure-related effects. Tremor was reported at long-term exposure to relatively low concentrations of mercury vapour (Fawer et al., 1983; Chapman et al., 1990), and mild tremor may constitute an early adverse effect (Biernat et al., 1999, Netterstrøm et al., 1996). Several studies failed, however, to show an increase of tremor at low level exposure (Roels et al. 1989, Langworth et al. 1992, Ellingsen et al. 2001).

### 6.3.1.3 Renal Effects

The kidney is, together with the CNS, a critical organ for exposure to mercury vapour. The kidney accumulates Hg to a larger extent than most other tissue with concentrations in occupationally unexposed groups typically of  $0.1 - 0.3 \text{ } \mu\text{g/g}$  (Drasch 1996, Barregard 1999, Hac 2000, Falnoga 2000). The critical kidney mercury concentration is not known, but levels in subjects with ongoing occupational exposure may be in the order of  $25 \text{ } \mu\text{g/g}$  (Kazantzis

1962, Borjesson 1995, Barregard 1999). Some of the mercury in the kidney is, however, bound to selenium, decreasing the toxicity, see section on interactions below.

High exposure may cause (immune-complex mediated) glomerulonephritis with proteinuria and nephritic syndrome. This has been shown at occupational exposure (Kazantzis 1962, Tubbs et al., 1982), as well as after use of mercury-containing ointment or skin-lightening creams (Becker et al. 1962, Kibukamusoke et al. 1974), but the reported cases are relatively few. Therefore, a specific genetic susceptibility is probably needed for a frank nephritis to develop, for a review see Enestrom and Hultman (1995).

More common at high exposure is proteinuria, glomerular (albumin) as well as tubular (low molecular weight proteins). Albuminuria is, however, generally not seen at exposure levels resulting in urinary mercury below 100 µg/g creatinine (Buchet et al., 1980, Roels et al., 1982, 1985, Langworth et al. 1992, Barregard et al. 1997, Ellingsen et al. 2000).

Effects on the renal tubules, as demonstrated by increased excretion of low molecular proteins like the proximal tubular enzyme NAG (N-acetyl-beta-D-glucosaminidase) have been shown at low-level exposure, and may constitute the earliest biological effect. This effect was previously shown at occupational exposure with urinary mercury of about 35 µg/g creatinine, equivalent to long term exposure to air levels of 25-30 µg/m<sup>3</sup> (Barregard et al., 1988, Langworth et al., 1992, Cardenas et al., 1993). In a recent report by Ellingsen et al. (2000), such an effect was, however, shown also in workers with urinary mercury of about 10 µg/g creatinine. Ongoing research (Wastensson G, personal communication, 2001) confirmed this in Swedish chloralkali workers, at levels above about 5 µg/g creatinine. This is only slightly higher than that found in the general population. The reversibility of these findings and the possible long term implications of tubular proteinuria are still open for discussion (Jarup et al. 1998).

Among male European mercury miners an increased mortality was observed from nephritis and nephrosis (SMR 1.55, 95 % CI 1.13-2.06) (Boffetta et al., 2001), whereas this was not shown among chloralkali workers (Barregard et al., 1990, Ellingsen et al., 1993).

#### **6.3.1.4 Respiratory Effects**

Respiratory toxicity in humans following exposure to elemental mercury vapors has been characterized by pulmonary edema and congestion, coughing, interstitial pneumonitis, and respiratory failure (Bluhm et al. 1992a, Taueg et al. 1992, WHO 1991). Barregard et al. (1990) and Ellingsen et al. (1993) found no associations between mortality from respiratory disease and mercury exposure among workers exposed to mercury in the chloralkali industry, although the power of the studies were low. Merler et al. (1994) found no excess mortality of respiratory disease in men (SMR, 0.67; 95% CI, 0.35 – 1.14) exposed to mercury in the fur hat industry. This was also true for mercury miners, except for pneumoconiosis (Boffetta et al., 2001).

### 6.3.1.5 Cardiovascular Effects

Signs of cardiovascular toxicity in humans after acute exposure to elemental mercury include tachycardia, elevated blood pressure and heart palpitations (Bluhm et al. 1992a; Snodgrass et al. 1981; Soni et al. 1992, Wossmann et al. 1999). Intermediate-duration exposure to elemental mercury vapors produced similar effects (i.e., tachycardia and elevated blood pressure) (Fagala and Wigg 1992; Foulds et al. 1987). Piikivi (1989) demonstrated a positive correlation between heart palpitations and urinary mercury concentrations in workers from a chloralkali plant. It is unclear from the available scientific literature, however, whether the effects on cardiovascular function are due to direct cardiac toxicity or to indirect toxicity (e.g., due to effects on neural control of cardiac function) of elemental mercury. Barregard et al. (1990) showed that Swedish chloralkali workers had increased mortality of ischemic heart disease and cerebrovascular disease. There were, however, no such findings in Norwegian chloralkali workers (Ellingsen 1993).

Among European mercury miners, increased mortality from hypertension (SR 1.46, 95 % CI 1.08-1.93) and from heart diseases other than ischemic (SMR 1.36, 95 % CI 1.20-1.53), and increased with time since first employment and with estimated cumulative mercury exposure. Findings were not consistent among countries. No increase was shown for ischemic heart disease or cerebrovascular diseases (Boffetta et al., 2001).

### 6.3.1.6 Gastrointestinal and Hepatic Effects

The most common sign of frank mercury poisoning is stomatitis, which is usually reported following acute, high concentration exposure to elemental mercury vapors (Bluhm et al. 1992a; Snodgrass et al. 1981). Other commonly reported gastrointestinal effects include nausea, vomiting, diarrhea and abdominal cramps (Bluhm et al. 1992a; Lilis et al. 1985; Sexton et al. 1978, Snodgrass et al. 1981, Vroom and Greer 1972). No increased mortality from the digestive system was observed in European mercury miners (Boffetta et al. 2001).

### 6.3.1.7 Effects on the Thyroid

The thyroid may accumulate mercury at exposure to Hg<sup>0</sup> (Kosta et al. 1975, WHO 1991, Falnoga 2000). It has recently been shown (Barregard et al. 1994, Ellingsen et al. 2000b) that moderate occupational exposure affects the deiodinase responsible for the deiodination of thyroxine (T<sub>4</sub>) to triiodothyronine (T<sub>3</sub>), a seleno-enzyme. This tends to increase T<sub>4</sub> and reverse T<sub>3</sub> levels, and increase the T<sub>4</sub>/T<sub>3</sub> ratio. The effects were seen at current urinary Hg levels of 15-30 µg/g creatinine (Barregard 1994, Ellingsen 2000b), thus at levels as low as the those where the first minor effects on the CNS and the kidneys were reported.

### 6.3.1.8 Immunological Effects

The ability of mercury to induce immune-mediated disease has been thoroughly investigated in mice and rats experimentally exposed to inorganic mercury compounds, in most studies divalent mercury, but also mercury vapour. The type of response depends on the strains, some of them being susceptible to autoimmune disease and some being resistant. It is therefore assumed that the genotype is probably important also for the potential immunological effects in humans, for a review see Enestrom and Hultman (1995).

Some studies in subjects occupationally exposed to moderate levels of  $\text{Hg}^0$  reported increase of antilaminin autoantibodies (Lauwerys 1983), alterations of certain T-lymphocyte populations, or increased immunoglobulin E (IgE) levels (Queiroz and Dantas 1997a,b, Dantas and Queiroz 1997, Moszczynski et al. 1995). One study showed increased autoantibodies to myeloperoxidase (Ellingsen et al. 2000a). In several studies no immunological effects were shown (Bernard 1987, Langworth 1992, 1993, Ellingsen 1994, Barregard 1997), and in particular anti-DNA or anti-nucleolar antibodies have not been reported except in one study (Cardenas et al. 1993). Cross-sectional studies of unselected populations may have low power to detect such effects if only a limited part of the populations is sensitive.

#### **6.3.1.9 Dermal Effects**

Exposure to elemental mercury vapors for acute or intermediate duration may elicit a response known as acrodynia or "pink disease", which is characterized by peeling palms of hands and soles of feet, excessive perspiration, itching, rash, joint pain and weakness, elevated blood pressure and tachycardia (Fagala and Wigg 1992, Karpathios et al. 1991, Schwartz et al. 1992). Rash and stomatitis have been reported after high inhalation exposures (Bluhm et al. 1992, Barregard 1996).

#### **6.3.1.10 Developmental Effects**

A study of the pregnancies of Polish dental professionals showed a high frequency of malformations of a nonspecified nature (Sikorski et al. 1987). In contrast, a study of Swedish dental professionals found no increases in malformations, abortions, or stillbirths (Ericson and Kallen 1989). An increase in low birth weight infants was noted in the offspring of female dental nurses (Ericson and Kallen 1989); however, in this same study similar effects were not observed for either dentists or dental technicians, and socioeconomic factors may have contributed to the effects observed.

#### **6.3.1.11 Reproductive Effects**

In occupational exposure studies, paternal exposure to metallic Hg does not appear to cause infertility or malformations (Alcser et al. 1989, Lauwerys et al. 1985). However, a study of pregnancy outcomes among the wives of 152 Hg-exposed men revealed an increased incidence of spontaneous abortions (Cordier et al. 1991). Preconception paternal urinary Hg concentrations above 50  $\mu\text{g/L}$  were associated with a doubling of the spontaneous abortion risk. Elghancy et al. (1997) compared the pregnancy outcomes of 46 Hg-exposed workers to those of 19 women who worked in nonproduction areas of the same factory. Women exposed to inorganic Hg had a higher rate of congenital anomalies. Concentrations were up to 0.6  $\text{mg/m}^3$ . No significant differences in stillbirths or miscarriage rates were noted between the two groups of women. Rowland et al. (1994) found that the probability of conception among female dental hygienists who prepared more than 30 amalgams per week and had at least five poor hygiene practices when handling Hg was only 63% of that among unexposed controls. Women with lower exposures, however, were more fertile than unexposed controls. A large study conducted in Norway compared reproductive success rates among 558 female dental surgeons with those of 450 high-school teachers (Dahl et al. 1999). They concluded that



exposure to Hg, benzene, and chloroform was not associated with decreased fertility except for a possible Hg effect on the last pregnancy of multiparous dental surgeons.

#### **6.3.1.12 Genotoxicity**

Two occupational studies (Anwar and Gabal 1991, Popescu et al. 1979) reported on workers inhaling inorganic mercury; the data were inconclusive regarding the clastogenic activity of inorganic mercury. Workers involved in the manufacture of mercury fulminate ( $\text{Hg}[\text{OCN}]_2$ ) had a significant increase in the incidence of chromosomal aberrations and micronuclei in peripheral lymphocytes when compared to unexposed controls (Anwar and Gabal 1991). There was no correlation between urinary mercury levels or duration of exposure to the increased frequency of effects; the study authors concluded that mercury may not have been the clastogen in the manufacturing process. In a study by Popescu et al. (1979), 18 workers exposed to a mixture of mercuric chloride, methylmercuric chloride and ethylmercuric chloride had significant increases in the frequency of acentric fragments. Barregard et al. (1991) demonstrated a correlation between cumulative mercury exposure and induction of micronuclei among a group of chloralkali workers, suggesting a possible genotoxic effect.

### **6.3.2 Organic Mercury Compounds**

Intoxications with alkoxialkyl or aryl compounds are similar to intoxications with inorganic mercury compounds, because these organomercurials are relatively unstable and are broken down to form mercuric mercury. Alkyl mercury compounds, such as methylmercury are more stable and result in entirely different adverse effects. As originally described by Hunter et al. (1940), the poisoned adult patient develops paresthesia in the fingers, the tongue and the face, particularly around the mouth. Later on, disturbances occur in the motor functions, resulting in ataxia and dysphasia. The visual field is decreased, and in severe cases the result may be total blindness, and impaired hearing may progress to complete deafness. Such cases were seen in Minamata, where fish was severely contaminated by effluents from a local chemical factory (Harada 1995).

In the following information is given on first on neoplastic effects and then on non-neoplastic effects from various organs/systems.

#### **6.3.2.1 Neoplastic Effects**

Direct SMRs for biliary tract cancer in the Japanese prefectures in 1975 were correlated with an environmental pollution index related to use of agricultural chemical products for the years 1962-66 (Yamamoto et al. 1986). In both men and women, only weak, non-significant correlations were found for exposure to mercuric compounds (such as phenylmercury acetate, used as a fungicide in Japan until 1971) converted to the dose of inorganic mercury.

The mortality pattern was studied in the population of a small area of the city of Minamata, Kumamoto Prefecture, Japan, which consisted mainly of fishermen and their families (Tamashiro et al. 1986) and where 70% of the 1612 confirmed cases (including 527 deaths) of Minamata disease in the Prefecture through 1983 were known to have occurred (see below for a description of Minamata disease). SMRs were computed for different causes of death in 1970-81 by using age-specific rates for the entire city for 1972-78. The SMR for cancer of the oesophagus was 2.05 (95% CI, 0.67-4.78), that of liver cancer was 2.07 (95% CI, 1.16-3.42)

and that of lung cancer was 1.52 (95% CI, 0.79-2.65). An elevated SMR was also seen for chronic liver disease and cirrhosis (2.16; 95% CI, 1.41-3.17; based on 26 cases). There was some evidence that alcohol consumption in the area was above the Japanese average, which might have contributed to the increased mortality from oesophageal and liver cancer.

Methylmercury chloride caused renal tumours in several studies in mice but not in rats, and the IARC judged that there is sufficient evidence for carcinogenicity of methylmercury chloride in experimental animals (IARC 1993). The overall evaluation for methylmercury compounds was that they are possibly carcinogenic to humans (group 2B).

### 6.3.2.2 Neurological and Developmental Effects

The original epidemiological report of methylmercury poisoning involved 628 human cases that occurred in Minamata, Japan, between 1953 and 1960. The overall prevalence rate for the Minamata region for neurologic and mental disorders was 59%. Among this group 78 deaths occurred, and hair concentrations of mercury ranged from 50–700 ppm. The most common clinical signs observed in adults were paresthesia, ataxia, sensory disturbances, tremors, impairment of hearing and difficulty in walking. Examination of the brains of severely affected patients that died revealed marked atrophy of the brain (55% normal volume and weight) with cystic cavities and spongy foci. Microscopically, entire regions were devoid of neurons, granular cells in the cerebellum, Golgi cells and Purkinje cells. Extensive investigations of congenital Minamata disease were undertaken, and 20 cases that occurred over a 4-year period were documented. In all instances the congenital cases showed a higher incidence of symptoms than did the cases wherein exposure occurred as an adult. Severe disturbances of nervous function were described, and the affected offspring were very late in reaching developmental milestones. Hair concentrations of mercury in affected infants ranged from 10 to 100 ppm (Harada 1995, Harada 1997, Tsubaki and Takahashi 1986, WHO 1990).

In 1971, an unknown number of people in Iraq were exposed to methylmercury-treated seed grain that was used in home-baked bread. Toxicity was observed in many adults and children who had consumed this bread over a three-month period, but the population that showed greatest sensitivity were offspring of pregnant women who ate contaminated bread during gestation. The predominant symptom noted in adults was paresthesia, and it usually occurred after a latent period of from 16 to 38 days. In adults symptoms were dose-dependent, and among the more severely affected individuals ataxia, blurred vision, slurred speech and hearing difficulties were observed. Signs noted in the infants exposed during fetal development included cerebral palsy, altered muscle tone and deep tendon reflexes, as well as delayed developmental milestones. Some information indicated that male offspring were more sensitive than females. The mothers experienced paresthesia and other sensory disturbances but at higher doses than those associated with their children exposed *in utero* (Bakir 1973, WHO 1990).

Thus, several neurological signs and symptoms are among the cardinal features of high-dose exposures to MeHg in adults. As no pathognomonic test is available to confirm the diagnosis of Minamata disease, cases were identified on the basis of a characteristic combination of symptoms (Harada 1997; Uchino et al. 1995). These included peripheral neuropathy, dysarthria, tremor, cerebellar ataxia, gait disturbance, visual-field constriction and disturbed ocular movements, hearing loss, disturbance of equilibrium, and subjective symptoms such as headache, muscle and joint pain, forgetfulness, and fatigue. The earliest effects due to

methylmercury in adults, such as paresthesias, seem to appear at hair Hg concentrations above 50 µg/g or blood mercury concentrations above 200 µg/l (WHO 1990).

Later studies of patients with Minamata disease reported increased pain thresholds in the body and distal extremities (Yoshida et al. 1992). Lebel et al. (1998) found that abnormal performance on the Branches Alternate Movement Task (BAMT) was significantly associated with all measures of Hg exposure, in adults from an Amazonian village, and abnormal visual fields were associated with mean and peak hair Hg concentrations. The authors stress that the dose-related decrements in visual and motor functions were associated with hair Hg concentrations below 50 ppm, a range in which clinical signs of Hg intoxication are not apparent.

The developing organism is much more susceptible to the toxic effects of methylmercury than the mature. Congenital methylmercury poisoning may result in a cerebral palsy syndrome, even though the mother remains healthy or suffers only minor symptoms due to the exposure (Davis et al. 1994).

Two large studies have been performed recently in order to assess the impact on the fetal brain from more moderate exposure to MeHg in pregnant women. The studies were performed in the Faroe Islands, and in the Seychelles Islands, comparing biomarkers of the MeHg exposure of the mother and foetus with neuropsychological and other endpoints at pre-school age.

The Faroe Island population was exposed to methylmercury mainly from pilot whale meat with relatively high concentration of methylmercury, around 2 µg/g (EPA 2001). The study of about 900 Faroe children showed that prenatal exposure to methylmercury resulted in neuropsychological deficits at 7 years of age (Grandjean et al., 1997). The brain functions most vulnerable seems to be attention, memory, and language, while motor speed, visuospatial function, and executive function showed less robust decrements at increased mercury exposures. The mercury concentration in cord blood appeared to be the best risk indicator for the adverse effects, which were apparently not due to a large number of covariates examined. Special concern was expressed with respect to the impact of PCB, which was present in the diet (in whale blubber) of these Faroe mothers. The results were roughly unchanged, however, when PCB levels were taken into account. Developmental delays were significantly associated with maternal hair mercury concentrations below 10 µg/g. Benchmark calculations based on the Faroe Islands data suggested that the lower 95 % confidence limit for a doubling of a 5% abnormality response occurred at maternal hair Hg levels around 10 µg/g and at cord blood levels corresponding to this hair level (Budtz-Jørgensen et al., 2000). However some models yielded much lower benchmark doses. Each doubling of the prenatal methylmercury exposure level was associated with a developmental delay of 1-2 months. Thus, on an individual basis the effects may seem innocuous, but they may have severe implications on a population basis.

Another prospective study was performed in the Seychelles islands, where the MeHg exposure was of similar extent. The fish consumption of pregnant women in the Seychelles is high, typically 10-15 meals per week (Shamlaye 1995), while the mercury concentrations in the ocean fish consumed is relatively low, with a mean of 0.2-0.3 µg/g (Cernichiari 1995). No effects on developmental tests up to 5.5 years of age were found to be associated with MeHg exposure, as measured by hair-Hg in the pregnant mothers (Davidson et al. 1998, Crump et al. 2000, Myers 2000, Axtell 2000, Palumbo 2000). The main longitudinal study was started in

1989-1990 and comprised about 700 mother-child pairs. Maternal hair (mean about 7 µg/g) and child hair, but not cord-blood levels were used as markers of MeHg exposure in this study. The benchmark calculations were similar to those used in the Faroe Island study. A reanalysis using raw scores rather than age standardized scores showed similar results. If anything, the results rather suggested a beneficial effect of mercury from the ocean fish consumption (Davidson 2001).

In addition there is a study from the New Zealand, suggesting an effect on the mental development of children at the age of 4 and 6-7 years. In a high-exposure group the average maternal hair-Hg was about 9 µg/g, and controls groups were selected with lower exposure levels. In total, about 200 children were examined at 6-7 years of age and a negative association was found between maternal hair-Hg and neuropsychological development of the children. This study was originally published as reports from the Swedish EPA (Kjellstrom 1986, Kjellstrom 1989), and was therefore less taken into account, but later the bench-mark analysis of the original data was published in a peer-reviewed journal (Crump 1998, EPA 2001).

Some cross-sectional studies using neuropsychological testing of older children in different settings, e.g. in the Amazonas and on the Madeira island also found significant associations with mercury exposure (for a review, see EPA 2001).

The studies mentioned, especially those in the Faroe Islands and the Seychelles are very important for the risk assessment of MeHg in humans and have been extensively evaluated, see section 6.7.

### 6.3.2.3 Renal Effects

Renal toxicity has rarely been reported following human exposure to organic forms of Hg. The only evidence of a renal effect following ingestion of Hg-contaminated fish comes from a death-certificate review conducted by Tamashiro et al. (1986). They evaluated causes of death among residents of a small area of Minamata City that had the highest prevalence of MD using age-specific rates for the entire city as a standard. Between 1970 and 1981, the number of deaths attributed to nephritic diseases was higher than expected among women who resided in that region (SMR, 2.77; 95% CI, 1.02 – 6.02) but was within the expected range (SMR, 0.80; 95% CI, 0.17 – 2.36) among men who resided in this region.

### 6.3.2.4 Cardiovascular Effects

Jalili and Abbasi's (1961) described EKG abnormalities in severely poisoned patients hospitalized during the Iraqi grain poisoning epidemic, and similar findings were reported in four family members who consumed ethylmercury-contaminated pork (Cinca et al. 1979). Salonen et al. (1995) compared dietary intake of fish and Hg concentrations in hair and urine with the prevalence of acute myocardial infarction (AMI) and death from coronary heart disease or cardiovascular disease in a cohort of 1,833 Finnish men. Dietary Hg intake ranged from 1.1 to 95.3 µg per day (mean 7.6 µg per day). Over a 7-year observation period, men in the highest tertile (at or more than 2 ppm) of hair Hg content had a 2.0-fold higher risk (1.2 – 3.1) of AMI than men in the two lowest tertiles. A later follow-up (Rissanen 2000) showed a protective effect of omega-3 fatty acids with respect to acute coronary disease, which was, however less evident in those with high hair Hg. The authors concluded that a high mercury

content in fish could attenuate the protective effect of these fatty acids. A recent study by Sørensen et al. (1999) showed an association between prenatal exposure to MeHg and cardiovascular function at age 7 in the children from the Faroe Islands. Diastolic and systolic blood pressures increased by 13.9 and 14.6 mmHg, respectively, as cord-blood Hg concentrations rose from 1 to 10 µg/L. In boys, heart-rate variability, a marker of cardiac autonomic control, decreased by 47% as cord-blood Hg concentrations increased from 1 to 10 µg/L.

### 6.3.2.5 Genotoxicity

Skervfing et al. (1974) found limited support for an association between chromosomal aberrations and mercury in red blood cells in subjects consuming large amounts of contaminated fresh-water fish. Wulf et al. (1986) reported an increased prevalence of sister chromatid exchange in humans who ate Hg-contaminated seal meat. However, information on smoking status and exposure to other heavy metals was not provided for those individuals, making interpretation of the study difficult. More recently, Franchi et al. (1994) reported a correlation between the prevalence of micronuclei in peripheral lymphocytes and blood Hg concentrations in a population of fishermen who had eaten Hg-contaminated seafood.

### 6.3.3 Interactions

Nutritional status and dietary interactions can affect the outcome of mercury studies, either by influencing the toxicity of mercury or by having effects on the endpoints measures. Protective effects of nutrients like selenium, vitamin E and omega-3 fatty acids might attenuate potentially harmful effects of mercury. At the other extreme, mal-nourishment could affect study results either by directly reducing the sensitivity of an end point tested or by exacerbating the effects of mercury and thereby increasing the sensitivity to mercury toxicity. Nutritional factors such as iron or folate deficiencies that disrupt neuronal development might increase the impact of mercury. Conversely adequate dietary iron and folate levels might reduce the impact of mercury. Pathways through which diet and nutrition might affect the results of mercury toxicity studies include 1) the potential for attenuating a mercury effect 2) exacerbating a mercury effect or 3) as confounders by causing toxicity due to other food-components or contaminants.

## Selenium

The essential micro-nutrient selenium is the best described food component that might protect against toxic effects from mercury. Numerous animal studies have documented a protective role of selenium against both inorganic and organic mercury (for reviews: Goyer 1997, Chapman and Chan 2000), however no protective effects have been confirmed in humans (NRC 2000). A few studies have addressed the human aspect. In workers occupationally exposed to elemental mercury Bulat et al. (1998) found significantly lower concentrations of the two antioxidative defence enzymes glutathione peroxidase (GPX) and superoxide dismutase (SOD) in mercury exposed workers compared to non exposed. This was, however, not the case in a previous study by Barregard et al. (1990) in chloralkali workers. In such workers with low exposure to mercury vapour Ellingsen et al. (2000) found the highest

activity in urine of N-acetyl-beta-D-glucosaminidase (U-NAG), a marker of effects on the renal tubules, in exposed workers with the lowest blood selenium concentrations.

Drasch et al. (1996) determined total mercury and selenium in kidney cortex samples of 195 deceased, non-occupationally exposed individuals. The molar ratio Se/Hg was high, up to 300 in cases with relatively low mercury concentrations, but decreased with increasing mercury to unity at mercury concentrations of 700-1000 ng/g, and remained constant at higher mercury concentrations. This means that mercury exposure decreases the reserve of free biologically active selenium. This is in accordance with observations by Falnoga et al. (2000) on autopsy samples of retired Idrija mercury mineworkers and non-exposed controls. In exposed individual a Se/Hg ratio of 1 in organs (thyroid, pituitary, kidney cortex, nucleus dentatus) was observed when the concentration of mercury was >1000 ng/g.

No observations on the Se/Hg ratio in humans with a documented intake of methylmercury have been reported, but will probably parallel what has been found in marine mammals. Dietz et al. (2000) found that selenium was present in molar surplus to mercury in molluscs, crustaceans, fish and seabirds. 1:1 molar ration was found in tissues of marine mammals with high mercury concentrations (above approx. 2000 n/g). This was most clearly demonstrated for liver and kidney. In liver samples from pilot whales Caurant et al. (1996) showed a molar ratio between selenium and mercury indicating the formation of an Hg-Se complex after demethylation of methylmercury. This is by the authors suggested as the major mechanism of detoxification.

Even if selenium protection of humans still is regarded controversial (WHO 1990), the experimental evidence in connection with existing data on molar ratios found in human tissues indicates that there is probably a protective effect. The amount of biological available selenium in the diet should be addressed in epidemiological studies of mercury exposure.

The mechanism by which mercury and selenium react has been studied by Sasakura and Suzuki (1998) who suggests that the interaction occurs through the general mechanism, i.e. mercury form the unit complex (Hg-Se)<sub>n</sub>, and then the complex binds to selenoprotein P to form the ternary complex (Hg-Se)<sub>n</sub>-selenoprotein P in the blood stream.

In a study of Latvian fish consumers Hagmar et al. (1998) showed correlations between fish intake, plasma-levels of selenium, selenoprotein P, glutathione peroxidase, and organic mercury in erythrocytes.

## Vitamin E

Kling et al. (1987) found that vitamin E was equal or superior to all synthetic antioxidants tested in alleviating the toxicity of organic mercury poisoning. The cause of observed antioxidant protection during organic mercury exposure is not known but the protection may result from the ability to scavenge free radicals generated by induction of *in-vivo* peroxidation by the mercury compound. The relevance of this to human exposure is unclear.

## Omega-3 Fatty Acids

Chalon et al. (1998) demonstrated that fish oil affects monoaminergic neurotransmission and behavior in rats. Omega-3 fatty acids might enhance neurotoxicological function and their deficiency might contribute to lower test results, which would confound MeHg toxicological studies in human populations. Individuals consuming less fish might perform more poorly. Individuals on a diet high in fish might demonstrate the competing effects of enhanced function from these fatty acids and reduced function because of the presence of MeHg in the same food source. A case-control study in Greece concluded that low fish intake is associated with an increased risk of cerebral palsy (Petridou et al. 1998). Populations eating diets rich in fish might have enhanced neural development that could mask adverse effects on development caused by MeHg. However, there is no evidence to date that supplementation of omega-3 fatty acid to the diet of a well-nourished term infant further enhances neurological development or attenuates the toxic effects of Hg.

## Alcohol

Ethanol has been shown to potentiate MeHg toxicity in mice and rats (Turner et al. 1981, Chapman and Chan 2000, Rumbelha et al. 1992, Turner et al. 1981, McNeil et al. 1988). Ethanol administered to male rats in conjunction with daily injections of MeHg chloride has resulted in a dose-dependent increase in tissue concentrations of both total Hg and MeHg in the brain and kidneys and in the morbidity and mortality of these animals. For effects of alcohol on the oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ , please see section 6.2.1.

## Garlic

Many compounds (or their metabolites) in garlic could act as metal chelating or complexing agents and increase methylmercury excretion. Such chemicals can be converted to thiols or include thiols, glutathione, vitamin C, and thiol amino acids, (Block 1985). Garlic also contains selenium (0.72-1.52  $\mu\text{g}$  of selenium per gram of garlic), which might influence Hg toxicokinetics.

## Other Dietary Factors

There are strong indications that wheat bran, but neither cellulose nor pectin, when consumed concurrently with MeHg administration, might reduce the Hg concentration in the brain. In a study of male BALB/c mice, a dose-response relationship between brain Hg concentrations and the percentage of wheat bran was seen across 0%, 5%, 15%, and 30% wheat bran in the diet. The highest dose of wheat bran decreased the half-time of Hg elimination by 43%, and decreased the brain Hg concentrations by 24%. Corresponding reductions were seen in the Hg concentrations in the blood of the bran-fed animals. Reductions of that magnitude have been associated with a lower incidence and severity of symptoms of neurotoxicity in rats. The effect has been attributed partially to binding of the Hg to bran, reducing its absorption from the gut and decreasing intestinal transit time. Using evidence of an increase in mercuric Hg in the large intestines of the bran-fed mice, it has also been hypothesized that wheat bran increased the rate of demethylation of organic Hg in the gut (Rowland et al. 1986). However,

the possible mechanisms of these interactions have not yet been elucidated. For review see Chapman and Chan (2000).

## 6.4 CRITERIA FOR SELECTING CRITICAL POPULATION GROUPS FOR RISK ASSESSMENT

The purpose of risk assessment is to protect the subjects most vulnerable to adverse effects of the pollutant in question. This assessment should not take into regard specific risks of increased exposure, e.g., through occupational processes or dietary habits, but should be based solely on the degree of susceptibility to the toxicity at particular levels of exposure.

For inorganic mercury, none of the toxicokinetic evidence suggests any variations in absorption or retention of mercury vapour or inorganic mercury compounds related to age or sex. Current information does not allow any judgment whether children or the fetus are any more vulnerable than is the adult human being. Risk assessment must there be carried out based upon the evidence available, although much of the information originates from occupational exposures of adult men. Appropriate consideration must be given to the concern that such working populations may exhibit a greater resistance to toxic effects than the general population. It should be noted, however, that immunological effects owing to exposure to inorganic mercury, e.g. glomerulonephritis, may affect preferentially humans with a certain genotype.

Organic mercury compounds are known to be particularly toxic during development, and they pass freely over the placental barrier. Children and the fetus therefore constitute the critical population group. Observations of severe congenital methylmercury poisoning cases revealed that the mother suffered limited clinical symptoms of the exposure, while permanent damage occurred to the fetal nervous system. Risk assessment should therefore appropriately focus on exposures during pregnancy.

## 6.5. RISK ASSESSMENT

The risk assessment done by the U.S. environmental Protection Agency (U.S. EPA) follows the paradigm established by the National Academy of Sciences (National Research Council. Risk Assessment in the federal Government: Managing the Process. Washington: National Academy Press 1983). This entails a series of interconnected steps including

Hazard identification uses available data on biological end points related to a material to determine if that material is likely to pose a hazard to human health. These data are also used to define the type of potential hazard.

Dose-response assessment uses data from human and animal studies to estimate the amount of material that is expected to produce a given effect in humans. In this step it is generally necessary to apply mathematical models to the data to calculate a quantitative risk estimate usable for low dose exposure.



Exposure assessment seeks to determine the extent to which a population is exposed to the material. Data limitations on the populations of interest often necessitate the use of models to provide relevant estimates of exposure.

Risk characterisation is the last step of the risk assessment process. This step evaluates assessments of human health and ecological effects, identifies human subpopulations or ecological species potentially at risk, and delineates areas of uncertainty, limitations, and assumptions made in the risk assessment.

### **6.5.1 Background**

This evaluation is properly based on national and international risk assessments carried out for this priority pollutant. The U.S. Environmental Protection Agency prepared a detailed Mercury Report to Congress (1997), which focussed on methylmercury. An extensive review was prepared by the U.S. Agency for Toxic Substances and Disease Registry (1999), which concluded in proposed exposure limits for mercury vapour, inorganic mercury, and methylmercury. Because of new information on the developmental effects of methylmercury, the U.S. National Institutes of Health convened an international group of experts, including several from the EU, to discuss the evidence in November, 1998. The report of the five working groups is available on the NIH server. This report was then followed by a comprehensive review carried out by an expert group under the auspices of the National Academy of Sciences in Washington (NRC 2000). The monograph was published in 2000 and then led to a revision of the U.S. EPA risk assessment for methylmercury, as documented in the 2001 report (EPA 2001).

### **6.5.2 Hazard Identification**

Mercury vapour easily penetrates the blood-brain barrier and is a well documented neurotoxicant. In addition there are effects on the kidney and thyroid. The evidence on possible carcinogenicity is limited. A critical effect on which risk assessment should be based is therefore the neurotoxic effects, e.g. the induction of tremor. The effects on the renal tubule should also be considered, even if this effect is probably less serious. The effect may well be reversible, but if the exposure to the general population is chronic, the effect is still relevant. For the thyroid, two studies suggested effects on the deiodination of thyroid hormones, but the impact on the thyroid is still less well described than that on the nervous system and the kidneys.

Methylmercury is a well documented neurotoxicant which may in particular cause adverse effects on the developing brain. This compound passes both the placental barrier and the blood-brain barrier, and exposures during pregnancy therefore constitute the main concern.

### **6.5.3 Methodology for Dose-Response Assessment**

Quantitative risk assessments for non-cancer effects are commonly based on determination of a NOAEL (No Observed Adverse Effect Level) from controlled studies in animals. In this context NOAEL is defined as the highest experimental dose that does not produce a

statistically or biologically significant increase in adverse effects over those of controls. An “acceptable safe” daily dose for humans is then derived by dividing the NOAEL by a safety factor, usually 10 to 1000, to account for sensitive subgroups of the population, data insufficiency, and extrapolation from animals to humans. Depending on its exact definition and application this value is referred to as the reference dose (RfD) by US-EPA, ADI by The Food and Drug Administration or MRL (minimum risk level) by Agency for Toxic Substances and Disease Registry (ATSDR).

In the event that the lowest experimental dose shows a significant difference from the control it is termed a LOAEL (lowest observed adverse effect level, and an extra factor of (usually 10) is used in the determination of the RfD, ADI; or MRL (EPA 1998).

Various reports have provided RfDs for methylmercury derived from animal studies (Rice 1992, Gilbert et al. 1993, Zelikoff et al. 1995, Rice 1996). Nonhuman primate studies indicate that adverse developmental effects in several outcomes occur at 50 microgram/kg per day maternal dose. Uncertainty factors of 10 were used for LOAEL to NOAEL and a safety factor of 100 to account for species and interindividual differences give a RfD of 0.05 µg/kg per day.

In recent years the use of the NOAEL has become controversial because of inherent uncertainties and there has been an increasing interest in new approaches based on dose-response modelling techniques. Crump (1984) suggested application of the lower 95% confidence limit of the dose corresponding to a predefined increase (usually 5%, or 10%) over the background rate. Crump (1995) defined the benchmark dose (BMD) as the estimated dose that corresponds to the specified risk above the background risk, while the BMDL is the corresponding lower 95% limit. This notation has now become standard usage in risk assessment. However, the benchmark calculations depend on the assumed dose-response model, and the results therefore should only be taken as indicative of approximate orders of magnitude (Budtz-Jørgensen et al. 2000).

Another obstacle is that in practice it is often difficult to differentiate the contributions of variability and uncertainty to the observed variation in the reported measurements of a particular parameter (Allen et al. 1996). Distinction between variability and uncertainty is important. Uncertainty can be defined as the possible error in estimating the “true” value of a parameter for a representative “average” person. Variability, on the other hand, should only be considered to represent true inter-individual differences. Understood in these terms, uncertainty is a defect (lack of certainty) which can typically be reduced by experimentation, and variability is a fact of life, which must be considered regardless of risk assessment method used. (Clewett et al. 1999)

#### **6.5.4 Dose-Response Assessment Scenarios in Europe**

The major source of exposure to mercury vapour for the general population of Europe is from dental amalgam fillings (WHO 1991). In addition, exposure may occur at inappropriate handling of mercury waste, and close to mercury mines and industrial plants using mercury, see Chapter 5. Some of these exposures are likely to be of a lasting nature, i.e., occurring over a protracted period of time. Evidence from long-term industrial exposure to mercury vapour is therefore highly relevant to exposure situations involving the general population.

Methylmercury exposure originates almost entirely from freshwater fish, marine fish and other seafood. Some population groups have a high exposure from marine mammals, but the most common source is fish, especially species high up in the food chain, see Chapter 5. Some governmental authorities have already taken action and recommended that pregnant women abstain from eating certain types of fish known to contain increased methylmercury concentrations.

While governmental monitoring deals with concentrations of mercury in food items, the main concern from a public-health viewpoint is the dose, i.e. amount ingested from a fish meal. The dose depends on the size of the fish meal and the frequency of such meals. Efforts to reduce the risks of methylmercury exposure must therefore not overlook the situation, however rare, of the pregnant woman who eats fish every day.

## **6.6 COMPARISON BETWEEN EUROPE AND IN OTHER PARTS OF THE WORLD**

Mercury vapour is a risk of decreasing importance in Europe, as mercury-containing thermometers and other instruments are being phased-out, and the emissions from the chloralkali industry have decreased. In addition, only one mercury mine remains in operation in Europe today. New developments in dental technology have resulted in filling materials that can substitute amalgam for many purposes. However, the information on safety and durability of these new materials is still rather limited, and amalgam fillings are therefore likely to remain in use.

The methylmercury risk will depend on the dietary habits and local sources of contaminated fish and seafood. The increased exposures documented in the Faroe Islands, Greenland and other northern populations are mainly due to ingestion of marine mammals. The extent of this problem within Europe is therefore limited. However, a study from the island of Madeira showed that the consumption of local black scabbard resulted in average methylmercury exposures that were even higher than on the Faroe Islands. Similarly, evidence on mercury in seafood from the Tyrrhenian Sea have shown concentration levels which overlap with those present in pilot whale meat. Thus, excess exposures occur in Europe, see Chapter 5, and may reach or even exceed levels observed in populations in which adverse effects on brain development have been documented.

## **6.7 LIMITS VALUES FOR MERCURY EXPOSURE SUGGESTED BY WHO AND OTHER ORGANISATIONS**

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) decided at a meeting in 1999 (WHO 1999) to maintain the provisional tolerable weekly intake (PTWI) of 3.3 µg/kg body weight. The committee considered data on intake, the quantitative relationship between daily intake of methylmercury and concentrations in blood and hair, and ongoing epidemiological studies. The information available was by the committee considered to be insufficient for evaluating the neurodevelopmental effects on offspring of mothers with low intakes of methylmercury. A clear indication of consistent risk was not detected in the ongoing epidemiological studies. The committee noted that fish (the major source of methylmercury in the diet) contribute importantly to nutrition, especially in certain regional

and ethnic diets, and recommended that the nutritional benefits are weighed against the possibility of harm, when limits on the methylmercury concentration in fish or on fish consumption are under consideration. The committee intends to reevaluate methylmercury in 2002 when the 96-month evaluation of the Seychelles cohort and other relevant data have become available.

The National Research Council (NRC 2000) recently reviewed the studies for the US EPA. The NRC found the basis for the US EPA reference dose (RfD) of 0.1 µg/kg body weight to be scientifically justifiable for the protection of public health. The NRC argued that the RfD should be derived from an analysis of data from the Faroe Islands study, instead of data from Iraq which was the case previously. The NRC review and the studies were again reviewed by an external expert panel, and then the EPA evaluation was finally presented in 2001 (EPA 2001), as part of a water quality criterion.

The EPA evaluation (EPA 2001) includes a thorough analysis of the above-mentioned studies, especially those conducted on children from the Faroe islands and the Sechelles islands. Since the results from these two studies disagree, the merits and weaknesses of the studies were discussed, as well as possible reasons for the conflicting results. Both studies were considered being of high scientific quality, and no serious flaws could be detected. In this situation, the EPA decided to rely on the Faroe island study, showing a negative effect of the exposure levels to methylmercury. The similar results from the smaller, and less well peer reviewed study from the New Zealand, as well as some later cross-sectional studies from other parts of the world, contributed to this conclusion.

The benchmark dose analysis used was based on the lower 95 % confidence limit for a 5 % effect level (above background) applying a linear model to dose-response data based on cord blood Hg. The cord blood data were converted to maternal intakes. Several of the neuropsychological tests used, and also an integrated analysis gave similar results with respect to benchmark doses. One test (the Boston Naming Test) was chosen for the formal calculations of the RfD. Other models for the benchmark analyses are possible (Budtz-Jørgensen et al. 2000) and resulted in lower benchmark dose limits, but the linear model was considered the most appropriate one. The EPA chose an uncertainty factor of 10 accounting for pharmacokinetic inter-individual variability, gaps of knowledge on possible long term effects, and uncertainty concerning the relationships between cord and maternal blood mercury concentration, and as mentioned, the EPA's final RfD was set at 0.1 µg/kg body weight and day (EPA 2001).

In contrast to the EPA's use of the Iraqi study, the Agency for Toxic Substances and Disease Registry (ATSDR) developed its proposed minimum risk level (MRL) of 0.3 µg/kg/day for methylmercury from the Seychelles Child Development data.

Based on an average daily intake of 17.5 gram of fish, the U.S EPA also calculated a Tissue Residue Criterion of 0.3 mg methylmercury per kg of fish. This limit is weighted on all fish and shellfish consumed. For higher intakes, a lower limit would be needed.

For mercury vapor, studies of occupationally exposed humans have shown slight adverse effects on the CNS and kidneys at long-term air levels of 25-30 µg/m<sup>3</sup> or equivalent urinary Hg levels of 30-35 µg/g creatinine. Based on the LOAEL for effect on the CNS, the US EPA determined a reference concentration (RfC) for mercury vapor of 0.3 µg/m<sup>3</sup> for the general population (EPA 1997). The RfC took into account a conversion from occupational exposure

to continuous exposure for the general population, lack of data on reproductive effects, the use of a LOAEL instead of a NOAEL, and susceptible subgroups. The US ATSDR established a minimum risk level (MRL) of  $0.2 \mu\text{g}/\text{m}^3$  based on the same occupational data.

## 6.8 CONCLUSIONS AND RECOMMENDATIONS

### 6.8.1 Elemental Mercury

For mercury vapor, studies of occupationally exposed humans have shown slight adverse effects on the CNS and kidneys, and probably also on the thyroid, at long-term air levels of  $25\text{--}30 \mu\text{g}/\text{m}^3$  or equivalent urinary Hg levels of  $30\text{--}35 \mu\text{g}/\text{g}$  creatinine. The US EPA determined a reference concentration (RfC) for mercury vapor of  $0.3 \mu\text{g}/\text{m}^3$  for the general population (EPA 1997). Recent studies suggested that the limit for adverse effects (LOAEL) in occupationally exposed subjects may be lower than indicated above. There is no universal agreement on which uncertainty factors to use. In ongoing work on a EU position paper on arsenic, cadmium, and nickel, factors of 5-10 were used for similar conversion from occupational exposure to continuous exposure, factors of 5-10 for the use of a LOAEL, and a factor of 10 for variation of susceptibility. The total factor was 500. A similar procedure would result in a limit value for elemental mercury of  $0.05 \mu\text{g}/\text{m}^3$ . We propose the use of  $25 \mu\text{g}/\text{m}^3$  as starting point, a factor of 10 for continuous exposure of the general population during a whole life-time, and uncertainty factors of 5 for the use of a LOAEL and 10 for individual susceptibility. The proposed limit value will then be  $0.05 \mu\text{g}/\text{m}^3$ , as an annual average. This air level is rarely exceeded in ambient air in Europe, however. A typical daily absorbed dose would be  $0.6\text{--}0.8 \mu\text{g}$  of Hg for adults. Exposure to  $\text{Hg}^0$  from dental amalgam in most cases represents a much higher daily uptake than this level would give rise to (WHO 1991).

### 6.8.2 Methylmercury

The developing brain is considered the most sensitive target organ for methylmercury toxicity, and data are available for assessment of exposure-response analyses. Effects on the adult population in general, e.g. increased risks of cardiovascular disease, cannot be excluded, but have yet to be substantiated. Therefore the risk assessment is based on neuro-developmental effects.

The basis for the US EPA's reference dose (RfD) has recently been re-evaluated and found scientifically justifiable for the protection of public health (NRC 2000). It is now derived from a benchmark dose analysis using the lower 95 % confidence limit for a 5 % effect level applying a linear model to dose-response data based on cord blood Hg from the Faroe islands study (EPA 2001). The cord blood data were converted to maternal intakes. Several neuropsychological tests were evaluated with similar results, and the formal calculations were based on one of them (the Boston Naming Test). Several models for the benchmark analyses are possible (Budtz-Jorgensen et al. 2000), but the linear model was considered the most appropriate one. The EPA chose an uncertainty factor of 10 accounting for pharmacokinetic inter-individual variability, gaps of knowledge on possible long term effects, and uncertainty concerning the relationships between cord and maternal blood mercury concentration.

We share the view of the recent evaluations by the US EPA and NRC. No new information has emerged that would change the risk assessment. Moreover, the considerations made for the US will be valid also for the European population.

We therefore consider the US EPA RfD of 0.1 µg per kg body weight to be appropriate for Europe. It should be noted that it is mainly relevant for fertile women, and that it includes an uncertainty factor.

The reference dose will be exceeded if a substantial amount of fish, contaminated with mercury, is ingested. As an example, if the weekly intake is about 100 g (one typical fish meal per week) of fish with > 0.4 mg/kg, the RfD will be exceeded. This suggests that fish Hg levels should be kept below this limit.

Fish is, however, a valuable part of the diet, in adults as well as in children, and a source of e.g. protein, vitamin E, selenium, and omega 3 fatty acids, see above. At high consumption of fish with low levels of mercury, like in the Seychelles Islands, the advantages and disadvantages may counterbalance each other. Because of the beneficial effects of fish consumption, the long-term aim is not to replace fish in the diet by other foods, but to reduce the MeHg concentrations in fish. If this is not possible, dietary restrictions with respect to fish with high levels of MeHg should be advised for pregnant women.

## 6.9 REFERENCES

- Aberg B., Ekman L., Falk R., Greitz U., Persson G., Snihs J. O. Metabolism of methylmercury (203-Hg) compounds in man. *Arch Environ Health* 1969;19:478-484.
- Ahlbom A, Norell S, Rodvall Y, Nylander M. Dentists, dental nurses, and brain tumours. *Br Med J* 1986;292:662.
- Albers J.W., Kallenbach L.R., Fine L.J., Langolf G.D., Wolfe R.A. Donofrio P.D., Alessi A.G., Stolp-smith K.A., Bromberg M.B. Neurological abnormalities associated with remote occupational elemental mercury exposure. *Ann Neurol* 1988;24:651-659.
- Alcser, K.H., Birx K.A., Fine L.J., Occupational mercury exposure and male reproductive health. *Am J Ind Med* 1989;15:517-529.
- Allen B., Covington T., Clewell H. Investigation of the Impact of Pharmacokinetic Variability and Uncertainty on Risks Predicted with a Pharmacokinetic Model for Chloroform. *Toxicology* 1996;111:289-303.
- Al-Shahristani H., Shihab K. Variation of Biological Half-Life of Methylmercury in Man. *Arch. Environ. Health* 1974;28:342-344.
- AMAP 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo Norway. xii+859pp.
- Anwar, W.A. and Gabal. M.S. Cytogenetic study in workers occupationally exposed to mercury fulminate. *Mutagenesis*. 1991;6:189-192.
- Aronow, R., Cabbage C, Wisner R, Johnson B, Hesse J, Bedford J. Mercury exposure from interior latex paint. *MMWR*. 1990 39(8):125-126.
- ATSDR. Toxicological Profile for Mercury (Update). Atlanta, GA: Agency for Toxic Substances and Disease Registry, 1999.
- Axtell C, Cox C, Myers G, Davidson P, Choi A, Chernichiari E, Sloane-Reeves J, Shamlaye C, Clarkson T. Association between methylmercury exposure from fish consumption and child development at five and a half years of age in the Seychelles child development study: an evaluation of nonlinear relationships. *Environ Res. Section A* 2000;84:71-80.
- Bakir, F., Damluji S.F, Amin-Zaki L, et al. Methylmercury poisoning in Iraq. *Science* 1973;181:230-241.
- Barregard, L., Sallsten G, Jarvholm B. Mortality and cancer incidence in chloralkali workers exposed to inorganic mercury. *Br J Ind Med* 1990; 47(2):99-104.
- Barregard L, Thomassen Y, Schütz A, Marklund S. Levels of selenium and oxidative enzymes following occupational exposure to inorganic mercury. *Sci Total Environ* 1990b;99:37-47.
- Barregard, L., Hogstedt B, Schutz A, Karlsson A, Sallsten G, Thiringer G. Effects of occupational exposure to mercury vapor on lymphocyte micronuclei. *Scand J Work Environ Health* 1991;17:263-268.
- Barregard L, Hultberg B., Schütz A., Sallsten G. Enzymuria in workers exposed to inorganic mercury. *Int Arch Occup Environ Health* 1988;61:65-69.
- Barregard L., Sallsten G., Shütz A., Attewell R., Skerfving S., Jarvholm B. Kinetics of mercury in blood and urine after brief exposure. *Arch Environ Health* 1992;47:176-184.
- Barregard L, Lindstedt G, Schütz A, Sallsten G. Endocrine function in mercury exposed chloralkali workers. *Occup Environ Med* 1994;51:536-540.
- Barregard L, Quelquejeu G Sallsten G, Haguenoer JM, Nisse C. Dose-dependent elimination kinetics for mercury in urine - observations in subjects with brief but high exposure. *Int Arch Occup Environ Health* 1996;68:345-348.
- Barregard L, Eneström S, Ljunghusen O, Wieslander J, Hultman P. A study of autoantibodies and circulating immune complexes in mercury-exposed chloralkali workers. *Int Arch Occup Environ health* 1997;70:101-106.

- Barregard L, Svalander C, Schütz A, Westberg G, Sallsten G, Blohmé I, Mölne J, Attman P-O, Haglind P. Cadmium, mercury, and lead in kidney cortex of the general Swedish population: a study of biopsies from living kidney donors. *Environ Health perspect* 1999;107:867-871.
- Barregard L, Sallsten G, Conradi N. Tissue levels of mercury in a deceased worker after occupational exposure. *Int Arch Occup Environ Health* 1999b; 72:169-173.
- Becker CG, Becker EL, Maher JF, Schreiner GE. Nephrotic syndrome after contact with mercury. *Arch Int Med* 1962;110:82-90.
- Bernard AM, Roels HR, Foidart JM, Lauwerys RL (1987). Search for anti-laminin antibodies in the serum of workers exposed to cadmium, mercury vapour or lead. *Int Arch Occup Environ Health* 59:303-309.
- Biernat H, Ellias S.A., Wermuth L., Cleary D., de Oliveira Santos E.C., Jørgensen P.J., Feldman R.G., Grandjean P. Tremor frequency patterns in mercury vapor exposure, compared with early Parkinson's disease and essential tremor. *Neurotoxicol* 1999;20:945-952.
- Bidstrup, P., J. Bonnell, D.G. Harvey, et al. Chronic mercury poisoning in men repairing direct current meters. *Lancet* 1951:856-861.
- Berlin, M, Mercury. In: *Handbook on the toxicology of Metals*, pp. 387-445, 2<sup>nd</sup> Ed. L. Friberg, G F Nordberg and V.B. Vouk, eds. New York. Elsevier 1986.
- Block, E. The chemistry of garlic and onions. *Sci Am.* 1985 252(3):114-119.
- Bluhm, R.E., Bobbitt R.G, Welch L.W, Wood A.J, Bonfiglio J.F, Sarzen C, Branch R.A. Elemental mercury vapour toxicity, treatment, and prognosis after acute, intensive exposure in chloralkali plant workers: Part I. History, neuropsychological findings and chelator effects. *Hum Exp Toxicol* 1992;11:201-210.
- Boffetta P, Merler E, Vainio H. Carcinogenicity of mercury and mercury compounds. *Scand J Work Environ Health* 1993;19:1-7.
- Boffetta P, Garcia-Gómez M, Pompe-Kirn V, Zaridze D, Bellander T, Bulbulyan M, Diego Caballero J, Ceccarelli F, Colin D, Dizdarevic T, Español S, Kobal A, Petrova N, Sallsten G, Merler E. Cancer occurrence among European mercury miners. *Cancer Causes and Control* 1998;9:591-9.
- Boffetta P, Sallsten G, Garcia-Gómez M, Pompe-Kirn V, Zaridze D, Bulbulyan M, Caballero J-D, Ceccarelli F, Kobal A, Merler E. Mortality from cardiovascular diseases and exposure to inorganic mercury. *Occup Environ Med* 2001;58:461-466.
- Börjesson J, Barregard L, Sallsten G, Schütz A, Jonson R, Alpsten M, Mattsson S. In vivo XRF analysis of mercury: the relation between concentrations in the kidney and the urine. *Phys Med Biol* 1995;40:413-426.
- Bornmann, G., Henke, g., Alfes, H., Mollmann, H. Intestinal absorption of metallic mercury (in German) *Arch Toxicol* 1970;26:203-209.
- Buchet, J., Roels H, Bernard A, Lauwerys R. Assessment of renal function of workers exposed to inorganic lead, cadmium, or mercury vapor. *J Occup Med* 1980;22:741-750.
- Budtz-Jørgensen E, Grandjean P, Keiding N, White R.F, Weihe P. Benchmark dose calculations of methylmercury associated neurobehavioural deficits. *Toxicol Lett* 2000; 112-113:193-199.
- Bulat P, Dujic I, Potkonjak B, Vidakovic A: Activity of glutathione peroxidase and sueproxide dismutase in workers occupationally exposed to mercury. *Int Arch Occup Environ Health* 1998; 71; Suppl. S37-39.
- Cardarelli JJ, Spitz H, Rice C, Buncher CR, Elson H, Succop P. Significance of radiation exposure from work-related chest x-rays for epidemiologic studies of radiation workers. Abstract book from X2001 – Exposure assessment in epidemiology and practice, 2001. Available on [www.niwl.se/ah/](http://www.niwl.se/ah/) (report 2001:10).



- Cardenas, A., Roels H, Bernard A.M, Barbon R, Buchet J.P, Lauwerys R.R, Rosello J, Hotter G, Mutti A, Franchini I. Markers of early renal changes induced by industrial pollutants. I. Application to workers exposed to mercury vapour. *Br J Ind Med* 1993;50:17-27.
- Cernichiari E, Toribara TY, Liang L, Marsh DO, Berlin MW, Myers GJ, Cox C, Shamlaye CF, Choisy O, Davidson P, Clarkson TW. The biological monitoring of mercury in the Seychelles study. *Neurotoxicology* 1995;16:613-628.
- Chapman L.J., Sauter S.L., Henning R.A., Dodson V.N., Reddan W.G., Matthews C.G. Differences in frequency of finger tremor in otherwise asymptomatic mercury workers. *Br J Ind Med* 1990;47:838-843.
- Caurant F, Navarro M, Amiard JC, Mercury in pilot whales: possible limits to the detoxification process. *Sci Total Environ* 1996;186:95-104.
- Chalon, S., Delion-Vancassel S, Belzung C, Guilloteau D, Leguisquet A.M, Besnard J.C, Durand G. Dietary fish oil affects monoaminergic neurotransmission and behavior in rats. *J Nutr* 1998;128:2512-2519.
- Chapman, L., and H.M. Chan. The influence of nutrition on methylmercury intoxication. *Environ. Health Perspect* 2000;108(Suppl.1):29-56.
- Cherian M.G., Hursh J.B., Clarkson T.W., Allen J. Radioactive mercury distribution in biological fluids and excretion in human subjects after inhalation of mercury vapor. *Arch Environ Health* 1978;33:109-114.
- Cinca I, Dumetrescu I, Onaca P, Serbanescu A, Nestorescu B. Accidental ethyl mercury poisoning with nervous system, skeletal muscle, and myocardium injury. *J Neurol Neurosurg Psychiatry* 1979;43:143-149.
- Clarkson T.W.. The toxicology of mercury. *Crit Rev Clin Lab Sci* 1997;34:369-403.
- Clewell H.J., Gearhart J.M., Gentry P.R., Covington T.R., VanLandingham C.B., Crump K.S. Shipp A.M. Evaluation of the Uncertainty in an Oral Reference Dose for Methylmercury Due to Interindividual Variability in Pharmacokinetics. *Risk Analysis* 1999;19: 547-558.
- Cordier, S., Deplan F, Mandereau L, Hemon D. Paternal exposure to mercury and spontaneous abortions. *Br J Ind Med* 1991;48:375-381.
- Crump K.S. A new method for determining allowable daily intakes. *Fundam Appl Toxicol* 1984;4:854-871.
- Crump K. Calculation of benchmark doses from continuous data. *Risk Anal* 1995;15:79-89.
- Crump K, Kjellstrom T, Shipp A, Silvers A, Stewart A. Influence of prenatal mercury exposure on scholastic and psychological test performance: statistical analysis of a New Zealand cohort. *Risk Anal* 1998;18:701-713.
- Crump K, Landingham C, Shamlaye C, Cox C, Davidson P, Myers G, Clarkson T. Benchmark calculations for methylmercury obtained from the Seychelles child development study. *Environ Health Perspect* 2000;108:257-263.
- Dahl J.E., Sundby J, Hensten-Pettersen A, Jacobsen N. Dental workplace exposure and effect on fertility. *Scand J Work Environ Health* 1999 25:285-90.
- Dantas, D.C., and Queiroz M.L. Immunoglobulin E and autoantibodies in mercury-exposed workers. *Immunopharmacol. Immunotoxicol.* 1997;19:383-92.
- Davidson P.W, Myers G.J, Cox C, Axtell C, Shamlaye C, Solane-Reeves J, Cernichiari E, Needham L, Choi A, Wang Y, Berlin M, Clarkson T.W. Effects of prenatal and postnatal methylmercury exposure from fish consumption on neurodevelopment: outcomes at 66 months of age in the Seychelles Child Development Study. *JAMA* 1998;280:701-707.
- Davidson P.W, Kost J, Myers G.J, Cox C, Clarkson T.W., Shamlaye C, Methylmercury and neurodevelopment: Reanalysis of the Seychelles Child Development Study outcomes at 66 months of age. *JAMA* 2001;285:1291-1293.

- Davis L.E, Kornfeld M, Mooney H.S, Fiedler K.J, Haaland K.Y, Orrison W.W, Cernichiari E, Clarkson T.W. Methylmercury poisoning: long-term clinical, radiological, toxicological, and pathological studies of an affected family. *Ann Neurol* 1994;35:680-688.
- Dietz R., Nielsen C.O., Hansen M.H., Hansen C.T. Organic mercury in Greenland birds and mammals. *Sci Total Environ* 1990;95:41-51
- Dietz, R, Riget, F., Born, E.W. An assessment of selenium to mercury in Greenland marine animals. *Sci Total Environ* 2000;245:15-24.
- Drasch G., Schupp I., Hofl H., Reinke R., Roeder G. Mercury burden of human fetal and infant tissues. 1994. *Eur J Pediatr* 153;8:607-610.
- Drasch G, Wanghofer E., Roeder G., Strobach S. Correlation of mercury and selenium in the human kidney. *J Trace Elem Med Biol* 1996;10:251-254.
- Ehrenberg, R.L., Vogt R.L, Smith A.B. Effects of elemental mercury exposure at a thermometer plant. *Am J Ind Med* 1991;19:495-507.
- Elghany, N.A., Stopford W, Bunn W.B, Fleming L.E. Occupational exposure to inorganic mercury vapor and reproductive outcomes. *Occup. Med. (Lond)* 1997;47:333-6.
- Ellingsen D, Andersen A, Nordhagen HP, Efskind J, Kjuus H. Incidence of cancer and mortality among workers exposed to mercury vapour in the Norwegian chloralkali industry. *Br J Ind Med* 1993;50:875-880.
- Ellingsen DG, Gaarder PI, Kjuus H (1994). An immunological study of chloralkali workers previously exposed to mercury vapour. *APMIS* 102:170-176.
- Ellingsen D.G, Efskind, J, Berg K.J., Gaarder, P.I., Thomassen, U. Renal and immunologic markers for chloralkali workers with low exposure to mercury vapor. *Scand. J. Work Environ. Health* 2000a;26:427-435.
- Ellingsen D.G, Efskind, J, Haug E, Thomassen, Y, Martinsen I, Gaarder, P.I. Effects of low mercury vapour exposure on the thyroid function in chloralkali workers. *J Appl Toxicol* 2000b;20:483-489.
- Ellingsen DG, Bast-pettersen R, Efskind J, Thomassen Y. Neuropsychological effects of low mercury vapor exposure in chloralkali workers. *Neurotoxicology* 2001;22:249-258.
- Eneström S, Hultman P. Does amalgam affect the immune system? A controversial issue. *Int Arch Allergy Immunol* 1995;106:180-203.
- Ericson, A. and Kallen B. Pregnancy outcome in women working as dentists, dental assistants or dental technicians. *Int Arch Occup Environ Health* 1989;61:329-333.
- EPA (U.S. Environmental Protection Agency). Guidelines for Neurotoxicity Risk Assessment. *Fed. Regist.* 1998; 63(93):26925-26954.
- EPA (U.S. Environmental Protection Agency). Mercury Report to Congress, Vol VI: Characterization of Human Health and Wildlife Risks from anthropogenic Mercury Emissions in the United States. EPA-452/R-97-001f. Washington. DC. U.S. Environmental Protection Agency, 1997.
- EPA (U.S Environmental Protection Agency). Water quality criterion for the protection of human health: Methylmercury. Washington, 2001. Available at [www.epa.gov/waterscience/criteria/methylmercury](http://www.epa.gov/waterscience/criteria/methylmercury).
- Fagala, G.E. and Wigg C.L. Psychiatric manifestations of mercury poisoning. *J Am Acad Child Adolesc Psychiat* 1992;31:306-311.
- Falnoga I, Tusek-Znidaric, M, Horvat, M., Stegnar, P. Mercury, Selenium, and Cadmium in Human Autopsy Samples from Idrija Residents and Mercury Mine Workers. *Environ Res* 2000;84:211-218.
- Fawer R.F., de Ribaupierre Y., Guillemin M.P., Berode M., Lob M. Measurement of hand tremor induced by industrial exposure to metallic mercury. *Br J Ind Med* 1983;40:204-208

- Foulds, D., Copeland K, Franks R. Mercury poisoning and acrodynia. *Am J Dis Child* 1987;141:124-125.
- Franchi, E., Loprieno G, Ballardini M, Petrozzi L, Migliore L. Cytogenetic monitoring of fishermen with environmental mercury exposure. *Mutat Res* 1994;320:23-29.
- Gilbert S.G., Burbacher T.M., Rice D.C. Effects of in utero methylmercury exposure on a spatial delayed alteration task in monkeys. *Toxicol Appl Pharmacol* 1993;123:130-136.
- Goyer, R.A. Toxic and essential metal interactions. *Annu. Rev. Nutr.* 1997; 17:37-50.
- Grandjean P, Weihe P, White R.F, Debes F, Araki S, Murata K, Sørensen N, Dahl D, Yokoyama K, Jørgensen P.J. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. *Neurotoxicol Teratol* 1997;19:417-428.
- Hac E, Krzyzanowski M, Krechniak J. Total mercury concentrations in human renal cortex, liver, cerebellum and hair. *Sci Total Environ* 2000;248:37-43.
- Hagmar L., Persson-Moschos, M., Akesson, B., Schütz, A. Plasma levels of selenium, selenoprotein P and Glutathione peroxidase and their correlations to fish intake and serum levels of thyrotropin and thyroid hormones: a study on Latvian fish consumers. *Eur J Clin Nutr* 1998;52:796-800.
- Halbach, S., Clarkson, T., W. Enzymatic oxidation of mercury vapor by erythrocytes. *Biochim Biophys Acta* 1978;523: 522-531.
- Hansen J.C., Reske-Nielsen E., Thorlacius-Ussing O., Rungby J., Danscher G. Distribution of dietary mercury in dog. Quantitation and localisation of total mercury in organs and central nervous system. *Sci Tot Environ* 1989;178: 23-43.
- Hansen J.C., Danscher G. Quantitative and qualitative distribution of dietary mercury in organs from Arctic sledgedogs: An atomic absorption spectrophotometric and histochemical study of tissue samples from natural long-term high dietary organic mercury-exposed dogs from Thule, Greenland. *Pharmacol Toxicol.* 1995;77:189-195.
- Hansen JC, Danscher G. Organic mercury: an environmental threat to the health of dietary exposed societies? *Rev Environ Health* 1997;12:107-116.
- Harada, M. Neurotoxicity of methylmercury: Minamata and the Amazon. Pp. 177-188 in *Mineral and Metal Neurotoxicology*, M.Yasui, M.J.Strong, K.Ota, and M.A.Verity, eds. Boca Raton, FL; CRC Press. 1997.
- Harada M. Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. *Crit Rev Toxicol* 1995;25:1-24.
- Hunter D., Bomford R., Russel D. Poisoning by methylmercury compounds. *Q J Med* 1940; 35:193-213
- Hursh, J.B. Partition coefficients of mercury (203-Hg vapor between air and biological fluids. *J Appl Toxicol* 1985;5:327-332.
- Hursh, J.B., Greenwood, M.r., Clarkson, T.W. Allen, J. Demuth, S. The effect of ethanol on the fate of mercury vapor inhaled by man. *J Pharmacol Exp Ther* 1980;214:520-527.
- IARC (International agency for research on cancer). IARC monographs on the evaluation of carcinogenic risks to humans. Vol 58. Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry. Lyon, 1993.
- Jalili, H.A., and Abbasi A.H. Poisoning by ethyl mercury toluene sulphonanilide. *Br J Ind Med* 1961;18:303-308.
- Jarup L (ed), Berglund M, Elinder C-G, Nordberg G, Vahter M. Health effects of cadmium exposure - a review of the literature and a risk estimate. *Scand J Work Environ Health* 1998;24 (suppl 1):1-52.
- Karpathios, T., Zervoudakis A, Thodoridis C. Mercury vapor poisoning associated with hyperthyroidism in a child. *Acta Paediatr Scand* 1991;80:551-552.
- Katz S. A., Katz R. B. Use of hair analysis for evaluating mercury intoxication of the human body: A review. *J Appl Toxicol* 1992;12:79-84.

- Kazantzis, G., Schiller K.F, Asscher A.W, Drew R.G. Albuminuria and the nephrotic syndrome following exposure to mercury and its compounds. *Q J Med* 1962;3:403-419.
- Kershaw T., Dhahir P., Clarkson T. The Relationship Between Blood Levels and Dose of MeHg in Man. *Arch Environ Health* 1980;35:28-36.
- Kibukamusoke JW, Davies DR, Hutt MSR. Membranous nephropathy due to skin-lightening cream. *Br Med J* 1974;2:646-647.
- Kishi, R., Doi R, Fukuchi Y. Subjective symptoms and neurobehavioral performances of ex-mercury miners at an average of 18 years after the cessation of chronic exposure to mercury vapor. *Environ Res* 1993;62:289-302.
- Kjellstrom T, Kennedy P, Wallis S, Mantell C. Physical and mental development of children with prenatal exposure to mercury from fish. Stage 1: Preliminary tests at age 4. Report 3080, National Swedish Environmental Protection Board, 1986.
- Kjellstrom T, Kennedy P, Wallis S, Stewart L, Friberg L, Lind B, Wutherspoon T, Mantell C. Physical and mental development of children with prenatal exposure to mercury from fish. Stage 2: Interviews and psychological tests at age 6. Report 3642, National Swedish Environmental Protection Board, 1989.
- Kling, L.J, Soares, J.H.jr. Haltman, W.A. Effect of vitamin E and synthetic antioxidants on the survival rate of mercury-poisoned Japanese quail. *Poult Sci* 1987;66:324-33.
- Langworth S., Almkvist O., Soderman E., Wikström B.O. Effects of occupational exposure to mercury vapor on the ventral nervous system. *Br J Ind Med* 1992;49:545-555.
- Langworth S, Elinder C-G, Sundqvist K-G, Vesterberg O (1992). Renal and immunological effects of occupational exposure to inorganic mercury. *Br J Ind Med* 49:394-401.
- Langworth S, Elinder CG, Sundqvist KG (1993). Minor effects of low exposure to inorganic mercury on the immune system. *Scand J Work Environ Health* 19:405-413.
- Lauwerys, R., Roels H. Genet P, Toussaint G, Bouckaert A, De Cooman S. Fertility of male workers exposed to mercury vapor or to manganese dust: A questionnaire study. *Am J Ind Med* 1985;7:171-176.
- Lauwerys R, Bernard A, Roels H, Buchet JP, Gennart JP, Mahieu P, Foidart JM (1983). Anti-laminin antibodies in workers exposed to mercury vapour. *Toxicol Lett* 17:113-116.
- Lebel, J., Mergler D, Branches F, Lucotte M, Amorim M, Larribe F, Dolbec J. Neurotoxic effects of low-level methylmercury contamination in the Amazonian Basin. *Environ Res* 1998;79:20-32.
- Letz R., Gerr F., Cragle D., Green C., Watkins J., Fidler A.T. Residual Neurologic Deficits 30 Years after Occupational Exposure to Elemental Mercury *Neurotoxicol* 2000;21:459-474.
- Liang, Y.X., R.K. Sun, Y. Sun, et al. Psychological effects of low exposure to mercury vapor: Application of a computer-administered neurobehavioral evaluation system. *Environ Res* 1993;60:320-327.
- Lilis, R., Miller A, Lerman Y. Acute mercury poisoning with severe chronic pulmonary manifestations. *Chest* 1985;88:306-309.
- Lind B., Friberg L., Nylander M., Preliminary studies on methylmercury biotransformation and clearance in the brain of primates. II. Demethylation of mercury in brain. *J Trace Elements Exp Med* 1988;1:49-56.
- Mathiesen T, Ellingsen D, Kjuus H. Neuropsychological effects associated with exposure to mercury vapor among former chloralkali workers. *Scand J Work Environ Health* 1999;5:342-250.
- McLaughlin JK, Thomas TL, Stone BJ, Blot WJ, Malke HS, Wiener JA, Ericsson JL, Malke BK. Occupational risks for meningiomas of the CNS in Sweden. *J Occup Med* 1987;29:66-8.
- McNeil, S.I., Bhatnager M.K, Turner C.J. Combined toxicity of ethanol and methylmercury in rats. *Toxicology* 1988;53:345-363.

- Merler E, Boffetta P, Masala G, Monechi V, Bani F. A cohort study of workers compensated for mercury intoxication following employment in the fur hat industry. *J Occup Med*. 1994;36:1260-1264.
- Miettinen J.K., Rahola T., Hattula T, Rissanen K. Tillander M. Elimination of <sup>203</sup>Hg-Methylmercury in Man. *Ann Clin Res* 1971;3:110-122.
- Moszczynski, P., Slowinski S, Ruthowski J, Bem S, Jakus-Soga D. Lymphocytes, T and NK cells, in men occupationally exposed to mercury vapours. *Int J Occup Med Environ Health* 1995;8:49-56.
- Myers G, Davidson P, Palumbo C, Shamlaye C, Cox C, Chernichiari E, Clarkson T. Secondary analysis from the Seychelles child development study: the child behavior checklist. *Environ Res. Section A* 2000;84:12-19.
- National Research Council. Committee on the Toxicological Effects of Methylmercury: Toxicological Effects of Methylmercury. National Academy Press, Washington DC 2000.
- Netterstrøm B., Guldager B., Heebøl J. Acute mercury intoxication examined with coordination ability and tremor. *Neurotoxicol Teratol* 1996;18:505-509
- Palumbo D, Cox C, Davidson P, Myers G, Choi C, Shamlaye C, Sloane-Reeves J, Chernichiari E, Clarkson T. Association between prebatal exposure to methylmercury and cognitive function in Seychelloise children: a reanalysis of the McCarthy scales of children's ability from the main cohort study. *Environ Res. Section A* 2000;84:81-88.
- Pedersen M.B., Hansen J.C., Mulvad G., Pedersen H.S., Gregersen M. Danscher G. Mercury Accumulations in Brains from Populations Exposed to high and Low Dietary Levels of Methylmercury. *Int J Circumpolar Health* 1999;58:96-107.
- Petridou, E., Moussouri M, Toupadaki N, Youroukos S, Papavassiliou A, Pantelakis S, Olsen J, Richopoulos D. Diet during pregnancy and the risk of cerebral palsy. *Br J Nutr* 1998;79:407-412.
- Piikivi, L. Cardiovascular reflexes and low long-term exposure to mercury vapour. *Int Arch Occup Environ Health* 1989;61:391-395.
- Popescu, H.I., Negru L, Lancranjan I. Chromosome aberrations induced by occupational exposure to mercury. *Arch Environ Health* 1979;34:461-463.
- Queiroz, ML. and Dantas D.C, B lymphocytes in mercury-exposed workers. *Pharmacol Toxicol.* 1997a;81:130-3.
- Queiroz, ML. and Dantas D.C, T lymphocytes in mercury-exposed workers. *Immunopharmacol Immunotoxicol.* 1997b;19:499-510.
- Rice D.C. Effects of pre-plus postnatal exposure to methylmercury in the monkey on fixed interval and discrimination reversal performance. *Neurotoxicology* 1992;13:443-452.
- Rice D.C.. Sensory and cognitive effects of developmental methylmercury exposure in monkeys, and a comparison to effects of rodents. *Neurotoxicology* 1996;17:139-154.
- Richardson R.J. Murpy S. D. Effect of glutathione depletion on tissue deposition of methylmercury in rats. *Toxicol Appl Pharmacol* 1975;31:505 –519.
- Rissanen T, Voutilainen S, Nyysönen K, Lakka TA, Salonen JT. Fish-oil-derived fatty acids, docosahexaenoic acid, and the risk of acute coronary events. *Circulation* 2000;102:2677-2679.
- Roels, H.A., Lauwerys R, Buchet J.P, et al. Comparison of renal function and psychomotor performance in workers exposed. *Int. Arch Occup Environ Health* 1982;50:77-93.
- Roels H., Gennart J.P., Lauwerys R., Buchet J.P., Malchaire J., Bernard A. Surveillance of workers exposed to mercury vapour: validation of a previously proposed biological threshold limit value for mercury concentrations in urine. *Am J Ind Med* 1985;7:45-71.

- Roels H., Abdeladim S., Ceulemans E., Lauwerys R. Relationship between the concentrations of mercury in the air and the blood or urine in workers exposed to mercury vapour. *Annals of occupational Hygiene* 1987; 31: 135-145.
- Roels H, Abdeladim S, Braun M, Malchaire J, Lauwerys R. Detection of hand tremor in workers exposed to mercury vapor: a comparative study of three methods. *Environ Res.* 1989 ;49:152-65.
- Roels H.A., Boeckx M., Ceulemans E., Lauwerys R.R. Urinary excretion of mercury after occupational exposure to mercury vapour and influence of the chelating agent meso-2,3-dimercaptosuccinic acid (DMSA). *Brit J Ind Med* 1991;48:247-253.
- Rowland, I.R., Mallett A.K, Flynn J, Hargreaves R.J. The effect of various dietary fibres on tissue concentration and chemical form of mercury after methylmercury exposure in mice. *Arch Toxicol* 1986;59:94-98.
- Rowland A.S., Baird D.D, Weinberg C.R, Shore D.L, Shy C.M, Wilcox A.J. The effect of occupational exposure of mercury vapour on the fertility of female dental assistants. *Occup Environ Med.* 1994;51:28-34.
- Rumbeiha, W.K., Gentry P.A, Bhatnagar M.K. The effects of administering methylmercury in combination with ethanol in the rat. *Vet Hum Toxicol* 1992;34:21-25.
- Sallsten G, Barregard L, Schütz A. Decrease of mercury concentration in blood after long-term exposure - a kinetic study of chloralkali workers. *Br J Ind Med* 1993;50:814-821.
- Sallsten G, Barregard L, Schütz A. Clearance half life of mercury in urine after the cessation of long term occupational exposure: influence of a chelating agent (DMPS) on excretion of mercury in urine. *Occup Environ Med* 1994;51:337-342.
- Sallsten G, Kreku S, Unosson H. A small dose of ethanol increases the exhalation of mercury in low-level-exposed humans. *J Tox Environ Health* 2000;Part A, 60:89-100.
- Salonen J.T., Seppanen K, Nyyssönen K, Korpela H, Kauhanen J, Kantola M, Tuomilehto J, Esterbauer H, Tatzber F, Salonen R. Intake of mercury from fish, lipid peroxidation, and the risk of myocardial infarction and coronary, cardiovascular, and any death in eastern Finnish men. *Circulation* 1995;91:645-55.
- Sasakura, C. Suzuki, K.T., Biological interaction between transition metals (Ag, Cd and Hg), selenide/sulfide and selenoprotein P.J. *Inorg Biochem* 1998;71:159-162.
- Schwartz, J.G., Snider T.E, Montiel M.M. Toxicity of a family from vacuumed mercury. *Am J Emerg Med* 1992;10:258-261.
- Sexton, D., Powell K, Liddle J, et al. A nonoccupational outbreak of inorganic mercury vapor poisoning. *Arch Environ Health* 1978;vol??:186-191.
- Shamlaye CF, Marsh DO, Myers GJ, Cox C, Davidson P, Choisy O, Cernichiari E, Choi A, Tanner MA, Clarkson TW. The Seychelles Child development study on neurodevelopmental outcomes in children following in utero exposure to methylmercury from a maternal fish diet: Background and demographics. *Neurotoxicology* 1995;16:597-612.
- Sherlock J., Hislop J., Newton D., Topping G., Whittle K. Elevation of Mercury in Human Blood from Controlled Chronic Ingestion of Methylmercury in Fish. *Hum Toxicol* 1984;3:117-131.
- Sikorski, R., Juskiewicz T, Paszkowski T, et al. Women in dental surgeries: Reproductive hazards in occupational exposure to metallic mercury. *Int Arch Occup Environ Health* 1987;59:551-557.
- Skerfving S. Methylmercury exposure, mercury levels in blood and hair, and health status in Swedes consuming contaminated fish. *Toxicology* 1974;2:3-23.
- Smith, R.G., A.J. Vorwald, L.S. Patel, et al. Effects of exposure to mercury in the manufacture of chlorine. *Am Ind Hyg Assoc J* 1970;31:687-700.

- Smith J., Allen P., Turner M., Most B., Fisher H., Hall L. The Kinetics of Intravenously Administered Methylmercury in Man. *Toxicol Appl Pharmacol* 1994;128:251-256.
- Snodgrass, W., Sullivan J.B, Rumack B.H, et al. Mercury poisoning from home gold ore processing: Use of penicillamine and dimercaprol. *JAMA* 1981;246:1929-1931.
- Soni, J.P., Singhanian R.U, Bansal A, Rathi G. Acute mercury vapor poisoning. *Indian Pediatr.* 1992;29:365-368.
- Sørensen N, Murata K, Budtz-Jorgensen E, Weihe P, Grandjean P. Prenatal methylmercury exposure as a cardiovascular risk factor at seven years of age. *Epidemiology* 1999;10:370-375.
- Suda I., Totoki S., Takahashi H., Degeneration of methyl and ethyl mercury into inorganic mercury by oxygen free radical-producing systems: Involvement of hydroxyl radical. *Arch. Toxicol* 1991;56:129-134.
- Suda I., Takahashi H. Enhanced and inhibited biotransformation of methylmercury in the rat spleen. *Toxicol Appl Pharmacol* 1986;82:45-52.
- Suda I., Takahashi H. Effect of reticuloendothelial system blockade on the biotransformation of methylmercury in the rat. *Bull Environ Contam Toxicol* 1990;44:609-615.
- Oskarsson A, Schütz A, Skerfving S, Palminger Hallén I, Ohlin B, Jönsson Lagerkvist B. Total and inorganic mercury in breast milk and blood in relation to fish consumption and amalgam fillings in lactating women. *Arch Environ Health* 1996;51:234-241.
- Tamashiro, H., Arakaki M, Futatsuka M, Lee E.S. Methylmercury exposure and mortality in southern Japan: A close look at causes of death. *J Epidemiol Commun Health* 1986;40:181-185.
- Taueg, C., Sanfilippo D.J, Rowens B, et al. Acute and chronic poisoning from residential exposures to elemental mercury. *J Toxicol Clin Toxicol* 1992;30:63-67.
- Tsubaki T., Takahashi H. Recent Advances in Minamata Disease Studies. Methylmercury Poisoning in Minamata and Niigata, Japan. Tokyo: Kodansha Ltd., 1986.
- Tubbs RR, Gephardt GN, McMahon JT, Pohl MC, Vidt DG, Barenberg SA, Valenzuela R. Membranous glomerulonephritis associated with industrial mercury exposure. *Am J Clin Pathol* 1982;77:409-413.
- Turner, C.J., Bhatnagar M.K, Yamashiro S. Ethanol potentiation of methylmercury toxicity: A preliminary report. *J Toxicol Environ Health* 1981;7:665-668.
- Uchino M, Okajima T, Rto K, Kumamoto T, Mishima I, Ando M. Neurologic features of chronic Minamata disease (organic mercury poisoning) certified at autopsy. *Intern Med.* 1995;34:744-7.
- US Public Health Service. Dental amalgam: A scientific review and recommended Public Health Service strategy for research, education and regulation. Department of health and human Services, USA, 1993.
- Vimy, M.J., Takahashi Y., Lorscheider, F.L. Maternal-fetal distribution of mercury (203-Hg) released from dental fillings. *Am J Physiol* 1990;258:R939-945.
- Vroom, F.Q. and Greer M. Mercury vapor intoxication. *Brain* 1972; 95:305-318.
- Warkany, J. and Hubbard D.M. Acrodynia and mercury. *J Pediatr* 1953;42:365-386.
- WHO. Environmental health criteria 101: Methylmercury. World Health Organisation Geneva, International Programme on Chemical Safety, 1990.
- WHO. Environmental health criteria 118: Inorganic mercury. World Health Organisation Geneva, International Programme on Chemical Safety 1991.
- WHO. Joint FAO/WHO expert committee on food additives. Fifty-third meeting, Rome 1-10 June 1999. Summary and conclusions. [www.who.int/pcs/jecfa/summary53revised.pdf](http://www.who.int/pcs/jecfa/summary53revised.pdf)
- Wossmann W, Kohl M, Gruning G, Bucsky P. Mercury intoxication presenting with hypertension and tachycardia. *Arch Dis Child* 1999;80:556-7.

- Wulf, H.C., Kromann N, Kousgaard N, Hansen J.C, Niebuhr E, Alboge K. Sister chromatid exchange (SCE) in Greenlandic Eskimos: Dose-response relationship between SCE and seal diet, smoking, and blood cadmium and mercury concentrations. *Sci Total Environ* 1986;48:81-94.
- Yamamoto R. Suzuki T., Satok H., Kawai K., Generation and dose as modifying factors of inorganic mercury accumulation in brain, liver, kidneys of rats fed methylmercury. *Environ Res* 1986;41:309-318.
- Yoshida Y, Kamitsuchibashi H, Hamada R, Kuwano Y, Mishima I, Igata A. Truncal hypesthesia in patients with Minamata disease. *Intern Med* 1992;31:204-7.
- Yoshida, M., Satho, H., Sumi, Y. Effect of ethanol pretreatment on mercury distribution in organs of fetal guinea pigs following in utero exposure to mercury vapor. *Toxicology* 1997;119:193-201.
- Zelikoff J.T., Bertin J.E., Burbacher T.M., Hunter E.S., Miller R.K., Silbergeld E.K., Tabacova S., Rogers J.M. Health risks associated with prenatal metal exposure *Fundam. Appl. Toxicol.* 1995;25:161-170.



## **CHAPTER-7. PRACTICAL OPPORTUNITIES AND TECHNOLOGIES AVAILABLE TO REDUCE ANTHROPOGENIC EMISSIONS OF MERCURY TO THE ENVIRONMENT**

### **7.1 INTRODUCTION**

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## 7.1 INTRODUCTION

Various international and national organizations have been involved in developing strategies and policies to reduce emissions of mercury to the environment. The element has been given priority in this process compared to other trace metals. Major international activity on reduction of mercury emissions has been carried out within the UN Economic Commission for Europe (ECE) Convention on Long-range Transboundary Air Pollution Transmission (LRTAP). The UN ECE Working Group on Heavy Metals is now preparing protocols on emission reduction for these pollutants. Mercury is considered as priority element in addition to cadmium and lead.

In Europe, there are at least three other conventions working on the basis of international agreements which aim at the reduction of environmental fluxes of various pollutants, including mercury as a priority compound. These three conventions operate within the following programs: Oslo and Paris Commissions (OSPAR) program on reduction of land-based pollutants transported to the North Sea and the sister programs for the Baltic Sea (Helsinki Commission - HELCOM) and for the Mediterranean Sea (Barcelona Convention). There are also a number of national programs in the European countries aiming at the emission reductions of mercury.

In North America, various activities have been launched to reduce emissions of toxic pollutants including mercury. In the United States, Section 112(n)(1)(B) of the Clean Air Act (CAA), as amended in 1990 requires that the U.S. Environmental Protection Agency (EPA) submits a study on atmospheric mercury emissions to the U.S. Congress. The Congress directed that the Mercury Study evaluates many aspects of mercury emissions, including the rate and mass of emissions, health and environmental effects, technologies to control such emissions, and the cost of such controls. There are also other activities at a federal and state level.

In Canada, Environment Canada has been involved in preparing emission surveys for mercury emitted from natural and anthropogenic sources. Various strategies for emission reductions have been prepared at a federal and provincial level.

## 7.2 CURRENT MEASURES TO REDUCE EMISSIONS OF MERCURY IN NORTH AMERICA, INCLUDING POLICY, LEGISLATION AND REGULATORY ACTIONS

This report focuses on mercury control technologies, costs, and financial viability estimates for the following industries:

- ❑ combustion of coal and oil to produce electricity and heat,
- ❑ production of iron and steel, cement, and non-ferrous metals,
- ❑ incineration of wastes, and
- ❑ production and uses of mercury.

These source categories were chosen on the basis of either their source category emissions in aggregate or their potential to be significant sources of emissions. Consideration was also

given to whether a particular source category was a feasible candidate for application of control technology.

### 7.2.1 Combustion of Coal and Oil

Mercury contained in fuel evaporates during fuel combustion in boilers operating at temperatures above 1100 C. Some of the gas may cool and condense as it passes through the boiler and the air pollution control system. Therefore, most of mercury emissions generated during the combustion process can be controlled by devices added on the installations to remove particles and acidic gases. The most commonly used devices to remove particles from exhaust gases in electric power plants and large industrial boilers are electrostatic precipitators (ESPs) and fabric filters (FFs). Various types of flue gas desulfurization (FGDs) are in use to control sulfur dioxide emissions.

ESPs currently employed in the utility and industrial boilers are not very efficient devices for the removal of mercury from the flue gas as major part of the element leaves the boiler in a gaseous form. Recent literature review of data from various power plants in the United States concluded that ESPs have a median mercury removal efficiency of 32% (U.S.EPA, 1997). It was also concluded that FFs are more efficient in removing mercury from the flue gas stream in power plants as part of the mercury may adsorb onto the fly ash cake collected on FFs. It was estimated that FFs have a median mercury removal efficiency of 42 (U.S. EPA, 1997).

Many of the U.S. and Canadian utility boilers are at present equipped with various types of FGDs. In such cases these boilers have an ESP or a FF before the wet FGD to collect the majority of particulate matter. Information collected by U.S.EPA (1995) indicates that FGD units have a median mercury removal efficiency of about 34% with a range from 18 % to more than 97 % removal.

A dry scrubbing system is also used in the U.S. utility boilers through the application of a spray dryer absorber (SDA). In such cases the SDA system is installed before an ESP or a FF. Tests performed on the SDA/ESP combined control system showed that the mercury removal efficiency was ranging from 23 to 83 % with a median efficiency of 67.3 % (Felsvang et al., 1993). Similar tests carried out for the SDA/FF system showed mercury removal efficiency ranging from 6 to 97 % with a median value of 30% (U.S.EPA, 1995; U.S.EPA, 1997).

The above presented data indicate that currently installed control devices, particularly combined systems of ESP or FFs with FGDs or SDAs can remove over 50 % of mercury from flue gases leaving the utility and major industrial boilers. Data on plant configuration, unit fuel usage, and stack parameters for the United States are available from the Utility Data Institute (UDI)/Edison Electric Institute (EEI) power statistics database. These data are collected on a yearly basis from electric utilities at the U.S. Department of Energy's Energy Information Administration.

### 7.2.2 Production of Iron and Steel, Cement, and Non-Ferrous Metals

Mercury can be emitted to the atmosphere during the production of metallurgical coke, which is used in iron and steel industry. ESPs or FFs and less frequently wet scrubbers are used in the coke production plants to control emissions, particularly those generated during quenching. This process is performed to cool down the coke and to prevent complete combustion of the coke upon exposure to air. Although no data are available for the performance of the ESPs or FFs in coke production plants it is expected that mercury removal is limited (U.S.EPA, 1993).

The primary sources of mercury emissions from Portland Cement Manufacturing are from the kiln and preheating/precalcining operations. The kiln operations consist of pyroprocessing (thermal treatment) of raw materials which are transformed into clinkers. Raw material processing differs somewhat for the wet and dry processes. Mercury is introduced into the kiln with fuels such as coal and oil which are used to provide energy for calcination and sintering. Other fuels, such as shredded municipal garbage, chipped rubber, petroleum coke, and waste solvents are also being used frequently.

The kiln emissions are controlled in the United States and Canada with either FFs or ESPs but only limited information is available on the efficiency of these devices with respect to the mercury removal. One source indicates (in U.S.EPA, 1993) that ESPs capture about 25 % and FFs capture up to 50 % of the potential mercury emissions as particulate matter. In general, it can be expected that the mercury removal efficiency in kilns will be comparable with the efficiency of the mercury removal by the same devices employed in utility boilers. Concerning the data collection on emissions of mercury from cement plants, cement kiln test reports are reviewed for facilities performing Certification of Compliance (COC) tests in the United States, required of all kilns burning waste derived fuel (WDF).

Primary lead and copper smelters can be regarded as sources of mercury as the element may be present in the ore. Non-ferrous smelters worldwide use high efficiency air pollution control devices to control particle and sulfur dioxide emissions from roasters, smelting furnaces, and convertors. ESPs are the most commonly used devices for removal of particles. Control of sulfur dioxide emissions is achieved by absorption to sulfuric acid in the sulfuric acid plants, which are commonly a part of the smelting plants. Mercury is emitted mostly in a gaseous form and therefore, the ESPs are not very effective in the element removal. The element does not end up in sulfuric acid plants and is, instead, emitted to the atmosphere from the smelter stacks. The amount of these emissions depends on the content of mercury in the ore. This content varies substantially from one ore field to another. Only limited information has been gathered on mercury emission rates from non-ferrous smelters by the U.S.EPA (1993).

### 7.2.3 Incineration of Wastes

As the content of mercury in wastes varies substantially from one type of waste and the area to another it is very difficult to generalize on mercury emissions from incineration of wastes. Three major groups of incinerators can be considered: municipal waste combustors (MWCs), medical waste incinerators (MWIs), and sewage sludge incinerators (SSIs).

An estimated number of 176 MWCs operating in the United States burn over 31 million tons of trash per year (Cole et al., 1992). More than 85 % of these incinerators with about 99 % of

the MWC capacity employ some kind of air pollution control devices. Various types of devices for removal of particles and acidic gases with different removal efficiencies are used according to the information collected by the U.S.EPA (1993). A great majority of mercury is emitted in a gaseous form. Parameters that increase the mercury removal during combustion of wastes are low temperatures at the typical air pollution control devices, such as ESPs, FFs, and scrubbers, the presence of an effective sorbent, such as carbon, and a method to collect the sorbent (Nebel and White, 1991). Recently, a method with the injection of activated carbon or sodium sulfide to the flue gas prior to the ESP or FF is becoming common in Canada, Europe, and Japan, but less so in the United States. This method is expected to remove between 50 and 95 % of mercury from the flue gas in MWCs.

Concerning emission regulations, the EPA's 1991 New Source Performance Standards and Emission Guidelines for MWCs call for new and existing facilities with certain processing capacities to meet certain emission standards for acidic compounds and metals. Regulations authorized by the Clean Air Act Amendments in the United States require that all MWC facilities with a processing capacity equal to or greater than 250 tons per day meet another set of emission standards for acidic compounds and metals. These requirements were proposed in the Federal Register in September 1994. MWCs with capacities larger than 250 tons per day are required to achieve 80  $\mu\text{g Hg}/\text{m}^3$  at 7 % oxygen or 85 % control, whichever is achieved first. Most of these facilities will install carbon injection along with SDA/FF or SDA/ESP. Facilities with processing capacities between 40 and 250 tons per day are required to have duct injection for acidic compounds and an ESP for particles.

At present, about 5000 MWIs is in operation in the United States, including veterinary facilities, nursing homes, and laboratories. It is estimated that at least 90 % of hospitals have an incinerator on-site. It is also assumed that at least larger MWIs are equipped with a simple or more efficient emission control devices. Most of the device systems employed in the medical waste incineration are either wet or dry systems. Wet systems typically comprise of a wet scrubber for controlling the emission of particles in combination with a packed-bed scrubber for removal of acidic gases and a high efficiency mist elimination. Dry systems include ESPs or FFs in combination with the sorbent injection. Concerning the removal of mercury, appearing mostly in a gaseous form, the efficiency of this process is rather limited. An improvement was obtained through adding activated carbon to the sorbent material in the sorbent injection/FF systems (U.S.EPA, 1993).

An improvement was also expected through adding sodium sulfide to the sorbent material in the sorbent injection/FF systems but the U.S. EPA tests showed that this method is not very effective in additional Hg removal. Sodium tetrasulfide is still untested on a commercial basis.

More than 200 SSIs operate in the United States. Most of them are equipped with some type of scrubbing system for the removal of particles. Quite often these systems consist of venturi scrubbers only or a combination of venturi scrubber/impingement scrubber. The latter system seems to be the most efficient in removing mercury, on the basis of comparison of emission factors presented by the U.S. EPA (1993). However, it is difficult to conclude on the efficiency of mercury removal from SSIs using different types of control devices.

### 7.2.4 Production and Use of Mercury

Mercury can be produced in primary and secondary processes. In primary processes mercury is produced from the ores while in the secondary processes from scrapped mercury-containing products.

At present, mercury is produced in the United States as a byproduct from the mining of gold ores and not from mercury ore. In 1991, there were 8 gold mines in the United States producing metallic mercury as byproduct, while the last mercury ore mine ceased the operation in 1990. On the basis of information from the U.S.EPA (1993), it can be concluded that the mercury emissions from the gold producing plants in the United States are quite well controlled, although no data are available on the amount of these emissions. In general, major sources of mercury emissions within the production process are at locations where furnaces, retorts, and other high temperature sources are employed and where the mercury is removed from the launders. Usually, the emission control installation consists of cyclones, removing larger particles, ESPs for removal of fine particles containing arsenic, mercury and other metals, and various types scrubbers to remove sulfur dioxide and other gaseous substances, including mercury. In the case of high content of mercury in the ore it is necessary to use an activated carbon adsorber bed.

Only about 10 % mercury in the United States is produced in the secondary plants. This production can be accomplished by one of the two general methods: chemical treatment or thermal treatment (U.S.EPA, 1993). The former process results in discharges of pollutants to the aquatic environment, while the thermal process emits various contaminants to the atmosphere.

Control devices in the thermal process based plants are mostly scrubbers but they are very much site-specific. As in the case of other industry branches, primary production plants are usually equipped with more efficient emission control devices than the secondary production plants. However, no details are available to the author on the efficiency of mercury removal from either type of plants in the United States.

Various inorganic mercury compounds are produced in North America using metallic mercury as the starting material. This production presents a potential source of mercury emissions to the atmosphere. No information is available on the amount of these emissions which are controlled mostly at the workplace. Information on removal of mercury from exhaust gases entering the ambient air is not available to the author.

Major uses of mercury include: 1) chlor-alkali production using the mercury cell process, 2) primary battery production, 3) production of measuring and control instruments, and 4) production of electrical lighting, wiring devices, and electrical switches. The use of the mercury cell process to produce chlor-alkali has decreased quite significantly over the past 10-15 years in North America. Already in 1988 this process accounted for only 17 % of all U.S. chlorine production. At present, this contribution is likely much lower. Major points of mercury emission generation in the mercury cell process of chlor-alkali production include: byproduct hydrogen stream, end box ventilation air, and cell room ventilation air. Typical devices/techniques for removal of mercury in these points are: 1) gas stream cooling to remove mercury from hydrogen stream, 2) mist eliminators, 3) scrubbers, and 4) adsorption on activated carbon and molecular sieves. The installation of the above mentioned devices can remove mercury with the efficiency of more than 90 %.

Mercury emissions data from chlor-alkali facilities in the United States can be obtained from Clean Air Act section 114 survey questionnaires (U.S.EPA, 1993). These data are also available from the Toxic Release Inventory (TRI).

The use of mercury in the battery production in the United States has decreased dramatically. Only between 1989 and 1992 the mercury use decreased by 94 % (Bureau of Mines, 1992) and currently only one type of battery, mercuric oxide batteries uses the element. Atmospheric emission of mercury from this source is low compared to other sources. Mercury emission on particles is controlled mostly by FFs, while some mercury vapor emissions from the anode processing and cell manufacturing areas are generally uncontrolled. An application of charcoal filter would likely remove of up to 75 % of these emissions.

Emissions of mercury during electrical apparatus and instrument manufacturing are quite low compared to emissions from other sources. Often these emissions can be controlled by using effective gaskets and seals to contain mercury in the process stream.

### **7.2.5 On-going Federal and State Activities on Mercury Reduction and Control in the United States**

Ongoing programs to control mercury uses, releases, and exposure under a spectrum of environmental laws are summarized at the Federal and State levels (in the EPA document after OECD, 1993). In general, these programs within Federal activities in the United States include:

- ❑ environmental media standards, specifying a maximum acceptable mercury concentration for different media,
- ❑ environmental source controls regulations that control mercury releases into the environment, including limits on air and water point sources, solid waste disposal restrictions, and requirements for reporting and public disclosure of releases,
- ❑ product control regulations for mercury-containing products, e.g. certain pesticides, special paper coatings, pharmaceuticals, cosmetics, and a variety of household products, and
- ❑ other standards and programs, for example regulating exposures to mercury in the workplace by establishing Permissible Exposure Limits (PELs).

Considering the scope of this work, the most relevant are environmental source regulations. Mercury and mercury compounds are regulated as Hazardous Air Pollutants (HAPs) under the 1990 Clean Air Act Amendments. National Emission Standards are established for three point source categories of mercury emissions: ore processing facilities, mercury cell alkali plants, and sewage sludge dryers. Major industrial sources may be subject to Maximum Achievable Control Technology (MACT) standards for stationary sources with emissions exceeding 10 tons/year and Generally Available Control Technology (GACT) standards for area sources. New regulations are proposed/implemented for MWCs and MWIs.

Concerning discharges to aquatic environment, mercury is listed as a toxic pollutant and its discharges from certain branches of industry are subject to technology-based effluent limits, under the Clean Water Act.

The U.S. EPA has established under the Resource Conservation and Recovery Act (RCRA) specific classification and disposal requirements for wastes that contain mercury. For example, any solid waste is considered a hazardous substance and prohibited from disposal in RCRA non-hazardous landfills if its leachate contains 0.2 mg Hg/liter or more; land disposal in RCRA hazardous landfills is allowed only after prescribed treatment to reduce mercury in extract to 0.2 mg/liter.

There are also other more general regulations. Any release of 1 pound or more of mercury to the environment in a 24-hour period must be reported immediately to the National Response Center as long as the release is not federally permitted. Certain facilities that release more than a reportable quantity of mercury must immediately report the release to State and local entities. Any release or transfer of mercury by facilities that exceed use or manufacturing thresholds is reportable under the Toxics Release Inventory.

### 7.3 REVISION OF CURRENT GUIDELINES ON TECHNOLOGICAL MEASURES

A broad review of the abatement techniques for heavy metal emissions from major industrial categories has been prepared for the UN ECE Task Force on Heavy Metals (ECE, 1994). The review is based on the concept of best available technology (BAT), defined as the latest stage of the development of processes, of facilities or of methods of operation which indicate the practical suitability of a particular measure for limiting emissions. In determining whether a set of processes, facilities, and methods of operation constitutes the best available technology in general or in individual cases, special consideration is given to:

- ❑ comparable processes, facilities, or methods of operation which have been recently tried out with successful result,
- ❑ technological advances and changes in scientific knowledge and understanding,
- ❑ the economic feasibility of such technology,
- ❑ time limits for installation in both new and existing plants,
- ❑ the nature and volume of the effluents of concern, and
- ❑ the precautionary principle.

The review concluded that a total dust retention of more than 99.75 % in major stationary sources, such as coal-fired power plants, smelters, cement kilns, and incinerators can be obtained with the use of ESPs and FFs. The contents of heavy metals, including mercury on particles in the flue gas can be reduced by at least 95.0 to 99.0 %.

Various techniques were proposed for capturing gaseous mercury from the flue gas. The application of selenium filter is proposed as a dry media process, which can be applied at both steel and non-ferrous metal smelters. The volatilized mercury is reacting with red amorphous selenium forming mercury selenide. The mercury reduction is never less than 90 %.

Selenium scrubber is a wet media process for removal of fairly large quantities of mercury from the flue gas. The gaseous mercury reacts with activated amorphous selenium, which is circulating in a scrubber with a 20 to 40 % sulfuric acid. The mercury removal efficiency is between 90 and 95 %. However, at low incoming Hg concentrations such as those seen in several utilities the removal efficiency can be less than 90 %.



Carbon filter is another dry media process. The mercury reduction efficiencies of 90 to 95 % have been obtained during measurements at one non-ferrous metal smelter in Sweden.

Lead sulfide process has also been recommended for removal of mercury. The flue gas containing mercury passes through a tower packed with lead sulfide coated balls. This method is used at the Mitsubishi smelter in Naoshima, Japan. The removal efficiency of 99.0 % has been measured.

Mercury content after cleaning of the flue gas with of the above mentioned techniques can be as follows:

<b>Cleaning Techniques</b>	<b>Mercury Content (mg m<sup>-3</sup>)</b>
Selenium filter	< 0.01
Selenium scrubber	0.2
Carbon filter	0.01
Odda chloride process	0.05–0.1
Lead sulfide process	0.01–0.05

The above mentioned Hg content after using the various control technologies listed above depends on the type of emission source and the uncontrolled Hg rate among other parameters. The UN ECE guidelines do not specify, however, this relationship.

More information on removal of mercury through the application of flue gas control devices is presented later in this work when discussing secondary measures of mercury emission reductions.

Concerning the BAT in chlor-alkali industry, the UN ECE Task Force on Heavy Metals guidelines recommend the membrane process. This technology is now gaining more recognition, although only 5.0 % of the total U.S. chlor-alkali was produced by this method in 1988. The membrane cell process is also more energy efficient compared to the diaphragm cell or mercury cell and produces a higher quality product. A conversion of existing membrane cell and diaphragm cell chlor-alkali plants to membrane cell operation is possible utilizing some of the existing equipment.

## **7.4 ASSESSMENT OF PRE-TREATMENT MEASURES OF MERCURY EMISSION REDUCTIONS**

Fuel washing and fuel substitution are the major pre-treatment measures to reduce emissions of various pollutants from coal combustion processes, including reduction of mercury. There are also some pollution prevention measures, such as materials separation to decrease emissions of mercury from waste incineration.

### 7.4.1 Coal Washing

Commercial coal cleaning (or beneficiation) facilities, particularly in the United States (e.g. NAPAP, 1990) are physical cleaning techniques to reduce the mineral matter and pyritic sulfur content. As a result, the product coal has a higher energy density and less variability (compared to feedstock coal) so that power plant efficiency and reliability are improved. A side benefit to these processes is that emissions of sulfur dioxide, as well as other pollutants including mercury can be reduced. The efficiency of this removal depends on the cleaning process used, type of coal, and the contaminant content of coal. Basic physical coal cleaning techniques have been commercial for over 50 years.

The cleaning of coal takes place in water, in a dense medium, or in a dry medium. Physical cleaning processes are based on either the specific gravity or surface property differences between the coal and its impurities. Jigs, concentrating tables, hydro-cyclones, and froth flotation cells are common devices used in current physical coal-cleaning facilities.

The mercury concentrations in the raw coal, the clean coal, and the present reduction achieved by cleaning have been presented by Akers et al. (1993) for coals from various regions in the United States. The removal efficiency ranged from 0 to 60 % with 21 % as average reduction. This efficiency is highly dependent on the type of coal and chloride content of the coal.

Concerning other fuels, the cleaning of crude oil occurs mostly through the residue desulfurization (RDS). However, the content of Hg in crude oil is usually very low and RDS is an inefficient method to even lower this content.

### 7.4.2 Fuel Switching

The following options of fuel substitution are often considered in the electric utilities:

- ❑ switching from high- to low-sulfur coal burnt in applicable coal-based generation (including switching directly from high-sulfur to low-sulfur supplies, blending high- and low-sulfur coal, cleaning high- and medium-sulfur coal, or a combination of cleaning and blending),
- ❑ increasing the use of natural gas, or oil, and
- ❑ increasing the use of alternate fuels or importing electricity to meet base load electric-generation requirements.

The two latter methods are the most interesting with respect to the reduction of mercury emissions. The substitution of coal by coal bed methane to produce heat and electricity would result in decrease of emissions of various air pollutants, including mercury. The following action would be needed in the case of the substitution:

- ❑ the modernization of existing utility and industrial heat producing plants,
- ❑ the development of new methane burning boilers, and
- ❑ the modernization of coal mines with respect to the better exploitation of coal bed methane.

Lower emissions of mercury from MWCs and MWIs can be achieved through a process called product substitution. Although this substitution is potentially applicable to a wide range

of components, batteries have received the greatest attention because of their significant contribution to total mercury content in municipal and medical wastes. Two initiatives were undertaken in order to reduce the amount of mercury used in battery manufacturing:

- ❑ an initiative towards reducing and eventually eliminating mercury in household batteries, and
- ❑ development of alternatives to mercury-zinc batteries, where small size and constant current supply are critical.

An important issue in this respect is State/ Provincial legislation prohibiting the sale of certain Hg-containing products, requiring manufacturer take back of Hg-containing products (except lamps), and requiring all medical facilities to segregate waste products containing Hg to the level of about 1 ppm. One additional HgO button battery/ ton of medical waste doubles the Hg concentration.

The applicability of the product substitution to other areas should be based on technical and economic feasibility. For example, reducing or eliminating the use of mercury in lighting systems could result in continued use of less efficient technology thereby requiring increased electricity generation and associated air emissions.

## **7.5 ASSESSMENT OF PRIMARY MEASURES OF MERCURY EMISSION REDUCTIONS**

Primary measures of emission reduction include solutions where emission reduction occurs at emission generation point, e.g. application of various modifications of combustion process may reduce emissions from a given burner. Technological modifications in chlor-alkali industry have already been discussed in this report.

### **7.5.1 Non-conventional Combustion Technologies**

Non-conventional methods of combustion, such as fluidized bed combustion (FBC) were found to generate comparable or slightly lower emissions of mercury and other trace elements compared to the conventional power plants (e.g. Carpenter, 1979, Abel et al., 1981). However, a long residence time of the bed material may result in increased fine particle production and thus more efficient condensation of gaseous mercury. Tests carried out in the former Federal Republic of Germany have shown that the residence time of the bed material can be regulated by changing the operating conditions of a given plant, the reduction of combustion temperature, coal size, moisture content, and bed flow rates (Munzner and Schilling, 1985). A literature review of information on the influence of various FBC techniques on emissions of trace elements has been presented by Smith (1987).

Quantities of atmospheric emissions from waste incineration depend greatly on the type of combustor and its operating characteristics. The mass burn/waterwall (MB/WW) type of combustor is often used. In this design the waste bed is exposed to fairly uniform high combustion temperatures resulting in high emissions of gaseous mercury and its compounds. Other types of combustors seem to emit lesser amounts of mercury as indicated by the comparison of the best typical mercury emission factors for municipal waste combustors

(U.S.EPA, 1993). It is also suggested that fluidized-bed combustors (FB) emit smaller amounts of mercury to the atmosphere compared to other sewage sludge incineration techniques, and particularly multiple hearth (MH) techniques.

### **7.5.2 Low NO<sub>x</sub> Burners**

Low NO<sub>x</sub> technologies are also likely to reduce mercury emission in the exhaust gases due to the lower operating temperatures. Very limited information on this subject is rather inconclusive. While some sources indicate that the reduction can be achieved, preliminary results of staged combustion in atmospheric fluidized bed combustion (AFBC) units indicated that low NO<sub>x</sub> had only little effect on trace element emissions (Smith, 1987). It should be noted, however, that low NO<sub>x</sub> technologies are far less used compared to the FGD systems.

## **7.6 ASSESSMENT OF SECONDARY MEASURES OF MERCURY EMISSION REDUCTIONS**

Secondary measures include technological solutions to decrease concentrations of pollutants in the flue gas. Major emphasis in this report is placed on the removal of mercury and its compounds by the application of flue gas desulfurization (FGD).

The distribution of trace elements in coal-fired boilers with wet and dry FGD was reviewed by Moberg et al. (1982) within the Swedish KHM project. Halogens, mercuric chloride and selenium dioxide, were removed with sulfur dioxide absorption. Large variations of mercury removal were found, probably due to differences in the behavior of specific mercury compounds. Formation of particles of chloride and sulfate salts was considered to be an important removal mechanism for mercury in the FGD process. This would be promoted by high Cl content in the coal and for mercury sulfate, and by low temperatures combined with the catalytic effect of activated carbon.

Two major types of FGD systems can be distinguished: wet and dry FGDs.

### **7.6.1 Wet FGD Systems**

Distribution of mercury within various streams of the wet FGD system was studied in various countries. As much as 70 % of mercury in exhaust gases has remained in the gas stream after passing through the FGD according to one German study (Gutberlet, 1984). In general, the trace element content of the gypsum and sludge is influenced by the solubility of the elements upstream, the settling behavior of solids in the thickener, and the waste water volume. In the waste water cleaning plant, the solubility of the trace elements is decreased by increasing the pH to the range of 8.0 to 9.5 so the waste water contains only very small amounts of the elements. Their concentrations in the waste sludge are at low levels (e.g. 6 ppm for Hg).

Removal of trace elements from exhaust gases by the wet FGD systems has also been studied in the Netherlands (Meij and Alderliesten, 1989; Meij, 1992), where only pulverized coal-fired dry-bottom boilers are used, equipped with high-efficiency electrostatic precipitators

(ESP) and FGD using a wet lime/limestone-gypsum process with prescrubber. Mostly bituminous coals imported mainly from US and Australia are burnt. In one study (Meij, 1992) the Hg concentration upstream of FGD was  $3.4 \mu\text{g}/\text{m}^3$  and downstream was  $1.0 \mu\text{g}/\text{m}^3$ . The relative distribution of mercury between bottom ash, collected pulverised-fuel ash and fly-ash in the flue gases and in the vapor phase was about 10% on fine particles and about 90% in vapor phase. Flue gases contained 87% of the mercury concentration found in coal, and up to 70% of that was removed by the wet FGD. About 60% of mercury removal takes place in the prescrubber and about 40% in the main scrubber.

In summary, the relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapor phase and thus to be removed from the flue gases. In general, removal efficiency for mercury ranges from 30 to 50%.

### 7.6.2 Dry FGD Systems

Retention of vapor phase mercury by spray dryers has been investigated in Scandinavia and the United States for coal combustors and for waste incinerators (Smith, 1987). The following conclusions have been reached in some of these studies:

- ❑ Brosset (1983): Water soluble mercury (40 to 80%) was partly bound in lime slurry and so mostly retained by the lime.
- ❑ Bergstrom (1983): 50–70% of the mercury from coal was retained in the ESP ash preceding the FGD spray dryer; 75% of the mercury from coal was retained overall.
- ❑ Nilsson (1981): 30–40% of gas phase mercury was retained.
- ❑ Karlsson (1986): 52–63% of mercury was removed, with 15–33% retained in the FGD unit (including baghouse).
- ❑ Moller and Christiansen (1985): inlet gas phase mercury concentrations of  $0.2\text{--}0.7 \text{ mg}/\text{m}^3$  reduced to  $0.1\text{--}0.01 \text{ mg}/\text{m}^3$  through the FGD unit.

An excellent retention of trace elements by spray dryer systems implies that fly ash or dry end product might contain high concentrations of mercury. Karlsson (1986) showed that precollection was beneficial for some elements. The pattern for carry over of trace elements from the ESP to the dry end product is complicated by condensation of some constituents and varying degree of enrichment and interactions among the elements. For example, a high Ca concentration led to high As, Cr and Hg concentrations but low concentrations of other elements.

In summary, the overall removal of mercury in various spray dry systems varies from about 35 to 85%. The highest removal efficiencies are achieved from spray dry systems fitted with downstream fabric filters.

It should be added that test results (for both wet and dry FGD systems) carried out before the 1990's are not to be considered as absolutely accurate. Some of the test methods were highly inaccurate, sometimes only capturing a half of the Hg present in the flue gas.

## 7.7 ASSESSMENT OF NON-TECHNOLOGICAL METHODS OF MERCURY EMISSION REDUCTIONS

Previous chapters of this work have dealt with technological methods to reduce mercury emissions, mostly with the methods often called End-of-Pipe solutions (EOP). An important aspect which needs not to be overlooked is the fact that in most cases EOP control technologies merely transfer the mercury from one form of waste to another. All of the add-on control technologies (carbon filter beds, wet scrubbing, activated carbon injection) generate a contaminated medium which must be disposed of either burning or landfilling, often in a hazardous waste landfill. This creates an additional charge of the pollutants, including mercury to the environment. Non-technological methods have the advantage over the EOP technologies because they do not generate the wastes.

The most known non-technological methods of mercury removal include: energy conservation and pollution prevention solutions. Energy conservation means using less energy to achieve the same level of energy service. Energy services include heat, light, sound, shaft power, and mobility. Decreasing energy production and use will result in the decrease of mercury emissions and provide additional benefits of reducing emissions of sulfur dioxide and other pollutants. A system of credits or vouchers could be developed and presented to the utilities for mercury reduction goals. Demand-side management (DSM) programs should be identified. The DSM refers to actions undertaken by an electric utility to modify customer demand patterns. The DSM programs consist of information dissemination, technologies, or financial incentives and are a component of Least-Cost Utility Planning.

A few solutions of pollution prevention can be presented for mercury, including:

- ❑ materials separation,
- ❑ product content bans,
- ❑ input taxes on the use of mercury in products, and
- ❑ labeling of products.

Material separation deals mostly with the separation of mercury containing materials from the waste streams of MWCs and MWIs. A very small portion of wastes (perhaps less than 1 %) containing very high content of mercury from batteries, fluorescent lights, thermostats and other electrical items needs to be separated from the rest of the wastes, such as paper, plastic, dirt, containing very low concentrations of the element. Several communities in the United States have already implemented household battery separation programs in an effort to reduce mercury in wastes to be incinerated. It is difficult to estimate what portion of batteries is recovered, but the U.S.EPA indicates a range from 3 to 25 % (U.S. EPA, 1991).

Labeling the mercury-containing products would help consumers to select the ones which are mercury-free. This is particularly important for switches and devices that most consumers would not expect to contain mercury.

## 7.8 COST-EFFECTIVENESS OF MERCURY CONTROLS

Information on investment, installation, and maintenance costs for mercury controls discussed in previous chapters has been obtained from previous projects of the author within the Baltic Sea Environment Program, the available literature on the subject, and pollution control technology vendors. Concerning North America, extensive studies on sources, exposure, and control measures are being carried out at the U.S. EPA. These studies include an evaluation of mercury control technologies, costs, and regulatory issues. The work is still in process and the results are expected soon.

It should be noted that the cost estimates presented in this report are in the 1990/91 US dollars.

### 7.8.1 Cost-Effectiveness of Mercury Removal from the Flue Gas

Cost effectiveness is an important part of the cost, impact, and benefit considerations associated with the control of air pollutant emissions, including mercury. In general, capital cost and maintenance cost are estimated separately for a given control technology, taking into account the size of emission generation unit, e.g. the size of boiler, type of the control technology employed, volume of the flue gas, the Hg concentrations before and after the control device, and a capacity factor. Capital cost consists of the cost of the purchased equipment, installation of this equipment, and indirect cost. The indirect is often calculated on the basis of the cost of purchased equipment.

More complicated is the estimation of the operating and maintenance cost. There are several parts of the cost which are rather uncertain and are usually assumed. In some countries the operating and maintenance cost is assumed to be a part, for example 4.0 % per year, of the investment cost, being a part of the capital cost (e.g. Amann et al., 1997). In other cases, operating and maintenance cost is calculated using available information and assumptions on costs of operating and supervision labor, maintenance labor and maintenance materials, operating materials, as well as costs of purchased materials, power, disposal, and various taxes. The operating and maintenance cost is annualized. An example of estimates of cost-effectiveness of mercury control measures in utility boilers and waste incinerators is presented in Table 1 after available data from the literature. The purpose for inclusion of this table was to inform the reader about the cost level rather than to give a cost rate for precise cost estimates in certain specific case of mercury control implementation. In the lastest case a thorough analysis of cost effectiveness would be needed. Examples of investment (capital) cost and annualized operating and maintenance cost estimates for power plants in Table 1 are given for a utility of ca. 1000 MW output. Application of carbon filter beds is a very efficient solution to remove mercury from flue gases but it also seems to be one of the most expensive methods; particularly the cost of purchased equipment is very high.

The effectiveness of the activated carbon injection and carbon filter beds in recovering different chemical species of mercury is still in the early stages of investigation. Without the activated carbon injection, a pilot SDA/ESP system removed 95 % of the ionic mercury from the flue gas of a coal-fired power plant (RTI, 1993). Activated carbon injection ahead of the SDA/ESP system would remove 90 % of the total mercury.

Information on total cost of mercury removal from the MWC flue gases in Table 1 is given for small units (a couple of hundred tons of wastes incinerated each day) and larger units (about 10 times more than small units), separately. Again, the employment of carbon filter beds seems to be very efficient but also very expensive solution for mercury removal from MWCs. Concerning the cost of mercury control in MWIs presented in Table 1, these estimates are for two unit sizes of combustors: around 60 and 460 kg wastes per hour. These preliminary estimates have been made for the U.S.EPA report to Congress (e.g. Radian, 1993; RTI, 1993).

Estimates of cost - effectiveness for mercury removal from the flue gas have also been made for other industrial sectors, particularly for non-ferrous metal smelters and chlor-alkali plants. Selenium filters are recommended for the removal of mercury from the flue gas stream upstream of the acid plant in non-ferrous metal smelters. These filters, developed already in the 1970's in Sweden would have removal efficiency of up to 90.0 %. The estimates of the annualized cost indicate a range from US\$ 10.0 to more than 50.0 per 1 tonne of copper produced. In the case of lead smelters this cost is about 50 % lower.

Estimates performed by Eurochlor, an umbrella organization representing the chlor-alkali industry, indicate that the conversion from mercury electrolysis to membrane electrolysis (no mercury involved) would cost about US\$ 1000.00 per tonne of chlorine (Eurochlor, 1993).

## **7.8.2 Cost-Effectiveness of Other Measures of Mercury Removal**

In general, direct abatement methods related to pre-combustion control, such as switch to or blend with fuels, and coal or oil cleaning cannot be recommended due to either low efficiency or high cost when used only to remove mercury. Cost - effectiveness for coal cleaning/benefication processes in the United States at the end of the 1980's ranged from US\$ 120.00 to 500.00 per tonne of sulfur dioxide removed, depending on the removal technique used and the type of coal cleaned (e.g. NAPAP, 1990). This method was found more expensive than the switch of fuels. A total retrofit cost of altering a coal-fired boiler for a seasonal use of natural gas has been conservatively estimated to be about US\$ 18000.00 per 1 MW. The cost of the pipeline must be added to the natural gas retrofit costs, ranging from US\$ 75.00 to 175.00 per 1 ft of pipeline.

A total retrofit cost of at least US\$ 42000.00 per 1 kg of mercury removed through the implementation of pre-treatment measures of control was estimated by Pacyna (1992) for the Baltic Sea Environmental Programme.



**Table 7.1** - Cost-effectiveness of mercury control measures in utility boilers and waste incinerators.

Control Options	Mercury Removal Efficiency %	Costs	
		Investment	Operating and Maintenance
<b>Power plant *1</b>			
- ESPs (only)	10	1.6	0.2
- FFs (only)	29	28.9	5.8
- ESP or FF + wet FGD	85	59.0	2.5
- dry absorber SDA+ESP	67	143.0	5.0
- ESP + carbon filter beds	90-95	264.0	62.0
- activated carbon injection +FF	50-90+	34.6	8.1
<b>Municipal Waste Combustor (MWC) <sup>(2)</sup></b>			
- ESP and FFs - as above			
- ESP or FF + carbon filter beds	99	31.7/80.0	6.5/15.6
- activated carbon injection + ESP or FF	50-90+	0.3/0.8	0.25/1.3
- polishing wet scrubber +ESP or FF	85	10.3/22.9	1.9/4.9
<b>Medical Waste Incinerators (MWI) <sup>(2)</sup></b>			
- ESP and FFs - as in p. 1.			
- activated carbon injection +FFs	50-90+	56.5/127.0	89.0/84.0
- polishing wet scrubber +FFs	85	400.0	100.0

(1) Investment cost in 1000 US\$/MWh, while operating and maintenance cost in 1000 USD/MWh/yr

(2) Investment cost in 1000 US\$/tonne of waste, operating and maintenance cost in 1000 USD/ ton-waste/yr. Two estimates are given for large plant/small plant

ESP =Electrostatic Precipitator

FF =Fabric Filter

FGD=Flue Gas Desulfurization

SDA= Spray Dryer Absorber

## 7.9 REFERENCES

- Abel W.T., Rice R.L., Shang J.Y., Turek D.G. and Ayers W.J. (1981) Combustion of western coal in a fluidized bed. DOE Report No. DOE/METC/RI-178, U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV.
- Akers D., Dospoy R. and Raleigh C. (1993) The Effect of Coal Cleaning on Trace Elements. Draft Report, Development of Algorithms. Prepared for Electric Power Research Institute, December, 1993.
- Amann M., Bertok I., Cofala J., Gyarfas F., Heyes C., Klimont Z. and Schopp W. (1997) Cost-effective Control of Acidification and Ground-level Ozone. Second Interim Report to the European Commission, DG-XI, International Institute for Applied Systems Analysis (IIASA), Laxenburg, Austria.
- Bergstrom J. (1983) Separation of mercury in electrostatic filters and by flue gas desulfurization. KHM Technical Report No. 89, The Swedish State Power Board Vallingby, Sweden, (in Swedish).
- Brosset C. (1983) Emissions of mercury compounds from flue gases. KHM Technical report No. 76, The Swedish State Power Board, Vallingby, Sweden (in Swedish).
- Bureau of Mines (1992) U.S. Industrial Consumption of Refined Mercury Metal, by Use. U.S. Department of Interior, U.S. Government Printing Office, Washington, D.C.
- Carpenter R.L. (1979) Fluidized bed combustion emissions toxicology program. Status report, October 1979. LMF-74 Report, Lovelace Biomedical and Environmental Research Institute, Albuquerque, NM.
- Cole H.S., Hitchcock A.L. and Collins R. (1992) Mercury Warning: The Fish You Catch May Be Unsafe to Eat. A Study of Mercury Contamination in the United States. Clean Water Fund. Clean Water Action. Washington, D.C., August, 1992.
- ECE (1994) Guidelines on Measures and Methods for Heavy Metal Emissions Control. In: the Task Force on Heavy Metals Emissions: the State-of-the-Art Report, the U.N. Economic Commission for Europe, Prague, June, 1994.
- Eurochlor (1993) Report of the Task Force Considering the Phase-Out of Mercury Cells by 2010. European Chlorine Industry Association.
- Gutberlet H. (1984) Measurement of heavy metal removal by a flue gas desulfurization plant working by the lime scrubbing method. Research report ENV-492-D (B). Commission of the European Communities, Luxembourg.
- Karlsson H.T. (1986) Spray dry scrubbing of secondary pollutants from coal burning. In Proceedings of 3rd Annual Pittsburg Coal Conference, Pittsburg, PA.
- Meij R. and Alderliesten P.T. (1989) The emission of inorganic trace compounds at coal-fired power plants equipped with wet flue gas desulfurization plants. In: Proc. 8th World Clean Air Congress, Man and his Ecosystem, Amsterdam, the Netherlands.
- Meij R. (1992) A mass balance study of trace elements in a coal-fired power plant with a wet FGD facility. In *Elemental Analysis of Coal and Its By-Products*, G. Vourvopoulos, ed., World Scientific, Singapore, 299-318.
- Moberg P.-O., Westermarck M., and Noling B. (1982) Migration of trace elements during flue gas desulfurization. KHM Report TR 28, The Swedish State Power Board, Vallingby, Sweden.
- Moller J.T. and Christiansen O.B. (1985) Dry scrubbing of MSW incinerator flue gas by spray dryer absorption: new developments in Europe. Presented at 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI.
- Munzner H. and Schilling H.-D. (1985) Fluorine and chlorine emissions from FBC enrichments in fly-ash and filter dust. In: the 8th Inter. Conf. on Fluidized Bed Combustion: Options and Issues, Houston, TX.

- NAPAP (1990) Technologies and Other Measures for Controlling Emissions: Performance, Costs and Applicability. National Acid Precipitation Assessment Program, NAPAP Rept. 25, Washington, D.C.
- Nebel K.L. and White D.M. (1991) A Summary of Mercury Emissions and Applicable Control Technologies for Municipal Waste Combustors. Prepared for the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, September, 1991.
- Nilsson B. (1981) Secondary cleaning effects in dry FGD scrubbing. KHM Technical Report No. 07, Studsvik Energiteknik AB, Sweden, (in Swedish).
- OECD (1993) Co-operative Risk Reduction Activities for Certain Dangerous Chemicals: Mercury. Organization for Economic Co-operation and Development, Paris, November, 1993.
- Pacyna J.M. (1992) The Topical Area Study for Atmospheric Deposition of Pollutants. Final Technical Report for the Baltic Sea Environmental Programme. NILU Rept. OR:46/92, Norwegian Institute for Air Research, Kjeller, Norway.
- Radian (1993) Mercury Control Technologies and Cost Report. Prepared for the U.S. Environmental Protection Agency by the Radian Corporation, Research Triangle Park, NC.
- Smith I.M. (1987) Trace elements from coal combustion – emissions. International Energy Agency, Coal Research, London.
- U.S. EPA (1991) Municipal Waste Combustion: Background for Materials Separation. EPA Rept. EPA/450-3-90-021, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (1993) Locating and Estimating Air Emissions from Sources of Mercury and Mercury Compounds. Final Rept. EPA-454/R-93-023, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- U.S. EPA (1995) Information obtained from discussions at the Review Workshop on the Mercury Study Report to Congress. U.S. Environmental Protection Agency, Cincinnati, OH, January 25-26, 1995.
- U.S. EPA (1997) Mercury Report to Congress. U.S. Environmental Protection Agency, Research Triangle Park, NC.