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

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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; Pirron 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 of 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., 1990).

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), Idrija (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 difficulty 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\(^{-1}\) (1992 estimate by Pirrone \textit{et al.}, 1996) to 1660 t yr\(^{-1}\) (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\(^0\)), 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, \textit{et al.}, 1998; Pirrone \textit{et al.}, 2000; Munthe \textit{et al.}, 2000; Wängberg \textit{et al.}, 2000; Munthe \textit{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 \textit{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\(^0\) in ambient air is mainly determined by the background concentration of around 1.3 – 1.5 ng m\(^{-3}\) in the Northern Hemisphere and 0.9 – 1.2 ng m\(^{-3}\) in the Southern. Hg(II) and Hg(p) are typically present in concentrations less than 1% of the Hg\(^0\). 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 \textit{et al.}, 2001). 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. In the presence of liquid water in the atmosphere (fog or cloud water or precipitation) small amounts of Hg\(^0\) are dissolved and can be oxidised in the aqueous phase by e.g. ozone (Munthe, 1991) or OH radicals (Gärdfeldt \textit{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\(^0\) 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 Hg0 and subsequent transfer back to the gas phase may also occur via reactions with dissolved sulphur dioxide and HO\(_2\) 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 Hg\textsuperscript{0} or 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 mg Kg\textsuperscript{-1} on calcareous and 6 mg Kg\textsuperscript{-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. podsolic 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 podsolic 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 podsolic 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 bout 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\textsuperscript{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 Hg\textsuperscript{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 patter 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^-3 and urban concentrations of 10 ng m^-3 (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^-3 during inhalation and less than 1,000 ng-Hg m^-3 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^-3 (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^{-1}, 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 immunoglobolins (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 (Hg$^0$), inorganic mercury (i.e., 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 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


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).


Palmberg 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)


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).

<table>
<thead>
<tr>
<th>Media</th>
<th>Elemental Mercury</th>
<th>Inorg. Mercury Comp.</th>
<th>Methylmercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>40-200&lt;sup&gt;b&lt;/sup&gt; (30-160)</td>
<td>0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Food:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fish</td>
<td>0</td>
<td>600&lt;sup&gt;d&lt;/sup&gt; (60)</td>
<td></td>
</tr>
<tr>
<td>non-fish</td>
<td>0</td>
<td>3600 (360)</td>
<td></td>
</tr>
<tr>
<td>Drinking water</td>
<td>0</td>
<td>50 (5)</td>
<td>0</td>
</tr>
<tr>
<td>Dental amalgam</td>
<td>3800-21000&lt;sup&gt;e&lt;/sup&gt; (3000-17000)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>3900-21000&lt;sup&gt;(3)&lt;/sup&gt; (3100-17000)</td>
<td>4200 (420)</td>
<td>2400 (2300)</td>
</tr>
</tbody>
</table>

<sup>a</sup> 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.

<sup>b</sup> Assumes an air concentration of 2-10 ng/m² and a daily respiratory volume of 20 m³.

<sup>c</sup> For the purposes of comparison, it is assumed that in the atmospheric concentrations of species of mercury other than mercury vapour are negligible.

<sup>d</sup> 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.