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THE ORIGIN AND FATE OF MERCURY SPECIES IN THE ENVIRONMENT

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The origin and fate of mercury species in the environment

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The origin and fate of mercury species in the environment

1. Introduction

1.1. Why mercury speciation?

The emissions, environmental fate and effects of mercury are to a large extent determined not only by the total amounts of mercury released or by the total concentration levels present in an environmental media, but also by the distribution of mercury between different chemical forms, i.e. the speciation.

Speciation of mercury has been a basic area of research for decades, both as an independent research topic and in combination with studies of emissions and environmental cycling of mercury. In some cases a mercury "species" is equivalent to a specific mercury chemical compound but in other cases it is an operationally defined form.

An example of the former is monomethylmercury (CH_3Hg^+) which is a species that can be identified analytically using e.g. gas chromatography. On the other hand it is an ion, which in any environment is bound to a ligand. The identification is, in this case, limited to the methylmercury group.

An example of the latter group is the commonly used term Reactive Gaseous Mercury (RGM) which is an operationally defined species in stack gases and ambient air. This is assumed to be $HgCl_2$ or similar species, see section 2.1.

Speciation influences the mobility of mercury in various media (air, water, soil), since different chemical species have different properties (e.g. volatility, water solubility). Furthermore, speciation and especially the methylmercury fraction, to a large extent determines the uptake and negative health effects of mercury in humans and wildlife.

1.2. Historical and current uses of mercury

Elemental mercury and some of its compounds have been known to man for more than 3000 years. The mineral cinnabar (HgS) is present in the ground at many places and could easily be collected. In the "History of Stones" the earliest preserved text on chemistry and metallurgy, Theophrastus of Eresus (371-286 B.C.) a student of Aristotle, describes how elemental mercury is obtained from cinnabar.

Very large quantities of mercury were found in Qin Shihuang's Mausoleum, the first emperor of China (259-210 B.C.). This silver shining liquid metal certainly attracted people's interest and fascination and it was probably collected and distributed as a curiosity in the beginning. However, HgS and other mercury compounds were used as pigments in paint in Egypt as early as 1500 B.C.

When the Romans began gold mining using mercury about 2000 years ago, the demand for mercury increased. It became commercially important and offered great prosperity to those who controlled the mercury mines. Later in the industrial era, mercury was found to be useful in many industrial applications. Elemental mercury constituted a vital part in a number of electrical and electro-mechanical devices as well as in many scientific instruments.

Since the middle of the 19th century mercury has been used extensively in dental amalgam. The chemical industry uses large amounts of mercury in chlor-alkali production although this use is being phased out in e.g. Europe. Compounds of the metal are still used as catalysts e.g. in the production of vinyl chloride in Asia. Organic mercury compounds have been used as fungicides in agriculture and the paper pulp industry. The mercury production reached a maximum during the 1960s with a global production of 10,000 tonnes per year.

The demand for mercury has since decreased dramatically. The total mercury consumption in 2000 amounted to 3390 tonnes (Maxson, 2006), whereof consumption of mercury for production of batteries and chlor-alkali contributed 55% (see Table 1). Another important use is in small-scale gold and silver mining constituting almost 20% of the total consumption.

Table 1. Global Mercury Consumption Year 2000 (Maxon 2006)

Mercury uses	Tonnes per year	%
Electrical control and switching	154	4.5
Lighting	91	2.7
Measuring and control	166	4.9
Dental amalgam	272	8.0
Batteries	1081	31.9
Chlor-alkali	797	23.5
Small-scale gold and silver mining	650	19.2
Other uses	175	5.2

1.3. The mercury problem

The toxicity of mercury and its compounds as well as the global aspects of mercury pollution are well known (UNEP, 2002; Mergler et al., 2007; Scheuhammer et al., 2007). Occurrences of mercury intoxication are known from both historical and modern times.

In modern times, the most well-known examples are the disasters in Iraq and in Minamata, Japan, where exposure to methylmercury via ingestion of grain treated with methylmercury-containing fungicides and severely contaminated sea-food, respectively, led to thousands of cases of death and serious neurological damage.

These events, although perhaps not representative of mercury problems globally, have become symbols of the risks associated with irresponsible use of mercury and have raised the awareness of mercury toxicity globally.

During the decades after the disasters in Iraq and Minamata, the focus of attention was very much turned to long-range environmental transport and increased levels in freshwater fish in Scandinavia and North America (Lindqvist et al., 1991). The driving force for this was the discovery that fish in remote lakes could accumulate methylmercury concentrations exceeding those causing adverse effects in humans, if consumed.

In recent years, the global trade of mercury and the (often illegal) use of large quantities of mercury in small scale gold mining leading to extensive local pollution and exposure, has been a source of concern. Environmental emissions and human exposure to mercury have thus been an active subject of research and policy development for several decades.

The environmental cycling of mercury is complex and not always well understood. Research has made significant progress over the last decade but as the focus of the problem shifts, new research needs appear to provide the basis for risk assessments and policy development.

1.4. General mercury chemistry

Mercury occurs naturally in the environment with 7 different stable isotopes (highest abundance ^{202}Hg at 29.9%, lowest ^{196}Hg at 0.15%). The principal mercury mineral in the Earth crust is cinnabar (HgS). Pure mercury is a shiny, silver-white liquid at room temperature (melting point 234 K) with a density of 13.6 g/cm^3. Mercury exists in three oxidation states (0), (I+) and (II+). The (I+) state is not common in the environment but exists in stable solid compounds such as calomel (Hg_2Cl_2).

Many stable mercury (II+) compounds are known. Examples are mercuric sulphide (HgS as mentioned above), oxide, and chloride. The sulphide and oxide are coloured solids insoluble in water whereas the chloride is a colourless salt slightly soluble in water.

Mercury(II+) halogens including $HgCl_2$ are sufficiently volatile to exist in the gaseous phase at ambient temperatures. When mercury combines with carbon, organic compounds "organomercurials" are formed.

There are a potentially large number of organic mercury compounds; however, by far the most common organic mercury compound in the environment is methylmercury (also known as monomethylmercury).

2. Mercury in the atmosphere

2.1. Mercury speciation in air

Mercury has physical properties unlike other heavy metals. The high vapour pressure of elemental mercury in combination with its thermodynamic stability allows it to be distributed in the air as a gas. To distinguish this form of mercury from other airborne mercury species it is denoted Gaseous Elemental Mercury (GEM). GEM is entirely monoatomic even in high concentrations, i.e. GEM = Hg^0.

The atmospheric lifetime of GEM has been estimated to be about one year. This is long enough for the metal to be transported on hemispherical or even global scales (Schroeder and Munthe, 1998).

Hence, mercury emitted from one European source may, one year later, be homogeneously distributed throughout the atmosphere of the northern hemisphere. This makes mercury a global pollutant in contrast to other heavy metals that have more local and regional impacts. This property of mercury is proven by measurements showing that the concentration of GEM is fairly uniformly distributed, around 1.7 ng m^{-3} in the northern hemisphere and 1.3 ng m^{-3} in the southern (Slemr et al., 2003). The lower value in the south is consistent with mercury sources being predominately located in the north.

Assuming homogeneous mixing ratios, the total amount of GEM in the troposphere can be estimated to be 4600 t. If the assumed atmospheric lifetime for mercury is correct it means that the overall sink of mercury from the atmosphere is about 4600 t per year which in turn must be balanced by an equal input. GEM is only dry deposited to ground or vegetation or washed out by precipitation to a small extent. However, Hg^0 is oxidised in the atmosphere forming divalent mercury species (Hg(II)) which are more easily removed from the atmosphere.

Hg(I) species may also be formed but are assumed to be of minor importance due their low stability in the atmosphere. Divalent mercury is found in both the gaseous and the particulate phase as well as in rainwater. However, the exact chemical compositions of these oxidation products are not yet known.

The gaseous fraction of oxidised mercury is referred to as "Reactive Gaseous Mercury" (RGM). RGM is operationally defined, as the fraction of gaseous mercury that can be sampled using a certain measurement method. Lately, a KCl-coated denuder technique has proven to be efficient and is now commonly used (Landis *et al.*, 2002).

The term reactive mercury denotes a class of divalent mercury species which, like for example $HgCl_2(aq)$, readily undergo reduction to Hg^0 by Sn^{2+} in diluted HCl solution (a procedure commonly used in the chemical analysis of mercury in water samples).

Although not yet proven, it is likely that RGM is constituted of species like $HgCl_2(g)$ and $HgBr_2(g)$ or mixed halides like $ClHgBr(g)$. Mercury halides have a covalent character and are low melting volatile solids that are only slightly soluble in pure water.

Their solubility is, however, increased in the presence of halogen ions (X^-) due to the formation of HgX_4^{2-} complexes. Their vapour pressure is relatively high, e.g. $P(HgCl_2) = 0.017$ Pa at 298 K (i.e. corresponding to 0.17 ppm). Due to the solubility of RGM, washout is an efficient removal process. It is also more easily dry deposited on water surfaces and on vegetation than Hg^0.

Total Gaseous Mercury (TGM) is another operational defined mercury fraction. This includes GEM plus other possible gaseous mercury species, such as RGM, that may also be detected when measuring gaseous mercury by the commonly used gold-trap method. In order to measure the actual concentration of GEM, the air must be purified by removing RGM and particulate mercury prior to adsorption on the gold trap. Although there are exceptions, TGM and GEM are often equal within a few percent.

Mercury is also found in aerosols in air. Particles emitted from coal fired power plants, for example, often contain mercury. Volcanoes and biomass burning are examples of natural sources that emit particulate mercury. GEM and, preferentially, RGM may also be adsorbed on already existing particles in the atmosphere.

The abbreviation TPM (Total Particulate Mercury) is used in the literature and it normally denotes the concentration of particulate mercury obtained with open face air filter samplers. Total particle mercury means that the sampling is not made in a size fractionated manner. If mercury in the fine mode (< 2.5 μm particle size) is sampled it is sometimes denoted Fine Particulate Mercury (FPM).

Dimethylmercury, CH_3HgCH_3 (DMHg) is formed in the oceans and its presence in the atmosphere is believed to be due to emission from ocean surfaces. Sewage plants, landfills etc. also emit DMHg, although these sources are of minor importance in comparison to the oceans.

Monomethylmercury (MMHg)) or methylmercury, CH_3HgX compounds are found in rainwater and have also been detected in the gas phase (see section 2.4.3 and chapters 3 and 4).

2.2. Sources of mercury

Mercury has both natural and anthropogenic sources. Natural emissions originate from mercury minerals in the Earth crust, especially cinnabar. The metal is released during volcanic activities and through weathering of rocks. However, most of the mercury in the atmosphere is believed to be a result of anthropogenic emissions.

Mercury is emitted from several industries, such as coal power plants and from production of chlor-alkali, cement and metals. It should be mentioned that not all chlor-alkali factories emit mercury, only those who use the Mercury Cell Chlor-Alkali (MCCA) process. Other sources are waste incinerators and various other industries using mercury.

Emissions from combustion of fuels, especially coal, constitute the most important mercury source category in Europe as well as in the rest of the world. Coal contains mercury in various concentrations (0.01 - 1.5 ppm). Without cleaning, all the mercury is emitted as gaseous or particulate mercury.

At present, many large European coal-fired power plants and incinerators etc. are equipped with cleaning facilities retrieving some of the mercury along with sulphur and other pollutants. But many small scale coal fired boilers without cleaning are still in use e.g. for domestic heating. In some areas these sources contribute significantly to the mercury emissions.

Due to the existence of a wide range of mercury sources, of which some are diffuse and others perhaps not even fully recognised, estimating the total emissions of mercury is difficult. However a lot of work has been done to identify important mercury sources in Europe.

Emission factors from various industrial sectors are also available from measurements. Using these parameters together with statistics on regional annual consumption of coal and other fuels and information on production of caustic soda, cement etc., the emissions of mercury have been estimated.

Figure 1 shows European mercury emission inventories for the period 1980 to 2000 (Pacyna et al., 2005a). The total emission of mercury in Europe has evidently decreased dramatically since 1980. The decrease corresponds to a 70% reduction, from 860 tonnes y^{-1} to 240 tonnes y^{-1} during 1980 to 2000.

There are several reasons for this. One is the implementation of Flue Gas Desulphurisation (FGD) technology in large coal-fired power plants. These facilities which are intended to reduce sulphur emissions also remove a variable fraction of the mercury.

Emission controls of mercury have also been implemented in other industrial sectors, especially in Western Europe. Another important factor is the change from centrally planned economies to market oriented economies that occurred in East and Central European countries in the

beginning of the 1990s. During this period many power plants and other heavy industries closed down.
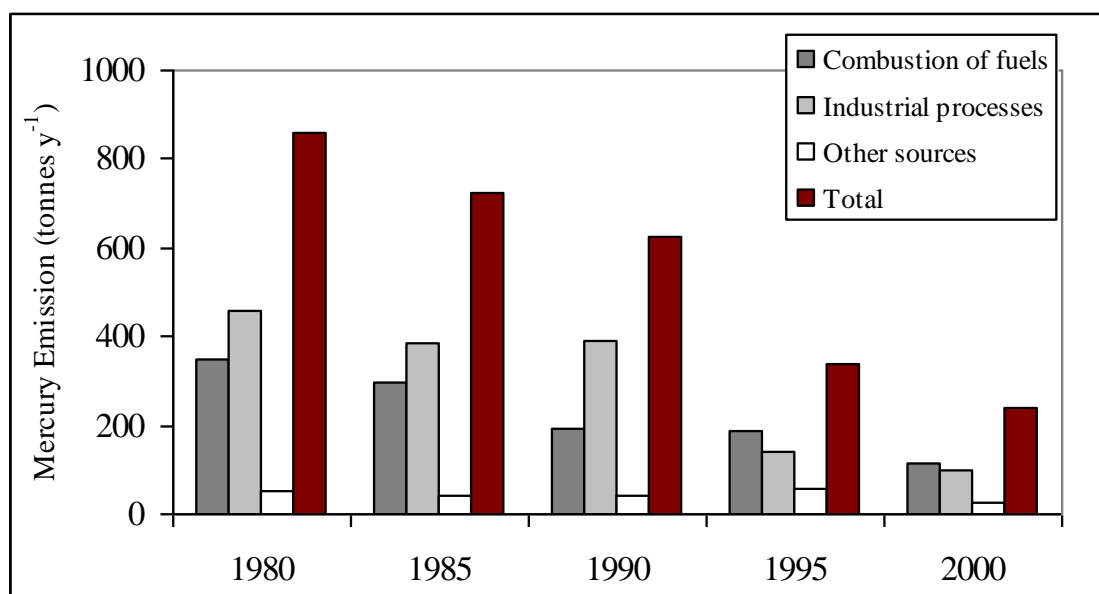

Figure 1. Change in total anthropogenic emissions of mercury in Europe since 1980, from Pacyna et al. 2005a.

According to Pacyna et al. (2005a) about 50% of the mercury emitted from coal and oil combustion is in the form of elemental mercury, 40% is RGM and 10% is TPM. These numbers are average values from limited speciation measurements and the variability is large between individual emission sources.

The corresponding values for smelters are 80% elemental mercury, 15% RGM and 5% TPM. Estimates for MCCA plants suggest that around 70% of the mercury emitted is Hg^0 and the rest (30%) is RGM (Pacyna, et al. 2005a). Recent speciation measurements show that the RGM fraction from MCCA plants may be much lower (1-2%) (Landis et al., 2004; Southworth et al., 2004; Wängberg et al., 2005).

Variations in RGM emissions are likely to be a result of how well the MCCA plant is maintained and the efforts made to reduce emissions to air. The local impact from mercury emission around MCCA plants is related to the amount of RGM and TPM emitted since these species, to a much larger extent than elemental mercury, are deposited near the source (Wängberg et al., 2005).

Several attempts to estimate global mercury emissions from natural as well as anthropogenic sources have also been made. Some of these estimates are shown in Table 2.

Table 2. Global emissions of Mercury in 1000 tonnes per year

Anthropogenic	Natural	Total	References
2	3 - 4	5 - 6	Fitzgerald, 1986
3.6	2.5	6.1	Nriagu & Pacyna, 1988
4.5	3	7.5	Lindquist et al.,1991
5.6	1.6	7.2	Mason et al.,1994
2.2	2.7	4.9	Pirrone et al., 1996
3	1.4	4.4	Lamborg et al., 2002
2.2*			Pacyna et al. 2005b

Anthropogenic re-emissions from oceans and land are not included.

According to a recent estimate (Pacyna et al., 2005b) 67% of the total global anthropogenic emission originates from stationary combustion. A large fraction of these emissions (52%) stems from sources in Asia.

There are obviously no direct means for determining global total mercury fluxes, hence these values are uncertain. From Table 2 it can be concluded that the total emission has been estimated to be in the range 4000 - 7000 tonnes per year.

The contribution from anthropogenic sources may range from 40 to almost 80%. The relation between natural and anthropogenic emissions is important since it gives some insight into the present environmental status concerning mercury pollution.

However, the behaviour of mercury in the environment is complicated. Oxidised mercury, once deposited to land and aquatic compartments, is to a large extent reduced back to elemental mercury and re-emitted to the atmosphere.

The total re-emission flux of mercury has been estimated to be of the same order of magnitude or greater than the global anthropogenic emission of mercury (Mason and Sheu, 2002; Selin et al., 2007). Lamborg et al. 2002 developed a concept to estimate global Hg fluxes by modelling the evolution of the mass of mercury in the atmospheric and the oceanic reservoirs. It is based on the observed interhemispheric TGM gradient and the change of deposition of atmospheric mercury since industrialisation.

Outputs from the model are mercury fluxes from the atmosphere to ocean and to the land surface as well the reverse fluxes. The results of Lamborg et al. are shown in Figure 2, where both the present mercury fluxes as well as natural fluxes (i.e. mercury fluxes 130 years ago) are shown.
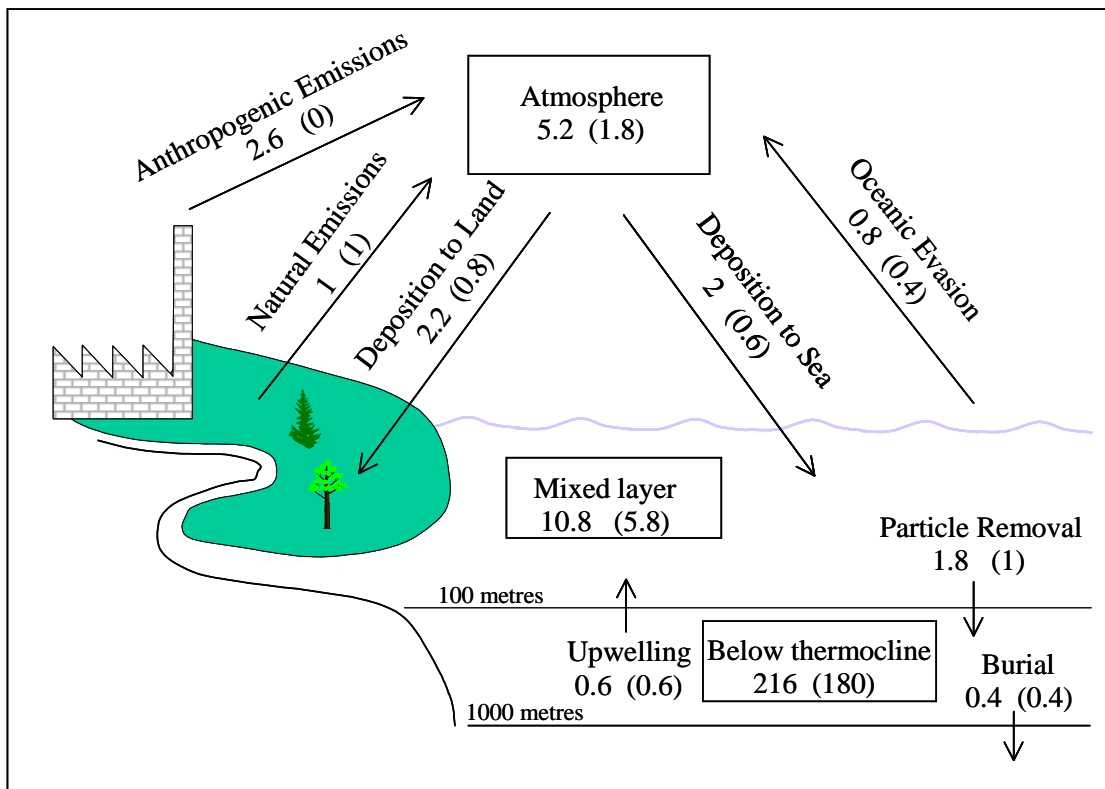
Figure 2. Global atmospheric - land - oceanic mercury fluxes as estimated by Lamborg et al., 2002. Numbers on arrows indicate the present mercury fluxes in 1000 tonnes y^{-1}. Numbers in frames correspond to the present mercury amounts in the different reservoirs in 1000 tonnes. The numbers in brackets correspond to pre-industrial mercury fluxes and mercury amounts.

According to the model, the total anthropogenic flux to the atmosphere is equal to 3 000 tonnes; 2600 tonnes (from industry + anthropogenic re-emission from land) + 400 tonnes (oceanic anthropogenic re-emission) i.e. about two times the natural emissions. Man made emissions have increased the total amount of mercury in the atmosphere from 1800 tonnes to the present amount of 5200 tonnes.

Higher atmospheric concentrations mean increased mercury deposition to oceans and land sites. Hence, according to the model, the deposition has increased by 2800 tonnes per year; from the pre-industrial value of 1400 tonnes per year to the present 4200 tonnes per year.

2.3. Sources of methylated mercury species in the atmosphere

Methylated mercury species have been identified in the atmosphere in a very limited number of investigations. Observed concentrations are usually at the low pg/m^3 level and methylated species are generally assumed not to play an important role in the atmospheric cycling of mercury.

The research interest is more related to the toxicity of these species and the potential role of the atmosphere as a source of methylmercury to aquatic ecosystems. To date, very few sources of methylated mercury species in the atmosphere have been defined.

The potential sources can be classified as: releases of dimethylmercury from natural surfaces (Pongratz and Heumann, 1999); releases from anthropogenic point sources or from soil affected by anthropogenic activities (Lindberg et al., 2005); and finally chemical formation in the atmosphere (Gårdfeldt et al., 2003).

In all cases, the availability of information is limited which makes an assessment of the overall importance of the individual sources difficult. In Table 3 a summary of the available information on sources of methylated mercury species to the atmosphere is given.

Table 3. Sources of methylated mercury species in the atmosphere

Source	Species	Rate of emissions/formation	Comments	Reference
Landfill gas	$(CH_3)_2Hg$	Concentration <100 ng/m^3 Estimated global emission: < 24 kg/yr.	Global emission calculated from landfill CH_4 emission estimates	Lindberg et al., 2005. See text below
Polar oceans	$(CH_3)_2Hg$ CH_3Hg^+	> 2300 tonnes/y	Estimate covers Arctic, Antarctic and Atlantic oceans.	Pongratz and Heumann, 1999.
Chemical formation	CH_3Hg^+ formed from Hg(II) and acetic acid	Rate of formation may explain a few percent of CH_3Hg in precipitation.	Minor importance but other reactions may contribute.	Gårdfeldt et al., 2003

The global emission estimate for methylated mercury species from landfill gas was made by assuming a constant ratio of methane and methylmercury species in landfill gas, and multiplying with a global estimate of methane emissions from landfills. The latter number was obtained from CDIAC (2005).

From the limited data available, releases from the ocean surface seem to be the dominating source of methylated mercury species in the atmosphere.

The estimated emission (>2300 tonnes per year) is within the range of estimates of total natural emissions (Table 2) and seems to be unrealistically high. This illustrates the difficulties in quantifying the global mercury cycle and emphasises the need for further research in this field.

2.4. Transformation and deposition of atmospheric mercury

The dispersion and deposition of mercury emitted from a point or area source is, to a large extent, dependent on the speciation of the emission.

In Figure 3 a schematic drawing of the dispersion and deposition of mercury species is given. Emissions of RGM and TPM will lead to deposition on local and regional scales whereas emissions of elemental mercury will disperse on hemispherical and global scales. These aspects need to be considered both when developing modelling tools and when designing (and evaluating results from) monitoring networks.
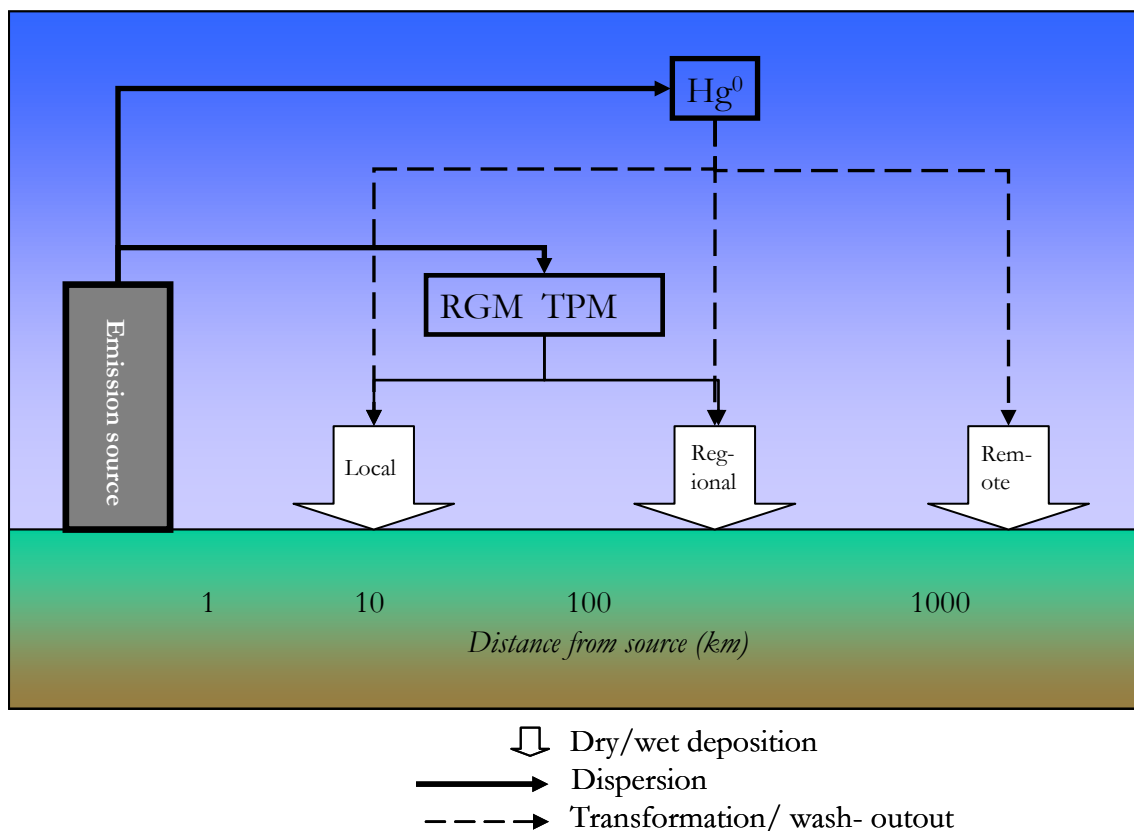
Figure 3. Schematic drawing of principal transport and deposition processes for mercury species.

Elemental mercury is the dominant form of mercury in the atmosphere and also from many emission sources. Deposition will occur mainly after oxidation to divalent species (i.e. RGM). Oxidation of elemental mercury in the atmosphere is generally a slow process. This allows mercury to be transported over long distances. Emissions to the atmosphere can thus affect the environment on local, regional and global scales.

The influence of a specific emission source on the global levels and impacts of mercury is difficult to quantify, since each individual source only contributes a very small amount of mercury to the global pool. Nevertheless, it has been estimated that anthropogenic activities have increased global background levels of mercury by a factor of about three.

2.4.1. Oxidation of mercury in the gas phase

Exactly how RGM is formed in the atmosphere remains a key question that is crucial to our understanding of atmospheric mercury chemistry and mercury cycling in the environment. The reactive capacity of the atmosphere is linked to photolysis reactions forming certain reactive radical species such as OH, HO_2, Br, etc.

The reaction rates between radicals and all kinds of hydrocarbons as well as many inorganic atmospheric constituents have been determined by laboratory experiments. This information has made construction of chemical-meteorological models possible. With the help of these models, important chemical and physical processes can be studied and verified by comparison with field measurements.

Several models including mercury chemistry have also been developed (see section 2.5.4). However, critical kinetic information on Hg^0 gas phase reactions is still lacking. This is partly because kinetic investigations on mercury are experimentally difficult to perform. Despite experimental problems, the reactivity between Hg^0 and several oxidants in the atmosphere has been investigated. These studies have included the gas phase reactions between Hg^0 and O_3, Cl_2, NO_2 and H_2O_2 as well as between Hg^0 and the radical species, OH, Cl, Br and NO_3.

Results from some of the most recent laboratory studies are shown in Table 4. In none of the studied reactions gaseous mercury containing products where reported to be found. The ability to identify products is, if not necessarily, at least very helpful when tying to prove a certain reaction.

Hence, product identification constitutes a principal problem concerning studying Hg^0 reactions. This difficulty has to do with the fact that the products are formed in low concentrations and also possess weak optical cross sections making detection by spectroscopic means difficult. In many investigations Hg containing products are assumed to be condensed on the reactor walls.

Table 4. Hg^0 gas-phase room temperature reaction rates and mid-latitude Hg^0 lifetimes

Gas phase reactions	Reaction coefficients k (cm^3 molecule^{-1} s^{-1})	Lifetimes[a] (k × [X])$^{-1}$ (days)	References
(1) Hg^0 + O_3 →	$3 \pm 2 \times 10^{-20}$	770	Hall (1995)
(1) Hg^0 + O_3 →	$\leq 8.5 \times 10^{-19}$	544	Tokos et al., 1998
(2) Hg^0 + OH →	$8.7 \pm 2.8 \times 10^{-14}$	130	Sommar et al., 2001
(2) Hg^0 + OH →	$\leq 1.2 \times 10^{-13}$	≥ 100	Bauer et al., 2003
(2) Hg^0 + OH →	$9.0 \pm 1.3 \times 10^{-14}$	130	Pal & Ariya, 2004
(3) Hg^0 + Cl →	$1.0 \pm 0.2 \times 10^{-11}$	230	Ariya et al., 2002
(3) Hg^0 + Cl →	$5.4 \pm 2.7 \times 10^{-13}$	4300	Deanna et al., 2005
(4) Hg^0 + Br →	$2.0 \pm 0.8 \times 10^{-13}$	115	Sommar et al., 1999
(4) Hg^0 + Br →	$3.2 \pm 0.4 \times 10^{-12}$	7	Ariya et al., 2002
(4) Hg^0 + Br →	$3.6 \pm 1.8 \times 10^{-13}$	64	Deanna et al., 2006
(5) Hg^0 + NO_3 →	$\leq 4 \times 10^{-15}$	≥ 960	Sommar et al., 1997

[a]$[O_3] = 5 \times 10^{11}$ molecules cm^{-3}, $[OH] = 1 \times 10^6$ molecules cm^{-3}, $[Cl] = 5 \times 10^3$ molecules cm^{-3}, $[Br] = 5 \times 10^5$ molecules cm^{-3}, $[NO_3] = 3 \times 10^6$ molecules cm^{-3}

Ozone is thought to react with Hg^0 to form HgO and O_2. With an O_3 concentration of 20 ppb a lifetime of Hg^0 of about two years is calculated based on the rate of reaction 1. According to Hall (1995) removal of Hg^0 in the reaction system was caused by both a gas phase reaction and heterogeneous gas-solid reactions occurring on the reactor walls. The present gas phase rate coefficient was obtained by separating these two components by varying the surface to volume ratio of the reactor.

The hydroxyl radical is one of the most important reactive species in the atmosphere and is therefore also a conceivable candidate for oxidising Hg^0. As shown in Table 4, the results from 3 different laboratory measurements of this reaction constant have yielded similar results. The implication of the rate constant is a lifetime with respect to OH in the order of 100 days.

However, the importance of reaction 2 is still not clear. Bauer et al. (2003) who have performed the most reliable investigation could not detect any reactivity and the value they presented is only an upper limit for reaction 2. Recombination reactions of this kind are complicated and require several steps in order to form stable products.

The Hg^0 + OH reaction is thought to proceed via a weakly bound intermediate (HgOH) which then reacts with O_2 to form HgO(g) and the HO_2 radical. (Sommar et al., 2001; Bauer et al., 2003). According to theoretical calculations (Goodsite et al., 2004) the HgOH intermediate will

undergo thermal decomposition rather than forming HgO as a result of reaction with O_2. Whether HgO exists in the gas phase or not is also a matter of debate.

HgO(g) has, according to other theoretical calculations (Shepler and Peterson 2003; Tossell, 2003) a very low bonding energy and is likely to photodecompose forming Hg^0 at atmospheric conditions (Tossell, 2003). Hence, according to theoretical results, HgO is not likely to be formed as a result of reaction 2 and if it does it will quickly photodecompose regenerating Hg^0.

How is it then that Hg^0 appears to react in relative rate experiments? By help of a chemical model Calvert and Lindberg, (2005) tried to simulate relative rate experimental systems. The modelling result indicated that the OH reactivity can be overestimated in a photolysis system with very high concentrations of reactants.

The authors suggested that the experiments are likely to provide a reasonable estimate of the Hg^0 + OH → HgOH reaction rate. On the other hand, decomposition of HgOH could be attenuated by competing reactions not occurring in the atmosphere where the concentrations of reacting species are many orders of magnitude lower.

Some experimental results from investigations of Hg^0 + halogen radical reactions (Sommar et al., 1999; Ariya et al., 2002) indicated that Cl and Br radicals react fast enough with Hg^0 to be important in the atmosphere. The Hg^0 + Br reaction would be the most important since the Br concentration in the atmosphere is much higher than that of Cl. Ariya et al. (2002) proposed that reactions between Hg^0 and Cl and Hg^0 and Br radicals are likely to yield $HgCl_2$ and $HgBr_2$, respectively since these compounds were identified when analysing material deposited on the walls of the reactor.

If the rate constants shown in Table 4 are correct, the free tropospheric lifetime of Hg^0 would be limited to 7 - 36 days. This seems to be in conflict with estimations from field measurements and mass balance calculations which suggest that the atmospheric lifetime of Hg^0 is around 1 year.

However, field measurements in polar regions indicate the existence of very fast atmospheric processes allowing GEM to be removed from the atmospheric ground layer within days. This phenomenon, called Mercury Depletion Event (MDE), was first reported by Schroeder et al. (1998).

The authors found that MDEs occur at certain conditions during polar springtime. Concurrent with decreasing GEM, increasing concentrations of RGM are observed as well as increasing mercury on particles. Mercury is thus rapidly oxidised in the air producing RGM, some of which quickly is deposited onto the ice and snow surface or scavenged on aerosols. This new finding triggered scientists to intensify the search for possible chemical reactions that are fast enough to explain the observations.
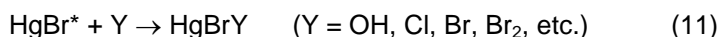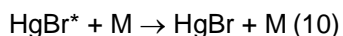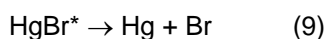
It is known that halogen chemistry is important during polar springtime. Ozone may also be completely depleted in the atmospheric boundary layer (Oltmans and Komhyr, 1986). Ozone is reacting with Br and Cl radicals according to reaction 6. The halogen radicals are recycled back according to reactions 7-8 making the ozone destruction very efficient (Barrie et al., 1988).

O_3 + Br (Cl) → BrO (ClO) + O_2 (6)

BrO (ClO) + HO_2 → OHBr (OHCl) + O_2 (7)

OHBr (OHCl) + h□□→ OH + Br (Cl)   (8)
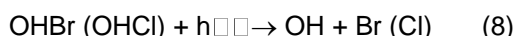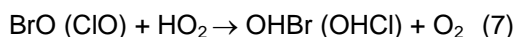
Recent Arctic and Antarctic field measurements showed an almost perfect match between removal of ozone and GEM (Lindberg et al., 2002; Steffen et al., 2002; Temme et al., 2003; Sommar et al., 2007; Gauchard et al., 2005). Therefore it has been suggested that Hg^0 also may be destroyed by Cl, Br or the BrO radical.

According to recent findings the Hg^0 + Br reaction constitutes an initial step during mercury depletion events. An excited intermediate, HgBr*, is formed as is shown in reaction 4. The HgBr* molecule may further react according to reactions 10-11 to form a stable gaseous Hg(II) compound.

Hg + Br → HgBr*   (4)

HgBr* $\rightarrow$ Hg + Br   (9)

HgBr* + M $\rightarrow$ HgBr + M (10)

HgBr* + Y $\rightarrow$ HgBrY   (Y = OH, Cl, Br, Br_2, etc.)   (11)

Whether this path will be significant or not is critically dependent on the stability of the intermediate. The excited molecule formed in reaction 4 may undergo thermal or photolytic decomposition, according to reaction 9 or, alternatively, it may react with other reactive atmospheric constituents.

If it decomposes quickly or reacts with oxygen it will not yield RGM. However, a theoretical study using RRKM theory and ab initio quantum calculations suggests that HgBr after stabilisation via reaction 10 indeed is a very stable molecule due to its high bond energy (Goodsite et al., 2004). Its half life is 126 s at 1 atm and 298 K and as long as 15 h at 265 K. It does not react with O_2, but may react with Br, OH or the I radical under Arctic conditions.

This theoretical result has been verified in a recent work by Deanna et al., 2006. Reaction 4 was investigated in an advanced flow reactor study using pulsed laser induced fluorescence to simultaneously measure Hg^0 and Br radicals. Both the pressure and temperature dependence of reaction 4 was investigated yielding a result consistent with a three-body recombination reaction according to reactions 4 and 10.

The reaction rate is shown in Table 4 and corresponds to a lifetime of Hg^0 in the free troposphere of 64 days if assuming an average Br concentration of 5×10^5 molecules cm^{-3}. During polar depletion events much higher Br concentrations are expected and Deanna et al. (2006) estimated the Hg^0 lifetime in respect to reaction 4 and 10 to be in the range of 6 h - 2.5 days.

Reaction 3, Hg^0 + Cl has also been investigated using the flow reactor pulsed laser induced fluorescence technique (Deanna et al., 2005). A reaction rate comparable to that of reaction 4 was obtained as shown in Table 4. Since the Cl radical concentration in the atmosphere is believed to be much lower than that of Br, reaction 3 is probably not important.

More research is needed before we know exactly how RGM is formed in the atmosphere. The fate of HgBr needs to be investigated to see if this radical intermediate may react to form RGM as exemplified by reaction 11.

2.4.2. Mercury reactions in the atmospheric water phase

Mercury is present in precipitation. The average mercury concentration in rain is around 10 ng L^{-1} according to measurements at EMEP (European Monitoring and Evaluation Programme) stations in northern Europe, 1999-2002 (Wängberg et al., 2007). Only a very small fraction (< 0.1%) should, according to the Henry's law constant for Hg^0, be present as dissolved Hg^0.

Hence, most of the mercury in rainwater is oxidised. Its appearance in raindrops and clouds is due to uptake of RGM and presumably also oxidation of Hg^0aq in clouds. Hg^0 reacts with O_3 in the aqueous phase according to reaction 12.

But Hg(II) may also be reduced as in reaction 16. Steady state calculations involving reactions 12 and 16 indicate that the O_3 reaction may yield Hg(II) concentrations in the range of 0.2 - 5 ng L^{-1} at different gas phase concentrations of SO_2 and O_3 (Munthe, 1992). Also the reaction between Hg^0 and the OH radical in aqueous aerosols seem to proceed fast enough to be important (Lin and Pehkonen, 1997; Gårdfeldt et al., 2001.).

Table 5. Mercury reaction rates at room temperature in the aqueous phase

Aqueous phase reactions	Reaction coefficients $M^{-1} s^{-1}$	References
(12) $Hg^0 + O_3 \rightarrow Hg(II)$	$4.7 \pm 2.2 \times 10^7$	Munthe, 1992
(13) $Hg^0 + OH \rightarrow Hg(II)$	$2.4 \pm 0.3 \times 10^9$	Gårdfeldt et al., 2001
(14) $Hg^0 + OH \rightarrow Hg(II)$	$2.0 \pm 0.3 \times 10^9$	Lin and Pehkonen, 1997
(15) $HgSO_3 \rightarrow Hg^+ + SO_3 \rightarrow Hg^0$	$0.6 \ s^{-1}$	Munthe et al. 1991*
(16) $Hg(OH)_2 + h\nu \rightarrow Hg^0$	slow	Xiao et al., 1994

An alternative mechanism and > 10 times slower reduction rate has been reported by van Loon et al. 2000.

2.4.3. Chemistry of DMHg and MMHg in the atmosphere

It has been suggested that MMHg may be formed in air and in aqueous aerosols in the atmosphere. The precursor could be DMHg and/or RGM. DMHg is rapidly oxidised by OH, Cl and also by the NO_3 radical. Products from these reactions may form MMHg by homogeneous or heterogeneous reactions. Sommar et al., (1997) studied the products formed from DMHg + NO_3 in the gas phase and reported that, except for minor yields of Hg^0, no other mercury containing products were detected.

The result excluded significant yields of organic mercury since the formation of HCHO and CH_3OH exactly accounted for the carbon loss of the DMHg reacted. According to Niki et al. (1983), MMHg actually constituted a major product from photolysis of a DMHg - Cl_2 mixture. It was assumed that the products found were due to Cl attack according to reaction 18.

$$Hg(CH_3)_2 + 2Cl \rightarrow CH_3HgCl + CH_3Cl \qquad\qquad 18$$

Gårdfeldt et al (2003) have shown that MMHg can be formed from reaction between Hg(II) and acetic acid in slightly acidic solutions i.e. at conditions relevant to clouds and rainwater. Celo et al (2006) found that MMHg can be formed from a variety of organic compounds. Although these reactions cannot explain observed concentrations of MMHg in rainwater, they demonstrate that such formation may occur.

MMHg has been shown to be degraded by sunlight in lake water (Sellers et al., 1996) whereas Siciliano and Beauchamp (2005) noted an enhancement of MMHg formation by sunlight in waters. Whether these reactions occur in atmospheric waters is not known.

2.5. Monitoring of atmospheric mercury and source-receptor relationships

In comparison to other major atmospheric pollutants, monitoring of mercury is performed at a limited number of sites and very little long-term data are available. The following discussion is focused on examples from monitoring performed within the OSPAR CAMP and EMEP networks in northern Europe. OSPAR is the convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") and CAMP is an abbreviation for the Comprehensive Atmospheric Monitoring Programme.

The quality of the OSPAR CAMP mercury data has been evaluated and has been reported to the Swedish Environmental Protection Agency (Wängberg and Munthe, 2001; Wängberg and Munthe, 2004). A trend analysis based on mercury data in air and precipitation measured during the period 1995-2002 has also been performed (Wängberg et al., 2007). The result from this evaluation is presented here.

2.5.1. Geographical and temporal variation in airborne mercury concentrations in northern Europe

Data on mercury in precipitation is available from six coastal stations within the OSPAR CAMP network. TGM data has been measured at three of these stations and also at three additional OSPAR CAMP measurement sites. The location of each station is shown in Figures 4 and 5.
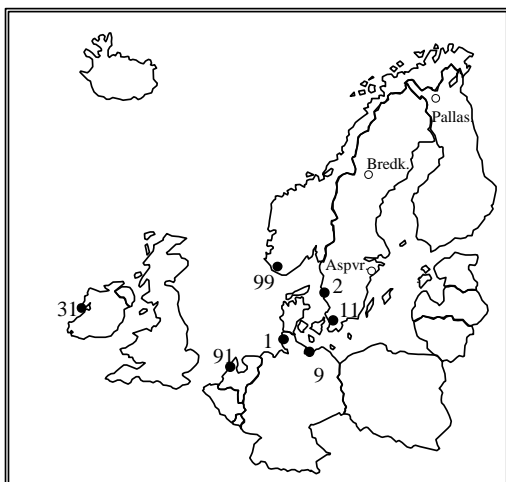

Figure 4. OSPAR CAMP stations. 1. Wenningstedt (GE), 2. Råö (SE), 9. Zingst (GE), 11. Vavihill (SE), 31 Mace Head (IR), 91 De Zilk (NE), 99. Lista (NO).
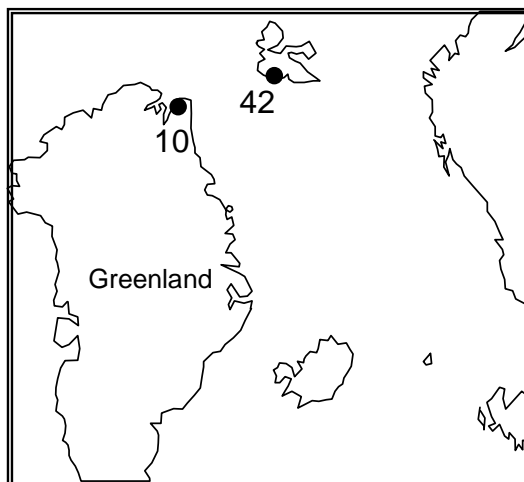
Figure 5. Northern OSPAR CAMP stations. 10. North Greenland (D), 42. Ny-Ålesund Spitsbergen (NO)

In addition, complete sets of TGM data covering the period 1995-2002 are available from Lista and Råö. In the data sets from Spitsbergen year 1995 is missing and from Mace Head year 1998 is missing. Only two years of data are available from Zingst (2000 and 2002) and North Greenland (2000 and 2001).

Annual deposition of Hg(tot) at the OSPAR sites is shown in Figure 6. Mercury deposition varies quite strongly from year to year. The decrease in Hg deposition when comparing average values from 1995-1998 and 1999-2002 is shown in Figure 7. Wenningstedt appears to be somewhat extreme.

Since the data obtained 1995-1998 at this station are very different in comparison to those from the other stations one may suspect that the early data from Wenningstedt are overestimated or alternatively reflect contributions from local sources. However, a substantial decreasing trend (16%) is obtained even when excluding the Wenningstedt data. The Hg(tot) concentration in precipitation is much the same at all stations. Lista is not an exception in this respect even though the greatest mercury deposition is measured there, see Figure 8.
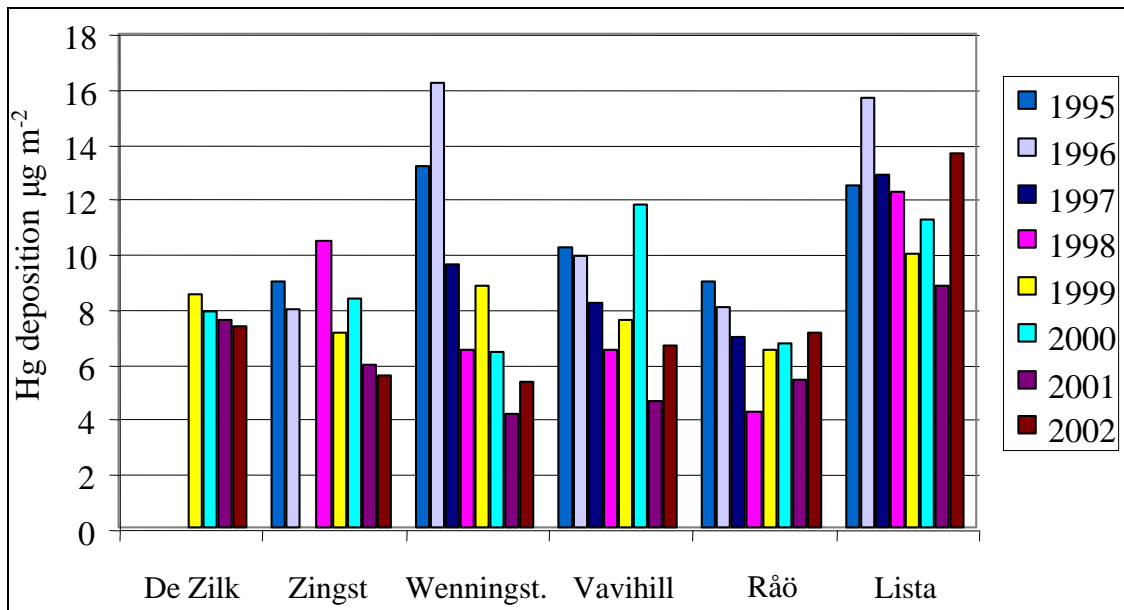
Figure 6. *Annual deposition of mercury at OSPAR CAMP measurement sites during the period 1995-2002. Deposition values from De Zilk are limited to the period 1999-2002.*
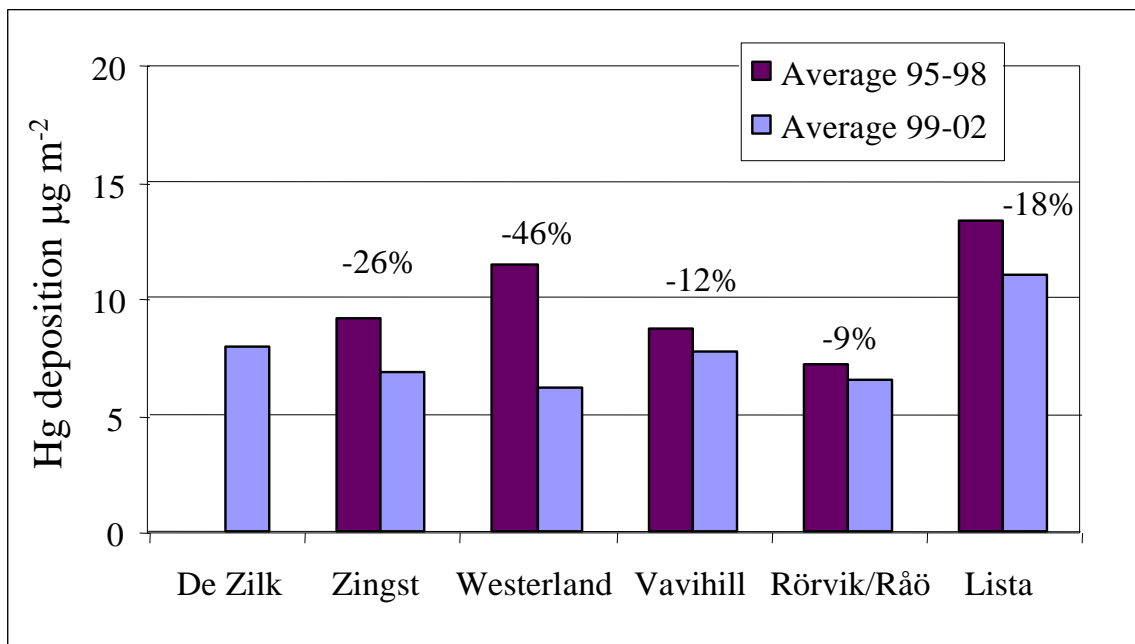

Figure 7. *Average Hg(tot) deposition during the periods 1995-1998 and 1999-2002.*
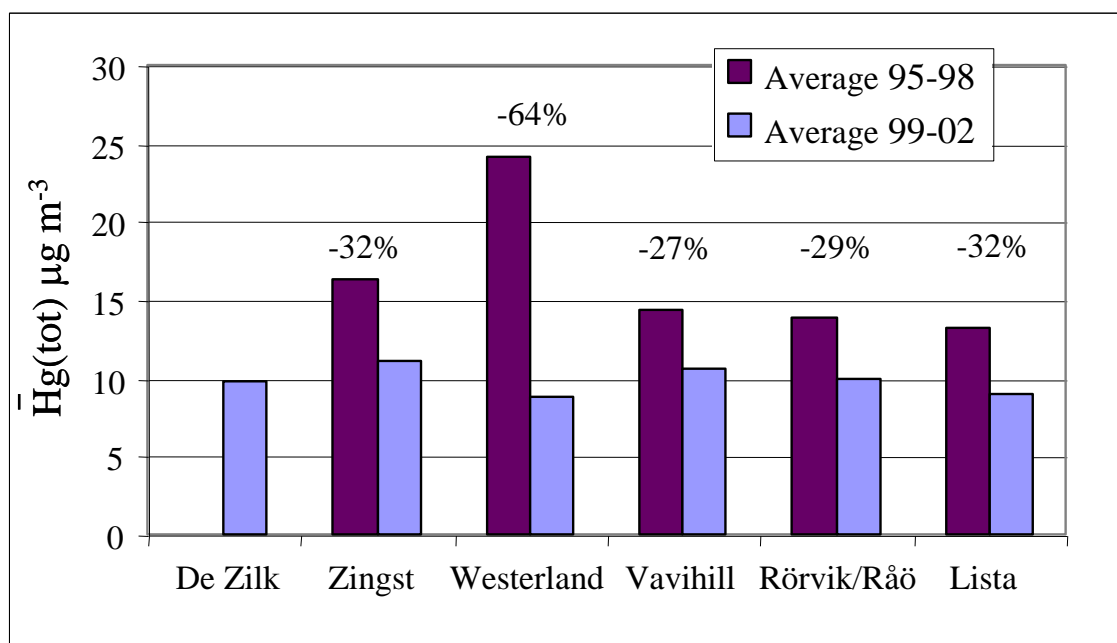
Figure 8. Yearly average mercury concentration in deposition.

The reason for the high mercury deposition at Lista is to a large extent a result of the high precipitation amounts received at this coastal station. In contrast, if using Hg(tot) concentrations as an indicator of mercury distribution then the lowest values are found at Lista. This station is dominated by winds from the west and Hg(tot) is likely to represent the westerly background input to Northern Europe.

The difference in Hg(tot) among the stations is marginal, but when comparing Zingst, Vavihill and Råö it is possible to see a south to north trend with lower Hg(tot) concentrations in the north. Considering measurement uncertainties the trend is too weak to be scientifically proven but is likely to reflect emissions from mercury sources in Poland and former East Germany.
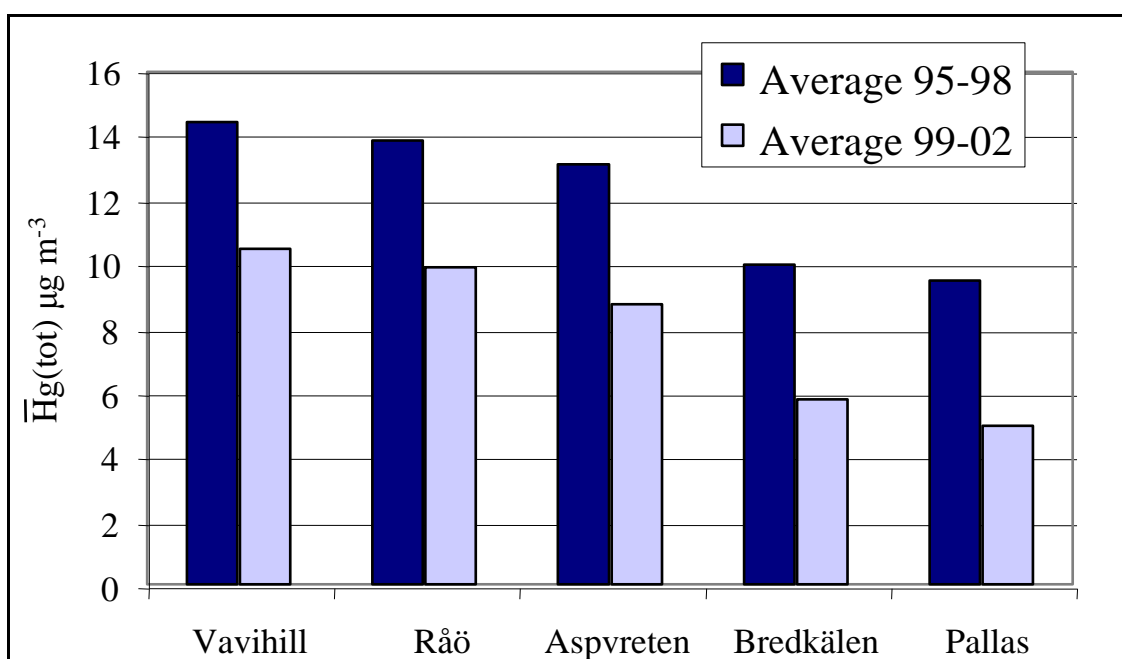

Figure 9. Yearly average Hg(tot) in precipitation from some Swedish and one Finnish EMEP sites. The locations of Aspvreten, Bredkälen and Pallas are indicated in Figure 4.

As a comparison one can look at data from some other EMEP stations as shown in Figure 9. There is a distinct gradient in Hg(tot) along a south-north transect in Scandinavia. The same is also true for Hg deposition at these stations. The lowest Hg(tot) is found at the Pallas station in northern Finland. The values measured at Pallas represent that of a real inland background site in Scandinavia and are 50% lower than some of the OSPAR CAMP sites. However, due to the inland character of this station a direct comparison may not be fully justified.
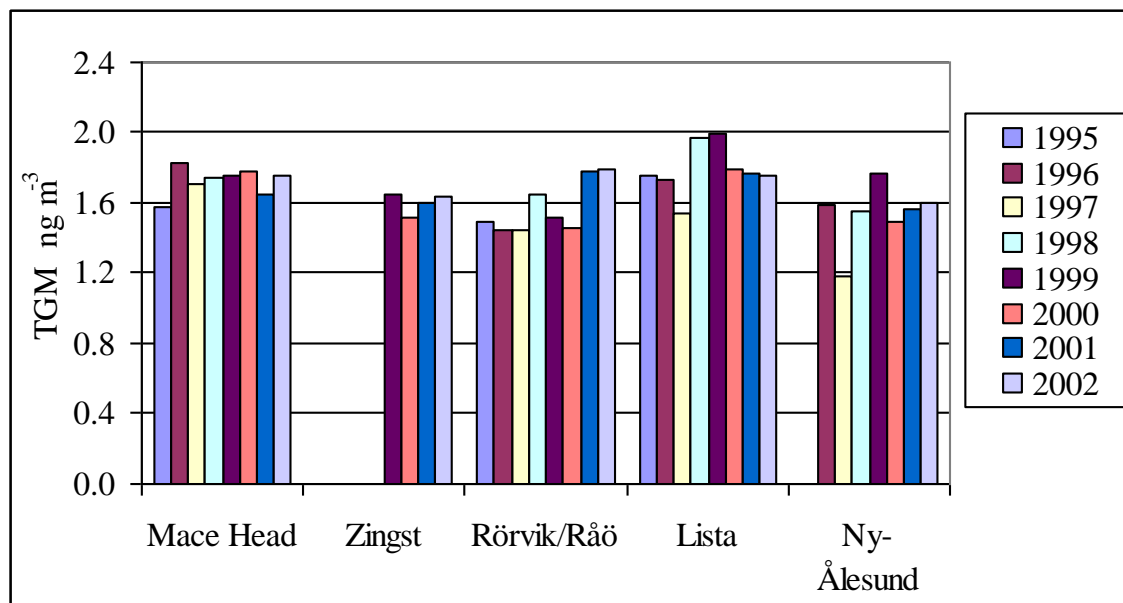

Figure 10. *Average yearly TGM values from 6 OSPAR CAMP sites during the period 1995-2002.*

Yearly average TGM values from five OSPAR CAMP sites are shown in Figure 10. One can see that the TGM values are confined within the range 1.2 to 2.0 ng m^{-3}. The lowest values were measured at the two polar stations, Ny-Ålesund and North Greenland. Due to certain atmospherically processes, elemental mercury may completely be removed from the atmosphere for limited time periods.

These are the so called mercury depletion events which occur in Polar areas during spring (see section 2.4.1). Yearly averages from these stations are therefore not directly comparable with those from stations located at lower latitudes.

Due to the relatively long atmospheric lifetime of mercury, TGM at background sites is considered to reflect the hemispherical background concentration. According to the present data, average TGM for the period 1995-2002 is 1.79 ng m^{-3} at Lista and 1.72 ng m^{-3} at Mace Head.

In a recent paper, Slemr et al., 2003, estimated the background TGM concentration in the Northern hemisphere to be 1.7 ng m^{-3} during 1996 to 2000. The average TGM in the Northern Atlantic Ocean was estimated to be somewhat higher, 1.88 ng m^{-3}, during the same period. It should be mentioned that these estimates are partly based on data from Lista and Mace Head, Ny-Ålesund and Råö but also from ship cruises and measurements at some additional sites.

However, the values from Lista, Mace Head are likely to represent that of the westerly border input of TGM to Northern Europe. On the other hand, the values from Råö and Zingst are more difficult to interpret. Due to the proximity to mercury sources in Europe one should expect the concentrations to be somewhat higher there than at the Atlantic sites, but according to Figure 10 it is the opposite. No plausible explanation is at hand at the moment.
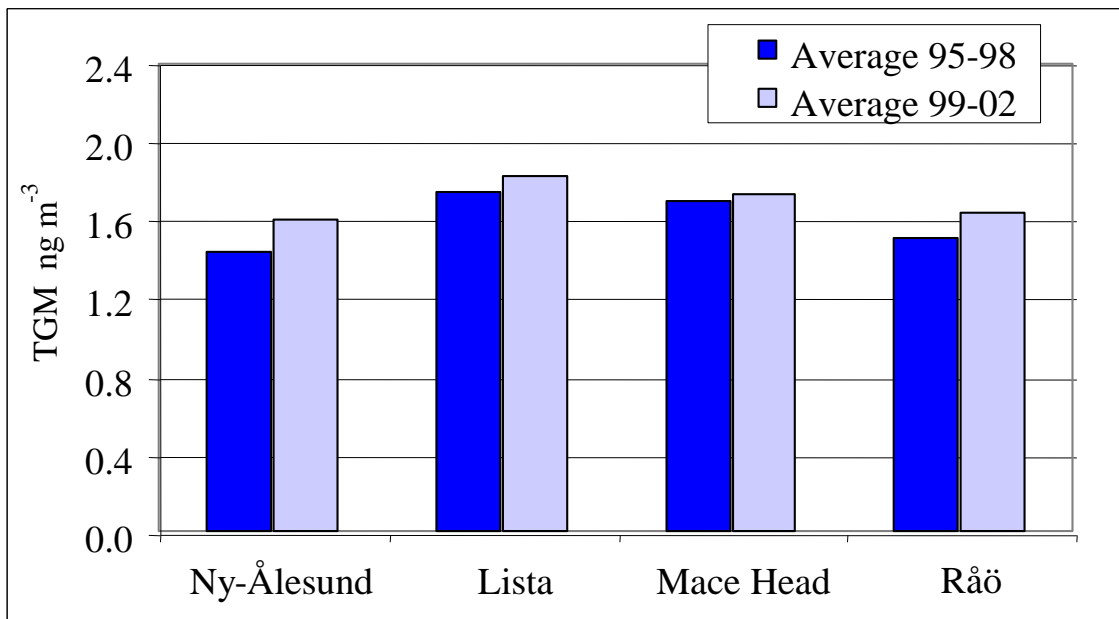
Figure 11. *Comparison of average TGM during the two periods 1995-1998 and 1999-2002.*

Average TGM concentrations from 1995-1998 and 1999-2002 are shown in Figure 11. TGM concentrations seem to increase slightly with time. However, the increases at Lista and Mace Head are small only 4% and 2%, respectively and comparison of the yearly values shows no increasing trend.

The change at Råö is 8% and is large enough to indicate that TGM really has increased during latter years. It can be concluded that TGM remained constant or slightly increasing in the OSPAR area during the period 1995-2002. On the other hand, Hg deposition decreased during the same period as shown above.

2.5.2. Impacts of anthropogenic activities on atmospheric mercury

To put the above result into perspective, it may be compared with earlier deposition measurements from the Rörvik/Råö station as shown in Figure 12. Unfortunately, there are no regular deposition measurements available from the period before 1989. However, the reduction of Hg deposition is likely to have been concurrent with the economic decline in Eastern and central Europe.

During the beginning of the 1990s many coal-fired power plants and other industries closed. As a result sulphur and also mercury emissions were greatly reduced. Measures to control emissions of sulphur were also implemented in the early 1990s which likely reduced mercury emissions further (via e.g. fuel changes and installation of wet scrubber systems) (Munthe et al., 2001).

Today the deposition of mercury at Rörvik/Råö is 4 - 5 times lower than before 1990. The present data indicate that regional anthropogenic mercury emissions are still declining, though at a much slower rate.

The present decrease in mercury deposition is likely to be an effect of further control mesaures in power production et cetera.

The earlier very high deposition of mercury was accompanied by high TGM concentrations. Thus, during the period 1985-1989 the average TGM concentration was reported to be 3.2 ng m^{-3} at Råö and 2.7 ng m^{-3} during 1990-1992 (Iverfeldt et al., 1995).

Iverfeldt et al. (1995) concluded that the decrease in atmospheric burden of mercury was due to decrease in Hg emissions from European source areas. In other words, changes in Hg deposition and TGM concentration was attributed to decreased regional Hg emissions.
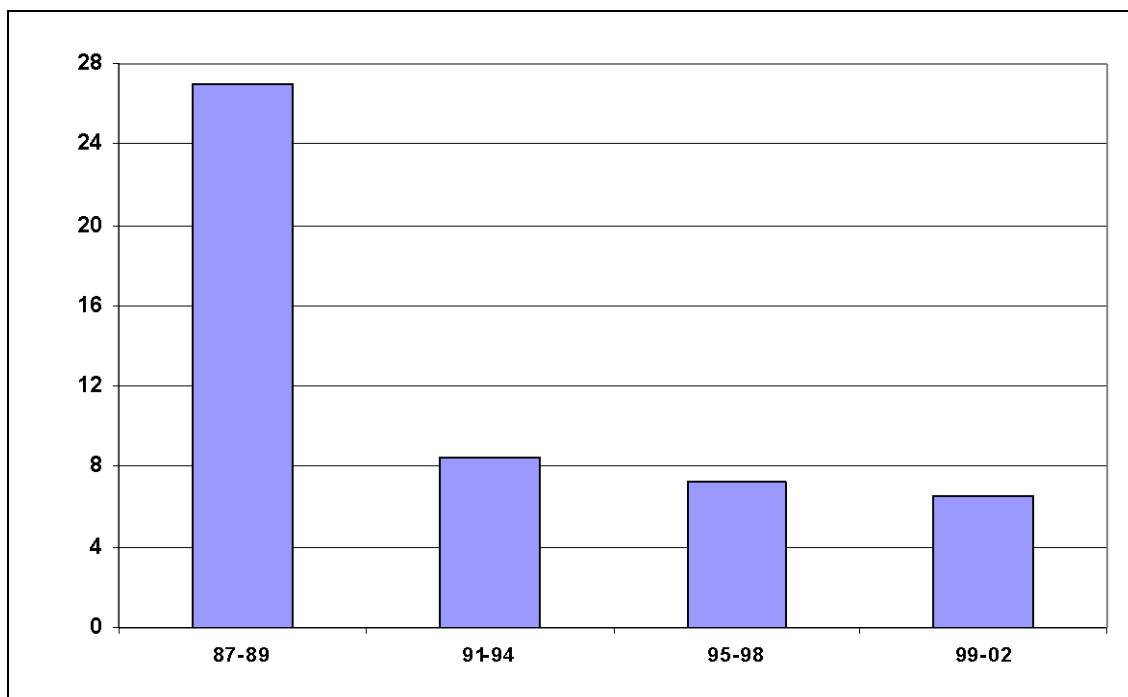
23

Hg (tot) deposition (µg/m^3)

Figure 12. *Average Hg(tot) deposition at the Rörvik/Råö station during 1989-2002.*

The reduction in Hg deposition as seen during 1995-2002 is also likely to be a result of reduced European Hg emissions as discussed above. The question is how to interpret the TGM trend. However, since TGM is influenced by both regional and global sources the regional contribution will gradually be less important if it is declining.

At a certain point the global influence will become dominating and trends in TGM will be governed by emissions on a global or hemispherical scale. Increasing TGM concentrations may thus indicate that mercury emissions are increasing globally.

2.5.3. Other monitoring networks and research activities

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) is a US nationwide network of precipitation monitoring sites. The NADP is three networks (NTN, MDN and AIRMoN), with NTN being the general chemistry deposition network (sulphate, nitrate, ammonia, other cations).

The network is a cooperative effort between many different groups, including the State Agricultural Experiment Stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities. The Mercury Deposition Network (MDN), currently with 109 sites was formed in 1995.

The objective of the MDN is to develop a national database of weekly concentrations of total mercury in precipitation and the seasonal and annual flux of total mercury in wet deposition. The data will be used to develop information on spatial and seasonal trends in mercury deposited to surface waters, forested watersheds, and other sensitive receptors. An example of annual deposition of total mercury is presented in Figure 13.
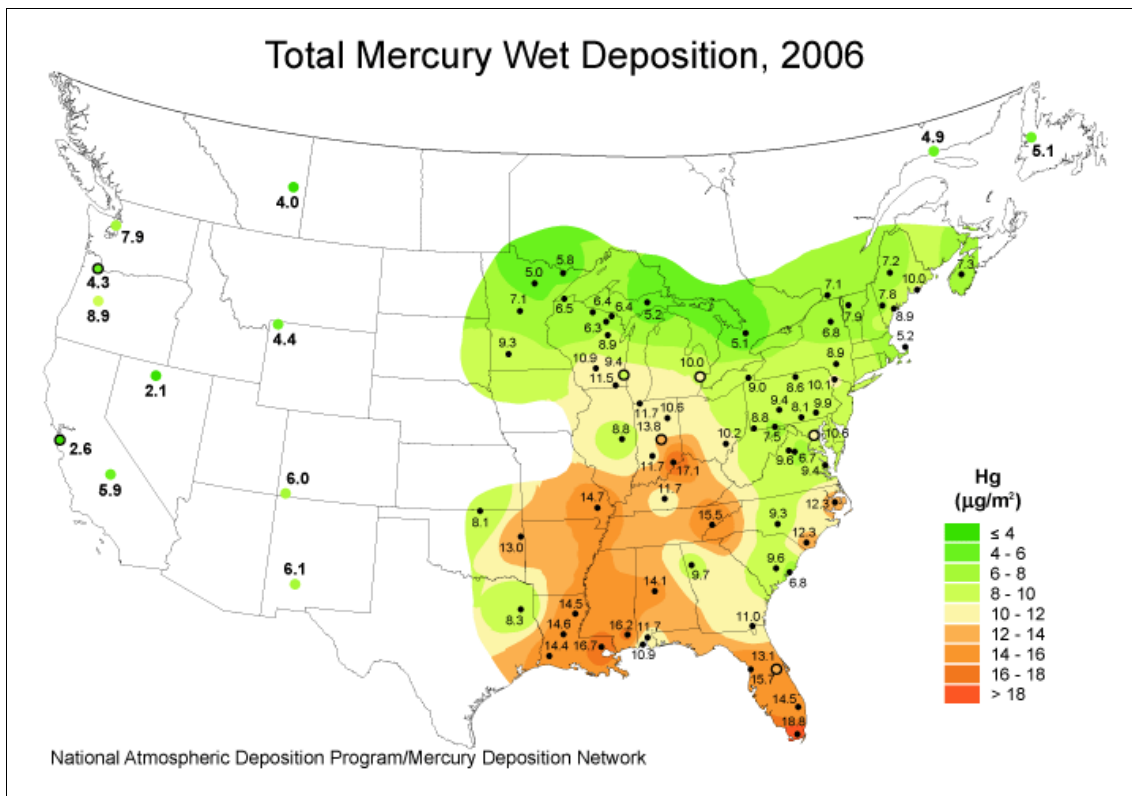
Figure 13. *Total mercury wet deposition from the US NADP/MDN network. Downloaded from http://nadp.sws.uiuc.edu/mdn/maps/, March 17, 2008*

2.5.4. Modelling atmospheric transport and deposition

Atmospheric models are used both as research tools to compile and assess the importance of e.g. atmospheric processes and emissions. They may also be used as policy tools to evaluate emission reduction measures. Depending on the purpose of the modelling, different levels of complexity are applied.

Models require inputs of meteorology, emissions of mercury species and parameterisation describing chemical and physical processes. The model then simulates transport of air masses, cloud formation and precipitation events, chemical conversions of mercury and dry and wet deposition.

Regional models describe emissions, transport and deposition of mercury on scales ranging from individual countries to continents. They are commonly used to develop and assess policies to reduce atmospheric emissions/deposition of Hg. One example is the modelling activity within the framework of the UN ECE Convention on Long Range Transboundary Air Pollution (http://www.unece.org/env/lrtap/).

The mercury model developed by the Meteorological Synthesizing Center - East (Travnikov and Ilyin, 2006) describes emissions, transport and deposition of mercury in Europe and has been employed to calculate e.g. how emissions in one country affect deposition in other. It is thus a useful tool for assessment on international policy options. Results from these modelling activities are available on the web (www.msceast.org).

An example is given in Figure 14 where the modelled distribution of total mercury deposition in Europe is presented. Other European models have been developed and employed in various research projects and national activities (e.g. Petersen et al., 2001; Pirrone et al., 2000; Hedegecock *et al* 2005). Similar model systems have been developed and applied in the US (e.g. Bullock and Brehme, 2002; Cohen et al., 2004).
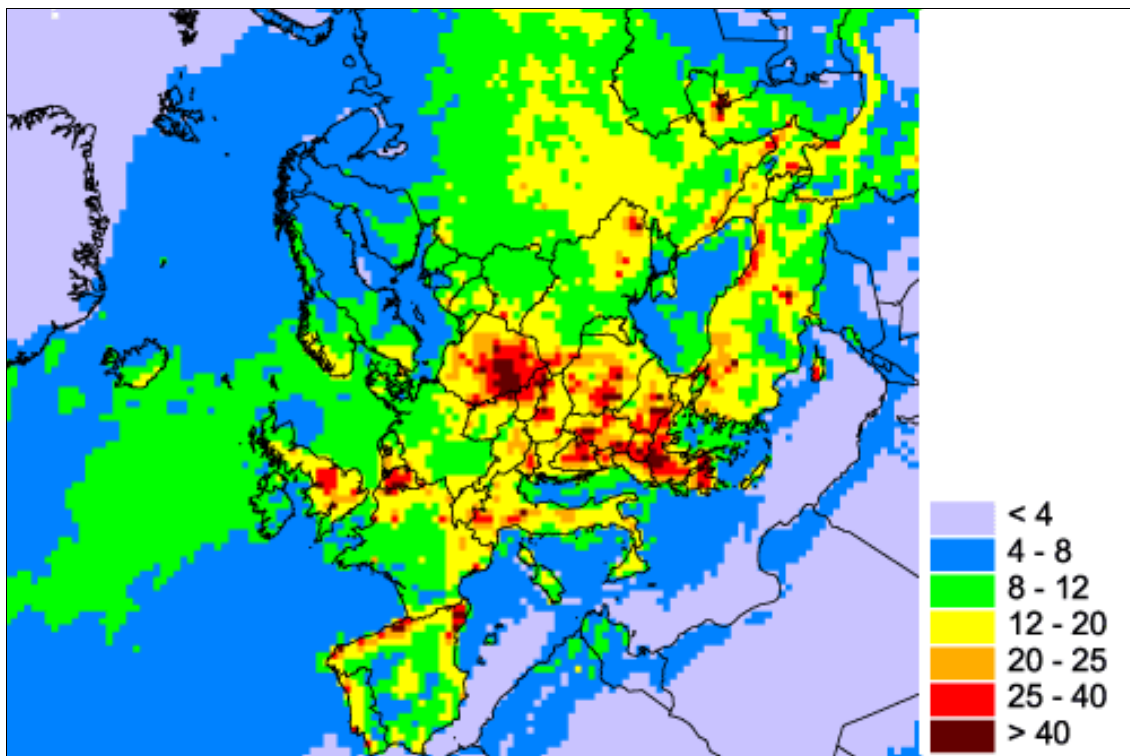
Figure 14. *Modelled annual total deposition of mercury in Europe in 2004. Units: g km^{-2}. Map courtesy of MSC-East (2006).*

Since mercury is a globally distributed contaminant, applications of global models are sometimes useful for assessment of intercontinental transport and global cycling.

One example of global models is presented in Dastoor and Larocque (2004) where modelling results of global TGM concentrations and deposition are presented.

MSC-East also operates a hemispherical model which is used both for simulating boundary conditions for the regional model and for assessing intercontinental transport of mercury (http://www.msceast.org/hemispheric/hemispheric_index.html).

To evaluate long term fluxes and pools, it is necessary to utilise multi-compartment models i.e. models that also describe pools of mercury in air, water and soils and fluxes between these compartments (Lamborg et al., 2002, see section 2.2).

3. Mercury species in terrestrial and aquatic ecosystems

3.1. Mercury fluxes in terrestrial ecosystems

Terrestrial ecosystems are an important link between atmospheric deposition and aquatic ecosystems. In forested ecosystems, deposition of mercury is often enhanced by a factor of 2-4 in comparison to open field wet deposition due to the role of dry deposition in the canopy.

The forest soil acts as a sink for deposited mercury and only a fraction of the deposited mercury is actually released to water ecosystem via runoff. Soils and especially wetlands can also act as sources of methylmercury via methylation and release of methyl mercury.

The enhanced deposition of mercury to forested ecosystems is mainly driven by air-canopy interactions. Mercury in the form of RGM and TPM are dry deposited to the forest canopy and then washed off by precipitation or deposited to the forest floor via litterfall (i.e. needles, leaves, branches), see Figure 15. A similar mechanism has been proposed for methylmercury.
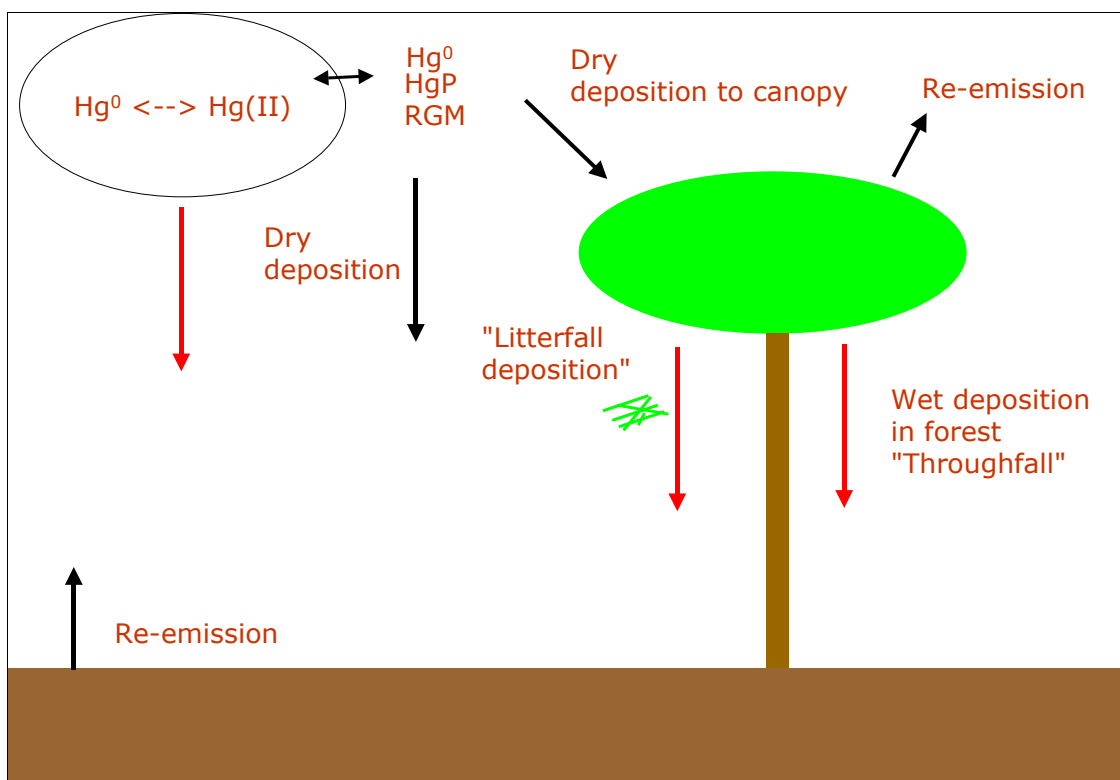
Figure 15. Mercury fluxes in terrestrial ecosystems.

A limited number of studies have been performed on this topic in Europe and North America, but all results point to the same enhancement of deposition. Research projects on the dynamics of Hg(tot) and CH_3Hg^+ in forested catchments and wetlands have been conducted in Sweden (Iverfeldt, 1991; Hultberg et al., 1994; Munthe et al., 1995a,b; Lee et al., 1994, 2000), North America (St Louis et al., 1996; Driscoll et al., 1998), and Germany (Schwesig and Matzner, 2000, 2001).

In Table 6, some examples of measured deposition fluxes of mercury and methylmercury are given.

Table 6. Deposition fluxes of Tot Hg and Me Hg in forested ecosystems.

Site	Wet deposition (open field), µg m^{-2} yr^{-1}		Total deposition (forest) µg m^{-2} yr^{-1}		Ratio Total/wet		Reference
	Tot Hg	Me Hg	Tot Hg	Me Hg	Tot Hg	Me Hg	
Steinkreuz, DE	27	0.08	61	0.26	2.3	3.2	Schwesig et al., 1999
Lehstenbach, DE	30	0.13	57	0.34	1.9	2.6	Schwesig and Matzner, 2000
Uraani, FI	6	0.12	37	0.48	6.3	4.0	Porvari et al., 2003
Svartberget, SE	7	0.08	33	0.47	4.7	5.9	Lee et al., 1994, 2000.
Gårdsjön, SE	10	0.12	46	0.75	4.6	6.3	Munthe et al., 1995
Sunday Lake, NY, USA	9.4	0.05	23	0.31*	2.5	-	Driscoll et al.1998
Walker Branch, TN, USA	10	-	44	-	4.4	6.2	Lindberg, 1996
ELA, CA	7	0.09	20	0.17	2.9	1.9	StLouis et al. 2001
Lake Huron, USA	8.7	-	21.9	-	2.5	-	Rea et al., 2001

The mechanisms in this deposition process are generally assumed to be dry deposition of RGM and TPM for total mercury, and dry deposition of gaseous CH_3HgX (X = Cl, OH) for methylmercury.

The mechanism to explain the enhanced deposition of total mercury is not completely understood. An evaluation of total (dry + wet) deposition fluxes calculated using a regional atmospheric model., using state-of-the-art parameterisation for dry deposition of mercury, could not reproduce the enhanced total deposition of mercury in forested ecosystems (Munthe et al., 2005).

Although results of only one model was evaluated, most models contain very similar parameterisations for dry depositions and the results suggest that the dry deposition of mercury to forest canopies is not fully described by our current knowledge. An alternative explanation is that the source of mercury in litterfall is not the atmosphere but rather the forest soil via root uptake and translocation from roots to needles/leaves.

No experimental evidence exists for this process occurring in forest trees, although it has been shown to be significant in wetland plants (Lindberg et al., 2005). Chamber experiments have also shown that plants can efficiently take up elemental mercury from air, although mainly at higher concentrations than normally found in ambient air.

The reverse (i.e. emissions of mercury from plants) has also been observed in measurements over forest canopies (Lindberg et al., 1998).

Mercury is also released from forest soils via re-emissions of previously deposited mercury. Only a few individual measurements have been performed on background soils in Europe and

North America. Flux chamber measurements in SW Sweden suggest that these fluxes are relatively small in comparison to deposition. Maximum summer values of approximately 1 ng/m^2 hr have been regarded (corresponding to 8.8 µg/m^2 yr) (Xiao et al., 1991). Much higher re-emission fluxes from soils can be found in areas where mercury occurs in the geological bed rock material (e.g. Gustin et al., 2003).

Mercury and to some extent methylmercury are efficiently accumulated in most soils. Mercury is strongly bound to the soil via reduced sulphur groups associated with organic matter. Depending on the characteristics of the organic material, the solubility and mobility of mercury will vary between different soils and soil types. Soil profiles of mercury usually follow the same profile as the organic matter.

Accumulated mercury in forest soils has recently been acknowledged as a potential toxicant to soil micro organisms (Bringmark and Bringmark, 2001). These results have been used to develop a biologically relevant critical limit for Hg concentrations in soil organic matter of 0.5 mg/(kg org), which is used as a basis for calculations of critical loads within the framework of the UN ECE Convention on Long Range Transboundary Transport of Air Pollutants (www.oekodata.com/icpmapping/).

Mercury and methylmercury are released from forest soils and transported via runoff water to rivers and lakes. The output is highly variable and depends on factors such as watershed size, run off amounts, hydrological pathways and catchment characteristics.

Particulate matter and Dissolved Organic Carbon (OC) are important carriers of mercury and methylmercury and any factors which influence the loss of these materials will enhance transport of tot Hg and Me Hg. Wetlands generally export higher proportions of methylmercury due to favourable conditions for methylation (anaerobic, high carbon content of soils).

An important factor when discussing export of mercury and methylmercury from soils to water is the role of land use and land use changes. Some studies have suggested that there is a lack of a clear linkage between annual mercury deposition and catchment export of tot Hg or Me Hg (Munthe and Hultberg, 2004).

Recent controlled Hg loading studies at the Experimental Lakes Area (ELA), Canada suggest that the total mercury exported in any given year is probably derived largely from old soil pools of mercury, rather than new Hg deposition.

Recent studies in Sweden and Finland indicate that the export of total mercury and especially methylmercury is more strongly influenced by catchment disturbance such as forestry and clear cutting than by changes in atmospheric Hg deposition (Munthe and Hultberg, 2004; Porvari et al., 2003). Land disturbances that are particularly relevant to Hg cycling include formation of wetlands and flooding of reservoirs (Rudd, 1995).

Therefore, measurements of catchment export of Hg must be regarded cautiously with respect to the use of this measurement as a reliable indicator of trends in atmospheric deposition.

The response of surface water Hg to changes in atmospheric Hg deposition will be influenced by the existing Hg pools in soil and by terrestrial processes that modify the transport of deposited Hg to surface waters (e.g., adsorption, vegetation uptake, mineralisation, reduction and emissions from soil and vegetation). In order to discern any change in loading to watersheds, multiyear studies will be necessary to detect real trends in the response of surface waters.

3.2. Mercury fluxes in aquatic ecosystems

The main sources of mercury species to aquatic ecosystems are direct deposition from the atmosphere input via streams and run off from the surrounding catchment. Direct inputs of methylmercury can potentially be taken up directly by the food-chain whereas inorganic mercury can undergo a number of transformations, including methylation.

In Figure 16 the main transformations and flows of mercury species in lake water are presented.
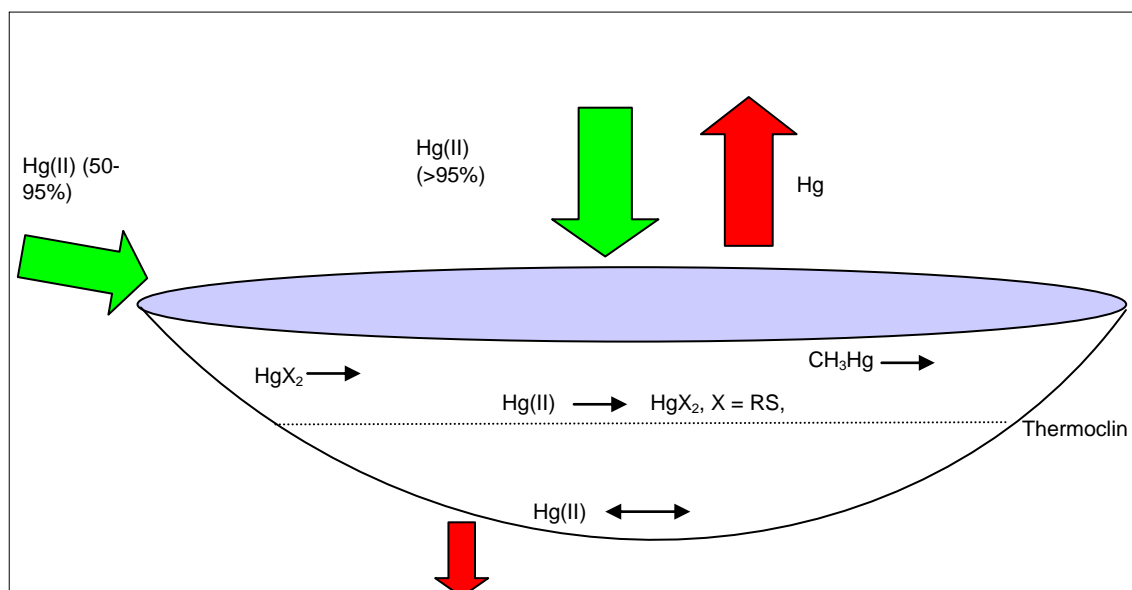

Figure 16. Schematic drawing of main transformations of mercury species in lake water. Input from atmosphere and catchments are represented by green arrows. Output via re-emission, sediment burial and runoff is represented by red arrows. Particulate phase species are not shown.

The relative importance of the two main external input pathways - catchment run off and atmospheric deposition - varies with the catchment-lake area ratio, the location and the characteristics of the catchment. In some specific cases, groundwater seepage can supply significant amounts of e.g. methylmercury to a lake.

Published values for annual catchment input of total mercury for a northern latitude lake are usually in the range 2-4 g/km^2 (Driscoll et al., 2007). For methylmercury, catchment input values are more variable and reported values range from < 0.01 to 0.1 g/km^2.

Direct atmospheric input is usually in the range 5-30 g/km^2 for total mercury and 0.05-0.2 g/km^2 for methylmercury. This means that catchment input will be the dominant source of total mercury in lakes with large catchments and small surface area. For methylmercury, atmospheric input will only dominate in very specific cases where the methylating capacity of the lake catchment area is low.

Having entered the aquatic system, mercury can undergo a series of different transformations. Divalent mercury and methylmercury in lake water will, to a large extent, exist in the form of complexes with dissolved organic compounds (humic or fulvic acids). A significant fraction may also be associated with particles.

Re-emissions have a major influence on the cycling of mercury in freshwaters. The process involves sunlight-induced reduction of Hg(II) and release of elemental mercury from the water surface. Field observations indicate that re-emissions may be of the same order of magnitude as wet deposition (e.g. Xiao et al., 1991).

Nearly all measurements of dissolved elemental mercury in surface waters (both fresh- and seawater) indicate that the water is supersaturated. This means that re-emissions occur from all waters. The rate is dependent on water temperature and on agitation of the surface water due to action of strong winds (on large open sea or lake areas) or strong currents in rivers and streams.

Methylmercury is degraded by sunlight in freshwaters (Sellers et al., 1996). The product is divalent mercury which can re-enter the cycle of methylation and is thus not removed from the ecosystem compartment.

The key process from environmental and risk assessment perspectives is methylation. Methylation has been investigated for many years and a number of processes and mechanisms have been proposed. The main current hypothesis is that inorganic mercury is methylated by sulphate reducing bacteria (SRB) in anoxic water layers or in sediments (Munthe et al., 2007).

The rate and extent of methylation of a pool of inorganic mercury is dependent on several variables. Under favourable conditions, methylation is a relatively fast process but it is balanced by demethylation occurring simultaneously. Current knowledge suggests that demethylation occurs via both biotic and abiotic pathways and that the rate is more independent of the environmental conditions.

The role of reduced sulphur is complex and of prime importance for the methylation. Methylation occurs primarily when the inorganic mercury is present in the form of neutral sulphide complexes (e.g. HgS(aq), $Hg(SH)_2$, HgOHSH). These species will only be present within a range of sulphide concentrations.

If the sulphide concentrations decrease or increase, the speciation of mercury will change e.g. to complexes with organic ligands containing sulphydryl groups or negatively charged sulphide complexes, respectively. These are not biologically available for methylation. The rate of methylation via SRB is also dependent on the presence of carbon in an available form.

The main hypothesis on the role of sulphides is that the neutral mercury complex can be transported through the cell wall and be methylated inside the cell (Benoit et al., 2003).

Other investigators have suggested that methylation occurs via cell exudates i.e. outside the cell walls (Parkman et al., 1994). In any case, the role of reduced sulphur is clear and to a large extent explains the variability of methylation rates at different locations.

3.3. Methylmercury in relation to total mercury in different environmental compartments

Since methylation of mercury is primarily a process both involving chemical constituents and microbes, predictions of production rates of MeHg are difficult. In addition to this complexity, demethylation also occurs thus limiting the overall rate of methylmercury production. In general, much less is known about demethylation than about methylation.

In Figure 17, a compilation of Hg and MeHg concentrations from sediments across North America is presented (modified from Benoit et al., 2003, logarithmic scale). For the whole dataset a weak relationship exists but the variability is large. For individual ecosystem types, the relationships appear to be stronger.
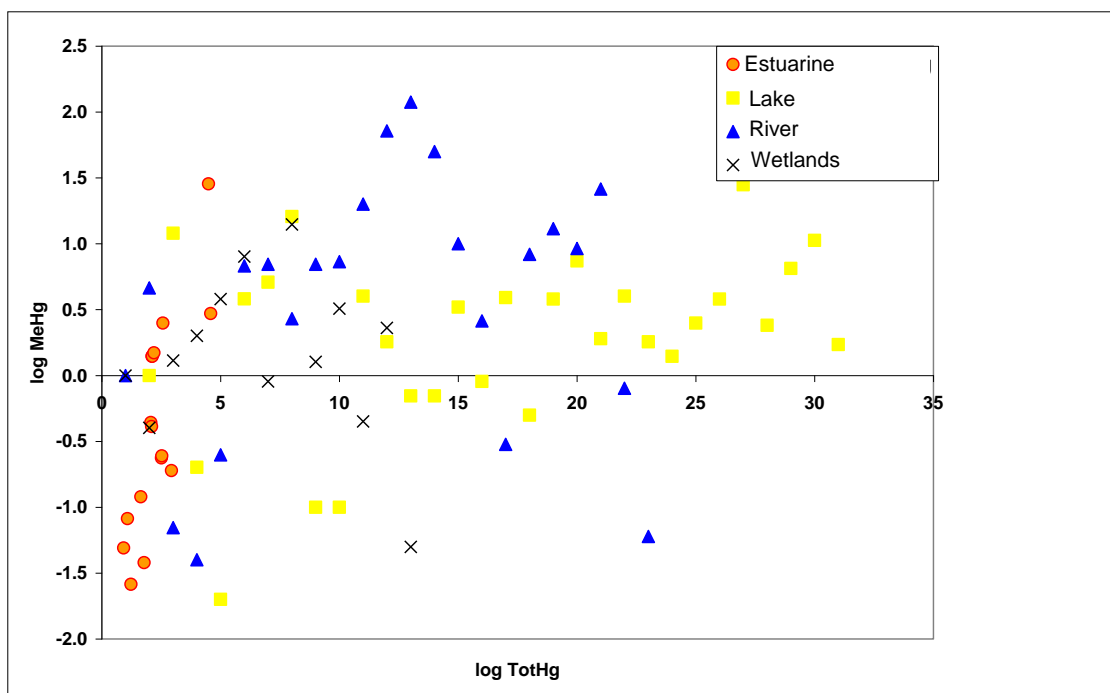
Figure 17. Relationship between total mercury (Tot Hg) and methylmercury (Me Hg) in sediments and soils from estuaries, lakes, rivers, wetlands.

To understand the complexity of these relationships, it is necessary to discuss the various factors affecting methylmercury production which are applicable in different situations. An obvious factor is the availability of mercury. Although some ecosystems show a linear response in methylation to Hg loading at relatively low levels (Orihel et al, 2006), it is evident that at higher Tot Hg levels, methylation can not occur as efficiently.

In most environmental compartments excluding biota, methylmercury only amounts to a very small fraction of the total mercury. This is mainly the result of the two competing processes methylation and demethylation. Methylation rates and processes have been much more thoroughly studied than demethylation and some major controlling factors have been identified. Methylation mainly occurs via SRB which are only active under anoxic conditions.

The presence of anoxic zones is thus an important controlling factor. Anoxia can occur in soils and wetlands as well as in sediments and bottom waters. In soils, the degree of water saturation is important and thus so is hydrology.

In soils with little connectivity to running water, even if methylmercury is formed, very little of it will be transported to the aquatic ecosystems. Sulphate availability is a pre-requisite for methylation via SRB and may be a controlling factor in remote terrestrial and freshwater systems. Acid deposition has also been suggested as a factor enhancing the rate of methylmercury formation in remote regions.

As described above, there are many factors affecting the formation of methylmercury under environmental conditions. Our current scientific understanding is sufficient to explain the main processes and controlling factors in individual ecosystems, but is far from complete. This limits our ability to make generalised risk assessments and predictions of recovery of contaminated ecosystems.

4. Conclusion and discussion – The role of mercury species in the environmental cycling of mercury

Mercury speciation has become a necessary part of research, assessment and policy making in the field of mercury. This is a consequence of the highly variable behaviour of different mercury species which affects its mobility and impacts. In recent years, most attention has been focussed on RGM (Reactive Gaseous Mercury) both in emissions from combustion processes and in ambient air.

The level of RGM in combustion flue gases greatly influences the removal efficiency in installations such as scrubbers for SO_2 removal and particle filters. Furthermore, an understanding of the speciation of the emitted mercury from point sources is necessary information for atmospheric modellers and thus for assessing the impacts of the emissions. RGM in ambient air partly originates from emissions and partly from formation in the atmosphere.

Understanding the dynamics of RGM in the atmosphere is a requisite for a more complete understanding of the transport and fate of mercury, and is consequently a prioritised subject for current and future research. A discussion of the current status of knowledge concerning atmospheric transport and deposition can be found in Lindberg et al. (2007).

Formation of methylmercury is the most critical process in the environmental cycling of mercury. Without this process, the toxicity and human health risks associated with mercury releases to the environment would be significantly lower. Ambient levels of methylmercury are a result of the competing processes of methylation and demethylation.

Demethylation effectively controls the amounts of methylmercury in aquatic ecosystems and is thus of equal importance as methylation. Although our understanding of these processes has increased greatly in recent years, large gaps still exist in our ability to predict methylmercury levels in a specific ecosystem at a given total load of mercury.

Anthropogenic emissions have affected levels of mercury on local, regional and global scales. The impact on a specific scale is largely dependent on the form of mercury released and on the methylation capacity of the local environment. Thus, a release directly to water or a release of RGM to air, in combination with favourable conditions for methylation, can have large impacts on a local scale. In contrast to this, releases of elemental mercury to air will only affect the local environment to a small extent.

This does not mean that releases of elemental mercury have not had an impact on the environment or on risks to human health. Over the industrial period, vast amounts of elemental mercury have been released leading to global increases of mercury in air and in all compartments of the environment (Expert Panel, 1994). The impacts in remote regions are, to some extent, a result of specific processes such as the polar sunrise depletion events which yield large inputs to polar ecosystems (Schroeder et al., 1998; Lindberg et al., 2002; Gauchard et al., 2005; Sommar et al., 2007) and the efficient methylation and biomagnification in remote lake ecosystems in the Boreal forest regions (e.g. Lindqvist et al., 1991).

The contribution to the global mercury contamination of any individual point source is, in most cases, very small. Anthropogenic contribution to the global mercury contamination today consists of a very large number of small sources with very differing characteristics. Combustion of coal for energy generation is a major source category but intentional use of mercury in industry, products and not least artisanal gold mining also contributes significant amounts.

In the richer parts of the world, use of mercury is being phased out. A safe and responsible handling of the surplus mercury thus generated is essential for the long-term protection of the environment.

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Other Euro Chlor Science publications

Focus on Chlorine Science

Electromagnetic fields in chlor-alkali production - Health effects and regulation – January 2009

Life Cycle Assessment – November 2006

Risk assessment and cycling of natural organochlorines – May 2006

Environmental fate and impact of chlorinated solvents – December 2005

Chlorination by-products – November 2005

Electromagnetic fields in chlor-alkali production – Health effects and regulation – January 2009

Key Science Information Sheets (KSIS)

Bioaccumulation – January 2005

Effluent testing: a review of current status – November 2004

Abbreviations used in (eco)toxicology – September 2004

Effluent testing with cell-based in vitro bioassays: use and limitations – July 2004

Marine Risk Assessment – October 2003

POPs & PBTs – February 2003

Naturally-occurring organochlorines – January 2003

Dioxins – April 2002

Water chlorination – February 2002

Children and exposure to highly chlorinated chemicals – August 2000

Science literature reviews

Bio-dehalogenation: Between 2001 and 2005, Professor James Field (University of Arizona, USA) provided Euro Chlor with quarterly updates of published scientific literature reporting on microbial (de)halogenations of key chlorinated compounds. There are 15 issues.

Natural organohalogens: From 1995 to 2002 Professor Gordon Gribble (Dartmouth College, Hanover, New Hampshire, USA) provided Euro Chlor with a series of periodic updates to the natural halogen literature, focusing on organochlorine compounds. There are 18 issues.

Marine Risk Assessments

1,2-Dichloroethane

1,1,2-Trichloroethane

Tetrachloroethylene

Trichloroethylene

Chloroform

Carbon tetrachloride

Dichloromethane

Hexachlorobenzene

Hexachlorobutadiene

1,2,4-Trichlorobenzene

1,1,1-Trichloroethane

Vinyl chloride

Monochloromethane

1,2-Dichlorobenzene

1,4-Dichlorobenzene

Mercury

Monochlorophenols (2-, 3- and 4-)

All the above and more are available on Chlorine Online at

www.eurochlor.org/science

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The Science Dossiers produced by Euro Chlor's Working Groups aim to improve the understanding of key topics related to the chlorine industry in order to support science-based decision-making. Science Dossiers are often dealing with chlorinated substances, both natural and man-made, explaining their formation, fate, occurrence or breakdown in the environment. Science Dossiers always intend to provide objective scientific information helping to improve the credibility and transparency of the chlorine industry. Many of our Science Dossiers have been the basis for peer-reviewed publications in scientific journals, written by specialists in the field.