

European Research Course on Atmospheres (ERCA) – Volume 5

Mercury as a Global Pollutant

Laurier POISSANT [§] Aurélien DOMMERGUE [†] and Christophe P. FERRARI ^{†, ‡}

[§] Service Météorologique du Canada, Processus Atmosphériques des Toxiques, Environnement Canada, 105 rue McGill, Montréal, Québec, H2Y 2E7.

[†] Laboratoire de Glaciologie et Géophysique de l' Environnement du CNRS, 54 rue Molière, BP 96, 38402 Saint Martin d'Hères, France.

[‡] École Polytechnique Universitaire de Grenoble, Université Joseph Fourier, 28 Avenue Benoît Frachon, BP 53, 38041 Grenoble, France.

Laurier POISSANT[§] Aurélien DOMMERGUE[†] and Christophe P. FERRARI^{†,‡}

Abstract. Mercury may be one of the best-documented hazardous substances utilised by man. Still the uncovering of the global human impacts on the environment through the use and mobilisation of mercury cannot be considered complete. Recent mercury depletion events observed in the Arctic have opened the horizon to numerous new aspects on mercury fate and cycling in the environment. This chapter browses various aspects of the extremely complex cycling and fate of mercury in the perspective of mercury as a global pollutant and discusses some new emerging research fields in mercury.

1. INTRODUCTION

Mercury (Hg: Greek for *hydrargyrum*) named after the Roman god of merchants and merchandise, sometimes being known as «quicksilver» is ubiquitous, being found in all environmental compartments because of its unique chemical and physical characteristics as a metal. Mercury was widely used because of its ability to dissolve silver and gold (amalgamation) and was the basis of many plating technologies. There are indications that it was prized and perhaps worshipped by many ancient civilisations such as the Chinese, Hindus, Egyptian, Greek and Roman. Mercury has been found in tombs dating back to 1500 and 1600 BC Theophrastus of Eresus (371-286 BC), head of the Lyceum in Athens from 322 BC, mentions in his book « On Stones » or « *De Lapidibus* » mercury extraction from cinnabar, its most widespread form in the geosphere. Since many centuries, mercury has played an important role in medicine and chemistry.

However, because of the extreme and pronounced toxicity of mercury, environmental contamination due to increased industrial use of the metal has resulted in many episodes of human poisonings. One of the earliest and best-known examples of environmental mercury poisoning occurred in Japan in 1953 with the first reported cases of « Minamata disease » [1]. Despite the recognition of the toxicity of mercury and mercury vapour in the 17th century in the Almadén (Spain) mercury mines, Minamata was the first identified example of the *in situ* methylation and bioaccumulation of mercury in fish.

As a consequence of the current human-health and environmental concerns associated with elevated levels of mercury (especially methylmercury) in freshwater and marine fish-eating fish, there has been refocused attention on mercury as a global pollutant as well as an expansion

in mercury research. Six international meetings dealing with mercury in the environment have occurred in recent years. The first was held in Gävle, Sweden, in 1990, and the last in Minamata, Japan, in 2001.

Mercury which is known to circulate throughout the earth's air and water, and can be concentrated to dangerous levels in fish consumed by humans is now of concern in many international scientific and policy issues. Mercury is a global pollutant requiring global initiatives.

2. CHEMICAL PROPERTIES

Mercury occurs naturally in the environment and exists in several forms. These forms can be organised under three headings: metallic mercury (also known as elemental mercury), inorganic mercury, and organic mercury. Metallic mercury is a shiny, silver-white metal that is a liquid at room temperature. Metallic mercury is the elemental or pure form of mercury (i.e., it is not combined with other elements). Metallic mercury metal is the familiar liquid metal traditionally used in thermometers and some electrical switches. At room temperature, some of the metallic mercury will evaporate and form mercury vapours. Mercury vapours are colourless and odourless. The higher the temperature is, the more vapours will be released from liquid metallic mercury. Mercury has an atomic number of 80, an atomic weight of 200.59, a melting point of $-38.87\text{ }^{\circ}\text{C}$ and a boiling point of $356.58\text{ }^{\circ}\text{C}$. These characteristics give it the unique property for a metal of being liquid at most environmental temperatures. Its chemical reactivity is generally low and the liquid metal has a very high surface tension that accounts for its high adsorptive properties to solids, in which it will form very small spheres.

Mercury has seven stable isotopes and four unstable radioactive isotopes. It can exist in three oxidation states: 0, +1 and +2. Mercury exists in the atmosphere mainly as elemental gaseous Hg with an oxidation state of 0 (Hg°). The +2 oxidation state is also found in the atmosphere (either in the gaseous form or attached to particles) but the +1 state has not been observed in the atmosphere. Figure 1 shows the common mercury transformation in the environment.

In water, soil, sediments and biota, most Hg is in the form of Hg salts (e.g., HgS) or organic forms (e.g., methylmercury). Very small concentration of Hg° is dissolved in the water system. The Hg° Henry's law constant is 0.29 (at $298\text{ }^{\circ}\text{K}$). Although all forms of mercury can accumulate to some degree in the food web, methylmercury accumulates to a greater extent than other forms of mercury.

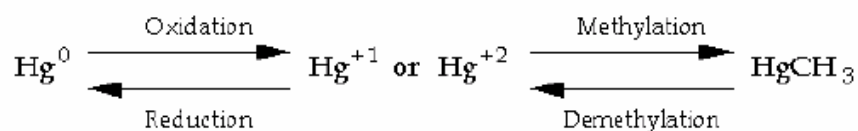


Figure 1. Common Mercury Transformation in the Environment

3. SOURCES OF MERCURY

There are many sources of mercury inputs to the biosphere (Figure 2) and various transport of mercury, which make mercury as a global pollutant.

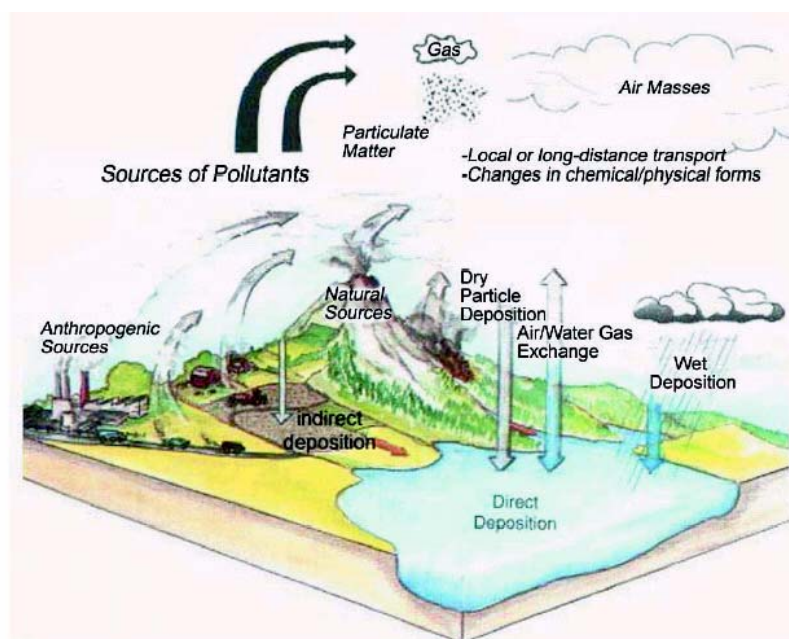


Figure 2. Schematic diagram showing the various transport of mercury as a global pollutant (source USA-EPA)

Natural sources are significant contributors, greater than man-made inputs in some areas, especially those where high concentrations of mercury exist in surface ores (e.g., Sierra Nevada). However, the contribution of mercury to the biosphere associated with human activities and from natural sources is a matter of great debate.

Anthropogenic sources of mercury might be categorised as both diffuse and point sources, the latter constituting the largest mercury emissions. Annual world emissions of anthropogenic Hg to the atmosphere are about 2200 t, which represents about 22 % of the world-wide mercury consumption. However, as there is a significant abundance of both crustal (Hg conc., 0.5 $\mu\text{g/g}$) and aquatic mercury, there is a natural amount of mercury in the atmosphere. The general world-wide distribution of mercuriferous belts tends to follow regions of geological activity and might be a significant source of natural mercury. Average atmospheric Hg emission from natural sources has been estimated to be 2500 t/yr [2] which is equivalent to an average

atmospheric concentration of 0.8 ng/m^3 [3]. About two hundred thousand (200 000 t) tons of mercury have been emitted to the atmosphere by human activities since the 19th century [4]. It is believed that “natural emission” from oceans is actually the re-emission of anthropogenically produced mercury [4].

4. ENVIRONMENTAL FATE OF MERCURY

Because of the high volatility of elemental mercury and some of its compounds, mercury is widely dispersed in the Earth's atmosphere. Emission sources, regional atmospheric chemistry and meteorology, and near-ground micrometeorological conditions may impact the distribution of the atmospheric mercury speciation and deposition. The average concentration in the troposphere is about 1.5 ng/m^3 . The dominant form of mercury in the atmosphere is gaseous elemental mercury (>97%) [5]. About 3% of the remaining atmospheric mercury species are reactive gaseous mercury (e.g., HgCl_2), particulate mercury and some organo-mercury forms (e.g., dimethylmercury) (e.g., [6-7]). Atmospheric mercury speciation is very important in the determination of the mercury atmospheric residence time. From one spectrum's side to another, elemental mercury can have a residence time of 1-2 years whereas RGM atmospheric residence time can be very short (few hours).

Cycling of atmospheric mercury (Figure 2) is an important source of mercury in the aquatic ecosystem [8]. Cycling of atmospheric mercury might proceed by gas exchange, particle settling or by rain scavenging. Wet deposition and particle deposition are considered to be unidirectional processes whereas Hg gas exchange is a bi-directional process. Wet and dry deposition occur mainly under Hg oxidised form, i.e. the Hg (II) species that is relatively immobile. Chemical, photolytic or biological reduction to elemental form can increase the mobility of mercury.

4.1 Atmospheric chemistry

The chemistry of atmospheric mercury, especially elemental mercury oxidation pathways by ozone, OH^\cdot , chlorine and bromine species, NO_3^\cdot and H_2O_2 were reviewed and discussed [9-13]. Accordingly, some chemical processes can affect the daily speciation, deposition and concentrations of mercury.

Ozone which is a daytime oxidant can oxidise Hg^0 efficiently through aqueous phase reaction (half-life is $\sim 30 - 40 \text{ s}$) [14] whereas it is less effective in gaseous phase chemistry [15]. Hydroxyl radical is also a daytime oxidant. Its oxidation reaction in aqueous phase leads to a Hg^0 half-life in natural conditions of $\sim 5 - 6 \text{ min}$ [16]. Oxidation of Hg^0 by chlorine species (Cl_2 , HOCl , Cl^\cdot) would be an important pathway [17] in the marine atmosphere. Reactive chlorine in the atmosphere is a night-time oxidant and usually reaches its peak concentration just before sunrise since both Cl_2 and HOCl can be photolysed by solar radiation [18]. Oxidation of Hg^0 by aqueous chlorine chemistry occurs rapidly in natural conditions (half-life $\sim 30 \text{ s}$). Gaseous phase

oxidation of Hg° by chlorine (Cl_2) might be possible [19], then the chemical half-life of Hg° would be ~ 2 months [20]. Oxidation of Hg° by NO_3^\cdot in gaseous phase [21] would be possible in night-time but kinetic reaction is low (half-life ~ 20 d). Oxidation of Hg° by H_2O_2 [12] would operate during daytime, however the kinetics of the gaseous phase oxidation reaction pathway is very low (half-life ~ 1 yr). In aqueous phase H_2O_2 can act as a reducing agent ($\text{pH} > 5.5$) as well as oxidising agent ($\text{pH} < 5.5$) [22].

Reduction processes occurring simultaneously in the atmosphere [23] may to some extent, balance oxidation of Hg° . Indeed, back-reduction of the oxidised Hg is likely to occur since the rate of oxidation of Hg° by ozone would lead to a depletion of mercury from the atmosphere [23]. For example, reduction of Hg (II) in the aqueous phase occurs through reaction with sulphite ions [12]. Photolysis reactions can also produce elemental mercury at a significant rate [12,24].

4.1.1 Mercury Depletion Events

Recent discovery on mercury depletion events in the high Arctic by Schroeder *et al.* [25] has shown that loss of gaseous elemental mercury is strongly correlated with ozone depletion in the Arctic boundary layer. Similar process has been observed in the sub-Arctic region in Kuujjuarapik, Québec, Canada (Figure 3).

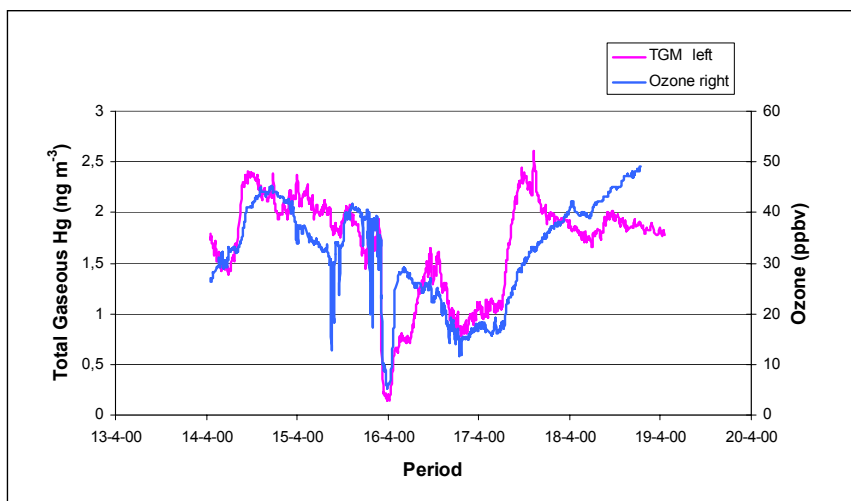


Figure 3. Time series of TGM and Ozone observed along the Hudson Bay (Kuujjuarapik, Québec, Canada) in April 2000.

Although, the two processes are not necessarily linked directly in a cause-effect

relationship. It is thought that Hg° is oxidised to $\text{Hg}(\text{II})$ by reactive halogen species (e.g., BrO) produced through photochemically initiated autocatalytic reactions [26].

Contrary to the high Arctic, the sub-Arctic around Kuujjuarapik, does not experience true polar night nor a rapid emergence of the sunlight. Nevertheless, MDEs have been observed at this location. Elevated concentrations of BrO have been observed in the air column by GOME satellite during the MDEs (Figure 4) which suggested BrO as a potential candidate responsible for elemental gaseous mercury oxidation during MDEs.

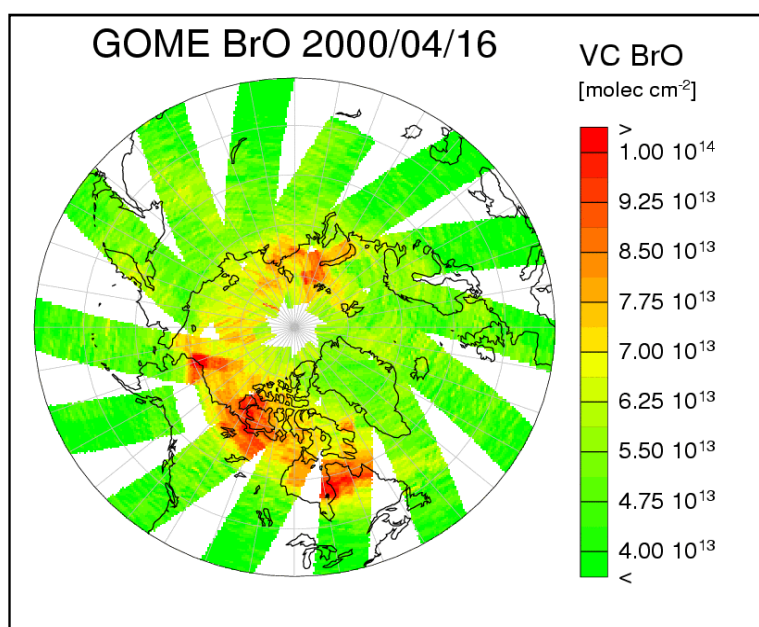


Figure 4. GOME global measurement of vertical columns of BrO during depletion event on April 16, 2000. (source: Dr. A. Richter, University of Bremen, Germany)

Lindberg *et al.* [27] presented a conceptual diagram (Figure 5) of proposed Hg° oxidation reaction sequences in the Arctic. There are several possible pathways and products. This schematic presents those that appear most favourable given the observations (dashed lines represent inter-phase transport; solid lines are reaction pathways).



and/or

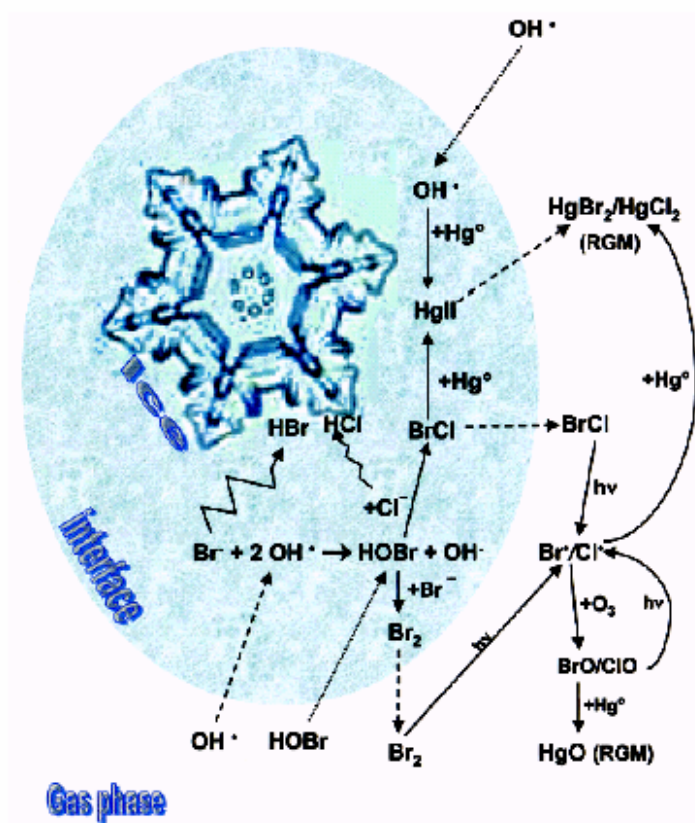


Figure 5. Potential Schematic chemical pathways during MDEs (source Lindberg et al.[27]).

Mercury species survey along MDEs (Figure 6) in Kuujjuarapik showed mercury conversion from gaseous elemental mercury to Reactive Gaseous Mercury and/or Particulate mercury.

Some snow surveys in the vicinity of Kuujjuarapik showed increase of mercury concentrations in snow-pack followed by a rapid lost through volatilisation back to the atmosphere (see below in section 4.6).

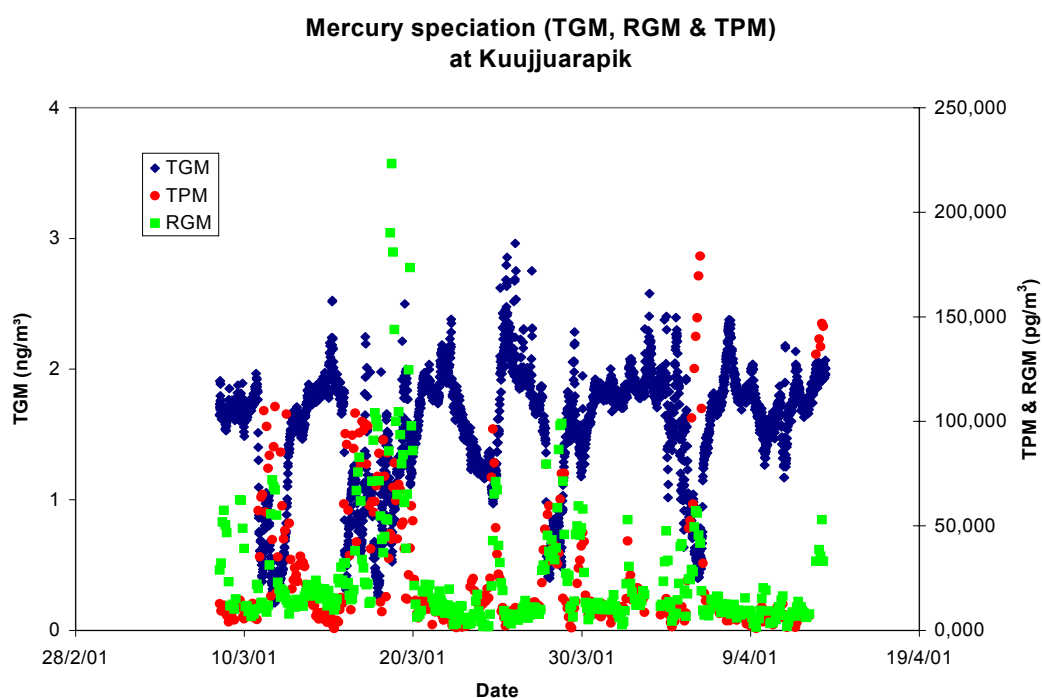


Figure 6. Time series of mercury species during MDEs in Kuujjuarapik .

4.2 Dry deposition

The dry deposition velocity of gaseous mercury (V_{dg}) is typically governed by three factors, namely, turbulent diffusive transport in the atmosphere, molecular diffusive transport through the quasi-laminar sub-layer at the ground surface and uptake by the surface or vegetation. Since Gaseous Elemental Mercury (GEM) is relatively inert, it is likely that GEM does not deposit at the ground surface or with a V_{dg} of less than 0.03 cm/s [28], although uptake by surfaces (e.g., water, vegetation), controlled by Henry's law might be significant. However, as mentioned below, aquatic and marine studies have demonstrated that the large majority of aquatic ecosystems have been found to contain dissolved gaseous mercury at concentration which are supersaturated relative to the equilibrium values predicted by Henry's law. Therefore, GEM evasion at the water-air interface is a major feature of the global mercury cycle [8]. Reactive gaseous mercury (RGM), expected to represent mainly $HgCl_2$, is assumed to be readily taken up by vegetation surfaces and deposited rapidly, with a deposition velocity (V_{dg}) that approaches the maximum rate possible by turbulence, similar to the atmospheric acids HNO_3 and HCl [28]. The ratio of the molecular diffusivity of $HgCl_2$ and HNO_3 may be estimated from the square roots of their molecular weights [29] as about 0.5. Consequently, the transport resistance through

the quasi-laminar sub-layer is about 75% larger than for HNO_3 [30], leading to an average deposition rate of about 2/3 the value for HNO_3 [28]. The deposition velocity of Particulate Mercury (PM) (V_{dp}) strongly depends on particle size, meteorology (atmospheric stability, relative humidity, and wind speed), and characteristics of the deposition surface. For example, deposition velocities of particles above short vegetation are about 3-5 fold less than above forest [31].

Milford and Davidson [32] compiled size-spectra of trace metals and inferred a mass median diameter (MMD) of $0.61 \mu\text{m}$ for Hg bound to particles, while Keeler *et al.* [33] observed an overall MMD of $0.80 \mu\text{m}$, originating from a bi-modal distribution centred around 0.68 and $3.8 \mu\text{m}$. The coarse mode of particulate mercury was correlated with the total aerosol mass and probably represents adsorption of gaseous mercury onto existing particles. With V_{dp} increasing more than linearly with particle size, the dry deposition flux of the coarse mode was estimated to be 4–5 times the fine PM flux.

Very few field studies account for atmospheric mercury speciation and deposition measurements (e.g., [6,7,34]). Mostly, mercury speciation and deposition are derived from modelling or/and surrogate estimation.

4.3 Rain scavenging

Wet removal of air pollutants from the atmosphere is significant (e.g., [35]) particularly for mercury (e.g., [36-39]). More precisely, wet scavenging and deposition of atmospheric mercury involves processes in both the gaseous and particulate phases.

Washout as well as rainout might be involved in the mercury scavenging process. The mercury concentration in precipitation is several orders of magnitude greater than that predicted by Henry's Law. Oxidation of elemental mercury (Hg^0) by ozone to a more soluble oxidation state (Hg II) followed by sorption mechanisms within the droplets might operate [14,37]. Particle-phase mercury might come from the adsorption of mercury onto soot particles within the droplets [40] as well as from the scavenging of atmospheric particles bearing Hg [38].

Mercury scavenging and deposition in precipitation are complex due to the physical mechanism involved, the volatility of mercury, its chemical speciation and reactivity (e.g., [41]).

Assuming an annual mean Hg^0 air concentration of 1.5 ng/m^3 and an annual average air temperature of $10 \text{ }^\circ\text{C}$, the concentration of the truly dissolved mercury should be around 0.02 ng/L . Hence, this suggests that less than 0.5 % of the total dissolved phase mercury is truly dissolved elemental mercury (Hg^0) whereas most of the « dissolved » mercury in precipitation, namely the « operationally-defined dissolved phase » (i.e., $< 0.45 \mu\text{m}$), is in colloidal particle form or in molecular complexes. As a whole, mercury wet deposition involves more colloids and molecular complexes than large particles. Mercury concentrations in precipitation are typically $\sim 3 - 15 \text{ ng/L}$.

4.4 Mercury gas exchanges

Until recently, mercury fluxes were quantified by estimations using mathematical models or by measuring the mercury accumulation in biological, soil and sediment samples. It is only in the last few years that technical improvements allowed a more or less direct measurement of mercury fluxes between air/soil and air/water compartments. Some of those methods are the micrometeorological techniques (such as the modified Bowen Ratio) and the dynamic flux chamber, which are simple and relatively reliable techniques.

4.4.1 Soil-air

Mercury fluxes have been measured in various locations in North America using both techniques coupled with an automatic mercury vapour phase analyser (namely, Tekran[®]). As a whole soil surface acted primarily as a source of atmospheric mercury, the most significant parameters correlated with soil-air Hg fluxes were turbulence and air temperature.

The temperature dependence of Hg fluxes over the soil surface is clearly shown by using the Arrhenius equation (Eq. 4),

$$k = A e^{-E_a/RT}, \quad (4)$$

where, k is the flux of Hg, R is the gas constant, temperature (T) is in degrees Kelvin, A is the preexponential factor and E_a is the activation energy.

4.4.2 Water-air

Transport of mercury from water bodies to the atmosphere (volatilisation) or atmospheric deposition are significant components for mercury budgets in lakes and rivers. Aquatic and marine studies have demonstrated that *in situ* synthesis of volatile Hg and its subsequent evasion at the water-air interface are major features of the global Hg cycle. Elemental mercury (Hg^0) and dimethylmercury are the most volatile mercury forms. In general, the dissolved gaseous mercury (DGM) fraction in lake water consists principally of Hg^0 , with no or few significant contribution from volatile organic Hg species. In-lake biological and chemical processes for Hg^0 and methyl Hg compete for the reactive Hg. Hg (II) is methylated and accumulates in the food chain. Once Hg^0 is produced in the aqueous phase, it is more or less unreactive but when the level exceeds saturation it is lost from the system. The large majority of aquatic ecosystems studied so far have been found to contain dissolved gaseous mercury at concentrations that are supersaturated relative to the equilibrium values predicted by Henry's law. Evasion of elemental mercury was suggested to occur over ocean and from inland waters but was only measured directly in a few cases. A few instances of net deposition were observed with flux chamber studies over inland waters.

From many field observations, the most significant parameter correlated with water-air Hg

fluxes was solar radiation suggesting photoreduction as an important aquatic process in the mercury water-air gas exchange.

4.4.2.1 Modelling approach: The mercury flux (F_m) across the water surface may be parameterised using a two-layer model (Eq. 5). The two-layer model is a convenient but not necessarily a mechanistically accurate model, which depends on empirical relationships reported for other chemicals. There are two main conditions required to apply the model: (1) the chemical does not undergo any reaction within the layers, and (2) the concentrations at the boundaries of the layers are kept constant long enough that the concentration profile reaches a steady state.

The model [42] is as follows:

$$F_m = K_{ol} (C_w - C_a RT/H) \quad (5)$$

where H is the Henry's Law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}$), C_a (ng/m^3) the mercury air concentration (GEM), C_w (ng/m^3) the dissolved mercury concentration (DGM) and K_{ol} is the overall mass transfer coefficient (m/h). R is the ideal gas law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$), and T is the temperature at the water-air interface (K°).

K_{ol} can be further broken down as (Eq. 6):

$$1/K_{ol} = 1/K_w + RT/HK_a \quad (6)$$

where, K_a and K_w are respectively the air and water mass transfer coefficients.

Since the Henry's Law for mercury is high ($H = 0.29$ or $729 \text{ Pa m}^3/\text{mol}$), most of the resistance to gas exchange lies in the water film ($> 99\%$). Hence, K_{ol} is expressed as K_w (after unit transformation).

The mass transfer coefficient (K_w) (cm/h) of Hg through the water layer can be correlated with the mass transfer of CO_2 across the interface as:

$$K_w \sim (0.45 U_{10}^{1.64}) [\text{Sc}_w(\text{Hg})/\text{Sc}_w(\text{CO}_2)]^{-0.5} \quad (7)$$

where U_{10} is wind speed at 10 m (m/s). This relationship is based on experiments with SF_6 , a volatile compound with dominant resistance to transfer through the water film and is normalised to the appropriate Schmidt number (Sc) for CO_2 and Hg in water.

It has been demonstrated by Poissant *et al.* [43] that Hg fluxes under supersaturation conditions were driven (modulated) by K_w and not by the degree of saturation.

4.5 Aquatic chemistry

Mercury in aquatic systems includes the study of freshwater ecosystems and marine environment. For these two compartments, a detailed description about the incorporation processes and about the behaviour of this pollutant will be given. The mercury cycle in aquatic

systems is summarised in Figure 7.

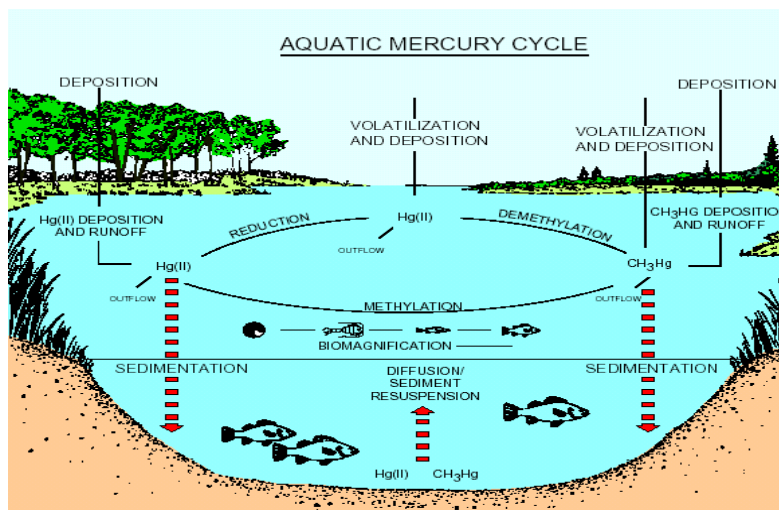


Figure 7. Mercury cycling pathways in aquatic environments are very complex. The various forms of mercury can be converted from one to the next; most important is the conversion to methylmercury (CH₃Hg⁺), the most toxic form. Ultimately, mercury ends up in the sediments, fish and wildlife, or evades back to the atmosphere by volatilisation. (from Lewis Publishers, an imprint of CRC Press).

4.5.1 Freshwater ecosystem

There are three main pathways by which mercury can enter the freshwater environment. Atmospheric deposition, by both wet and dry processes, of Hg (II) and methylmercury can directly enter water reservoirs. Runoff can be also a pathway for Hg (II) and methylmercury introduction in water bodies, especially bound to suspended soil/humus or adsorbed to dissolved organic carbon. At last, leaching of groundwater flow in the upper soil layers can be a source of Hg (II) and methylmercury in the freshwater ecosystems.

In freshwater reservoirs, mercury species will be mainly bounded to organic matter (from ~25% to ~60 %), as for example fulvic and humic acids, carbohydrates, carboxylic acids, amino acids and hydrocarbons [41]. Common measured mercury concentrations in surface fresh water range from 0.04-74 ng/L for lakes and 1-7 ng/L for rivers and streams [44] and 0.3-25 ng/L for drinking tap water in USA. Total mercury in lake waters are lower than the levels found in precipitation.

Once introduced in water reservoirs, mercury can be lost through drainage water, revolatilised to the atmosphere, stored in sediments or accumulated into the food chain. Methylmercury can represent up to 10 % of total mercury in freshwater bodies. These toxic compounds can be formed in the water column by both microbial action and abiotic processes. This is the first step for mercury introduction into the food chain [45]. Bioconcentration factors

for accumulation of methylmercury (nearly 100% of mercury is methylmercury in fish

can reach values up to 10^5 - 10^6 in fish [46].

Bacterial methylation rates increase when anaerobic conditions, low pH and high temperatures [44,47]. Hg^0 can be produced in the water by humic acid reduction or demethylation of methylmercury under sunlight. This elemental mercury can remain in the dissolved phase or volatilize. The main pathway for mercury removal from water is sedimentation of Hg (II) and methylmercury bound to particulate matter [48]. Total mercury concentrations tend to increase in lake waters especially in Canada and Northern countries. It has been shown that total mercury concentration increases when the pH of water decreases and when organic matter concentration in water increases.

4.5.2 Marine Environment

Marine environments can be divided into three reservoirs: coastal zones, areas of upwelling and open oceans. The open oceans, upwelling regions and coastal zones represent up to 90 %, 10% and ~0.1 % of the total area of the oceans respectively. Ocean waters and ocean sediments represent the largest reservoir of mercury on the planet even if mercury concentrations can range from undetectable to over 1 $\mu\text{g/L}$ [49].

In these three compartments, elemental mercury is deposited to the ocean waters by wet deposition. These precipitations allow the deposition of oxidised form of mercury produced in the clouds in the frame of complex oxidating chemistry. Mercury in ocean waters and specifically coastal zones can originate from riverine systems. Mercury upwelling can be a significant source to open oceans.

In the upper layers of the ocean, reactive mercury can be transported through attachment to particles to areas where oxygen content is lower and then can be methylated. Monomethylmercury is then produced in these anoxic regions (called mixed layer) below the thermocline (< 100 m above the surface) where it can be incorporated into the food chain [50-51]. The methylation rate appears to be correlated with the primary productivity [51]. In the subthermocline waters, reactive mercury can both form monomethylmercury and dimethylmercury under biotic factors. In the upwelling zones, methylmercury is converted in elemental mercury leading to a supersaturation of the elemental species in surface waters. The rate of volatilisation of elemental mercury from open oceans has been evaluated up to 1 % per day [52]. 10 to 30% of the reduction is attributed to abiotic factors, especially with sunlight in presence of fulvic and humic acids. For biotic factors, Mason *et al.* [52] estimate that bacteria and cyanobacteria could be responsible of mercury reduction.

In coastal zones, methylation of mercury can take place both in the water column near the oxycline and in the sediments [53]. The monomethylmercury formed in these places is transported to mixed layer where it can be accumulated in the food chain. This accumulation can be observed in community leaving in sediments and community leaving in the water column such as phytoplankton and zooplankton.

4.5.3 Aquatic ecosystem changes with industrialisation.

During pre-industrial times, Mason *et al.* [8] estimated that rivers injected ~ 60 tons/year to the ocean. Atmospheric deposition of mercury over the oceans represented ~600 tons/year balanced by ~600 tons/year evasion from the oceanic surfaces. The mixed layer of the ocean represented a pool of mercury of about 3,600 tons where 200 tons/year have been transferred to sediments. The current mercury budget in aquatic systems has changed. The mixed layer reservoir of mercury has increased by a factor of 3 while in the same period atmospheric emission have increased by a factor of 5. The mercury transported to deep ocean and the particulate removal has increased by a factor of 3.4. Rolfus and Fitzgerald [53] have concluded that increase in anthropogenic emissions of mercury would result in an increase of mercury deposition, and finally enhanced food chain bioaccumulation and higher concentrations of mercury in marine fish.

4.6 Mercury cycle in snow

The snow-pack is a medium that greatly interacts with a variety of atmospheric gases. Its role in the mercury depletion events in arctic and sub-arctic regions seems to be crucial though it is poorly understood. Furthermore, an understanding of the chemical and physical behaviour of Hg in snow is also required to interpret properly profiles from snow and ice cores [54].

4.6.1 Contamination of arctic regions by Mercury Depletion Events?

Experiments conducted in Arctic and sub-Arctic regions in spring have pointed out the rapid conversion (known as mercury depletion events, see section 4.1.1) of elemental mercury into more reactive forms [25,55]. These reactive forms are rapidly deposited onto snow surfaces resulting with higher mercury content observed in snow collected after mercury depletion events. The fate of deposited mercury is a question of high concern since large quantities of this toxic compound could contaminate water systems during snowmelt and then could enhance mercury levels in Arctic biota. Consequently, native population with a high dietary component of fish and/or sea mammals such as Inuit and Cree Indians in Canada could be particularly exposed to this persistent pollutant.

Before addressing the question of mercury contamination, the fate of the deposited mercury must be elucidated. A part of deposited mercury will certainly be exported to water systems during snowmelt. However some chemical and physical processes that are not really understood, may affect mercury exchanges between snow and atmosphere. Thus the study of Hg behaviour in snow-pack has a predominant role in the understanding of the mercury cycle.

4.6.2 Processes at the origin of mercury exchanges between snow and atmosphere

The snow mantle is a dynamic medium: both physical and chemical processes can alter its chemical composition.

4.6.2.1 Physical processes: Complex processes occur in snow-packs: reactions on snow grains, photochemical reactions, diffusion, sorption and desorption [56]. The snow-pack is subject to temperature changes and air movements that can affect chemical species concentration and transport. Diffusion is thought to be a relatively slow transport process that is constrained by gradients in concentration and temperature. Another physical process, the ventilation, is of advective nature. Ventilation is caused by pressure variations from wind blowing over an uneven surface or from wind turbulence [57]. Ventilation is a phenomenon that increases the rate of chemicals transfer and exposes large part of a snow mantle to chemical exchanges [58].

4.6.2.2 Mercury chemistry in snow: Once deposited onto the surface or incorporated into the snow-pack, a part of Hg could be accumulated in water systems and become available for methylation. However chemical transformations of mercury in snow through redox reactions have become recently evident.

Observations realised by Ferrari *et al.* [59] in Greenland snow before the polar sunrise have shown a rapid decrease with depth of gaseous elemental mercury concentration present in the air of the snow-pack. The consumption of Hg⁰ in the snow mantle could be the result of fast oxidation processes involving strong oxidative agents (e.g. halogen species).

On the other hand, supporting recent observations of atmospheric Hg⁰ production during snowmelt [26], Hg⁰ measurements made in the first centimetres of the snow-pack [60], it appears that mercury could be emitted from the snow-pack. Furthermore, several authors have already pointed out the question of mercury reactivity in snow [61-62]. Photoreduction processes and/or photo-induced reductions of divalent mercury complexes could be the chemical pathways at the origin of Hg⁰ reemission from the snow-pack.

In Kuujuarapik (a sub-arctic site, along the Hudson Bay), such processes may be illustrated by gaseous elemental mercury production in the snow-pack (Figure 8). These measurements show a diurnal cycle of mercury production, with a fast response to light suggesting a process of photochemical origin [63].

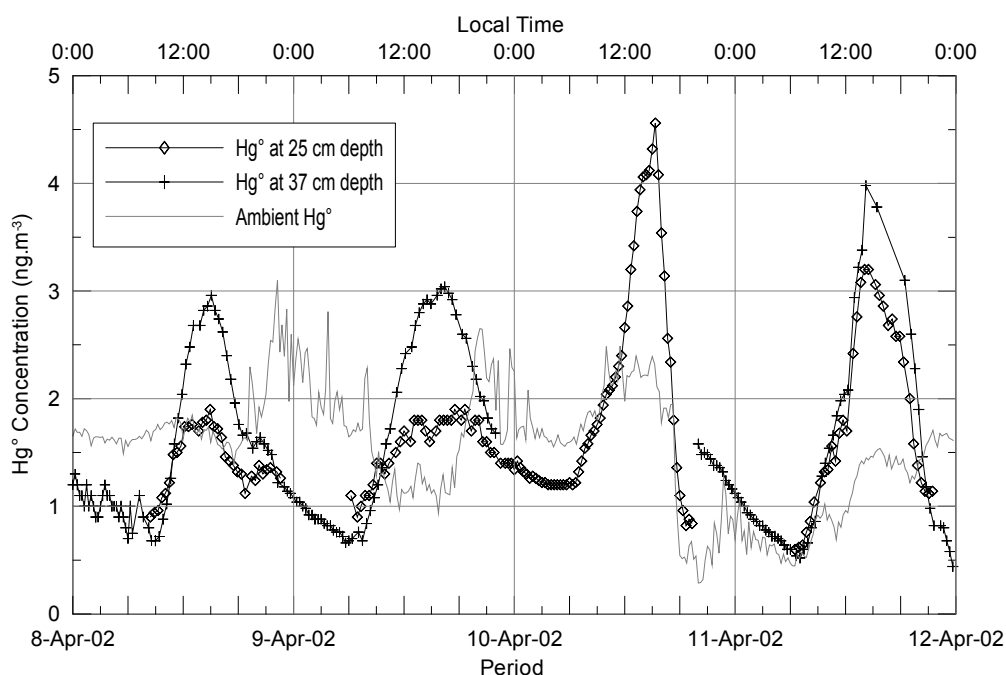


Figure 8: Diurnal cycle of gaseous elemental mercury present in the air of the snow-pack at Kuujjuarapik, Québec in April 2002. Hg° concentration measured at 25 and 37 cm below the snow surface shows higher levels than ambient air during the daytime. The maximum of Hg° production within the snow-pack occurs concurrently with the maximum of irradiation (around 3 PM).

The cryosphere is undoubtedly a major component in the mercury cycle in the environment, but its role is complex and not well known. The snow-pack can collect deposited mercury and can transfer it to water reservoir, acting thus as a sink for atmospheric Hg. On the contrary, we have now evidences that snow-pack is also a source of Hg since Hg° can be released into the atmosphere at the snow-melt and in sunlight-irradiated snow-packs.

4.7 Mercury Cycle in Sediments

Freshwater sediments and ocean sediments particularly constitute a large reservoir of mercury on earth. Moreover, sediments provide unique data of past and present Hg levels and allow the reconstruction of Hg deposition to water bodies.

4.7.1 Mercury incorporation in sediments

Once entering a freshwater system, mercury can remain in the water column or be lost from the water system. The loss occurs through the drainage water, the Hg volatilisation into the atmosphere, the incorporation in the food chain and Hg settling into the sediment [64]. High

affinity of mercury for organic ligands on particles and colloids implies that Hg is easily transported to bed sediments from the water column. Since many organisms live in or are in contact with bed sediments, they may assimilate the bioavailable mercury and consequently expose the whole food chains to this toxic compound. For many lakes, sedimentation of Hg^{2+} and methylmercury bound to particulate matter is a dominant process for removal of Hg from the water column [45]. In a marine environment, owing to the long water mixing cycles, the sedimentation rates are very low, thus the removal of Hg from the water is expected to be slower.

4.7.2 Mercury species and transformations in sediment

Once present in sediments, mercury can undergo physicochemical and biological transformations leading to its accumulation in the sediment or its release to the water body. Additionally, diffusion and advection are some physical processes likely to affect Hg distribution and mobilisation in sediments.

It is often not clear whether HgCl_2 or $\text{Hg}(\text{OH})_2$ organic complexes (more susceptible to methylation) will be the predominant species of mercury, or HgS and HgO (unreactive forms) will predominate [64]. Recently, it has been demonstrated that most of the mercury (85%) present in lake sediments is bound to the NaOH-extractable organic matter [65]. In anoxic sediments, Hg major form is HgS , as cinnabar (red) or metacinnabar (black). Mercury sulphide (HgS) is a stable compounds extremely insoluble that remains unreactive in anoxic conditions. It can adsorb to or co-precipitate with acid sulphide and pyrite. This fraction of mercury is poorly available for uptake by organisms.

In sediment, incorporated divalent mercury can be reduced to elemental mercury (Hg^0) and released back to the water system or it can be involved in methylation-demethylation cycles. Methylated mercury (e.g. monomethylmercury CH_3Hg^+) can also be reduced to Hg^0 or be released into the water reservoir (Figure 9)

Methylation of inorganic mercury species is the key step in the entrance of Hg in the food chains. This process favoured under anoxic conditions in freshwater sediments lead to the formation of a Hg specie bioavailable with the ability to magnify. Indeed, inorganic Hg can be transformed to monomethylmercury through biotic process. The sulphate-reducing bacteria *Desulfovibrio desulfuricans* may be the primary group of organism responsible for this reaction [66]. Mercury bioavailabiliy and its behaviour in sediments depends upon several factors (pH, redox potential and temperature), moreover the geochemical composition (particle size, organic matter content, metal oxide and sulphide contents) and biological factors (feeding behaviour and uptake rate) are parameters affecting the bioavailabiliy of Hg [67].

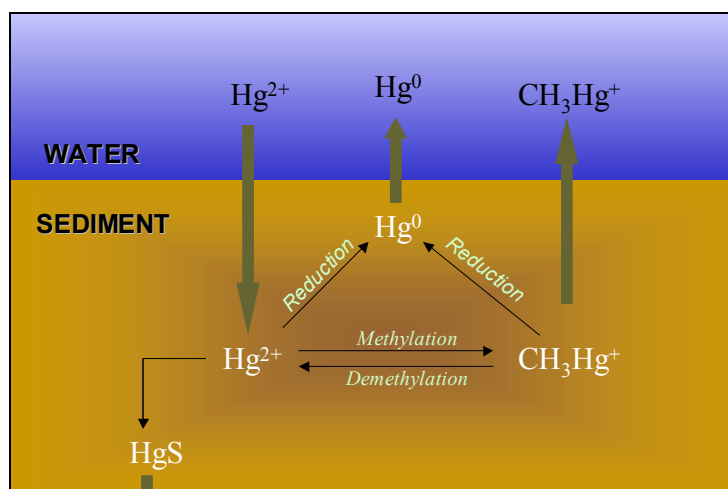


Figure 9: Conceptual diagram of mercury cycling in sediment.

4.7.3 Sediments as an archive of past Hg deposition

Lake sediments constitute an archive of past and present inputs of Hg to a lake. When lake sediments are carefully dated, they provide a recording over long periods of the total mercury concentration. Then, a reconstruction of local and regional trends in Hg deposition to water bodies is possible. For instance, Hg concentration profiles in sediment cores from a natural lake on the Upper Mississippi River record the history of the lake contamination that began with European settlement in the early 1800^s, peaked after the second world war and declined to current levels [68]. Lake-sediment records have also shown that atmospheric Hg deposition could have increased by a factor 3-4 since pre-industrial times [69].

Nevertheless the use of sediments as an archive implies that once sedimented Hg does not undergo migration by remobilization during diagenesis [70]. These chemical, physical, and biological changes that affect sediment after its initial deposition and during and after its slow transformation into sedimentary rock can alter the information contained in the sediment core. In this particular case, the sediment cores do not faithfully reflect atmospheric trends and fluxes in their Hg profiles.

5 INTERNATIONAL REGULATION

Mercury is a global pollutant requiring global initiatives. Its mitigation has to be addressed under a sustainable approach embracing the “Act locally: think globally” paradigm. In that spirit, the Governing Council of the United Nations Environment Programme (UNEP), under the Governing Council decision 21/5, undertakes a global assessment of mercury and mercury compounds, in co-operation with other members of the Inter-Organization Programme for the

Sound Management of Chemicals (IOMC). The Governing Council of the United Nations Environment Programme requests ongoing actions and compile information about future plans at the national, sub-regional or regional levels for controlling releases, and limiting use and exposures, including waste management practices on mercury. It is showed in the *UNEP- Global Mercury Assessment report* that the environmental authorities in many countries consider mercury to be a high-priority substance with recognised adverse effects. They are aware of the potential problems caused by use and release of mercury and mercury compounds, and have found it necessary to protect health and the environment from its adverse effects by implementing measures at national level to limit or prevent certain uses and releases. However, it is also clear that because of mercury's persistence in the environment and the fact that it is transported over long distances by air and water, crossing borders and often accumulating in the food chain far from its original point of release, a number of countries have concluded that national measures might not be fully sufficient. These countries have initiated measures at regional, sub-regional and international level to identify common reduction goals and ensure co-ordinated implementation for international regulation of mercury.

6. CONCLUSION

Mercury has an extremely complex cycle in the environment as presented in this chapter. All the environmental bodies are active for mercury. They can be either a source or a sink of this pollutant. They can be compartments where inorganic mercury can be transformed in organic mercury, directly bioaccumulated in the food chain, leading to toxicological and ecotoxicological effects.

The atmosphere appears to be a key reservoir for mercury transport and deposition to other bodies like oceans, biosphere, and ice caps. As presented in this chapter, mercury has particular physical and chemical properties. It is a really volatile metal, and its volatilisation is directly connected to temperature conditions. Global warming is a subject of major concern since a decade. The climate scientific community agrees to say that in the next century the global temperature of the atmosphere would probably increase from about 1.5 to 4 °C. What would be the result of such an increase on the biogeochemical cycle of mercury? What would be the changes in mercury emission fluxes to the atmosphere from upper layers of the oceans? From soils dramatically contaminated by human activities like in North and South America? This global warming might have also consequences on the water cycle and especially the cloud cover. What would be the changes in mercury atmospheric chemistry in clouds?

This global warming might have also consequences on seasonal snow precipitation (intensity and duration). What would be the result of this evolution on mercury chemistry in polar places and the transfer of mercury to ecosystems when snowmelt?

This question of the relation between global warming and mercury cycle appears to be a new and exciting field of research for the mercury community.

Acknowledgements

We would like to thank the Consulat de France in Québec and especially M. Alain Péguy for its help for North Canada Arctic Research and exchanges between French and Québec teams. LP would like to thank the St. Lawrence Action Plan (Environment Canada) and the Northern Contaminant Programme (Department of Indian Affairs and Northern Development) for their financial support. Special thanks to Martin Pilote (research assistant) for his wonderful field and laboratory research support, Dr. A Richter, University of Bremen, Germany, for the Gome BrO mapping and Pr C. Boutron and Dr C. Ferrari for their invitation for the oral presentation during ERCA 2002. AD & CF would like to thank the French polar institute, Paul Emile Victor Institute (I.P.E.V.) for its financial support (Program CHIMERPOL n°399) for the Arctic expeditions and researches on mercury. Great thanks also addressed to our partners, the Royal Danish Air Force (R.D.A.F.) and especially John Lau Hansen, Arctic coordinator, the crew of Station Nord, Greenland (Jakob O. Larsen, Thomas A. Iversen, Asger Mathiesen, Martin R. Arvensen and Dennis P. Christensen), the National Environmental Research Institute (N.E.R.I.) from Roskilde (Denmark), the Agence de l'Environnement et de la Maîtrise de l'Energie (A.D.E.M.E.) and finally the French Ministry of the Environment.

References

- [1] Imura N., Sukegawa E., Pan S.K., Nagao, K., Kim J.Y., Kwan T., Ukita T., *Science*, **172** (1971) 1248–1249.
- [2] Nriagu J.O., *Nature* **338** (1989) 47-49.
- [3] Pirrone N., Keeler G., and Nriagu J.O., *Atmos. Environ.* **30** (1996) 2981-2987.
- [4] Olmez I. and Ames M.R., *Pure Appl. Chem.* **69** (1997) 35-40.
- [5] Slemr F., Seiler W. and Schuster G. J., *Atmos. Chem.* **3** (1985) 407-434
- [6] Johnson D.L. and Braman, R.S., *Environ. Sci. Technol.* **8** (1974) 996-1003.
- [7] Lindberg S.E. and Stratton W.J., *Environ. Sci. Technol.* **32** (1998) 49-57.
- [8] Mason R.P., Fitzgerald W.F. and Morel F.M.M., *Geochim. Cosmochim Acta* **58** (1994) 3191-3198.
- [9] Ariya P.A., Khalizov A. and Gidas A., *J. Phys. Chem. A.* **106** (2002) 7310-7320.
- [10] Lin C.J. and Pehkonen S.O., *Atmos. Environ.* **33** (1999) 2067-2079.
- [11] Sommar J., Atmospheric chemistry of mercury: kinetics, mechanisms and speciation 1997 Department of inorganic chemistry, Göteborg University, Chalmers, Sweden, report OOK 97:01.
- [12] Seigneur C., Wrobel J. and Constantinou E., *Environ. Sci. Technol.* **28** (1994) 1589-1597.
- [13] Schroeder W.H., Yarwood G. and Niki H., *Water Air Soil Pollut.* **56** (1991) 653-666.
- [14] Munthe J., *Atmos. Environ.* **26A** (1992) 1461-1468.
- [15] Hall B., *Water Air Soil Pollut.* **80** (1995) 301-315.

- [16] Lin C.J. and Penkonen S.O., *Atmos Environ.* **31** (1997) 4125-4137.
- [17] Kobayashi T., *J. Japan Soc. Air Pollut.* **22** (1987) 230-236.
- [18] Impey G.A., Shepson P.B., Hastie D.R., Barrie L.A. and Anlauf K.G., *J. Geophys. Res.* **102D** (1997) 16005-16010.
- [19] Menke R. and Wallis G., *Am. Ind. Hyg. Assoc. J.* **41** (1980) 120-124.
- [20] Lui P.Y., Rasmussen P.E., Roussel P.B. and Lin X., A study of the atmospheric transport, transformation and deposition of mercury 1994, Canadian Electrical Association, report No. 9237G950.
- [21] Sommar J., Hallquist M., Ljungström E. and Lindqvist O., *J. Atmos. Chem.* **27** (1997) 233- 247.
- [22] Brosset C., *Water Air Soil Pollut.* **34** (1987) 145-166.
- [23] Munthe J. and McElroy W.J., *Atmos. Environ.* **26A** (1992) 553-557.
- [24] Xiao Z.F., Strömberg D. and Lindqvist O., *Water Air Soil Pollut.* **80** (1995) 789-198.
- [25] Schroeder W.H., Anlauf K.G., Barrie L.A., Lu J.Y., Steffen A., Schneeberger D.R. and Berg T., *Nature* **394** (1998) 331-332.
- [26] Lindberg S.E., Brooks S., Lin C.-J., Scott K., Meyers T., Chambers L., Landis M., and Stevens R., *Water Air Soil Pollut.* **5-6** (2001) 295-302.
- [27] Lindberg S.E., Brooks S., Lin C.-J., Scott K.J., Landis M.S., Stevens R.K., Goodsite M., Richter A., *Environ. Sci. Technol.* **36** (2002) 1245-1256.
- [28] Lee D.S., Nemitz E., Fowler D., Hill P., Clegg S. and Kingdon R.D., Sources, Sinks and Levels of Atmospheric Mercury in the UK, Defense Evaluation and Research Agency, report DERA/AS/PTD/CR000114, August 2000, 133 p.
- [29] Wesley, M. L., *Atmos. Environ.* **23** (1989) 1293-1304.
- [30] Garland J.A., The dry deposition of sulphur dioxide to land and water surfaces. Proceedings of the Royal Society of London A 354 (1977) pp. 245-268.
- [31] Caffrey P.F., Ondov J.M., Zufall M.J. and Davidson C.I., *Environ. Sci. Technol.* **32** (1998) 1615-1622.
- [32] Milford J.B. and Davidson C.I., *J. Air Pollut. Control Assoc.* **35** (1985) 1249-1260.
- [33] Keeler G.J., Glinsorn G. and Pirrone N., *Water Air Soil Pollut.* **80** (1995) 159-168.
- [34] Malcolm E.G. and Keeler G.J. *Environ. Sci. Technol.* **36** (2002) 2815-2821.
- [35] Poissant L., Schmit J.P. and Béron P., *Atmos. Environ.* **28** (1994) 339-346.
- [36] Lindqvist O. and Rhode H., *Tellus* **37B** (1985) 136-159.
- [37] Iverfeldt A., *Water Air Soil Pollut.* **56** (1991) 251-265.
- [38] Lamborg C.H., Fitzgerald W.F., Vandal G.M. and Rolffhus K.R., *Water Air Soil Pollut.* **80**, (1995) 189-198.
- [39] Burke J., Hoyer M., Keeler G. and Scherbatskoy T., *Water Air Soil Pollut.* **80** (1995) 353-362.
- [40] Petersen G., Iverfeldt A. and Munthe J., *Atmos. Environ.* **29** (1995) 47-67.
- [41] Lindqvist O., Johansson K., Aastrup M., Anderson A., Bringmark L., Hovenius G., Hakanson L., Iverfeldt A., Meili M., and Timm B., *Water Air Soil Pollut.* **55** (1991) 1-261.

- [42] Liss P.S. and Slater P.G., *Nature* **247** (1974) 181-184.
- [43] Poissant L., Amyot M., Pilote M. and Lean D.R.S., *Environ. Sci. Technol.* **34** (2000) 3069- 3078.
- [44] New Jersey Department for Environmental Protection and Agency. Final report on Municipal Solid Waste incineration. Volume II: Environmental and Health Issues 1993.
- [45] Sorensen J.A., Glass G.E., Schmidt K.W., Huber J.K. and Rapp J.G.R., *Environ. Sci. Technol.* **24** (1990) 1716-1727.
- [46] Bloom N.S., *Can. J. Fisher. Aq. Sci.* **49** (1992) 1010-1017.
- [47] Winfrey M.R. and Rudd J.W.M., *Environ. Toxicol. Chem.* **9** (1990) 853-869.
- [48] Fitzgerald W.F. and Clarkson T.W., *Envir. Health Perspec.* **96** (1991) 159-166.
- [49] Nriagu J.O., *The Biogeochemistry of Mercury in the Environment*. Elsevier/North Holland. Biomedical Press : New York (1979).
- [50] Mason R. and Fitzgerald W., *Deep Sea Res.* **40(9)** (1993) 1897-1924.
- [51] Mason R. and Fitzgerald W., Sources, Sinks and Biogeochemical Cycling of Mercury in the Ocean. In *Global and Regional Mercury Cycles : Sources, Fluxes and Mass Balances*. Edited by : W. Bayesens, R Ebinghaus, and O. Vasiliev. Kluwer Academic publishers (1996), (Netherlands), 249-272.
- [52] Mason R., Fitzgerald W. and Egmond H., *Water Air Soil Pollu.* **80** (1995) 775-787.
- [53] Rolfus K. and Fitzgerald W., *Water Air Soil Pollu.* **80** (1995) 291-297.
- [54] Boutron C.F., Vandal G.M., Fitzgerald W.F. and Ferrari C.P., *Geophys. Res. Lett.* **25** (1998) 3315-3318.
- [55] Poissant L., 2001. Atmospheric mercury transport, oxidation and fallout in northern Québec (Nunavik) : an important potential route of contamination. pp. 125-129: Northern Contaminants Program, Synopsis of Research 2000-2001, Indian and Northern Affairs Canada.
- [56] Dominé F. and Shepson P.B., *Science* **297** (2002) 1506-1510.
- [57] Colbeck S.C., *J. Glaciol.* **35** (1989) 209-213.
- [58] Albert M.A. and Shultz E.F., *Atmos. Environ.* **36** (2002) 2789-2797.
- [59] Ferrari C.P., Dommergue A. and Boutron C.F., *J. Geophys. Res.* (2002) submitted.
- [60] Steffen A., Schroeder W.H., Bottenheim J., Narayana J. and Fuentes J.D., *Atmos. Environ.* **36** (2002) 2653-2661.
- [61] Ferrari C.P., Dommergue A., Veysseyre A. Planchon F. and Boutron C.F., *Sci. Total Environ.* **287** (2002) 61-69.
- [62] Lalonde J.D., Poulain A.J. and Amyot M., *Environ. Sci. Technol.* **36** (2002) 174 -178.
- [63] Dommergue A., Ferrari C.P. Poissant L. and Boutron C.F., *Environ. Sci. Technol.* (2003) 37, 10.1021/es026242b..
- [64] United States Environmental Protection Agency, Mercury Study Report to Congress. EPA-425/R-97-003, Office of Air Quality Planning and Standards, Office of Research and Development, US Government Printing Office, Washington, DC, December 1997.
- [65] Dmytriw R., Mucci A., Lucotte M. and Pichet P. *Water Air Soil Pollu.* **80** (1995) 1099-

1103.

- [66] Compeau G.C. and Bartha R., *Appl. Environ. Microbiol.* **50** (1985) 498-502.
- [67] Canadian Council of Ministers of the Environment, Canadian sediment quality guidelines for the protection of aquatic life: Mercury. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- [68] Balogh S.J., Engstrom D.R., Almendinger J.E., Meyer, J.L. and Johnson, D.K., *Environ. Sci. Technol.* **33** (1999) 3297-3302.
- [69] Swain E.B., Engstrom D.R., Brigham M.E., Henning T.A. and Brezonik P.L., *Science* **257** (1992) 784-787.
- [70] Gobeil C., Macdonald R.W. and Smith B., *Environ. Sci. Technol.* **33** (1999) 4194-4198.