Atmospheric and catchment mercury concentrations and fluxes in Fennoscandia

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Preface

The Nordic countries have played an important role in raising international awareness about contamination of remote ecosystems by mercury by supporting research efforts on emissions, long range transport and biogeochemical cycling of this toxic element. The Nordic countries have also made significant efforts to reduce the use and the environmental emissions of mercury thus providing a good example on the international scene. Research initiated in the Nordic countries has supported the establishment of international agreements on atmospheric mercury within the UN ECE Convention for Long-Range Transboundary Air Pollution (CLRTAP) as well as European Union directives. The Nordic countries have also contributed significantly to research focussed on mercury in the Arctic environment and not least to the on-going work with preparation of the Arctic Monitoring and Assessment Program (AMAP) mercury assessment report.

The Nordic countries have also made significant efforts to establish a procedure for negotiation of a global treaty on mercury within UNEP Chemicals. This process formally started in June 2010 with the first meeting of the International Negotiation Committee. The negotiations are in an early stage, and many more meetings will take place over the coming years, but the final goal is to establish a global agreement on reducing mercury use and emissions within a few years.

This report contains several examples of monitoring and research activities which provide important input to the on-going assessments and negotiations. It covers several different areas including trends and geographical patterns of atmospheric mercury, the cycling of mercury in terrestrial ecosystems and the complex behaviour of mercury in the Arctic atmosphere.

Environmental contamination of mercury can be significantly reduced by controlling use and emissions from a number of different sources. Different strategies to achieve this are the focus of the discussions in the on-going UNEP process. Research and environmental monitoring is needed to follow up the effects of emission reductions and to increase our understanding of the environmental pathways of mercury and can thus provide input to further development of strategies to reduce the environmental impacts.

Ingvar Wängberg (PhD)

Project leader

Summary

Measurements in Southern Fennoscandia show a weak declining trend in mercury deposition which can be attributed to reduction controls in EU countries. Deposition of mercury in Arctic areas is likely to be governed by the amount of mercury in background air and therefore largely dependent on mercury emissions from mercury sources in the northern hemisphere. As a consequence of reduced mercury from European sources concentrations of gaseous elemental mercury (Hg^0) in Northern Europe is also to a much larger degree than before governed by the background level of mercury. This is consistent with mercury being a global pollutant. Hence, further reduction in anthropogenic emissions of mercury will also require control measures on a global scale.

The so called atmospheric mercury depletion events (AMDE's) are occurring during polar spring. During AMDE mercury is rapidly oxidised and deposited on snow and ice and thereby constituting a source of mercury to the vulnerable Arctic environment. However, a significant part of the freshly deposited mercury may be reduced to the elemental form and be re-emitted back to the atmosphere. How much of the deposited mercury that remains contra is re-emitted to the atmosphere is crucial for assessing the importance of AMDE in the Arctic environment.

Mercury deposited to boreal forest areas tend to accumulate in forest soils. Part of the mercury is re-emitted back to the atmosphere as a course of reduction mechanisms in the soil. Forest fires also constitute a source of mercury. When the soil is heated a great part of the accumulated mercury is re-emitted as Hg^0 and hence recycled back to the atmosphere. The re-emission fluxes from forest fires are small in comparison to anthropogenic mercury emissions from the Fennoscandian countries, but cannot be ignored in the global mercury cycle.

Forest soils are an important sink for mercury deposited from the atmosphere. This sink can be affected by perturbations which lead to a mobilization of the stored mercury. Forestry practices which cause changes in the soil water table and may damage soil structures can lead to increased leaching of MeHg and TotHg via both increased run off and (for MeHg) by creating conditions suitable for methylation of mercury. Similar effects can be expected in areas where climate change results in large increases in precipitation amounts. The processes governing these changes in mobilization are to some extent unknown and general predictions of the magnitude of the changes are thus associated with a large degree of uncertainty.

1. Introduction

One of the most specific properties of mercury regarding environmental concerns is its ability to appear as a diluted gas in the atmosphere. Both anthropogenic and natural mercury emissions constitute to the most part of Hg^0 , gaseous elemental mercury (GEM). The atmospheric residence time of mercury has been estimated to be around 0.7–1.4 year (Schroeder and Munthe, 1995; Selin et al., 2007 and references therein) which is long enough for distribution on hemispherical scales before it eventually is oxidised and deposited to ground and water surfaces (Schroeder and Munthe, 1998). According to measurements GEM appears to be fairly uniformly distributed with concentrations of around 1.7 ng m^{-3} in the northern hemisphere and 1.3 ng m^{-3} in the south (Slemr et al., 2003). The higher values in the north are consistent with major mercury sources being predominately located in the northern hemisphere. This makes mercury a global pollutant in contrast to other heavy metals that have more local or regional impact. GEM is only, to a small extent, dry deposited to ground and vegetation or taken up in cloud water and removed from the atmosphere via wet deposition. On the other hand, mercury is slowly oxidised in the atmosphere forming divalent mercury species (Hg(II)) which are more easily dry deposited and also prone to wet deposition. Divalent mercury is found in the gas phase as well as in rainwater and snow. The exact chemical compositions of these oxidation products are not yet known, however. The gaseous fraction of oxidised mercury is referred to as Reactive Gaseous Mercury (RGM) or Gaseous Oxidised Mercury (GOM). RGM is operationally defined, as the fraction of gaseous mercury that can be sampled using a certain measurement method. Although not yet proven, it is likely that RGM is constituted of species like HgBr_2 , HgCl_2 or mixed halides and related compounds. Total Gaseous Mercury (TGM) is another operational defined mercury fraction. It 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. Although there are exceptions, TGM and GEM are often equal within a few percent. Mercury is also found in aerosols. Particles emitted from coal fired power plants, for example, 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 ($< 2.5 \mu\text{m}$ particle size) is sampled it is sometimes denoted Fine Particulate Mercury (FPM).

As an effect of photolytically initiated biotic or abiotic processes oxidised mercury may be reduced back to its elemental state. Due to this phenomenon, sea and lake surface water tend to be supersaturated with Hg^0 and as a consequence mercury can be re-emitted back to the atmosphere. Similar processes also occur on terrestrial surfaces; hence a significant part of the mercury once deposited on ground and vegetation as well as on snow and ice tends to return to the atmosphere. This promotes atmospheric transport of mercury and makes environmental cycling of mercury even more complicated. Early studies in boreal regions have showed the importance of the terrestrial environment as a significant mercury source in the global mercury cycle (Schroeder et al., 1989; Mason et al., 1994; Carpi and Lindberg, 1997). Today, it is estimated that as much as 80% of the mercury that is deposited on the terrestrial surface is re-emitted back to the atmosphere through surface emission (Grigal, 2002). Mercury emission from the terrestrial surface occurs as a result of natural and anthropogenic-related atmospheric deposition and soil/surface mercury enrichment (Gustin et al., 2000).

The Arctic is believed to be a global sink of mercury due to a set of extraordinary circumstances occurring during Polar spring where GEM is rapidly transformed following sudden depletion in the atmosphere (Steffen et al., 2008 and references therein). This phenomenon, termed atmospheric mercury depletion event (AMDE), is a circum polar phenomenon. During AMDE's, GEM is rapidly oxidised by halogen radicals through a chain of photochemical and heterogeneous processes leading to formation of RGM and PHg which in turn are quickly lost from the atmosphere resulting in large seasonal deposition fluxes of Hg onto snow and ice surfaces (e.g., Lindberg et al., 2002; Steffen et al., 2008). AMDE's are only reported during polar spring in association with sea ice, and research today commonly agree that refreezing ice in open leads provides a halogen source that drives the AMDE chemistry (Lindberg et al., 2002, Kaleschke et al., 2004, Simpson et al., 2007). It is estimated that AMDE's can lead to deposition fluxes up to 300 tons pr year to the Arctic (Ariya et al., 2004, Skov et al., 2004).

The major environmental concern regarding anthropogenic emissions of mercury is enrichment of the metal in for example forested ecosystems and the risk of methyl mercury (MeHg) formation and subsequent uptake into the food chain. Recently Munthe et al. (2007) provided a comprehensive compilation and assessment of available data on mercury in air, precipitation, sediments and fish in Fennoscandia with the focus on lake sediments and fish. The main conclusion was that mercury levels in Nordic ecosystems continue to be affected by long-range atmospheric transport, but the geographical patterns of mercury concentrations in both sediments and fish are strongly affected by ecosystem characteristics and by historical pollution.

The evaluation of mercury in precipitation clearly showed that long-range transport from European sources continued to deliver mercury to Nordic ecosystems. The data on air concentrations, however, suggested that

sources on the hemispheric scale also contributed to the long-range transport (Munthe et al. 2007).

This paper presents the results from the continued and enlarged monitoring of mercury in air and in precipitation with the evaluation of the AMDE phenomenon and re-emission from forest floor. The paper also presents an overview of catchment mercury studies trying to quantify the mass balances of mercury in catchments as well as the effect of environmental characteristic and human activities determining the output fluxes of mercury and methyl mercury (MeHg) from the catchments to receiving surface waters.

Abbreviations used in text:

- AMDE: Atmospheric mercury depletion event is a phenomenon encountered at some Arctic and Antarctic sites during springtime. Due to the action of halogen chemistry may elemental mercury entirely or partly be oxidised and depleted from the atmosphere.
- EBAS: Is a database hosting observation data of atmospheric chemical composition and physical properties. EBAS is developed and operated by the Norwegian Institute for Air Research (NILU). [<http://ebas.nilu.no/>].
- GEM: Gaseous elemental mercury (Hg^0). This specie is the principal form of mercury in the atmosphere often contributing to more than 98%.
- MeHg: Mono-methyl mercury, $\text{CH}_3\text{-Hg}^+$ which is one of the most poisonous mercury species. MeHg bound to various ligands is the mercury form that undergoes bioaccumulation.
- RGM: Reactive gaseous mercury also denoted gaseous oxidised mercury (GOM) is believed to consist of divalent mercury species HgX_2 where X are halogen species like Br and Cl.
- TGM: Total gaseous mercury is an operational defined parameter which is measured when trapping mercury gaseous species from pre-filtered air on gold traps. TGM is often equal to GEM.
- TPM: Total particulate mercury or PHg denotes mercury bound to atmospheric particles.

Units used in the text:

- $\text{pg} = 10^{-12} \text{ g}$, $\text{ng} = 10^{-9} \text{ g}$, $\mu\text{g} = 10^{-6} \text{ g}$, $\text{mg} = 10^{-3} \text{ g}$

2. Air mercury measurements and measurement sites

Sites at which airborne mercury is measured are shown in Figure 1. At most of the sites mercury is measured on a permanent basis within the EMEP and AMAP monitoring network. Whereas at Andøya, Kise and Amderma mercury data from measurement campaigns of 1 to 3 years duration are available, see Table 1. TGM is measured using an automatic method (Tekran 2 537 instruments) with high time resolution at most of the sites except at in Sweden sites, where a manual method is used. Earlier this also was the case in Pallas but since end of 2007, both the manual method and a Tekran instrument is used.

Figure 1. Mercury measurement sites. All sites discussed in the text are shown except the Danish sites, Station Nord and Nuuk on Greenland.

In addition to TGM measurements, mercury in deposition is measured at all German, Swedish and Finnish sites as well as at Lista/Birkenes in Norway. The only Arctic site from which there exists long time series of mercury in precipitation is the Pallas station in Finland. Virolahti and Hyytiälä are two relatively new measurement sites in southern Finland. Automatic TGM

measurements were started at these sites in 2006 and 2008 and mercury deposition measurements in 2008 and 2009, respectively. In order to investigate geographical trends regarding distribution of mercury from European sources data from three sites in Germany and Mace Head on the West coast of Ireland also are evaluated. All data used for analysing total gaseous mercury and mercury deposition trends were obtained from the EBAS – data base [<http://ebas.nilu.no>]. The measurement methods applied from the different measurement sites and the quality of the data have previously been examined in respect to reliability and consistency (Wängberg et al., 2007).

To evaluate AMDE's TGM or GEM data with high temporal resolution is required. Hence, for the purpose of this report, only data from stations that applied continuous measurements using Tekran 2 537, which allows for 5 min time resolution, during at least one spring have been considered. The data was extracted from the EBAS data base. The data covers in total 10 years from January 1, year 2000 to December 31, 2009. For data evaluation 1 hour averages has been used. An overview of stations and data collection periods are given in Table 1. Nord, Ny-Ålesund and Amderma are termed high Arctic locations whereas the remaining sub-Arctic locations. Though Andøya and Amderma are located at the same latitude, only Amderma is termed a high arctic location due to the proximity to sea ice.

Table 1. Overview of Arctic monitoring stations from which TGM data is available

Country	Station	Location	Measurement periods	AMDE year
Denmark	Nord (Greenland)	81°N, 16°W	01.01.00–23.08.00	2000
			14.02.01–23.08.01	2001
			27.04.02–29.06.02	2002
			10.09.08–30.12.08	
Denmark Skov et al., 2004	Nuuk (Greenland)	64°N, 51°W	01.10.01–07.02.02	2003
			01.10.02–01.07.03	2004
			01.04.04–30.06.05	2005
Finland	Pallas	68°N, 24°E	12.12.07–31.12.09	2008, 2009
Norway	Andøya	69°N, 16°E	08.03.04–10.06.05	2004 2005
Norway	Ny-Ålesund (Spitzbergen)	79°N, 12°E	08.02.00–31.12.09	2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009
Russia	Amderma	69°N, 61°E	28.06.01–09.10.02	2002,
			28.02.03–27.12.03	2003,
			03.04.05–20.10.05	2005

The Tekran Gas Phase Mercury Analyser (Model 2537A; Tekran Inc., Toronto, Canada) was used to measure TGM or GEM at all sites in Table 1. Details on the instrumental setup applied at the various sites are reported in Skov et al., 2004 and Skov et al., 2005 (Nord and Nuuk, respectively). Berg et al., 2008 (Andøya). Schallbach et al., 2009 (Kise). Berg et al., 2003 (Ny-Ålesund). Steffen et al., 2005 (Amderma).

3. Results

3.1 Total gaseous mercury in Northern Europe

Yearly average TGM concentrations from five Northern European sites and from Ny-Ålesund are shown in Figure 2. The data covers the period 1995 to 2006 and shows that all values with few exceptions are confined into the relatively narrow range of 1.4–1.9 ng m⁻³. The background concentration of TGM in the Northern Hemisphere was estimated to be around 1.7 ng m⁻³ during the period 1996–2000 with somewhat higher values over the Northern Atlantic Ocean (Slemr et al., 2003). Hence, this indicates that the present TGM values to a large degree reflect the northern hemispheric background concentration of mercury. Earlier TGM was much higher in for example southern Sweden due to the proximity to European mercury sources (Iverfeldt et al., 1995; Wängberg et al., 2007). The highest values are observed at Mace Head and at Lista/Birkenes and during later years also at Råö. Whereas TGM values appears to be slightly lower at especially Pallas and Ny-Ålesund. The reason for this difference is not clear, but the same pattern has been observed earlier and attributed to re-emission from the Atlantic Ocean (Kock et al., 2005).

Figure 2. Yearly average time series of TGM from Ny-Ålesund on Svalbard and five North European sites.

Some average yearly TGM values measured at the Arctic sites Andøya in the Northern Norwegian archipelago and at Amderma on the Arctic Ocean coast in Russia are shown in Table 1 and compared to those at Pallas and Ny-Ålesund. Only one yearly data is available from Andøya covering the period April 2004 to April 2005. The TGM values from Amderma are higher in comparison to both Pallas and Ny-Ålesund and resemble those from Råö and Lista and the early data from Mace Head.

Table 2. Yearly average TGM data from some Arctic sites

Site	2001	2002	2003	2004	2005
Pallas	1.41	1.48	1.57	1.49	1.63
Andøya				1.64	
Amderma	1.68	1.71	1.71		1.66
Ny-Ålesund	1.61	1.63	1.63	1.52	1.61

As shown in Figure 2, TGM values appear to vary more or less randomly from year to year. To investigate temporal trends, four year average TGM values were calculated. Thus, TGM values covering three periods, hereafter referred to as period 1, 2 and 3 are obtained, as shown in Figure 3. The result suggests an increasing trend at some of the investigated sites. The opposite seems, however to be the case at Mace Head and Ny-Ålesund.

Figure 3. Changes in TGM concentrations over time.

3.2 Mercury deposition

Yearly average deposition of mercury from nine North European measurement sites is shown in Figure 4.

Figure 4. Times series of mercury deposition at nine North European measurement sites.

Figure 5. Four year average mercury deposition values, in the text referred to period 1, 2 and 3.

Also in this case temporal trends are investigated by comparing values from three four year periods as shown in Figure 5. The result indicates that mercury deposition is decreasing at most of the investigated sites.

However, since deposition is a result of precipitation amounts times mercury concentration we need to look at these two parameters as well. Let us first compare period 1 and 2. A decrease in deposition at all sites is shown in Figure 5. This occurs simultaneously with decreasing mercury concentration in precipitation and constant or increasing precipitation amounts as shown in Figure 6 and 7, respectively. Hence, the decrease in mercury deposition when comparing period 1 and 2 is due to decreasing concentrations of mercury in precipitation.

Figure 6. Four year average mercury concentration values.

Figure 7. Four year average precipitation amounts.

When comparing period 2 and 3, in Figure 5 it seems like the declining trend is continuing. However, the situation is somewhat more complicated since the precipitation amounts at many of the sites are lower during period 3 in comparison to period 2. At Zingst, Westerland, Vavihill and Lista/Birkenes is the declining trend an effect of a significant decrease in precipitation amounts combined with decreasing mercury concentrations as shown in Figure 6 and 7. Mercury deposition at Evo is also declining, but in this case it is solely an effect of decreasing mercury concentration in precipitation. At Breckälén, the small increase in mercury deposition is only an effect of increased precipitation amounts. At three of the sites, De Zilk, Råö and Pallas mercury concentration in precipitation has increased, but the mercury deposition is hampered by lower precipitation amounts. Both Råö and Pallas are believed to be dominated by background air and the reason for increasing mercury in precipitation at these sites is difficult to explain.

The mercury concentration in precipitation is similar at most of the studied sites. The northernmost sites, Breckälén and Pallas are exceptions to that which presumably is due to their distance to mercury sources in the south. The highest mercury deposition is received at Lista/Birkenes. This is to the most part due to the very high precipitation amounts received there, as is consistent with the relatively low mercury content in precipitation found there, see Figure 6.

3.3 AMDE studies

Time series of GEM concentration values from all Arctic monitoring stations and Kise are displayed in Figure 8. The longest high resolution time series of GEM available in Europe is from Ny-Ålesund and covers almost 10 years of data collection. Continuous GEM measurements have also been performed at other locations, though it should be noted that data from the

other locations do not entirely overlap in time and the time record at the other locations is much shorter than for Ny-Ålesund. At all the high Arctic locations (Ny-Ålesund, Nord and Amderma) the reoccurring spring phenomenon, AMDE, is observed with repeating periods of low concentrations values of GEM. AMDE have been operationally defined to occur when GEM concentration values falls below 1 ng/m^3 (Steffen et al., 2002) as marked in Figure 8 as a horizontal straight line. The remaining locations (Nuuk, Pallas, Kise and Andøya) also observe repeated low GEM concentration values during spring, but to a much less extent.

Figure 8. Time series of GEM concentration values from all Arctic monitoring stations. The black line in each panel at 1 ng/m^3 represents the operationally defined cut-off value for AMDE.

Figure 9. Box and whisker plots of monthly GEM concentration values of data collected at each monitoring station. The middle line in the box represents the median value, whereas the square is the mean value. The boundary of the box closest to zero is the 25th percentile and the boundary farthest from zero is the 75th percentile. The whiskers above and below the box indicate 5 and 95 percentiles and the crosses indicate 1 and 99 percentiles

The box and whisker plots as presented in Figure 9 represent the interquartile range as an estimation of the dispersion of GEM concentration values per month from the different monitoring stations. The high Arctic locations (Ny-Ålesund, Amderma and Nord) exhibit a stronger seasonal modulation as compared to the sub-Arctic locations. The high Arctic locations show a spring depression (March, April and May) followed by a slight increase in summer (June and July) and low variability in fall and winter (October to February). This seasonal modulation is similar to what is observed at Alert, in Canada where the seasonality is even stronger (Steffen et al., 2005). The sub-Arctic locations also show a spring depression but not as pronounced as for the high Arctic locations as is expected for locations with far distance to sea ice.

Figure 10 shows the result from measurements of GEM, RGM and PHg at Ny-Ålesund during the period 2000–2005. GEM was continuously measured during the whole time using an automatic instrument (Tekran 2 537) whereas manual methods were used to measure RGM and PHg. These two mercury fractions were only measured during springtime, when AMDE's were expected to occur. As is shown in Figure 10 elevated concentrations of oxidised mercury (i.e., RGM and PHg) in combination with very low levels of GEM are repeatedly observed each spring time. The highest RGM and PHg values were observed during the AMDE in spring 2003. GEM was almost entirely depleted while RGM and PHg each reached concentrations of approximately 300 pg/m³. But as shown in Figure 10 the concentration of oxidised mercury during most of the depletion events was much lower. The amount of oxidised mercury found during AMDE's at Ny-Ålesund is also lower in comparison to that observed at some other Arctic sites. As dis-

cussed in the next section, observations of low levels of oxidised mercury has been attributed to transport of air masses already depleted from mercury before reaching Ny-Ålesund.

Figure 10. Atmospheric mercury depletion events at Ny-Ålesund, 2000–2005.

3.4 Transport of depleted air masses

The relative distribution of RGM and PHg formed during AMDE's differs between the Arctic locations (Steffen et al., 2008). For instance, at Alert the overall predominant specie in air is PHg (Steffen et al., 2002), whereas in Barrow RGM predominates (Lindberg et al., 2002). In Ny-Ålesund studies have shown that there seem to be no predominance of either specie (Gauchard et al., 2005, Sprovieri et al., 2005). RGM exists in the gas phase but due to its hygroscopic character it is likely to adsorb onto aerosols present in the air (Ariya et al., 2004) to form PHg. Scientists have suggested that the distribution of RGM and PHg is an indication of the age of the air mass. (Lindberg et al., 2002, Sprovieri et al., 2005) while others suggests that the distribution is an indication of local versus transported events (Wängberg et al., 2003, Gauchard et al., 2005). Studies performed in Ny-Ålesund suggests that at this site both local and transport events are observed (Gauchard et al., 2005, Steen et al., 2009).

The following examples show how mercury depleted air masses may be transported to areas where depletion normally is not occurring. Back trajectories were used to study which path the air masses had taken before reaching Ny-Ålesund on May 13, 2004 and Andøya on May 14, 2004. Figure 11 indicates that the air masses prior to enter to the two sites had passed the north coast of Siberia, an area with high BrO activity. GEM likely reacted

with Br/BrO radicals in the Siberian air and the air masses, depleted in respect to mercury, were then transported to Ny-Ålesund and Andøya.

Figure 11. BrO map showing average BrO column 13 May 2004. 7 days air mass trajectory arriving at Zeppelin (500 m.a.s.) 13 May 2004 at 12:00, and 7 days air mass trajectory arriving at Andøya (500 m.a.s.) 14. May 2004 at 12:00 (Source Berg et al., 2008).

At April 25, an AMDE with a duration of several days was observed at Ny-Ålesund. Traces of this AMDE were also observed at Andøya April 27. The air masses originated from far northwest of Ny-Ålesund, but had passed through large areas east and west of Svalbard before reaching Andøya. The BrO map (Figure 12) shows that high activity was observed in the area where the air masses had passed as well as in the Svalbard area. It is likely that the depletion of GEM measured at Ny-Ålesund occurred at Svalbard as a local event. May 15 an AMDE started simultaneously both at Andøya and Svalbard: At Andøya it was short-lived, while it lasted for several days at Ny-Ålesund.

Figure 12. BrO map showing average BrO column 26 April 2005. 7 days air mass trajectory arriving at Zeppelin (500 m.a.s.) 26 April 2005 at 00:00, and 7 days air mass trajectory arriving at Andøya (500 m.a.s.) 27 April 2005 at 18:00. (Berg et al., 2008)

Air masses depleted from mercury have been observed as far south as at Kise as shown in Figure 13 and 14. It should be mentioned that remnants of depletion events observed at Andøya and Kise unlikely lead to enhanced mercury deposition fluxes in these areas due to depletion events, because of the short atmospheric lifetime of oxidized mercury forms. The oxidized mercury is presumably already scavenged from the atmosphere elsewhere before the air masses reach the measurements site. This is likely the case also for Pallas and Nuuk, though a thorough investigation has not been performed.

Figure 13. GEM concentration values from Kise and Ny-Ålesund.

Figure 14. Back trajectories for air masses arriving at Kise, April 21, 2007 (Source Schlach et al., 2009).

Figure 15. Concentrations of Hg (ng g^{-1}) in moss in Norway, year 2000 (Berg et al. 2008).

Total Hg in moss has shown a pronounced tendency toward higher concentrations along the northwest coast of Norway compared to areas farther inland, see Figure 15. Since measurements started in 1985, a trend which appears to be particularly strong in the northernmost area has been discerned (Steinnes et al., 2003; Steinnes and Sjøbakk, 2005). This trend is not due to higher wet deposition along the coast. Measurements of GEM in the same region indicate that this pattern could be due to transport of inorganic Hg from AMDE's to the mainland of Norway (Berg et al., 2008). Coincident measurements of RGM are required before the extent of AMDE Hg contributions to moss can be firmly established. Similar results have not been seen in moss surveys in the other Nordic countries.

3.5 Deposition and re-emission fluxes

3.5.1 Mercury emission from forest floor

Mercury emissions from background forest floor and wetland was studied in Evo natural reserve area in Finland in summer 2007 (Kyllönen et al., 2010). Fluxes were measured at five separate plots by a flux chamber technique coupled with an automatic mercury vapour analyzer. Most of the flux data was collected during daytime. However, diurnal flux behaviour was studied at one site. Airborne TGM was measured during the project to ensure background conditions at the site.

Figure 16. Daytime fluxes in $\text{ng m}^{-2} \text{h}^{-1}$ with air temperatures at the three sites (a, site F1; b, site F2; c, wetland). Flux1 and Flux2 denote sequential measurements while Plot 1–3 denote adjacent experiment plots. A missing bar indicates no flux.

The fluxes varied between -1.0 – $3.5 \text{ ng m}^{-2} \text{h}^{-1}$ at the forest floor sites (see Figure 16) and were mainly positive i.e. Hg was emitted from the forest floor to the air. No flux was detected at some occasions (29% of samples) while negative fluxes were observed rarely (7% of samples). In August, when a majority of the experiments were conducted, an average flux of $0.9 \pm 1.1 \text{ ng m}^{-2} \text{h}^{-1}$ was calculated from the measured values. The measured fluxes are very similar to those in Swedish and Canadian studies (Xiao et al., 1991; Lindberg et al., 1998; Poissant & Casimir, 1998; Schroeder et al., 2005), which could be expected due to similarities in vegetation and latitude.

Fluxes at the verdant forest floor site (F1) were always greater than at the litter-rich site (F2). This is likely to be due to different plot vegetation and differences in solar radiation affecting the chamber plot since the substrate Hg concentration is expected to be fairly consistent in the study area. The F1 site was rich in vegetation of moss while the F2 site was covered with forest litter and much dryer than F1. Xiao et al. (1991) postulated that when the

forest soil is covered with litter, any Hg emanating from the soil might be trapped by litter via direct adsorption or via formation of complexes with humic materials. During the diurnal flux measurements, a clear cycle with afternoon maximum and night minimum was observed.

At the wetland site, the surface acted both as a source and as a sink. However, the fluxes were very small (-0.3 – 0.6 $\text{ng m}^{-2} \text{h}^{-1}$), even though the measurement days at the wetland site were generally warm and sunny. Since the measurements were limited to summer time, the real annual net balance at the site is difficult to quantify. One should note that the measurement occasions partly favoured emission conditions since most of them were conducted during daytime.

As mentioned above, the mercury flux from forest floors has a pronounced diurnal variation which needs to be considered when assessing the importance of this phenomenon in terms of environmental cycling of mercury. In addition, seasonal variations are also likely to be important. During the winter, for example, the snowpack act as a dynamic system that links atmospheric deposition and ecosystem cycling through deposition and emission of deposited mercury. To assess the seasonal behaviour of Hg surface exchange, it is also important to determine the magnitude of the emissions during the non-summer months when the quantity of incoming solar radiation and ambient temperatures are reduced compared to the summer months. This may be of particular importance in Fennoscandia due to the rather short summer season and long winters with snow covered surfaces in large areas.

Figure 17a: Diurnal and seasonal variations in the mercury flux at a open field site in Southern Norway during January to december 2009. Figure 17b: The resulting cumulative mercury flux at the same site.

Continuous surface flux measurements have recently been performed at a forest site at Brekkebygda in Southern Norway applying a flux-gradient method. The flux-gradient approach which measures the turbulent transfer coefficient (K), is based on Monin-Obukov (MO) similarity theory involving near-simultaneous measurements of GEM at two heights above the surface (Edwards et al., 1997; Edwards, 2005). The measurements were performed during 2009 covering all seasons over a full year. Preliminary results from these measurements see Figure 17a–17b, indicates that both diurnal and seasonal variation in the mercury flux is significant and that both deposition and emission of Hg to and from the surface occurs through out the year. Fluxes varied between $-90 \text{ ng m}^{-2} \text{ hour}^{-1}$ and $90 \text{ ng m}^{-2} \text{ hour}^{-1}$. During the whole year diurnal fluxes occur, with a daytime maximum and night time minimum, as also observed in the Finnish study referred to previously in this report. Considering the annual cumulative flux it is evident that a net deposition occurs in the winter and spring months when the surface is snow covered. This observation is consistent with studies from the Arctic reporting a strong emission flux from snow covered surfaces (Steen et al., 2009, Ferrari et al., 2005). However, as soon as the snow thaws deposition dominates, indicating that atmospheric Hg is being incorporated into foliar plant tissue, possibly through nonstomatal pathways (Stamenkovic and Gustin, 2009).

The preliminary flux results from the study at Brekkebygda are high in comparison to other comparable studies and the actual magnitudes of the flux values shown in Figure 17 need further verification. However, one has to keep in mind that Hg fluxes are widely variable in both magnitude and direction depending on site differences such as soil and air concentrations, vegetation type and local Hg sources. In addition, measurement technique and set-up as well as meteorological conditions make it complicated to compare individual studies (Steen et al., 2009, Converse et al., 2010). Based on this, extrapolating the results from single studies to large scale is a challenge and to predict the effect of a changing climate on surface emissions will inevitably be somewhat speculative.

3.6 Mercury emission from forest fires

Current climate change scenarios indicate dry seasons during summers in large areas in Europe. Due to drier summers, the amount of forest fires is expected to increase. Wildland fires take place every spring and summer in Europe, and they are especially common in Western Russia from where the smoke plumes travel to e.g. Nordic countries. The fires have a negative effect on human health and safety, air quality and economy.

Besides Russia, the amount of forest fires is expected to increase in the Nordic countries. Projections from a 100-year simulation with the SMHI-RCA Regional Climate Model starting from 2001 have been used for determining future changes in fire danger over Finland, Sweden and the Baltic

Region, focusing on the fire season, April–September (Morse et al., 2009). This analysis shows that a statistically significant trend towards an increased danger of fire can be observed. The forest fire danger is rated applying Finnish Forest Fire Risk (FFI), which has an index value of 1–6. If the $\text{FFI} \geq 4$, an official forest fire warning is given via weather forecasts in Finnish media. According to Morse et al. (2009), the number of days with very high fire risk ($\text{FFI} \geq 5$) is expected to almost double during the current century. The highest number of days with fire risk is predicted to occur in the south, see Figure 18. However, the highest relative increases in fire risk are estimated for the northernmost areas. The modelled trends are given for IPCC A2 and B2 scenarios.

Figure 18. Number of days with very high forest fire risk projected for northern Europe during the 21st century. (Morse et al., 2009)

Forests are sinks for atmospheric mercury originating from anthropogenic and natural sources. Forest fires have been observed to enhance the release of mercury (Friedli et al., 2003; Sigler et al., 2003; Cinnirella and Pirrone, 2006). This effect has also been observed at the Finnish station Virolahti (Anttila et al., 2008; Paatero et al., 2009), which is located close to north-west Russia, areas where extensive forest fires have occurred during recent years. TGM concentrations peaked during the forest fire period in August 2006 (see Figure 19). The TGM peaks also coincided with airborne particle concentrations ($\text{PM}_{2.5}$) remarkably well. This strongly suggests that the elevated mercury concentrations were due to mercury released from soil and vegetation during the fires. The measured TGM concentrations are so far among the highest measured at the station. The concentration of TGM more than doubled during the episode compared to the typical summer concentration level.

Figure 19. Hourly averaged time series of TGM (left axis) and $\text{PM}_{2.5}$ measured at Virolahti in 2006 during the Russian forest fire period.

Cinnirella and Pirrone (2006) have estimated the annual mercury emissions from forest fires in Europe and the Russian Federation. According to their preliminary assessment for 1990–2004 the annual average emission from the countries Sweden, Finland, Norway and Denmark corresponds to 20 (2.8–45.1), 4.2 (0.9–8.6), 3.6 (0.5–9.4) and 0.4 (0.0–1.8) kg y⁻¹, respectively. Closer emission rates would be expected when comparing Sweden and Finland. However, the emission rate from the Nordic countries is small in comparison to that for the Russian Federation, for which an average value as high as 9910 kg Hg y⁻¹ was estimated. This corresponds to 7 mg ha⁻¹ y⁻¹ which is an order of magnitude higher than that for Sweden (0.5 mg ha⁻¹ y⁻¹) for example. Cinnirella and Pirrone (2006) also report potential mercury emission rates (i.e., rate of mercury emission when forest areas are burning) in the range of 5–7 g Hg ha⁻¹ y⁻¹ for the Nordic countries. This, corresponds to 60–70% of the average rate for Europe. In recent years in e.g. Finland, 360–1600 hectares of forests were burned during 2004–2008 (Kokki and Tiittanen, 2009), which results in a rough estimate of 2–8 kg of Hg released annually when using the Hg emission rate of Cinnirella and Pirrone, 2006. Hence, this is within the same range as the preliminary assessment for 1990–2004 given above. For comparison, the Finnish annual mercury emission from anthropogenic sources was 0.6–1.0 tonnes in 2000–2008 (Finnish Environment Institute, 2010). One should note that forest fires only constitute a part of all biomass fires. In Finland, forest fires were 20–40% of the total biomass fires (forest + land) in 2004–2008 (Kokki and Tiittanen, 2009). Since there are no estimates for the projected change in the extent of burned areas it is difficult to predict the future Hg emissions from biomass burning. It is clear however that with the current estimates of increasing forest fire days, Hg emissions from forest fires will increase.

3.7 Results from mercury catchment studies

3.7.1 Boreal forest catchment as Hg source for lakes

Boreal forest catchments, especially those containing wetlands are sources of total mercury (TotHg), but can also be important sources of methyl mercury (MeHg) for downstream aquatic systems (Rudd, 1995). However, the proportion of MeHg from TotHg in surface waters coming from soils via runoff may vary substantially (Rudd, 1995; Kelly et al. 1995). Moreover, it is still unclear how TotHg/MeHg in runoff enters the food chain. Studies conducted in Finland and Sweden have shown that the amount of MeHg in fish can be significantly related to the catchment/lake ratio with higher concentrations in fish in lakes with high catchment-lake ratio (Verta et al., 1986; Lindqvist et al., 1991). This suggests that the characteristics of catchment may play an important role for the accumulation of Hg/MeHg in lakes, and consequently, for the bioaccumulation of MeHg in fish.

The concentrations of substances in lakes and streams are maintained by a dynamic balance of inputs and outputs. Climatic and hydrologic conditions are important factors in such dynamics, but fluxes of most substances from catchments into lakes are also markedly affected by a variety of geologic, edaphic, and landscape factors. Among the landscape factors, the abundance of wetlands may cause a particularly strong impact because in many lake-catchment systems they act as the principal source of dissolved organic carbon (DOC). This, in turn, serves as the transport mechanism for substances like Hg associated with or bound to it (Grigal, 2003).

3.7.2 Input-output of Hg in forested catchments

Munthe et al. (2004) summarized a number of deposition and export data from nine catchments in Europe and North America (Figure 20). For Hg in all catchments and for MeHg in most catchments litterfall dominated over throughfall and open field precipitation in input. The higher deposition flux in throughfall in comparison to open field is attributed to dry deposition of Hg in the canopy which is washed off by rainfall. This may involve surface adsorption of RGM and/or deposition of Hg^0 via stomatal uptake or canopy surface oxidation (Munthe et al. 2004). The source of Hg in litterfall is most likely due to dry deposition as well.

Figure 20. Input and output of Hg and MeHg in forested catchments in Europe and in North America (Munthe et al. 2004).

Generally the output of Hg via runoff was less than 5% (Munthe et al. 2004) but higher in catchments with wetlands indicating that a substantial fraction of the deposited Hg may be retained in the catchment vegetation and soils as discussed earlier. Recently Larssen et al. (2008) estimated clearly higher output ratio (26%) in a catchment in southern Norway with a sparse forest and low productivity. This further suggests that catchment processes are of greater importance for surface water export of Hg than the current atmospheric input. Although some studies on re-emission of Hg from forest soils have been done (see deposition and re-emission fluxes above), there exist no quantitative estimate in Scandinavia or elsewhere of the complete mass balance of Hg in forested catchments including all fluxes.

3.7.3 Differences in Hg concentrations and fluxes according to forest catchment type

In order to evaluate the role of different type of forest catchment as a source of ToHg and MeHg to downstream lakes all available catchment Hg data from Finland and Sweden was compiled and compared with results from North American studies (Table 3). Only few studies have been reported on TotHg/MeHg concentrations and loads from forest catchments in Fennoscandia (Table 3). These results show that TotHg concentrations and output fluxes vary generally within an order of magnitude between different types of forested catchments whereas both the fraction and TotHg present in the form of MeHg (MeHg %) and the MeHg load, vary substantially more. The highest MeHg %, MeHg concentrations and fluxes are found in runoff waters from peatland catchments. Upland catchments with partial peatland

coverage have somewhat less MeHg and pure uplands have the least MeHg, in outflowing water.

Catchments with peatlands appear to be more effective MeHg sources than pure upland catchments or uplands with a minor area of peatland. Swedish, Canadian and American estimates of MeHg output fluxes are comparable at sites with forests and wetlands, but clearly lower at pure upland sites (Table 3). As in the case of concentrations, the output fluxes of TotHg in Sweden and Finland were at the same level as reported for Canada and USA (Table 3).

Table 3. Comparison of TotHg and MeHg concentrations (ng l^{-1}) and MeHg% in runoff waters and output fluxes ($\text{g km}^{-2} \text{a}^{-1}$) in studies made in Finland, Sweden and North America.

Location	Concentration ng l^{-1}		MeHg/TotHg%	Output flux $\text{g km}^{-2} \text{a}^{-1}$		Reference
	TotHg	MeHg		TotHg	MeHg	
Valkea-Kotinen, S. Finland						
upland/peatland	4.86±2.32	0.47±0.33	10.8±7.06	0.81–1.36	0.075–0.177	SYKE, unpublished
S. Finland, upland/peatland	5.6±2.7	0.30±0.30	6.5±5.5	1.6	0.053–0.22	Porvai & Verta, 2003
C. Finland, peatland	4.8±2.3	0.77±0.61	19±13	1.0–1.8	0.11–0.33	Porvai & Verta, 2003
Minnesota, USA						
Upland	20.6±1.8			2.2±0.37		Grigal, 2003
Peatland	12.9±2.2			4.4±0.42		Grigal, 2003
Wisconsin, USA						
Upland				0.043		Hurley et al., 1995
Wetland/forest	3.88±2.61			5.5	0.12	Hurley et al., 1995
Wetland	0.9–5.9	0.08–0.21		3.1	0.035	Krabbenhoft et al., 1995
Agriculture/forest	3.92±2.92			1.6	0.024	Hurley et al., 1995
Agriculture	2.73±1.84					Hurley et al., 1995
Adirondack, New York, USA						
Riparian wetland	2.3 ±0.26	0.10–0.40		2.2	0.17	Driscoll, et al., 1998
ELA, Ontario, Canada						
Upland	8.8–13	0.031–0.055	0.23±0.06	2.0	0.007	St. Louis et al., 1994; St. Louis et al., 1996
Upland/riparian wetland	12±0.73		1.58±0.16	2.3	0.032	St. Louis et al., 1994
Upland/riparian wetland	6.3–11	0.18±0.012	2.0±0.29	1.9	0.035	St. Louis et al., 1994; St. Louis et al., 1996
Upland /headwater wetland	3.5–4.8	0.25–0.36	13±2.42	1.2	0.096	St. Louis et al., 1994; St. Louis et al., 1996
		0.46–0.73				
Gårdsjön, SW. Sweden						
Upland/ wetland	~2–6	<0.1–0.6	6	1.8	0.030	Hultberg, et al., 1994; Hultberg, et al., 1995
Svartberget, N. Sweden						
Upland/ wetland	3.5	<0.2–0.8		1.0–3.4	0.050–0.14	Lee, et al., 1998; Lee et al., 2000
Colorado, USA						
Alpine tundra/boreal forest	0.4–2.5	<0.04		1.55	0.019	Shanley et al., 2008
Wisconsin, USA						
Forested temperate		0.04–1.1		0.25	0.037	Shanley et al., 2008
Buskerud, SW Norway						
Upland/peatland	2.5–4.0	0.04–0.12		2.5	0.04	Larssen et al., 2008
Alaska, USA						
Treeless tussock tundra					0.04–0.33	Hammerschmidt et al., 2006
Balsjö, N. Sweden						
upland/peatland 1	6.4	0.16		0.40	0.025	Bishop et al., 2009
upland/peatland 2	5.7	0.30		0.29	0.013	Bishop et al., 2009

The indication that wetlands are effective hot spots of MeHg output from the terrestrial ecosystem has been corroborated by studies that identify the output of MeHg from different parts of the landscape. Wetlands, and especially the organic-rich riparian zones commonly found bordering boreal watercourses, have much higher outputs of MeHg, per unit area, than well-drained forest soils. Other research has shown a significant spatial gradient in sulphate concentration across the upland-peatland interface, suggesting high levels of sulphate reduction (Mitchel, 2007; Mitchel et al., 2005). Because the activity of sulphate reducing bacteria is directly related to MeHg production (Gilmour et al., 1992; King et al., 1999), the delivery of sulphate from the adjacent upland is at least part of the reason that MeHg% values are high in the upland-peatland interface. It is likely that the low sulphate concentrations generally found in the peatland interior are limiting to the bacteria responsible for mercury methylation. Other research suggests that the carbon delivered in upland runoff is more labile to sulphate-reducing bacteria than that derived from peatlands, driving higher rates of net MeHg production (Mitchel et al., 2008).

7.3.4 The effects of forestry on Hg dynamics

In the recent paper Bishop et al., 2009 summarized all research data of forest harvest impacts on Hg. Watershed manipulations can result in an increase of downstream MeHg concentrations (Munthe et al., 2004) and fish Hg levels by an order of magnitude, without any additional input of Hg (Garcia and Carignan, 2005). This can be attributed to increased mobilization of existing MeHg from catchments and/or an increased net methylation of natural and anthropogenic Hg stored in soils. Removal of trees raises the water table and warms the soil during summer/autumn (Rosen et al., 1996). The disturbance associated with logging also increases the hydrological connectivity along superficial flow pathways as well as the output of dissolved organic matter (DOM) and nitrate, among other effects (Kreutzweiser, et al., 2008). Thus, there is a process-level explanation for increased export of MeHg/Hgtot from catchments as a result of forest operations, as well as an increase in the net production and bioaccumulation of MeHg in lakes.

The pioneering studies from Finland and Sweden remain the only ones that have studied the effects of harvesting on concentrations and fluxes of Hgtot and/or MeHg in runoff. The first study that showed increased Hg in runoff was made in Finland by Porvari et al., 2003, see Table 4. Harvesting of a 7 ha stand increased Hg fluxes by a factor of four and MeHg by a factor of six. The increased fluxes resulted from both a doubling in runoff and concentration increases. It was difficult to distinguish the effect of the harvest itself from the subsequent site preparation. Recent, unpublished data show that the harvest effect on this site has persisted for over 12 years (Table 4).

Table 4. Comparison of TotHg and MeHg concentrations (ng l⁻¹) in runoff waters and output fluxes (g km⁻² a⁻¹) in forest disturbance studies made in Finland, Sweden and Canada.

Location	Period	Concentration ng l ⁻¹		Output flux g km ⁻² a ⁻¹		Reference
		TotHg	MeHg	TotHg	MeHg	
S. Sweden						Munthe & Hultberg, 2004
Gårdsjön, F1 before track	1994–1998	3.6	0.05	2.3	0.03	
Gårdsjön, F1 after track	1999–2001	4.3	0.22	3	0.15	
Gårdsjön, F2, harvested 1999	1999–2006	8.1	0.53	–	–	Munthe et al., 2007
Götaaland						Munthe et al., 2007
Coniferous forest	1987–2004	4.1	0.12	–	–	
Clear-cut	1999–2006	7.5	0.51	–	–	
Balsjö						Sørensen et al., 2009
Before harvest	2005–2006	5.7	0.3	0.29	0.013	
Reference	2005–2006	6.4	0.4	0.4	0.025	
S. Finland						Porvari et al., 2003
Before harvest	1994–1997	8.1	0.15	0.81	0.02	
After harvest	1998–2000	12	0.35	3.44	0.13	
After harvest	2001–2008	11	0.83	1.29–4.46	0.10–0.64	Porvari et al., 2010
Reference	1994–1997	4.9	0.33	0.64	0.03	
Reference	1998–2000	4.7	0.33	0.74	0.04	
Reference	2001–2008	5.3	0.30	0.51–1.71	0.025–0.11	Porvari et al., 2010
Canada, Ontario						
Before harvest	2003–2004	7.2	0.16	7.3	0.016	Allan pers. comm.
After harvest	2004–2006	6.2	0.37	–	–	
	2004			1.3	0.083	
	2005			6.2	0.14	
	2006			0.6	0.013	

In Sweden, a temporary logging track inadvertently placed across a small brook in the long-term Gårdsjön reference catchment increased outputs of MeHg by a factor of over five (Munthe and Hultberg, 2004) for more than half a decade (Table 4). There has also been an increase in Hg, but the largest effects on Hg were observed during the first year, as was also the case for dissolved organic matter (DOM).

While a large harvesting effect is clear in these published studies, initial results from two newer harvest studies, one in northern Sweden (Sørensen et al., 2009.), and one in Ontario, Canada (C. Allan pers. comm.), have found the effect on Hg and MeHg fluxes to be limited to increases in runoff (35–100%), without significant concentration increases (Table 3). The range of Hg responses to harvesting should not be a surprise given the large variability in the outputs from different catchments and uplands in comparison to riparian soils (Tables 3 and 4). However, there is a clear indication that forest harvesting leads to increases in Hgtot and MeHg loading. In some cases this effect might last more than a decade. Increased bioaccumulation in downstream aquatic biota has also been reported (Garcia and Carignan, 1994, 2000, 2005; Desrosiers et al., 2006)

On a broad scale, factors such as wetland area in forested catchments and the DOM concentrations have previously been correlated with higher levels of Hg in fish (Grigal, 2002; Meili, 1997). The indication that wetlands are effective hot spots of MeHg output from the terrestrial ecosystem has been

corroborated by studies that identify the output of MeHg from different parts of the landscape. Wetlands, and especially the organic-rich riparian zones commonly found bordering boreal watercourses, have much higher outputs of MeHg, per unit area, than well-drained forest soils (Table 3). The difference between outputs of MeHg from organic soils and mineral soils is comparable to that between harvested and unharvested catchments (Table 3 and Table 4). However, the area of wetlands is relatively constant for a catchment, whereas new areas are impacted by forestry every year.

While only a few relevant studies have been conducted, they are consistent in pointing to forestry operations increasing the total loading of Hg to aquatic ecosystems. From these studies, Bishop et al., 2009 estimated that one-tenth to one-quarter of the Hg now in the fish of forested, high-latitude landscapes can be attributed to forest harvest operations.

The few studies of forestry impacts on leaching of Hg and MeHg from forest soils document extremely variable responses and a key area for research is the causes of this variability. Another topic for further research is how other forest practices impact the retention of Hg in forest soils during the growth period. Forestry is not the primary source of the mercury and forest management activities may increase the retention of Hg during the growth period via e.g. enhancing growth of the mor layer and lowering the water table. Long-term studies of Hg retention and leaching in managed and unmanaged forests are thus needed to determine the impacts of forestry over a forest stand life cycle.

4. Discussion

4.1 Atmospheric mercury trends

Deposition of mercury is regulated by precipitation amounts and mercury concentration in deposition. The variation of the latter is to some degree due to the proximity to major mercury sources as well as to meteorology, e.g. wind transport patterns. The former East Countries still constitute a source area for airborne mercury. In Southern Poland, for example, the mercury deposition may during winter be more than 10 times higher than in Southern Sweden (Zielonka et al., 2005). Mercury deposition appears to decrease at many of the investigated sites, but at a slower rate than during the 1990-ties. The decreasing trend is likely to be an effect of reduced anthropogenic emissions in Europe. This started already in the beginning of the 1990-ties as a consequence of the economical breakdown in the former east block (Munthe et al., 2001) when many coal power plants and other industries were closed. As a result sulphur and also mercury emissions were strongly reduced. Today the deposition of mercury at for example Råö is 2–3 times lower than before 1990 (Wängberg et al., 2007). Nowadays the reduction in mercury emission in Europe is due to reduction controls in EU countries. That is control measures in coal power plants that are mainly intended for reduction of emissions of SO₂ and particles also have a reducing effect on mercury emissions.

Mercury occurring in precipitation is likely to compose of two components, whereof one is oxidised or particulate bound mercury emitted from, for example, coal combustion. The other is mercury originally emitted as Hg⁰ that later oxidised in the troposphere to form RGM. This mercury may be of both natural and anthropogenic origin and since the residence time of Hg⁰ is relatively long (Schroeder and Munthe, 1998) this component is more or less evenly spread in the atmosphere. Hence, emission of oxidised mercury from human sources has a regional impact, whereas emitted Hg⁰ can be considered to have a more global effect on mercury deposition. The latter is therefore to a great part governed by the global emission of mercury.

Regarding TGM no clear trend is seen during recent years, but the data indicates a weak increase during the period 1995–2006. Before year 1990 the average TGM concentration in Southern Sweden was about twice as high as today (Iverfeldt et al., 1995), but then rapidly decreased to about the present values in conjunction to the reduction of European mercury sources as mentioned above. The TGM levels we see today more or less reflect that of the northern hemispherical background and is thus to a significant degree controlled by anthropogenic emissions from Europe and other continents.

4.2 Deposition and re-emission of mercury due to AMDE

At the onset of the AMDE research, AMDE's were believed to be the missing link between atmospheric mercury and accumulation of mercury in Arctic ecosystems. Despite more than a decade of effort to measure and understand AMDE's the connection of mercury deposition and entry into food webs remains tenuous and poorly understood (McDonald and Loseto, 2010). The post-depositional fate of mercury is continuously under debate in terms of how much of the deposited mercury is emitted as GEM through photoreduction and how much remains in snow (Steffen et al., 2008).

Studies have shown that the concentration of mercury in snow increases during and following AMDE where oxidized atmospheric mercury is thought to have been deposited (Lu et al., 2002, Lindberg et al., 2002). In Ny-Ålesund, it is observed that concentrations of mercury in snow increases from the low polar winter concentrations of approximately 2 ng L^{-1} (Berg et al., 2003, Sommar et al., 2007) up to almost 400 ng L^{-1} (Dommergue et al., 2010) during AMDE's. These values are similar to those observed in Barrow (AK, US) where local production of Hg(II) usually exists (Lindberg et al., 2002, Johnson et al., 2008). In another study from Ny-Ålesund in 2003, it was demonstrated that of seven ADMEs no increase in the surface mercury concentration was observed and the authors suggests that the origin on the AMDE plays a significant role in the amount of mercury deposition that is observed (Ferrari et al., 2005).

It is also observed that within 24 hours after deposition of mercury from the atmosphere a fraction is re-emitted back to the atmosphere as GEM (Lalonde et al., 2002, Dommergue et al. 2003), thus adding uncertainties to the net deposition. Once deposited to snow and ice surfaces, mercury species can undergo photolytically mediated reactions in which oxidised mercury is reduced to Hg^0 . This is consistent with observations in Ny-Ålesund (Sommar et al., 2007, Dommergue et al., 2010, Steen et al., 2009).

Ferrari et al., 2008 estimated that more than 80% of the deposited mercury was re-emitted back to the atmosphere during the days following a depletion event. Dommergue et al., 2010 found that most of the up to $2160 \text{ ng deposited Hg/m}^2$ was lost to the atmosphere via photochemical processes, however an important amount remained in the snow and they estimated that spring melt contributed to an input of upto 3.6 kg of Hg to the surrounding fjord. This accounts for approximately 15% of the total Hg content in the fjord. Steen et al., 2009 reported a net loss of GEM from the snow pack which by far exceeded the estimated deposition of total mercury and discovered that depending on the measurement protocol considerable sources of error in the GEM flux may be introduced. Consequently, care should be taken when comparing different Arctic locations and when scaling up mass budgets for mercury in the Arctic.

4.3 Climate change effects on AMDE

Because atmospheric mercury is almost entirely gaseous (Hg^0) it is tempting to assume that the polar regions might be global sinks simply due to low temperature and accordingly to make projections on the effects of climate change based on this fact alone. AMDE perturbs this simple comprehension.

Modeling and predicting the loading of Hg to polar ecosystems is challenging because there are several drivers of the Hg cycle currently undergoing rapid change. Firstly, the source regions of Hg in the Northern hemisphere are shifting from North America and Western Europe to Asia. Models have shown that air currents from Asia occur in the springtime when atmospheric Hg chemistry is in full swing and any increases in the amount of Hg from this important source region will, no doubt, affect the Hg cycle of the Arctic. Secondly, and very importantly, the extent of sea ice is in marked decline in certain Arctic regions and the degree to which this decline occurs is predicted to be high. It is tempting to draw the conclusion that with a decline in sea ice extent, the frequency and geographical extent of AMDE's would also decline. However, sea ice drives the major meteorological components of the Arctic system (precipitation, temperature, winds, and regional circulation) and these parameters largely control the entry and subsequent scavenging of atmospheric contaminants including Hg. Changes in the timing and extent of sea ice will no doubt affect AMDE dynamics. It is essential to fully comprehend the role that sea ice plays in AMDE chemistry and subsequent deposition to the ocean (Steffen et al., 2008).

As the Arctic undergoes dramatic change due to reduced sea ice and warming temperatures it is crucial to understand how climate change may alter the frequency and magnitude of AMDE's in the future in order to predict future inputs of mercury to polar regions. There is already some evidence suggesting that mercury oxidation rates by halogen radicals are influenced directly and indirectly by climate. Theoretical calculations predict that the net oxidation of Hg^0 to HgBr_2 by bromine radicals – a likely oxidation pathway during AMDE's – will be much faster at low temperatures (Goodsite et al., 2004). The origin of high levels of bromine radicals, so called bromine explosions, appears to be heterogeneous reactions with bromide ions in snow and ice and/or aerosols where sea salt is the original source of bromide. Bromine explosion and hence AMDE's may be tied to snow and ice characteristics through frost flowers (Kaleschke et al., 2004), first-year sea ice (Simpson et al., 2007) and inland snow pack chemistry (Simpson et al., 2007, Piot and von Glasow, 2008) all of which would be sensitive to climate change.

4.4 Mercury emission from forest floor – Effects of climate change

Hg flux from soil is influenced by e.g. solar radiation (Poissant & Casimir, 1998; Bahlmann et al., 2004a), soil and air temperature (Gustin et al., 1997; Poissant & Casimir, 1998), soil moisture (Bahlmann et al., 2004b) and wind speed (Gustin et al., 1997). The emission rate limiting factors are abiological and biological formation of Hg^0 (and possibly $(\text{CH}_3)_2\text{Hg}$) in the uppermost soil layers in background areas, and thus, the evaporation rate is probably also strongly influenced by deposited airborne mercury (Schlüter, 2000). Given the situation of climate warming and the shorter duration of snow cover in large areas of the boreal forest zone, the terrestrial mercury emissions will likely change in the future. In the study by Kyllönen et al., 2010, the flux was found to correlate strongly with air temperature ($R^2 = 0.86$). With increasing temperature, Hg emissions are expected to increase in the future. Furthermore, clear cutting is enhancing with the current focus on the usage of logging residues as biofuels in the effort to reduce anthropogenic carbon emissions. It has been already proven that clear cutting can effectively transport Hg through different media (Porvari et al., 2003). According to preliminary data from Kyllönen et al. (2008, not published), clear cutting will also increase Hg emission from the disturbed forest floor.

4.5 Mercury emission from forest fires – Implications of climate change

The amount of Hg released from forest fires in the Nordic countries is small compared to anthropogenic sources such as energy production and other industrial processes, mainly because the fires are limited in duration and size. These fires pose a more severe threat to human health in countries where extensive areas are burned (in e.g. Canada, Russia). Sigler et al., 2003 report an average annual release of 3.5 tonnes Hg from Canadian boreal forest fires equalling 30% of inventory estimates of annual anthropogenic Hg emissions. They also estimate a global average of 22.5 tonnes Hg released annually from boreal forest fires while Turetsky et al., 2006 estimate an Hg emission of 53.5 tonnes using the same circumboreal annual burn area. Furthermore, Turetsky et al., 2006 suggest that 340 tonnes of Hg is annually emitted across the circumboreal region when the boreal peatland soils, which possess great stocks of mercury, are included in the calculations. Thus, mercury released from biomass fires presents an important source in regional and global mercury balances and cannot be excluded from model calculations assessing environmental cycling of mercury.

With the warming climate, changes in precipitation amount and other climate variables are predicted, too. The increases in precipitation in the summer months would weaken the occurrence of forest fires, and thus, the

effect of increasing mercury emissions. However, during the next few decades the influence of the enhanced GHG (greenhouse gas) effect on precipitation in Finland is expected to be much weaker in comparison with natural variability than the influence on temperature according to Jylhä et al., 2009. The increase in precipitation amount is changing slowly, and there is still a probability of about 25% that the mean annual precipitation in Finland in the decade 2011–2020 will be lower than that in 1971–2000. By the end of this century, precipitation amounts will increase in Finland; in winter by 10–40%, and in summer by 0–20% accompanied with increases in temperature. In relative terms, the changes in the north will exceed those in the south, see Figure 21. Similar changes are likely in the other Nordic countries. The changes in precipitation shown in Figure 21 were calculated as an average of IPCC A1B scenario calculations of 19 global climate change models. In spite of slight increases in summertime rainfall, water resources may not increase, since evaporation will also intensify in a warmer climate. In conclusion, the effect of increasing precipitation is small in comparison to the effect of increased occurrence of forest fires.

Figure 21. Predicted change (in percentages) in precipitation (1971–2000 → 2070–2099) in the summer season (Jun to Aug) (Jylhä et al., 2009).

4.6 The effect of climate change on Hg concentrations and fluxes from catchments

The possible effect of climate change on Hg concentrations and fluxes could be both due to direct (increased precipitation and runoff from catchments) and indirect effects. Indirect effects are linked to organic carbon chemistry. Organic carbon export simulations based on climate change scenarios and neural networks indicate increasing DOC fluxes in headwater streams (Holmberg, 2003). Further, elevated leaching and increasing trends in DOC concentrations in streams and lakes across Europe and North America have already been reported (e.g. Stoddard et al. 2003, Skjelkvåle et al. 2005, Vuorenmaa et al. 2006) probably because of decreasing SO_4 deposition and improved acid-base status in soils. Because Hg flux correlates positively with

stream discharge, increased precipitation and runoff with increased C (DOC, TOC) concentrations may increase Hg and MeHg export to lakes and affect concentrations in fish. Dissolved organic carbon is an important factor controlling the bioavailability of Hg(II) and its increased export may have a pronounced effect on the Hg cycle. Generally, DOC may affect MeHg formation in three ways: a) DOC is a carrier of Hg(II) (e.g. Grigal 2002, Skjellberg et al. 2003); b) fresh DOC enhances the biological activity, serving as an organic substrate for microbes (Barkay et al. 1997); c) binding of Hg (II) and MeHg by DOM decreases its bioavailability for methylation and for bioaccumulation (Barkay et al. 1997).

On the other hand increased nutrient (N, P) export, partly associated with TOC export may boost fish growth and further lead to biodilution of Hg and lower bioaccumulation. Consequently the overall response of climate change is very difficult to predict and field measurements may sometime be contradictory.

An experiment with an artificial precipitation to a small forested catchment was performed as a part of European research project on climate change effects in lakes (Euro-limpac) in southern Sweden in 2005 (Munthe et al., 2010, manuscript in preparation). The total precipitation added was about three quarters of the annual natural precipitation. A significant part of soils in the catchment became water saturated for extensive period of time which lead to the formation anoxic conditions in the soils favouring Hg methylation. A sharp increase in MeHg concentration and flux was measured within a few months after irrigation but also in later years indicating long term changes in soil properties resulting to enhanced formation and release of MeHg.

The increase in MeHg in runoff are generally associated with low SO_4 concentrations (Galloway and Branfireun, 2004; Porvari et al., 2010) indicating that sulfate reducing bacteria are mainly responsible for the methylation of Hg in soils which has also been shown for freshwater lakes (e.g. Gilmour et al., 1992). Since sulphate is an important factor affecting MeHg production, its concentration may be the rate determining factor for microbial sulphate reduction in low sulphate systems. Thus climate change may affect Hg cycling in catchments by increased weathering in the watersheds and liberating sulphate from the mineral phase, and by producing poor oxygen systems favourable for sulphate reduction and MeHg formation.

5. Conclusions

Wet deposition of mercury show a weak declining trend in Southern Fennoscandia which can be attributed to regulation of emissions of sulphur and particles, which also reduces mercury emissions. Unfortunately, until now Pallas in northern Finland is the only Arctic site at which mercury in deposition regularly is being measured. The data obtained at Pallas indicates that mercury deposition there to the most part is governed by the atmospheric mercury background level. It is likely that this also is the case regarding other Arctic areas. In addition to that, AMDE's also contribute to deposition of mercury in certain polar areas. The TGM concentration in the investigated area is now to a greater degree than before governed by the background concentration of mercury in the atmosphere, which in turn is due to the sum of natural and anthropogenic emissions of Hg^0 . The data presented here indicates that the background level of atmospheric mercury in Fennoscandia has been fairly constant during recent years or might be slightly increasing. Rising emissions of mercury is conceivable considering the increasing demand for electricity and heat in the developing economies in Asia and elsewhere. On the other hand, according to a recent mercury emission inventory (AMAP/UNEP-report, 2008) the emissions of mercury from human sources declined during the period 2000 to 2005 on all continents including Asia. However, the inventory is based on estimates involving certain uncertainties. As much as 66% of the anthropogenic mercury to the atmosphere is assumed to come from Asia. The annual emission from Asia corresponds to 1280 tonnes with an uncertainty range of 840–1760 tonnes. The uncertainties regarding anthropogenic mercury emissions from Europe and other continents are also relatively large (AMAP/UNEP-report, 2008).

AMDE's are large scale polar phenomenon occurring during springtime at which Hg^0 is oxidised and deposited on snow and ice as well as on open sea surfaces. The chemical mechanisms causing AMDE is still not entirely understood, but Hg^0 is likely to be oxidised by halogen radical species where especially bromine originating from sea salt probably is involved. Deposition of the oxidised mercury occurs locally but air masses enriched by oxidised mercury may also be transported far away from where the depletion event took place, thereby having the potential of affecting large areas. How much of the deposited mercury that remains contra is re-emitted back to the atmosphere is crucial for assessing the importance of AMDE in the Arctic environment. The complexity of mercury biogeochemistry indicates that climate change will alter the exposure of Hg to the ecosystems. However, the exact coupling between climate change, AMDE processes and mercury deposition in the Arctic is yet unknown.

Since forest fires are expected to increase due to climate change, it is likely that Nordic countries will be exposed to more fire plumes containing hazardous substances like mercury. Since most of the mercury emitted is in the gaseous elemental form (Friedli et al., 2003), the mercury in the plumes is effectively transported to large areas and concurrently diluted. Given the long residence time of gaseous elemental mercury (Schroeder and Munthe, 1998), these short-time elevated levels of the pollutant are not likely to affect the human health directly. However, during fires, mercury (both natural and once deposited anthropogenic Hg) is released into the biogeochemical cycle and part of it may eventually be enriched in the food chain as highly toxic methyl mercury. Not only changes in temperature but also in other climate variables such as precipitation amount are expected with the current climate change scenarios. If the precipitation amounts increase, the occurrence of forest fires are likely to decrease resulting in lower mercury emissions. However, the estimates of precipitation amount changes are uncertain. Also evaporation will increase in a warmer climate weakening the effect of increased precipitation. In conclusion, the effect of increasing precipitation is small in comparison to the effect of increased occurrence of forest fires.

We conclude that environmental changes such as forestry treatments in forested catchments lead to increased TotHg/MeHg concentrations and output fluxes. The magnitude of these effects may vary substantially and the research is far too limited to make any clear conclusion. Still there is a strong indication that soil disturbances and changed hydrology may play a central role in Hg dynamics and as a regulator of Hg methylation. The new forestry treatment methods like stump harvest and logging residue removal from the clear-cut sites are causing more and more disturbances to the soil. These widely used practices mean more visits to the harvested forest by heavy machinery. Also the climate change in the form of warmer and wet climate combined with an increased removal of logging residues and stumps may boost the adverse effect and further result in deeper tracks with wetter soil conditions. This in its turn may imply severe risks for the water quality (erosion and leakage), soil permeability, hydrology and further leakage of Hg and MeHg and enhanced Hg methylation.

The possible effect of climate change on Hg concentrations and fluxes in catchments is even more complex and it cannot be easily judged how the changes of temperature and precipitation will change Hg dynamics in boreal forested catchments. The predictions for precipitation amounts are highly uncertain and include probabilities for both increase and decrease of summer precipitation but with higher probability to increase. Judged from the Gårdsjön experiment the summer precipitation amount may be the main contributor to MeHg formation in soils. Thus climate change will likely increase the export of Hg, MeHg, DOC and nutrients from watersheds to boreal lakes.

The knowledge of the effects of environmental changes on Hg levels in biota is very limited. Even if the MeHg concentrations and output fluxes would increase due to disturbances in catchment there may exist other ef-

fects like biodilution and enhanced fish growth, which end up in reverse consequences and may compensate the negative effects.

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Sammanfattning

Mätningar av kvicksilverdeposition i södra Fennoskandia indikerar en svag neråtgående trend vilket kan antas vara en effekt av minskade mänskliga emissioner av kvicksilver i EU-området. Deposition av kvicksilver i Arktis är beroende av kvicksilverhalten i bakgrundsluft vilket i sin tur beror på emissioner av kvicksilver i norra hemisfären. En konsekvens av minskade emissioner av kvicksilver från Europeiska källor är att koncentrationen av elementärt kvicksilver (Hg^0) i Fennoskandia i högre grad än tidigare bestäms av den globala bakgrundshalten av kvicksilver. Det här betyder att fortsatt reduktion av kvicksilver i Norra Europa förutsätter minskade emissioner på global, eller åtminstone hemisfärisk nivå.

Tillfällena med utarmning av atmosfäriskt kvicksilver, vilket på engelska benämns ”mercury atmospheric depletion events” (AMDE’s) förekommer under våren i Arktis och Antarktis då solen återigen stiger över horisonten. Kviksilver i atmosfären kan under kort tid i det närmaste kvantitativt oxideras och deponeras till snö och is. Emellertid reduceras en betydande del av det deponerade kvicksilvret till Hg^0 och emitteras tillbaka till atmosfären. Hur mycket kvicksilver som blir kvar och hur mycket som emitteras är fortfarande en fråga som avgör betydelsen av det här speciella fenomenet.

Kviksilver deponerat till barrskogsbältet tenderar att ackumuleras i skogsmark. På grund av vissa reducerande mekanismer som förekommer i markens ytskikt kan en del av det deponerade kvicksilvret återföras tillbaka till atmosfären i form av gasformigt Hg^0 . Skogsbränder ger också upphov till emission av kvicksilver. När det brinner värms marken upp och då kan betydande del av det ackumulerande kvicksilvret i marken reduceras och avgå tillbaka till atmosfären. Bidraget av kvicksilver från skogsbränder i Fennoskandia är litet i förhållande till mänskliga emissioner, men fenomenet antas vara av betydelse i ett globalt perspektiv.

Ackumulering av kvicksilver i skogsmark utgör en sänka för atmosfäriskt kvicksilver. Senare upptäckter visar dock att markstörningar orsakade av skogsmaskiner i samband med avverkning m.m. kan leda till en ökad mobilisering av kvicksilver och även gynna bildning av metylkvicksilver. Kviksilver bundet i marken kan då läcka ut till vattendrag och sjöar. Liknande effekter befaras också kunna ske på platser med ökad nederbörd till följd av klimatförändringar. Fortfarande saknas dock tillräcklig kunskap om de processer som styr mobilisering av kvicksilver i skogsmark varför de kvantitativa uppskattningar som kan göras utifrån olika klimatscenarier blir osäkra.