Sufficiency and Effectiveness Review of the 1998 Protocol on Heavy Metals, UN/ECE Convention on Long-range Transboundary Air Pollution

Best Available Scientific Information on the Effects of Deposition of Heavy Metals from Long-Range Atmospheric Transport

Prepared by the Task Force on Heavy Metals
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Executive Summary

This chapter describes atmospheric transport, ambient concentrations and depositions of heavy metals, observed and modelled concentrations and temporal trends of heavy metals in environmental media and biota and comparisons, as appropriate, with effects indicators of significance. It provides, moreover, an assessment of effects on ecosystem and human health from the deposition of heavy metals from long-range atmospheric transport with a focus on cadmium, lead and mercury.

Heavy metals are a natural component of the earth's crust and as such they cycle throughout the environment in varying concentrations as a result of natural processes. In the post-industrial age, however, human activities have unlocked previously sequestered heavy metals from stable matrices, and released them into the atmosphere where to some extent they are transported across national boundaries. This has resulted in an enrichment of heavy metals in environments that are far from emission sources. While atmospheric deposition contributes to this enrichment, and potential harmful effects to the environment, other sources and site-dependent chemical and physical factors are also important for ecosystem accumulation.

Mercury. Of the three metals that are the focus of this review, mercury displays the greatest potential for long-range atmospheric transport. Mercury is emitted primarily in the gaseous elemental state (Hg(0)) and various compounds of ionic mercury [Hg(II)]. The Hg(II) compounds tend to deposit closer to the emissions sources, but elemental mercury can remain in the atmosphere for as long as 2 years and is easily transported over long distances. Concentrations of atmospheric mercury at remote locations in the UNECE region are fairly consistent (about 1.5 ng/m^3). Long-term data sets are scarce, however; data from stations located around the North Atlantic suggest that levels reached a peak in the 1980s, decreased by more than 50% by the late 1990s, and then stabilized. These findings are generally reflected in sediment, bog and glacier cores. Within Europe, EMEP modelling suggests, in general a 2-fold decrease in deposition between 1990 and 2003 as a result of reduced emissions, and that up to 50% of anthropogenic mercury deposition are derived from transboundary European sources, whereas between 25% and 60% may be derived from intercontinental sources. North American models suggest an even greater contribution from intercontinental sources to some regions of North America.

Recent results from the International Cooperative Programme on Integrated Monitoring (ICP-IM) suggest that remote forest catchments of northern and central Europe continue to accumulate deposited mercury. Studies in Scandinavia found that mercury

concentrations were associated with microbial effects in surface soils. Mercury concentrations in terrestrial wildlife (those that are not part of the aquatic food chain), however, are generally low and do not present a risk to wildlife or humans who consume them.

In the majority of lakes and rivers in North America and Scandinavia, methylmercury (a particularly hazardous form that biomagnifies up food chains) remains elevated in predatory fish. These levels may cause adverse neurobehavioural effects in fish-eating birds, mammals and humans that consume notable amounts of these fish. Generally, there is little evidence in remote locations that fish mercury concentrations have decreased over the past 10-15 years.

Mercury concentrations are also elevated at the top of marine food chains. Scientific evidence indicates that current levels of mercury in marine mammals are significantly elevated over pre-industrial levels. As in freshwater ecosystems, however, levels over the past 10-15 years appear relatively unchanged. The highest levels of mercury (mostly in the form of methylmercury) are found in long living predatory fish and marine mammals. The more highly contaminated marine mammals can exceed thresholds for effects in wildlife.

The primary source of human methylmercury exposure is from the consumption of fish, particularly larger and older predatory freshwater and marine species. It is recognized however, that fish is an important, beneficial food for many populations and moderate consumption of a variety of fish (following established consumption guidelines) is not likely to result in exposures of concern. Guidelines consider factors such as species, fish size, and waterbody as well as age and gender of human consumers. For example, guidelines are generally more restrictive for women of childbearing age because of potential adverse effects to fetuses. Nonetheless, people who consume high amounts of contaminated fish or marine mammals may be highly exposed to methylmercury, and therefore may be at risk.

Human exposure to elevated levels of mercury, especially in the form of methylmercury, can cause adverse effects, such as neurodevelopmental effects in newborns and young children. Among the general population estimated levels of dietary intake are not high enough to exceed guidelines set by national health agencies and the World Health Organization. It is probable, however, that some populations that consume fish and/or marine mammals may have exposures that exceed the intake guidelines. For example, studies have shown that blood mercury concentrations regularly exceeded American and

Canadian guidelines among women of childbearing age in Arctic populations that consume marine mammals.

Cadmium. Cadmium is emitted to the atmosphere primarily in the particulate phase. While the majority of larger diameter particles are deposited relatively close to the source, the finer particles have the potential for long-range transport. Deposition of cadmium resulting from long-range atmospheric transport has been reported in remote areas. Evidence suggests that deposition rates in remote areas peaked at several times pre-industrial rates during the 1960s and 1970s and has since decreased to levels only slightly higher than pre-industrial. These results are consistent with results of EMEP modelling and monitoring in Europe, which suggest, in general, a two-fold decrease in atmospheric concentrations and deposition between 1990 and 2003. EMEP modelling suggests that 10-80% of deposition in European countries is derived from emissions in other European countries.

Recent results from the International Cooperative Programme on Integrated Monitoring (ICP-IM) suggest that remote forest catchments of northern and central Europe continue to accumulate deposited cadmium. In general, soil cadmium concentrations in remote regions do not exceed thresholds for adverse effects on microbiota or vegetation. Vegetation, which accumulates cadmium from a number of sources, including atmospheric deposition, is the primary source of cadmium exposure for terrestrial herbivores that tend to accumulate cadmium in their liver and kidneys. Available information indicates that levels of cadmium in terrestrial wildlife are generally low and do not exceed thresholds of effects.

Cadmium is relatively mobile in freshwater ecosystems and can be accumulated by freshwater biota. However, unlike mercury, cadmium does not biomagnify in freshwater ecosystems. While lakes in northern Europe were found to contain elevated concentrations of cadmium as a result of long-range atmospheric transport, the levels that were reported do not exceed the estimated thresholds for toxic effects. Overall there appears to be generally a low risk of adverse effects due to environmental exposure to cadmium through freshwater ecosystems. However, under conditions of very soft water there is concern that there may be some risk because the "estimated thresholds" may not be sufficiently protective for these water conditions.

In marine ecosystems cadmium can achieve relatively high levels in some marine mammals. The contribution of anthropogenic cadmium to marine ecosystems, however, is thought to be relatively small. The vast majority of cadmium circulating in the world's oceans arises from natural sources and processes.

Food is the greatest source of human cadmium exposure, accounting for about 99% of cadmium intake in non-smokers, on average. Cereals, potatoes and leafy vegetables, represent the greatest source of dietary cadmium; however, consumption of organ meats and shellfish can also represent a significant dietary source. Cadmium-containing fertilizers, natural soil content, and atmospheric deposition all contribute to levels in food crops. In general, levels of dietary intake of cadmium are below applicable consumption guidelines for the prevention of kidney damage and there does not appear to be any risk of adverse effects to the general population as a result of long-range atmospheric transport. However, the safety margin for human health effects due to current exposures is considered to be small. Thus, further accumulation of cadmium in agricultural lands could result in exposures of concern.

Lead. Lead is emitted to the atmosphere primarily in the particulate phase. While the majority of larger diameter particles are deposited relatively close to the source, the finer particles have the potential for long-range transport. Organic forms of lead, such as tetraethyl and tetramethyl lead, are significantly more volatile than inorganic forms of lead and are more amenable to atmospheric transport. Evidence suggests that atmospheric deposition rates of lead in remote regions peaked during the 1970s and early 1980s at levels up to 200 times higher than historic background. Deposition rates appear to have decreased rapidly since the early 1980s. This is consistent with results of EMEP monitoring and modelling in Europe, which suggest a general two to three-fold decrease in atmospheric concentrations and deposition between 1990 and 2003. EMEP modelling suggests transboundary transport within Europe can account for 10-90% of deposition in European countries. In North America, lead air concentrations decreased greatly in the 1980s and early 1990s, and continued to decline through the mid- to late-1990s, although at a slower rate. Results from Arctic monitoring indicate that lead concentrations in air generally decreased since the 1980s, though recent average levels are relatively stable.

Recent results from ICP-IM indicate that atmospherically deposited lead is accumulated in forested catchments of Northern and Central Europe. Concentrations of lead measured in some forest humus layers and reported by the International Cooperative Programme on Forests (ICP-Forests) may exceed thresholds for effects in soil organisms. However, these ICP-Forests sites are not necessarily in remote locations. Lead does not appear to reach concentrations of toxicological significance in terrestrial wildlife as a result of deposition from long-range atmospheric transport.

Concentrations of lead in freshwater ecosystems influenced by long-range atmospheric transport are relatively low and are not considered a toxicological threat to aquatic

organisms. Lead poisoning from ingestion of lead shot, or sinkers, however, is a serious threat to aquatic wildlife. Available information indicates that lead from atmospheric deposition does not represent an ecological risk to marine ecosystems.

The general population can be exposed to atmospherically deposited lead primarily through the diet, mainly cereals and leafy vegetables, but this likely does not contribute substantially to exceedences of exposure guidelines. Children are also exposed to lead through the ingestion of lead-containing dust and other particles (e.g. deteriorating paint chips, residential soil). In a 1999-2002 survey of children in the United States, 1.6% exceeded the Centers for Disease Control and Prevention (CDC) current blood guideline for the prevention of neurodevelopmental effects (10 µg/dL), but these exceedences are not likely attributable to long-range transport.

Among aboriginal populations in Northern Canada and Greenland, the use of lead shot to harvest wildlife is thought to be the dominant source of dietary lead. In a survey of Inuit women, up to 12% of women exceeded the CDC blood guideline. The source of lead exposure does not appear to be related to deposition of lead from long-range atmospheric transport.

Other metals. The main group of other metals that were considered are those for which some Parties have collected and voluntarily reported emissions data including: arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se) and zinc (Zn). Other metals, though not reported on by Parties, for which new information on long-range transportation exists include platinum group metals (platinum (Pt)), palladium (Pd), and rhodium (Rh)), and antimony (Sb). Evidence suggests that all of the aforementioned metals have the potential for long-range atmospheric transport and to some extent are enriched in remote environments. It should be noted however, that nickel and chromium display a lower potential for long-range atmospheric transport compared to the other metals. Atmospheric concentrations and deposition of most metals appear to be stable or decreasing in remote environments with the exception of platinum, palladium, rhodium and antimony, which have increased in recent years. Studies from ICP-IM suggest that copper and zinc are accumulating in forested catchments of Northern and Central Europe. Presently, available information indicates that none of these "other" metals achieve high enough concentrations as a result of long-range atmospheric transport and deposition to cause adverse effects on wildlife or human health.

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1 Introduction

The following paper is intended to provide a synopsis of the best available scientific information on effects of deposition of Heavy Metals in the UNECE region. It has been prepared to support the Review of Sufficiency and Effectiveness of the obligations set out in the Heavy Metals Protocol to The Convention on Long-Range Transboundary Air Pollution (LRTAP). As specified by the Task Force on Heavy Metals, this paper considers the best available scientific information on atmospheric transport and deposition, levels in environmental media, and the potential toxicological effects that these levels may cause in wildlife and humans. Information relating to heavy metal emissions are not discussed.

The majority of the information in this paper has been drawn from existing reports that have previously been reviewed and accepted by a variety of international organizations (e.g. EMEP, WHO and AMAP) that have, themselves, condensed and synthesized primary sources of scientific information on the effects of pollutants. Where necessary, information from primary peer reviewed literature is included in an attempt to make the review as complete and as current as possible.

All regions of the UN ECE are potentially impacted by the deposition of heavy metals from long-range atmospheric transport. The sources of heavy metals include those that are regional, hemispheric and global in nature. In the more populated and industrial regions of the UN ECE, however, it can be difficult to distinguish the influence of local, and often direct inputs of heavy metals, from those of long-range transport (LRT). Therefore, this paper pays particular attention to the Arctic as a remote environment that receives anthropogenically released heavy metals primarily from LRT and not local sources. The processes involved have been comprehensively studied by the Arctic Monitoring and Assessment Programme (AMAP) over the last fifteen years making the Arctic especially informative for the sufficiency and effectiveness review. Information from non-Arctic regions is also presented and discussed, and provides a valuable perspective relating to the influence of nearby or regional LRT sources, for example, the particular influence Northern European sources have in Scandinavian countries.

2 Mercury

2.1 Background

Mercury is emitted in three major forms (elemental gaseous mercury, ionic mercury, or particulate bound mercury). As mercury moves through environmental media (e.g., air, sediments, water), it undergoes complex transformations. As stated in the 1997 US EPA's Mercury Study (US EPA, 1997c):

> "Mercury cycles in the environment as a result of natural and human (anthropogenic) activities. Most of the mercury in the atmosphere is Hg^0 vapor, which circulates in the atmosphere for up to a year, and hence can be widely dispersed and transported thousands of miles from likely sources of emission. Most of the mercury in water, soil, sediments, or plants and animals is in the form of Hg^2 salts and organic forms of mercury (e.g., methylmercury). Inorganic mercury, when either bound to airborne particles or in a gaseous form, is readily removed from the atmosphere by precipitation and is also dry deposited. As it cycles between the atmosphere, land, and water, mercury undergoes a series of complex chemical and physical transformations."

The air transport and deposition patterns of mercury emissions depend on various factors including the chemical form of mercury emitted, stack height, topography, and meteorology. The mercury emitted to the air is transported through the atmosphere and eventually deposited onto land or waterbodies. The chemical and physical properties of different mercury forms determine how they behaviour in the environment and the pattern of deposition. For example, ionic mercury, also known as reactive gaseous mercury, is water soluble and relatively reactive and therefore is much more likely to deposit within a short distance from the emitting facility, especially if it is raining or snowing. On the other hand, elemental mercury tends to disperse long distances and may not deposit until it has travelled hundreds or thousands of miles.

Once deposited to soils and sediments mercury can be methylated as a consequence of bacterial metabolism. Methylmercury is toxic and particularly prone to biomagnification through food webs, especially the aquatic food web (such as in fish and animals that eat the fish). Various studies indicate that anthropogenic releases of mercury from industrial and combustion sources contribute to the levels of methylmercury in fish. However, also contributing to these fish levels are existing background concentrations of mercury, which may consist of mercury from natural sources, as well as historic anthropogenic mercury which has been re-emitted from the oceans or soils (US EPA, 1997a, 1997c; UNEP, 2002).

2.2 Atmospheric Transport, Distribution and Deposition of Mercury

2.2.1 Modelled mercury concentrations and depositions

Modelling of mercury concentrations, deposition rates and transboundary fluxes over Europe for 1990 – 2003 was performed on the basis of official emissions and expert estimates (*Berdowski et al.*, 1997), using the Meteorological Synthesizing Centre – East Heavy Metals model (MSCE-HM). The geographic scope of this work generally covers the region defined by the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP).

Modelled concentrations of mercury in precipitation for 1990 are mainly within the range of 12 to >40 ng/L over central and eastern parts, and within 6 – 12 ng/L in the northern and south-western parts of Europe (Figure 2.1a). For 2003 modelled concentrations ranged from 6 to 12 ng/L over most of Europe, and from 12 to >20 ng/L in the eastern part of Europe, and were generally lower than the1990 values (Figure 2.1b).
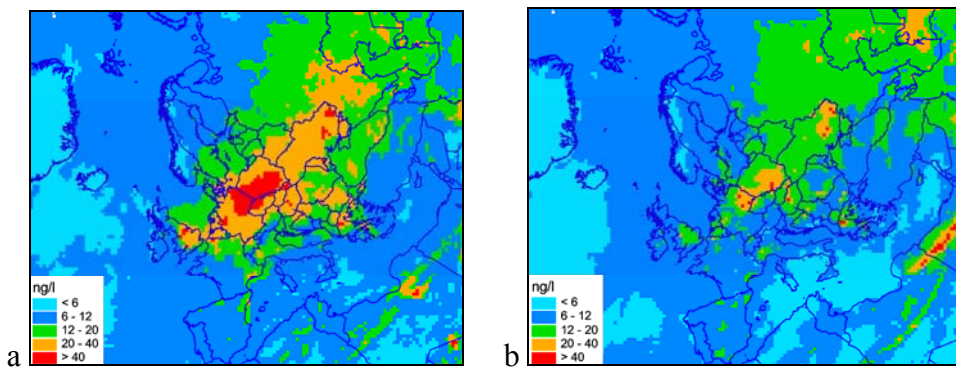
Figure 2.1. Modelled concentrations of mercury in precipitation over the EMEP region in 1990 (a) and 2003 (b)

For Europe as a whole the decrease in deposition for 1990 – 2003 was an estimated 1.6 times. The decrease in depositions for individual countries varied, reaching about three times in Germany, Czech Republic, Republic of Moldova and Slovakia (Figure 2.2). In 11 countries an estimated two-fold decrease took place. In 12 countries the depositions decreased by about 1.5 - 2 times.
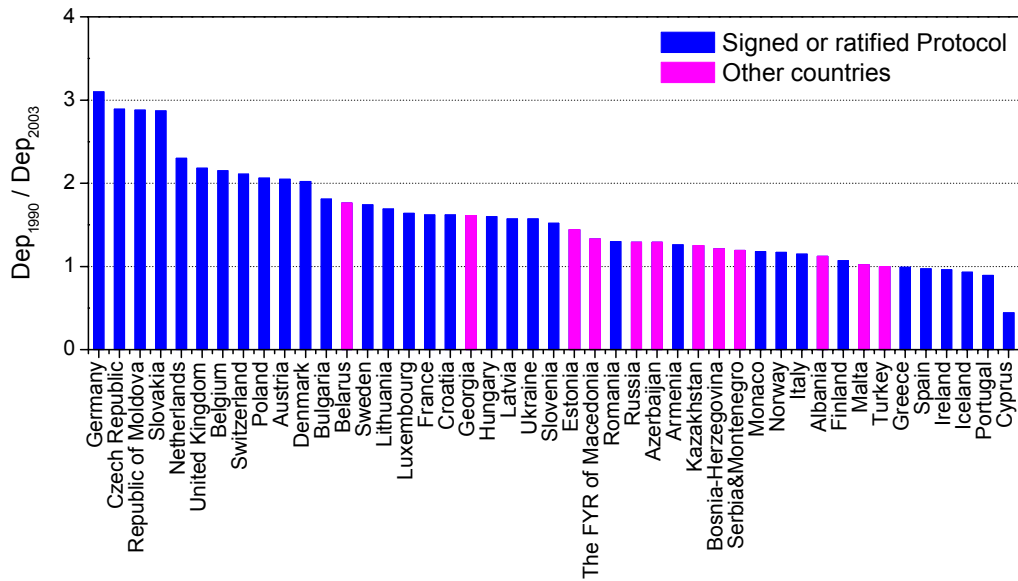
Figure 2.2. Ratio of modelled total depositions of mercury in 1990 to those in 2003 in countries of Europe

Contributions of mercury depositions to European countries from external anthropogenic European sources vary from 2 to 55% (Figure 2.3). In 11 countries this contribution made up more than 30%. The contribution of natural sources, global sources and re-emissions of mercury is higher compared to that of lead or cadmium: it ranges from 20% in Poland to 98% in Iceland. This high contribution is explained mainly by the global character of mercury atmospheric pollution.
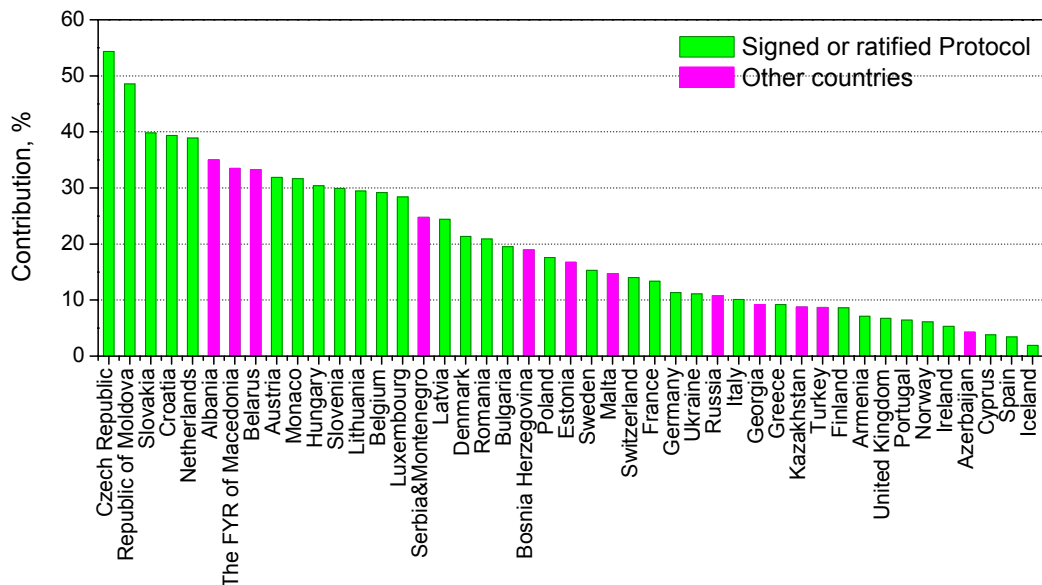
Figure 2.3. Contribution of external European anthropogenic sources to depositions of mercury in Europe countries in 2003

Recently in the U.S.A., modelling was conducted to serve as input to the benefits analysis for the 2005 Clean Air Mercury Rule (CAMR) for power plants. U.S. EPA used the Community Multiscale Air Quality (CMAQ) modeling system (a sophisticated photochemical air quality model) to predict the levels of mercury deposition from all sources (U.S. anthropogenic sources plus global sources) for years 2001, and 2020. The 2020 results reflect estimates of the co-control of mercury from implementation of the Clean Air Interstate Rule (CAIR) as well as emission reductions from (CAMR). CMAQ is a three-dimensional grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales. CMAQ accounts for spatial and temporal variations as well as differences in the reactivity of Hg emissions. Results are shown in Figure 2.4a, b. U.S. EPA estimates that most of the reductions (shown in Figure 2.4) will occur by 2010 due to the CAIR rule, which reduces a large portion of the ionic mercury (details are described in *U.S. EPA* (2005a and 2005b)).

To evaluate the modeling results, the results were compared with measured data from MDN. This comparison found that averaged annually over all MDN monitoring sites, CMAQ underestimates mercury wet deposition with a fractional bias of approximately -23 percent. This underprediction bias is well within a factor of 2 (*U.S. EPA*, 2005a).
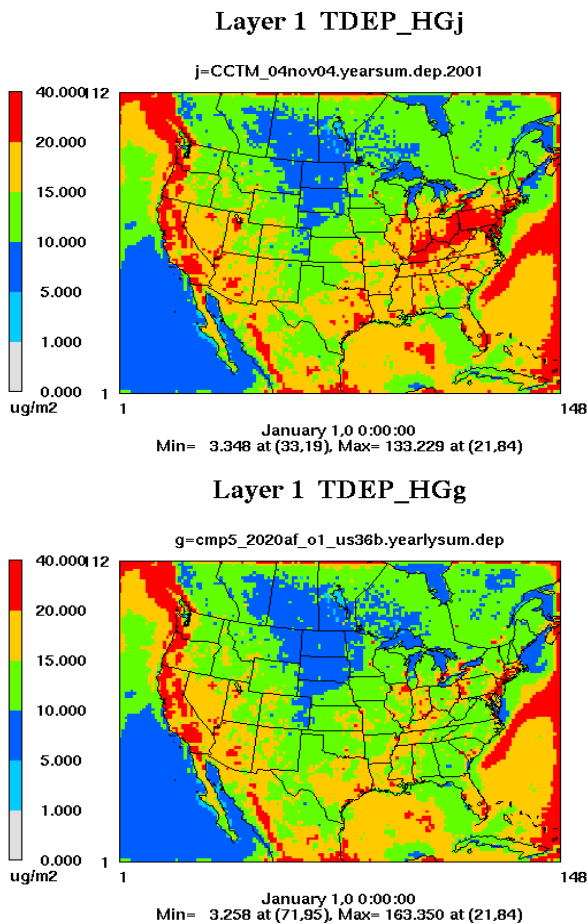
Figure 2.4. Modeled Mercury Deposition in U.S. From All Sources: in 2001 (a) in 2020 with CAIR & CAMR (b)

In the U.S.A., the National-Scale Air Toxics Assessment (NATA) is conducted by U.S. EPA to assess air quality, human exposures and risks for a range of chemicals. NATA includes modeling ambient air concentrations of 33 air toxics (including mercury). The NATA results for mercury are based on 1996 and 1999 emissions data and show modeled annual average concentrations (U.S. EPA, 2002; and U.S. EPA, 2006)." The NATA results are available on the U.S. EPA website, at: http://www.epa.gov/ttn/atw/nata/.

Intercontinental transport of mercury

Evaluating the contribution of intercontinental mercury transport to deposition levels over Europe and North America was achieved with the hemispheric version of EMEP/MSC-E model (MSCE-Hg-Hem). Figure 2.5 shows the modelled contributions of different continents to deposition of mercury in Europe for 1996. These results indicate that emissions from Asia contribute 15% to depositions in Europe, and emissions from North America contributed about 5% to deposition in Europe. The contribution from sources within Europe is about 60%.

The contribution of mercury in Europe from intercontinental transport varies from 2.5 to 10 g/km^2/y (Figure 2.6). The Relative contribution of mercury from emission sources outside Europe to depositions in Europe is spatially inhomogeneous (Figure 2.7). In the central part of Europe the contribution is about 25% while on the periphery of the region it exceeds 60%.
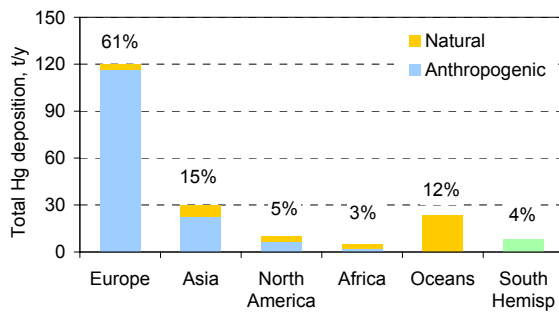
Figure 2.5. Contributions of global sources to mercury depositions in Europe in 1996
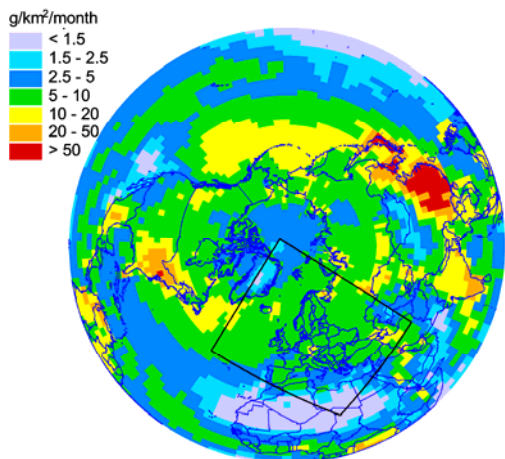
Figure 2.6. Spatial distribution of modelled annual deposition of mercury in the Northern Hemisphere (except for the deposition from European emission sources). Black line delineates the EMEP region
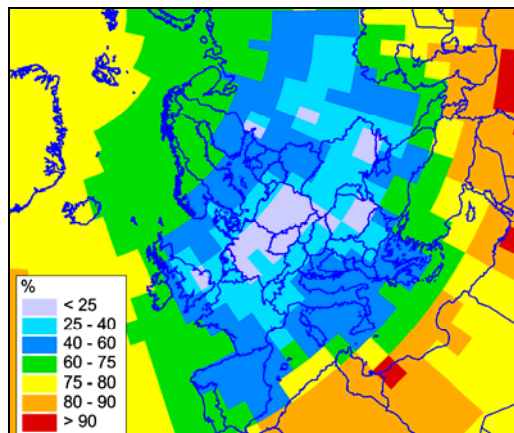
Figure 2.7. Relative contribution of non-European sources to mercury deposition in Europe in 1996

Mercury is capable of being transported over thousands of kilometres and depositing in remote regions like the Arctic. According to calculations of EMEP/MSC-E (Dutchak et al., 2003), more than 30% of depositions to the Arctic are caused by sources located in Asia, and more than 20% are from Europe (Figure 2.8). The contribution of the North American sources is estimated to be about 10%.

Modelled depositions over continental parts of the Artic range from 4 to 20 g/km^2/y (Figure 2.9). Over marine parts the depositions vary from 2 to 8 g/km^2/y.
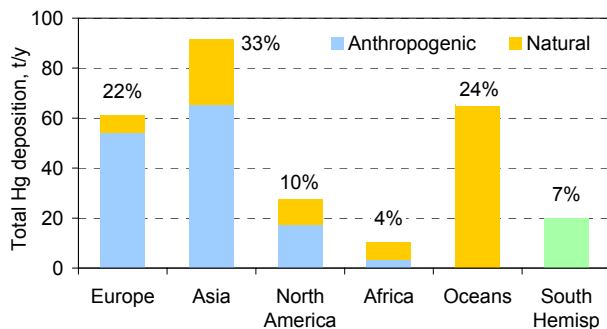
Figure 2.8. Contribution of different regions to the total annual deposition of mercury to the Arctic in 1996
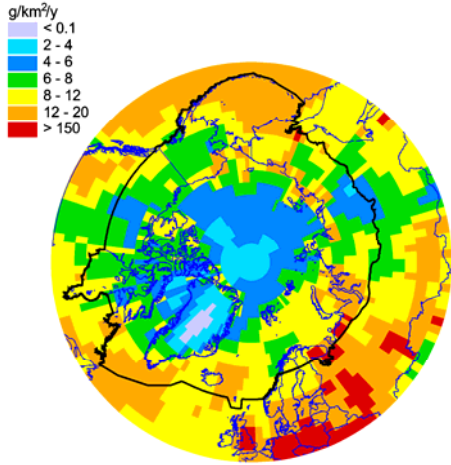
Figure 2.9.   Spatial distribution of annual mercury deposition fluxes in the Arctic. Black line delineates the Arctic boundary as specified by AMAP

The U.S. EPA used the CMAQ model to estimate the contribution to deposition in the U.S. from global sources. Figure 2.10a shows the modeled deposition in year 2001 from global sources (i.e., current anthropogenic emissions from sources located outside U.S.A, plus global natural sources, plus re-emissions of historic global anthropogenic releases). Figure 2.10b shows the modeled deposition in 2001 from all sources (i.e., global sources plus U.S. anthropogenic emissions for year 2001). The results indicate that a significant portion of the mercury deposition in the U.S.A. originates from the global sources. The contribution from global sources varies considerably in different areas of the U.S. Nonetheless, based on this modeling, U.S. EPA estimates that on average over 75% of the mercury deposition in the U.S. is from "global sources" (*U.S. EPA,* 2005c).
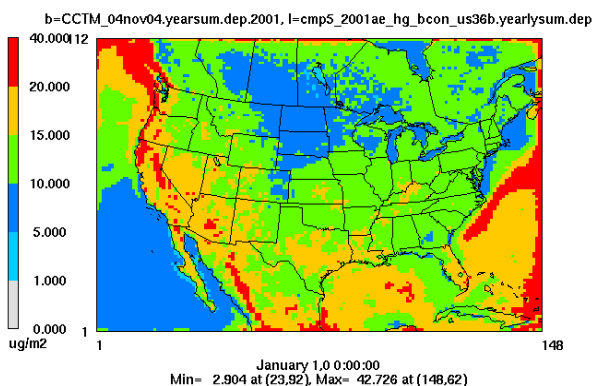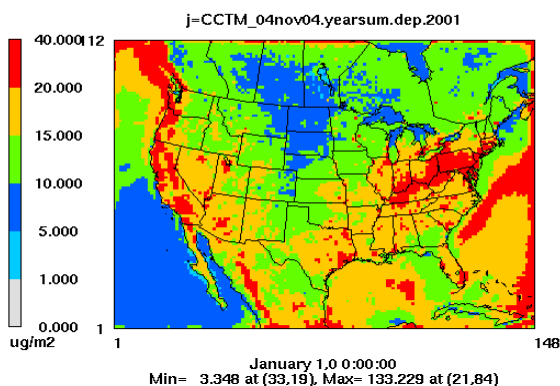
Figure 2.10. Modeled Mercury Deposition in U.S. in 2001. a: from global sources; b: from all sources.

Evaluation of modelling results

Evaluation of the MSCE-HM model uncertainties demonstrates that the intrinsic model uncertainty (uncertainty of model without emission data) varies over Europe from 15 to 20% for concentrations in air, from 30 to 70% for concentrations in precipitation and from 20 to 60% for total depositions (*Ilyin and Travnikov*, 2005).

Multi-stage mercury intercomparison study has shown that the participated models could predict the observed concentrations of elemental mercury with accuracy within ±20%. The accuracy for wet deposition is within a factor of two, whereas discrepancy between the models did not exceed 40%. Detailed description of the mercury intercomparison results is available in the scientific paper (*Ryaboshapko et al.,* 2002) and MSC-E reports (*Ryaboshapko et al.*, 2003, 2005).

Concentration levels of mercury in air and in precipitation are well reproduced by the MSCE-HM model based on available official emission data and expert estimates. Few mean annual values of modelled total gaseous mercury (TGM) concentrations differ from the observed ones more than by 30%. As much as 80% of modelled values agree with

measurements within the range ±50% of measured value. However, the model tends to somewhat overestimate mercury concentrations in precipitation.

The U.S. EPA evaluated the CMAQ modeling results by comparing the modeled deposition rates with measured data from MDN. This comparison found that averaged annually over all MDN monitoring sites, CMAQ underestimates mercury wet deposition with a fractional bias of approximately -23 percent. This underprediction bias is well within a factor of 2 (*U.S. EPA*, 2005a), which indicates that concentration levels in precipitation are also well reproduced by the CMAQ model.

2.2.2 Atmospheric Monitoring

As described above, emissions of elemental mercury can disperse great distances and stay in the atmosphere for between six and 24 months according to various estimates (Steffen et al., 2005). Given this long residence time, anthropogenically released elemental mercury easily undergoes (long-range atmospheric transport) LRAT and is dispersed throughout the atmosphere.

In 1990, information on measured concentrations of mercury in Europe was available from 7 stations, located in five countries. By 2003 the number of mercury monitoring stations in Europe increased to 15 spread over 8 countries.

Mercury is a global pollutant. Spatial and temporal variability of its air concentrations at a regional scale is not high. According to measurement data from EMEP stations for the period 1990-2003, measured air concentrations of mercury ranged from 1.3 to 2 ng/m^3.

In 1990, measurement data on concentrations in precipitation were too scarce to draw any conclusions about spatial patterns. The concentration averaged over a few stations was around 15 ng/L. In 2003, concentrations typically were 5 – 10 ng/L in northern and 6 – 10 ng/L in central parts of Europe.

There are only a few stations in Europe providing long-term measurements of mercury. Concentrations of mercury in air do not demonstrate any noticeable long-term trend. Concentrations in precipitation based on these limited data have been reduced by about 2-fold in central and northern Europe (Figure 2.11a, b)
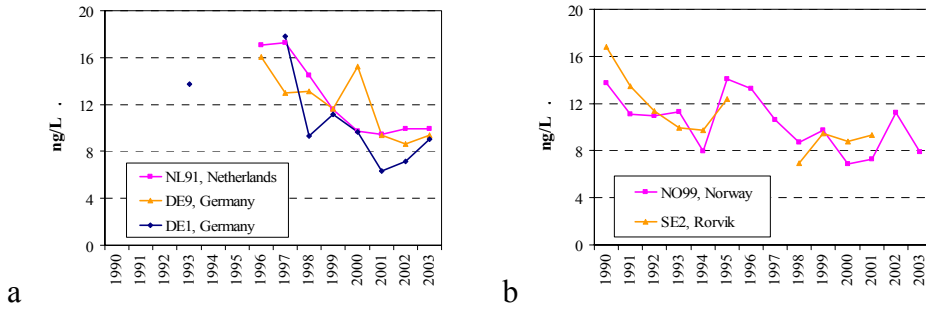
Figure 2.11. Observed concentrations of mercury in precipitation at stations in central (a) and northern (b) parts of Europe

In North America, mercury concentrations in precipitation (and wet deposition) are measured through the Mercury Deposition Network (MDN). The MDN began in 1995 with 13 sampling sites. In 2005, there were about 75 sites in the U.S.A., 10 sites in Canada, and 2 sites in Mexico (MDN 2006). The MDN is partly intended to provide information on the geographic distribution of mercury deposition and long-term trends. At a few selected sites, MDN is also serving as a location for mercury dry-deposition research, trace-metals wet-deposition and other monitoring research. Before the MDN, in the early 1990s, there were only a few mercury monitoring stations in operation in North America. Measured levels of mercury in precipitation over North America for the period from 1998 to 2004 can be characterized by data collected at the MDN. The northwest and east of the USA is characterized by concentrations of about 4 - 8 ng/L (Figure 2.12). The concentrations in the southern and central parts of the country typically ranged from about 10 to 15 ng/L. Based on information in Figure 2.12, there appear to be no distinct temporal trends of mercury concentrations in precipitation for 1998-2003.
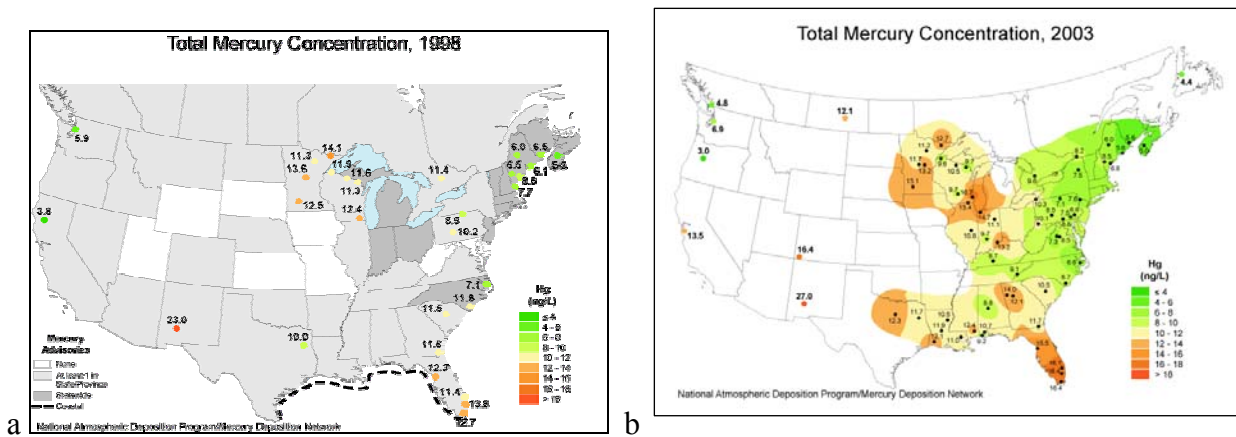
Figure 2.12. Mercury concentrations in precipitation in 1998 (a) and 2003 (b) from Mercury Deposition Network

Prestbo et al. (2003) investigated annual trends of mercury wet-deposition for each MDN site with 5 or more years of data over the years 1996 to 2002. There were 32 sites with 5 years of data or more. At the 90% confidence level, no significant trends were observed.

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However, a Maine site showed a significant decrease over time, but with only 4 years of data. A downward trend was also noted for a Florida site over the period 1993 to 2002. The overall lack of significant trends for MDN from 1996 to 2002 is in contrast to the overall decreasing rates of anthropogenic emissions in the last 14 years in the U.S.A. and Canada. However, *Prestbo et al.* (2003) explain that the discrepancy could be partly due to lack of consistency in the timeframe of their analysis (1996-2002) and the time of decreases in anthropogenic emissions (which began in earlier years), and that if high-quality mercury wet-deposition measurements started as early as 1990, a more distinct downward trend may have been observed (*Prestbo et al.,* 2003). The lack of trends is also likely due, in part, to the large contributions to mercury deposition from the Global Pool (as shown in Figure 2.10).

In an attempt to characterize global mercury trends in the late 20th century, Slemr et al. (2003) compiled atmospheric monitoring data from land based monitoring stations and ship cruises. Results for sites located around the North Atlantic indicated a rise in total gaseous mercury (TGM) concentrations that peaked at 3.5 ng/m^3 in the 1980s and then steadily declined and have remained relatively constant since about 1996 at about 1.7 ng/m^3 (Figure 2.13).
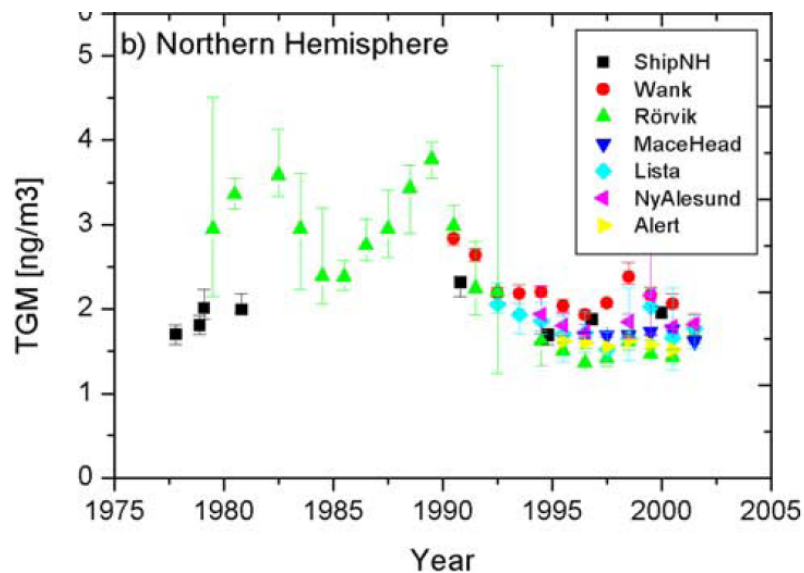
Figure 2.13. Trends of TGM concentrations in the northern hemisphere. The points and bars represent the annual medians (or cruise medians) and the 95% confidence intervals, respectively (adapted from Slemr et al., 2003)

In the Arctic, far from emissions sources, atmospheric mercury concentrations have been monitored since the early 1990s at several Arctic stations including: Alert (Canada), Barrow (Alaska), Svalbard (Norway), Station Nord and Nuuk (Greenland), Torshavn (Faroe Islands) and Amderma (Russia). Annual mean total gaseous mercury concentrations at each of these stations show little variation around 1.5 ng/m^3 (AMAP 2005). Temporal trends have been assessed at two stations where decent temporal datasets exists. No discernable long-term trends were observed at either Alert between

1995 and 2002 or Svalbard between 1994 and 2000 (Steffen et al., 2005), which is consistent with the findings of Slemr et al. (2003).

The 2002 AMAP assessment report on heavy metals (AMAP 2005) reports on mercury concentrations in rainwater for several Scandinavian sites. The data from these monitoring stations reported in 1991 indicated a strong decreasing south-to-north gradient in wet deposition of mercury, with much of the mercury being associated with particulate. At southern stations mercury was strongly correlated with sufate and pH which is indicative of anthropogenic sources. A substantial decrease in mercury wet deposition, from 27 $\mu g/m^2/yr$ to 10 $\mu g/m^2/yr$, was observed between 1987-89 and 1990-92, which coincided with the dramatic political and economic changes that occurred in Eastern Europe. In the late 1990s the decreasing south-to-north gradient in mercury deposition persisted but weakened as rates of wet deposition decreased throughout Scandinavia.

At the majority of the Arctic monitoring stations the annual record of gaseous elemental mercury (GEM) concentrations is characterized by a similar seasonal pattern. At Alert, where seasonal mercury trends have been studied extensively, the seasonal pattern is characterized by levels of GEM near background and little variability during the winter, however, variability starts to increase with the approach of spring. Spring is punctuated by frequent, large fluctuations in GEM, the onset of which coincides with polar sunrise. In early summer GEM concentrations are elevated and the variability decreases. Towards late summer and early fall, GEM returns to background concentrations and low variability that carry on through winter (Figure 2.14) (Steffen et al., 2005). The fluctuations experienced in spring, referred to as mercury depletion events (MDEs), represent the rapid conversion of GEM to a reactive form of gaseous mercury, Hg(II), which is then deposited onto particulate and the terrestrial surface (i.e. snow). The MDEs can last several days and appear to result from chemical interactions between solar radiation, GEM, ozone, and marine halogens (e.g. Br, and maybe Cl). It is hypothesized that MDEs could be an important mechanism whereby a pulse of mercury is delivered to Arctic ecosystems every spring. The timing of this sudden influx of bioavailable mercury, which coincides with a period of intense biological activity, provides optimal conditions for food web uptake and bioaccumulation.
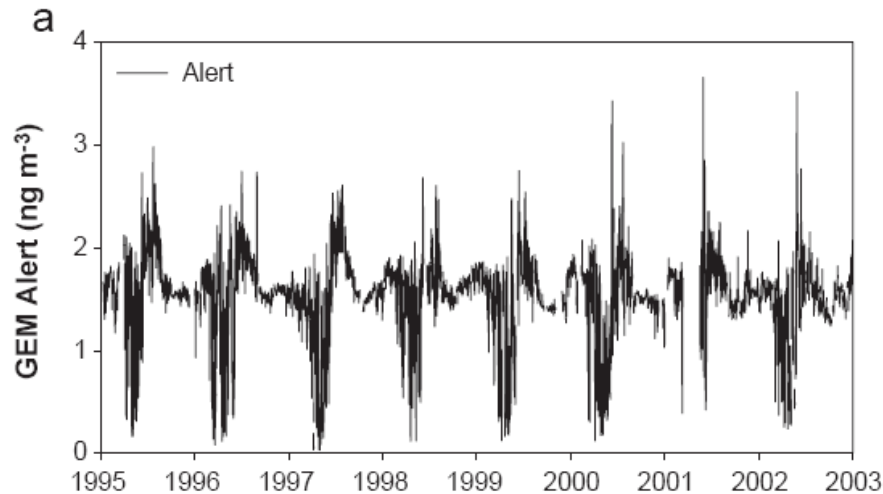
Figure 2.14. Time series of gaseous elemental mercury at Alert (1995 – 2002). (From Steffen et al., 2005)

Research at Barrow Alaska suggests that while some of the mercury deposited during MDEs is converted back to GEM and re-emitted to the air, the majority (60-80%) remains at snowmelt. During snowmelt, mercury, some of which is bioavailable, is delivered to the surrounding tundra through runoff and percolation at concentrations of roughly 30 ng/L (AMAP 2005). Results from other research, however, suggests that the majority of MDE deposited mercury is quickly converted back to GEM and then re-emitted to the air (St. Louis et al., 2005) implying that MDEs transfer little mercury to surrounding ecosystems. It seems likely that MDEs are responsible for the delivery of some mercury to Arctic ecosystems, however, how much mercury is actually transferred and in what form, i.e. bioavailable or not, remains uncertain.

Estimates of mercury input to Canadian Arctic waters, that include both standard deposition and deposition from MDEs, range from 50 – 300 t/yr (Lu et al., 2001; Lindberg et al., 2002). These estimates of annual mercury deposition are equal to approximately 6-10% of the total estimated anthropogenic mercury emissions worldwide (about 2235 t/yr). The fact that this deposition occurs over only 1-2% of the earth's surface suggests that the Arctic is somewhat of a sink for mercury deposition (AMAP 2005), perhaps due to the occurrence of MDEs, which are unique to polar regions.

2.2.3 Atmospheric deposition as documented in natural archives

This section examines historic rates of atmospheric mercury deposition as documented in natural archives of metal deposition such as lake sediments, peat bogs, and glaciers. Each of these media can be particularly useful as they integrate both dry and wet deposition of metals into layers of sediment, peat and ice that are formed year after year. Each of these media can be sampled by various coring techniques that preserve the historical record of deposition that is stored through the depth of the core. The depositional record is interpreted by aging the layers of the core, thereby developing an

historic timeline for the formation of the core layers, and combining that with measured concentrations of metals. A cautionary note about interpreting trends from sediment cores comes from the AMAP 2005 report: The mercury concentrations in these media could be influenced by chemical diagenesis, thereby distorting the temporal record of mercury deposition. Diagenesis refers to the biogeochemical changes that sediments undergo after they are deposited. Concerns about diagenesis are greatest for marine cores, which generally aren't as reliable for the assessment of recent historical records as lake sediments are. Chemical diagenesis and it's implications for lake sediment cores is a topic of recent and ongoing study, however the extent to which these processes may influence the temporal record is still uncertain.

Sediment cores

Atmospheric deposition of mercury into aquatic ecosystems is recognized as the most important source of mercury to these sensitive environments (Swain et al., 1992; Fitzgerald et al., 1998). In a study of remote lakes in Minnesota and Wisconsin, USA, Swain et al. (1992) found that the deposition of atmospheric mercury increased 3.4 fold (from 3.7 to 12.5 $\mu g/m^2/yr$) between 1850 and 1990. The findings for the period late-1970s to late-1980s agreed with the peaking of atmospheric mercury concentrations reported by Slemr et al. (2003) discussed above. Swain et al. (1992) were also able to demonstrate how the entire increase in mercury input could be accounted for by increases in atmospheric depositions, and implied that pre-industrial atmospheric mercury levels were approximately 4-times lower than levels in 1990. More recently, Perry et al. (2005) conducted a similar study on numerous lakes in the North Eastern United States and derived estimates of current and historical atmospheric mercury deposition rates. Perry et al. (2005) also compared results between several other studies on North American lakes and found relatively good agreement, with estimates for peak atmospheric mercury deposition rates generally falling between those of Swain et al. (1992) and their own upper estimates of 60 $\mu g/m^2/yr$ for years 1980 to 2000. Historic deposition profiles, as interpreted from lake sediment cores, imply that Hg deposition peaked sometime between 1970 and 1990 and then generally appear to level off or decrease during the 1990s (Figure 2.15). The implied levelling off of mercury deposition rates in the North Eastern USA and Eastern Canada over the past 10-20 years is also supported by the lack of recent trends in atmospheric mercury concentrations and measured deposition rates in Vermont (Keeler et al., 2005). However, Engstrom and Swain (1997) found declining levels of deposition through the 1980s and 1990s in lake sediments from remote areas of Minnesota.
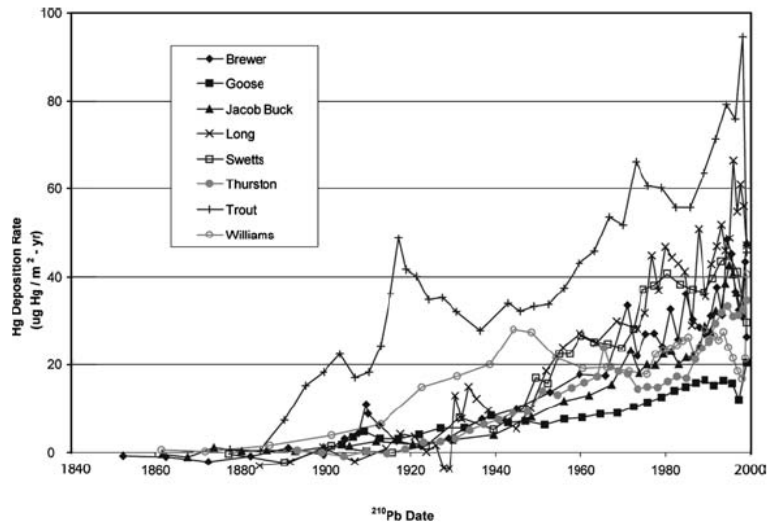
Figure 2.15. Corrected anthropogenic Hg deposition rates (HgA,F) in a cluster of eight Maine lakes, central Maine, USA. (From Perry et al., 2005)

Sediment cores from Arctic lakes have also demonstrated higher rates of mercury deposition in modern versus pre-industrial sediments. A study of sediment cores from a lake on Devon Island, Canada, indicates a 2-fold increase in deposition rates from a range of 2.5 – 5.9 µg/m^2/yr to a range of 6.8 – 10.9 µg/m^2/yr, in pre-industrial versus modern sediments, which is similar in magnitude to the increases seen in other Arctic lakes (Outridge et al., 2005a; AMAP 2005). Analyses of sediments in the high Arctic lakes indicated increased mercury deposition without the levelling off or declines that were found in sediment studies in some more southern lakes to which results were compared (e.g. Lake Winnipeg) (AMAP 2005). Arctic sediment cores have recently been examined for climate change related effects on the observed increases in mercury concentrations. In some lakes (e.g. DV-09 on Devon Island) there is evidence that climate induced increases in phytoplankton productivity may be responsible for increased mercury scavenging in the water column, thereby increasing the deposition of mercury to sediment (Outridge et al., 2005a). This hypothesis is supported by a correlation between mercury and diatom concentrations in sediment over the past 400 years, and the fact that recent trends seen in the cores do not reflect the recent declines reported for anthropogenic mercury emissions that are seen in lake sediments (and other temporal records like glacial ice cores and ombrotrophic peat bogs) from other remote regions. Outridge et al. (2005a) suggest that climate related changes in limnology may be driving the mercury trend observed in high Arctic lake sediments, but that mercury trends in sediments of lakes further to the south, which have not seen the same magnitude of change, are probably more reflective of anthropogenic emissions. A study by Muir et al. (2005) looked at similar indicators of lake productivity in cores from eight Arctic lakes and did not observe the same associations between micro-fossils and mercury that Outridge et al. (2005a) reported in the core from Devon Island. A levelling off or decreasing trend in mercury deposition through the 1990s was evident in seven of the eight cores examined by Muir et al. (2005), which was not the case for the Devon Island cores.

Muir et al. (2004) looked at sediment core records of mercury deposition in a large number of North American lakes that extended from the high Arctic south to Massachusetts and from Yukon east to Labrador. Not only did the authors analyze a large number of cores, but they also include a good review of other recently reported results to develop comparisons on a continental scale. Mercury concentrations in surface sediments were compared to concentrations in sediment layers formed in pre-industrial times to produce enrichment factors. Enrichment factors measured for this survey ranged from 0.62 to 3.3, which is in good agreement with results from other studies (AMAP 2005). The sediment core profiles also implied that depositions had declined or levelled off during the 1990s. Increased enrichment was observed from west to east and suggests the influence of emission sources in eastern North America.
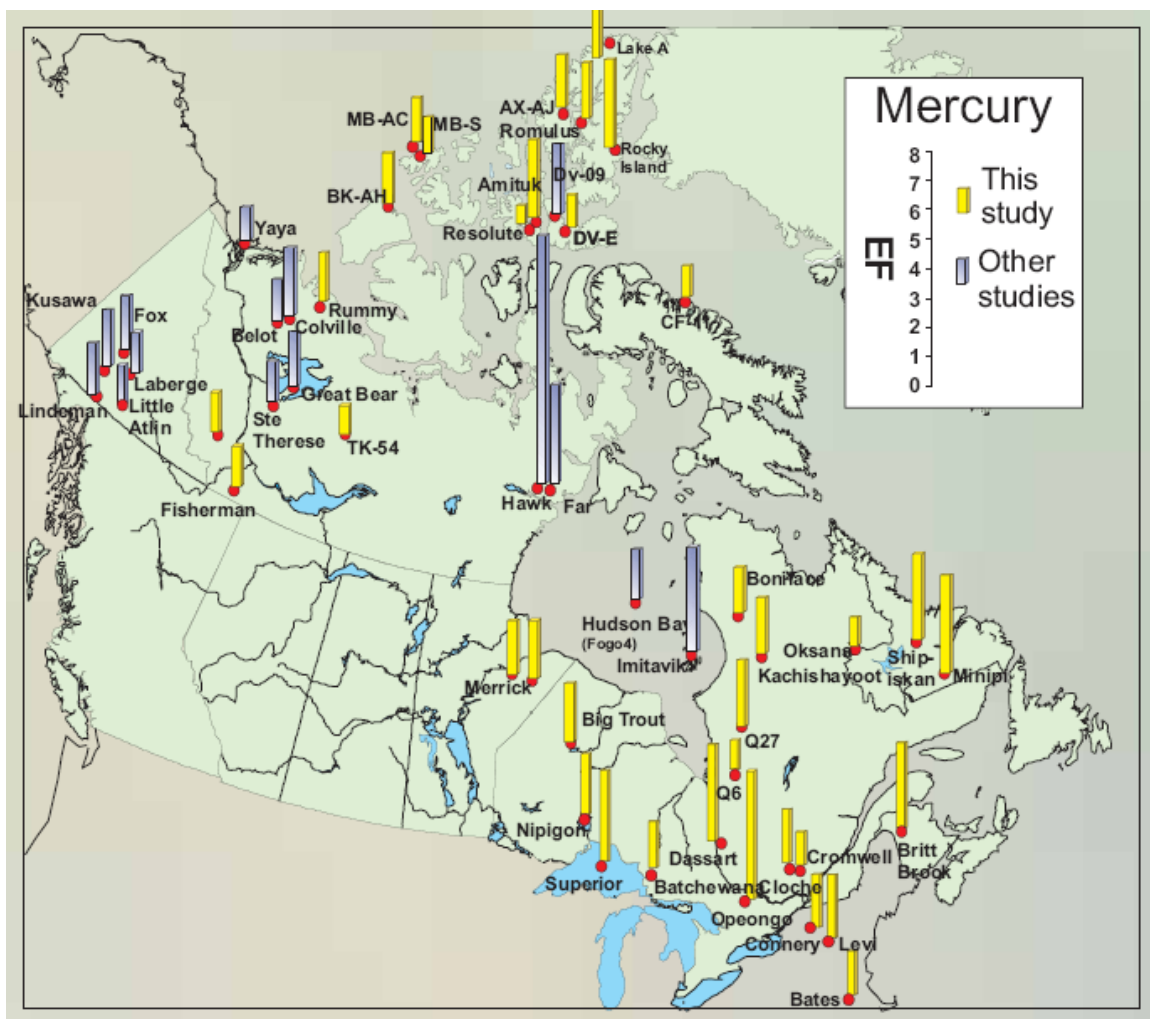
Figure 2.16. Geographical trends in mercury enrichment factors (EF) in lake sediments. (taken from Muir et al., 2004)

A number of studies have also been conducted on European lakes, including lakes in Greenland, Sweden, Finland, Norway and Russia. The majority of these studies found

that recent, post-industrial deposition of mercury to lake sediments was significantly higher than pre-industrial deposition. In some of the regions, eg. Alaska, whwere enrichment factors are low, it is thought that high levels of local geologic mercury masks the anthropogenic signal (AMAP 2005).

A decreasing south to north gradient in mercury enrichment factors was observed in Scandinavian countries, reflecting perhaps the closer proximity of southern lakes to source regions. Another study carried out in Greenland compared enrichment factors in a transect of lakes stretching from the coast inland to the edge of the ice sheet. The results demonstrated higher enrichment factors near the coast, and suggested this was due to the occurrence of mercury depletion events, the chemistry of which require marine halogens. While inland lakes displayed lower enrichment factors, a series of lakes adjacent to the ice sheet, and the furthest inland, had the highest enrichment factors of the whole transect. The authors speculated that meteorological conditions unique to the ice sheet edge were responsible for enhanced deposition and retention of atmospheric mercury (AMAP 2005).

The results of these studies all demonstrate that, while anthropogenic influences on atmospheric mercury deposition contributes to observed post-industrial mercury enrichment, there are numerous environmental factors that also seem to affect the accumulation of mercury in lake sediments and likely other media as well. Caution must therefore be used when interpreting the causal factors influencing the sediment record.

Peat Bogs
In a recent assessment of peat cores from Ireland, Coggins et al. (2006) found peak deposition of mercury occurred sometime between 1950 and the 1970s. Mercury deposition rates calculated from the Irish bogs were similar to those measured in North America though slightly lower than what had been measured in remote bogs from Europe (Coggins et al., 2006). Based on the sampling locations and similarity with trends measured in America, the authors suggest that the study site was influenced primarily by transatlantic transport of atmospheric mercury emitted in North America. Recent rates (1993-1996) of mercury deposition were in the range of 6-24 $\mu g/m^2/yr$. Cores have also been collected from Arctic and sub-Arctic sites including Canada, Greenland, Norway and the Faroe Islands. In all instances the core profiles showed increased mercury levels in post-industrial layers of the cores, ranging from 7 to 17-fold in cores from Arctic Canada and up to 14-fold in Greenland (AMAP 2005).

Ice Cores
One of the most impressive temporal records of mercury deposition to remote environments comes from an analysis of ice cores collected from the upper Fremont Glacier, Wyoming USA (Schuster et al., 2002). The core captures a record of mercury deposition to the surface of the glacier between 1720 and 1993, and highlights both increases in atmospheric deposition related to anthropogenic emissions, as well as natural events, like volcanic eruptions (Figure 2.17). Consistent with the results from lake cores, the ice core suggests mercury deposition peaked in the early 1980s and then decreased

through the last ten years captured by the core. Peak deposition rates inferred from the ice-core suggest a 20-fold increase over pre-industrial deposition levels.
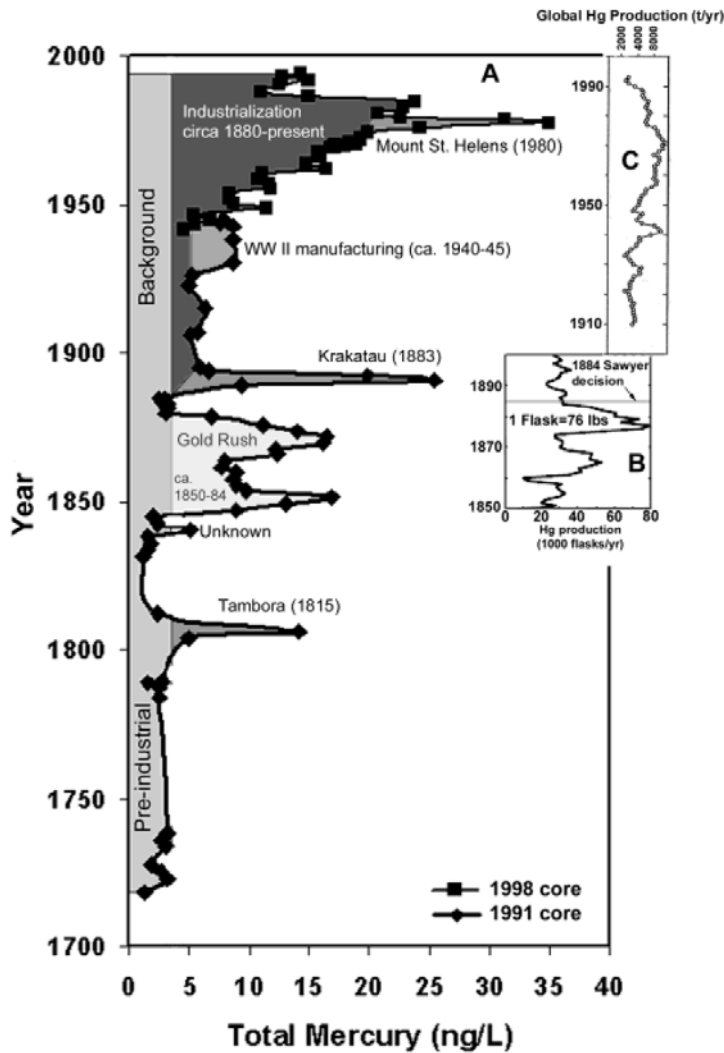
Figure 2.17. A) Profile of historic concentrations of Hg in the Upper Fremont Glacier. A conservative concentration of 4 ng/L was estimated as preindustrial inputs and extrapolated to 1993 as a background concentration. Age-depth prediction limits are ±10 years (90% confidence level); confidence limits are 2-3 years. (Schuster et al., 2002)

2.3 Levels and Trends of Mercury in Terrestrial Ecosystems

Terrestrial food chains derive the majority of their heavy metal exposure from the consumption of plants by herbivores. Plants can take metals up directly from the soil and water contained in the soil matrix through root systems and they can also take metals directly from the air.

2.3.1   Soils

Retention of mercury in various European forest catchments was estimated at a number of International Cooperative Programme on Integrated Monitoring (ICP-IM) sites by comparing output fluxes resulting from runoff (RW) to input fluxes from deposition. Total deposition was assumed to be the sum of throughfall (TF) and litterfall (LF). A ration of RW/(LF+TF) that is greater than 1 implies that the catchment is actually giving up mercury, whereas a ration less than 1 implies the catchment is accumulating mercury. In four Swedish catchments (ICP IM sites: Gardsjon, Aneboda, Kindla, Gramtratten) output fluxes were lower than input fluxes in the late 1990s and the early 2000s, with ratios (RW/(LF+TF)) of 0.074; 0.055; 0.04; 0.19, respectively, indicating retention of mercury in these catchments (Bringmark and Lundin 2004).

Little data on metals in soils from remote areas of the Arctic have been reported by AMAP. Based on data from Greenland, background concentrations of mercury in soils have been estimated at <0.01 – 0.03 mg/kg (AMAP 1998). Extensive sampling of surface humus layers of forest soils has been carried out in Norway where results showed a slight decreasing gradient from south to north (AMAP 2005). This relatively minor north-south trend was notably weak compared to the strong gradient seen in wet-deposition (See section 2.2.2). The AMAP (2005) report hypothesizes that mercury is retained more effectively in the colder soils of the north, thereby reducing the influence of lower wet deposition rates. Under warmer conditions re-emission from the soil would be more rapid.

2.3.2   Plants

Information on Hg contents in higher plants is rather scarce. The valuation of literature data resulted in a range of 0.01 to 0.1 mg/kg (dw) for grassland species and crops under background conditions (De Vries and Bakker 1998, Nagel et al. 2000). Alrikson et al. (2002) reported Hg contents in spruce of 0.004 mg/kg (dw, stem wood) and 0.008 mg/kg (dw, stem and bark) (ICP Modelling and Mapping Manual 2004).

There is substantially more information on metals in mosses and lichens. Mosses and lichens are particularly useful for the assessment of atmospheric deposition of heavy metals since they lack substantive root and vascular systems, and therefore primarily accumulate metals directly from the atmosphere. Twenty-eight European countries and

almost 7000 sites have been involved in the most recent survey of heavy metals in mosses 2000/2001 in Europe. The survey was coordinated by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). Mercury concentrations in mosses were ranging from < 0.02 mg/kg to 0.08 mg/kg in the predominant part of Central and North Europe. High concentrations up to > 0.24 mg/kg occur in individual 50 x 50 km grid cells over Europe, but mainly in East Europe (Harmens et al. 2003, WGE 2004).

Extensive surveys of mercury in moss from northern Scandinavia found levels generally ranged between 0.02 and 0.04 mg/kg dw, and from the Faroe Islands levels were slightly higher and ranged from 0.02 to 0.07 mg/kg. In southern parts of Sweden and Finland, however, concentrations were about 2.5 times higher and more variable with levels up to 0.14 mg/kg dw. Similar north-south differences were not observed in Norwegian samples. As discussed in the previous paragraph this could be due to enhanced retention in colder climates. The differences could also be due to a combination of different patterns of climate, precipitation, and atmospheric transport pathways (AMAP 2005).

Mosses from Alaska and the Taymir Peninsula, Russia, had higher concentrations of mercury than the Scandinavian mosses. Concentrations ranged from 0.02 – 0.11 mg/kg dw and 0.12 – 0.55 mg/kg dw respectively.   These general trends seem to also apply to different species of moss and lichen. Greenland samples were generally similar to results from the Faroe Islands and slightly lower than samples from Alaska.

The metals that plants remove from the air may be of a LRTAP origin, however, they may also originate from local wind blown dust. This was investigated further by comparing the ratios of mercury to other metals both in the plant and in the surrounding soil. The resulting enrichment factors that were calculated for the Alaskan mosses were relatively high, suggesting that the mercury concentrations were the result of sources other than local soils and dust (AMAP 2005).
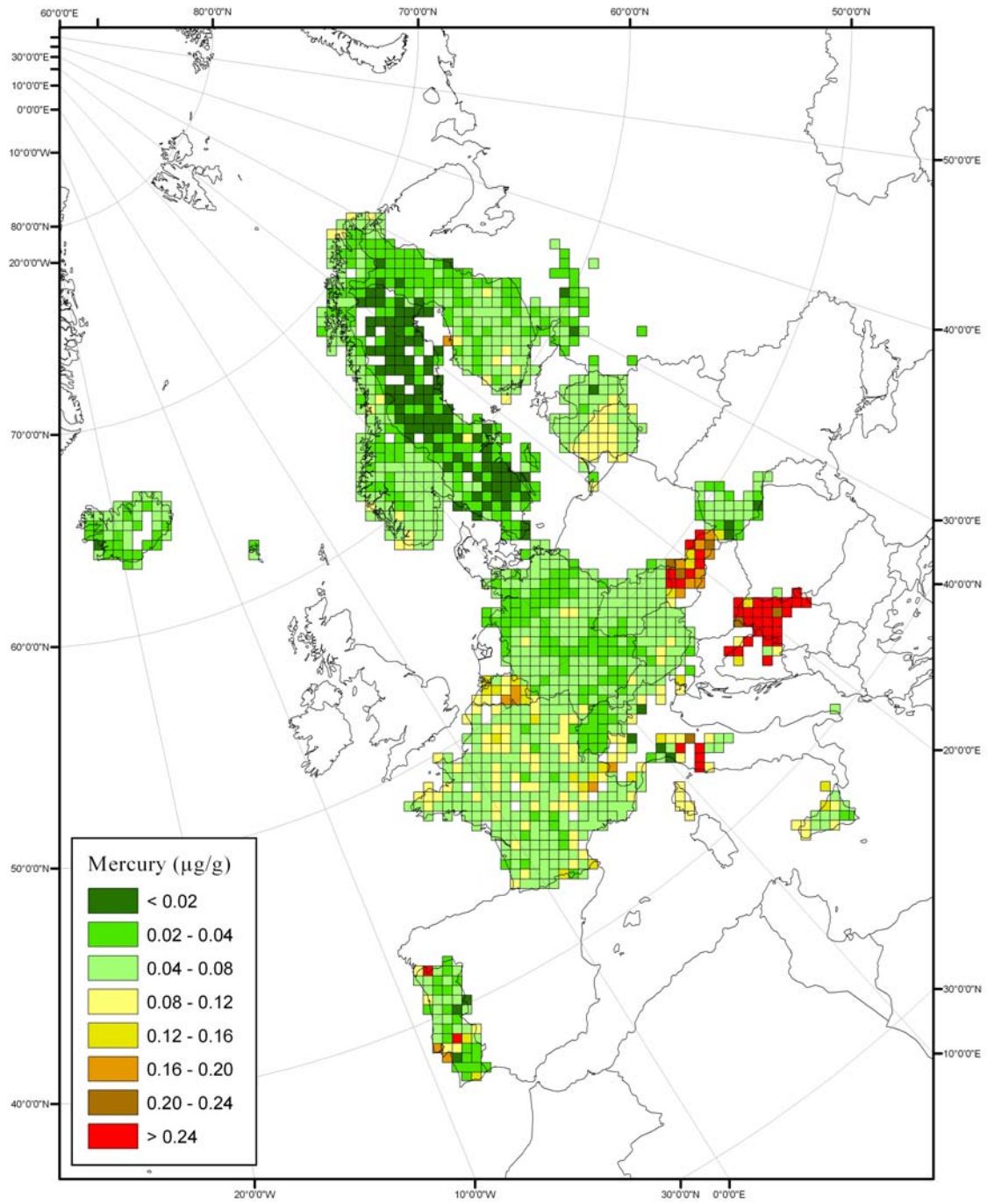
Figure 2.18. Mercury concentrations in moss in Europe, 2000/2001 survey (WGE 2004).

2.3.3 Birds

Circumpolar data on mercury in ptarmigan, a widely distributed non-predatory terrestrial bird, reported that mercury concentrations in breast muscle were generally below detection limits. Higher levels were observed in liver and kidneys, with concentrations ranging from 0.006 to 0.04 mg/kg wet weight (ww) across all regions of the circumpolar Arctic. Only the Taymir peninsula, Russia, had a set of ptarmigan livers with higher levels, mean 0.093 mg/kg ww (AMAP 2005).

2.3.4 Mammals

Reindeer/caribou and moose are the most widely studied terrestrial mammals. As with most other species, these ungulates tend to accumulate Hg in the kidney, liver, and muscle, to respectively decreasing concentrations. Concentrations in liver were lowest among reindeer from the Scandinavian countries and Russia, ranging from 0.013 – 0.4 mg/kg ww (Figure 2.19). The highest levels of mercury in liver were reported for North American caribou where concentrations ranged from 0.38 – 0.7 mg/kg ww (AMAP 2005). The comparison did not speculate about the influence of anthropogenic sources on measured mercury concentrations in caribou liver. A number of factors may influence the concentrations of mercury measured in the caribou, including the age of the animal, the season in which it was collected, local geology and diet. In the AMAP (2005) report, the availability of lichen as winter forage was identified as an important factor to be considered when interpreting temporal trends.

Data on other terrestrial herbivores are fairly scarce but AMAP (2005) does report some data for lamb, sheep, muskox and hare, all of which had mercury concentrations in either liver or kidney that were about an order of magnitude lower than the values reported for caribou and reindeer.

Mercury and cadmium were measured in terrestrial carnivores in Arctic Canada including mink, fox, wolverine and wolf (Figure 2.20). Mercury concentrations in wolf and wolverine were low (around 0.1 mg/kg ww in liver) reflecting their exclusively terrestrial diet. Mink and fox, however, displayed liver mercury concentrations in the range of 0.3 – 1.6 mg/kg ww, indicative of consumption of prey from freshwater and marine ecosystems. The highest levels of mercury were measured in fox from a coastal population known to scavenge the remains of ringed seal (Gamberg et al., 2005a). Results for cadmium are discussed further in Chapter 3. Results for Mink are discussed further in Section 2.4.3 in the context of freshwater ecosystems.
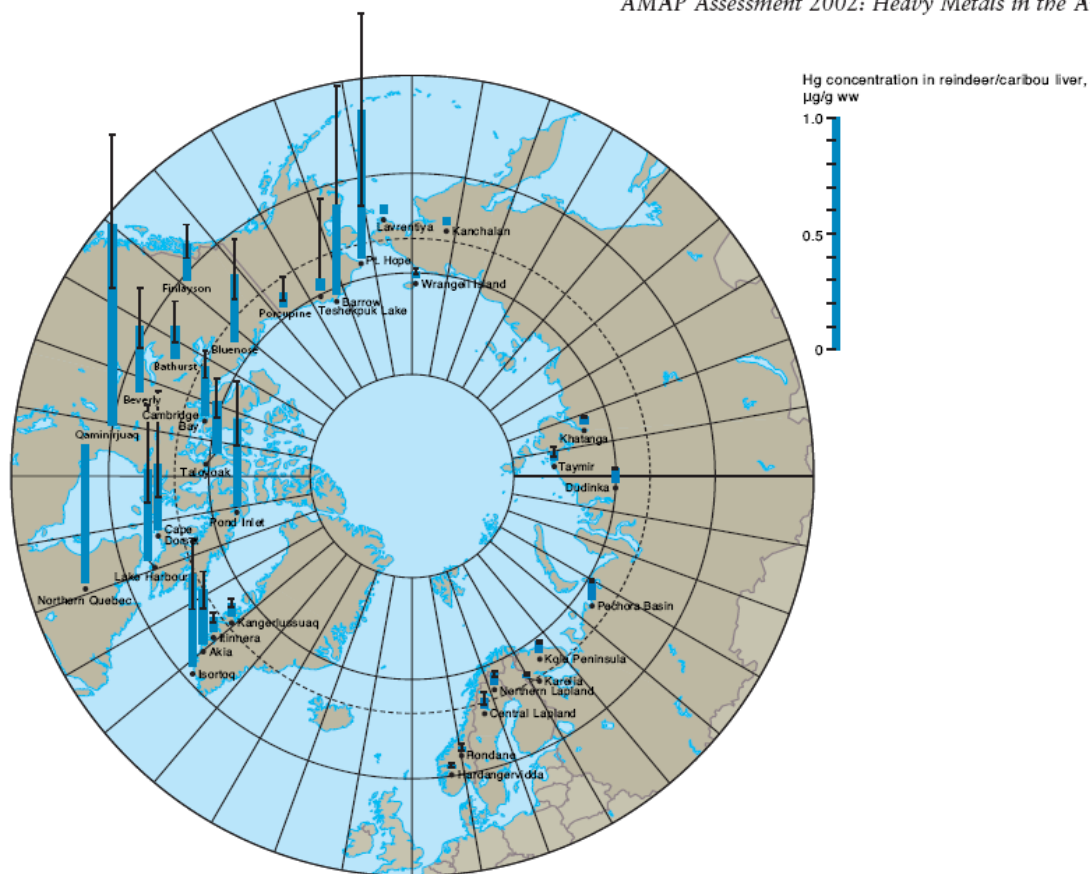
Figure 2.19. Concentrations of mercury in caribou and reindeer (AMAP 2005).
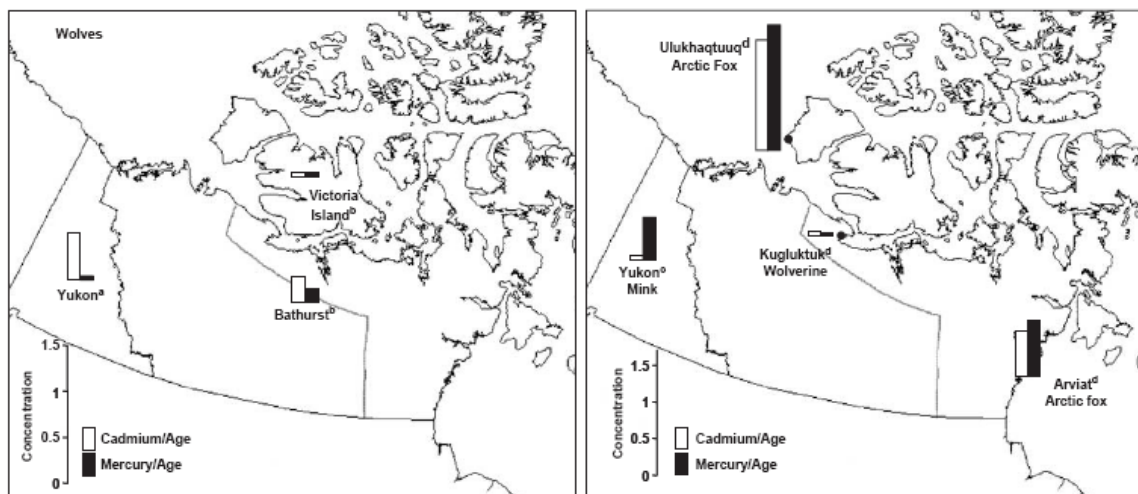
Figure 2.20. Mean concentrations of liver cadmium/age (mg/kg dry weight/year) and mercury/age (mg/kg wet weight/year) in carnivores from the Canadian Arctic.

2.4 Levels and Trends of Mercury in Freshwater Ecosystems

In aquatic environments atmospherically deposited inorganic mercury can be converted to organic forms of mercury, particularly methylmercury, which is bioaccumulative and toxic. Methylmercury is easily accumulated by invertebrates and subsequently passed up the food chain, biomagnifying with trophic level. For this reason, long lived predatory fish can accumulate relatively high levels of methylmercury in their flesh. A number of factors related to specific freshwater ecosystems can influence the rate of mercury methylation thereby influencing the rate of food chain uptake. While mercury concentrations in surface sediment may be a factor, they are quite poor at predicting mercury concentrations in fish.

Mercury methylation rates reflect a combination of environmental factors that influence: 1) bioavailability of inorganic mercury (Hg(II)) in water and sediments and 2) the activity of methylating microbes responsible for converting inorganic mercury into methylmercury (Sunderland et al. 2006).   In general, methylation rates are a complex function of the specific biogeochemistry of each aquatic system that affects the supply and distribution of organic carbon (e.g. algal productivity), sulfur (both sufate and sulfide species), and the supply of inorganic mercury (Benoit et al., 2003). A comprehensive discussion of the latest research in this area is beyond the scope of this discussion. Rather, the following section will focus on levels and trends of mercury in freshwater ecosystems.   Freshwater fish are a particularly important source of nutrition to certain human populations, however, this food source can also be a primary route of exposure to methylmercury for these populations. Concentrations of mercury in freshwater fish are a function of the availability of methylmercury in freshwater ecosystems both from in situ production and the watershed, as well as the diet composition and tropic level of each species (Harris et al. 1998). Because methylmercury bioaccumulates in the food web and is effectively retained by most aquatic species over their lifetime, older (and therefore often large), slow growing piscivorous fish have the highest concentrations of mercury (Doyon et al. 1998).

2.4.1   Fish

One of the most complete surveys of mercury in Arctic freshwater fish exists for land-locked Arctic char. AMAP (2005) reports mercury levels in muscle of land-locked char from lakes in northern Canada, Greenland, Iceland, Faroe Islands, Sweden and Finland (Figure 2.21). Unlike sea-run char, land-locked char spend their entire lives in lakes and can have mercury concentrations that are three to fifteen times higher than sea-run char. Mean concentrations reported in AMAP (2005) range from 0.013 mg/kg ww in Iceland to highs of 0.8 mg/kg ww in a lake in Greenland.

In Northern Canada, mercury data have been collected for a number of species including lake whitefish, lake trout, walleye, northern pike, white sucker and burbot. Lake whitefish is relatively plentiful and an important food species that occupies a relatively low trophic position. Consequently, mercury concentrations in whitefish are relatively low and generally fall within the range of 0.02 – 0.2 mg/kg ww. Lake trout is also an

important food species, however, it is a long lived predatory species and can have mercury concentrations that usually exceed 0.2 mg/kg ww and regularly exceed 0.5 mg/kg ww.   Other predatory species like pike and walleye tend have mercury concentrations that are similar if not higher than in lake trout. These levels are significant relative to Canadian food consumption guidelines that set 0.2 mg/kg as the limit for subsistence consumers and 0.5 mg/kg as the limit for commercial sale.
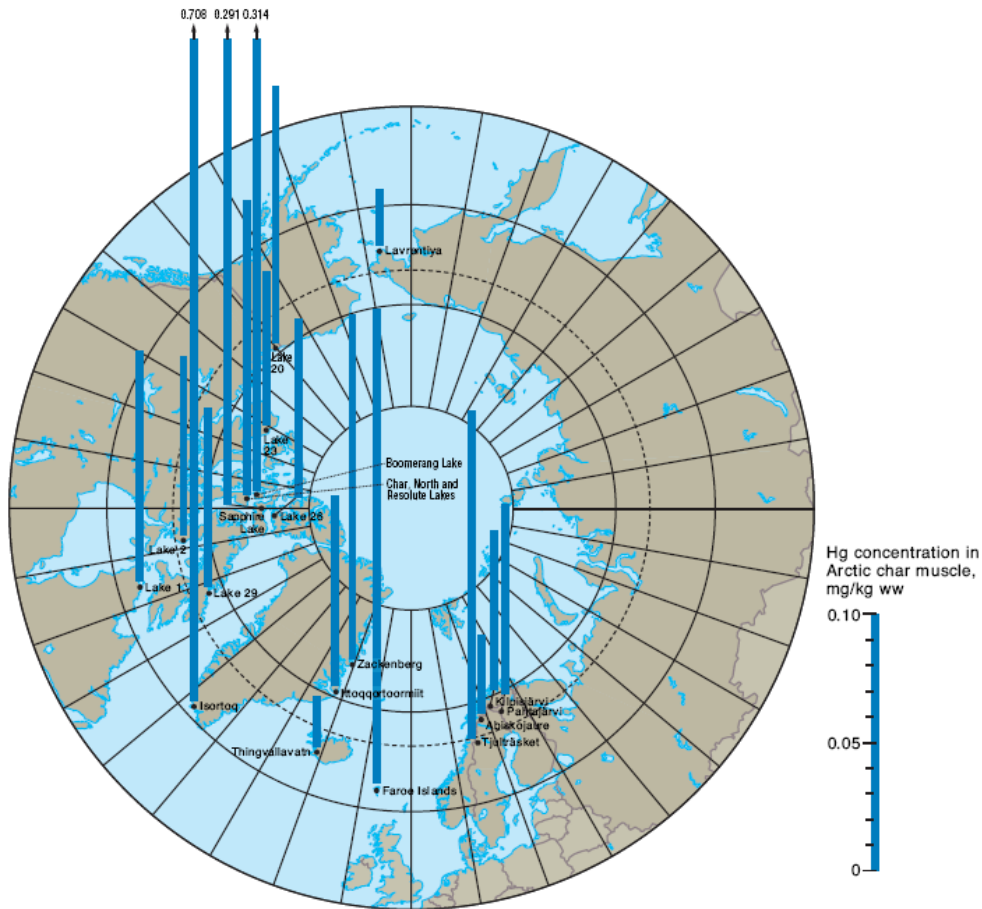
Figure 2.21. Concentrations of total mercury in muscle of Arctic char from lakes in various Arctic and subarctic regions (AMAP 2005).

Lockhart et al. (2005a) reviewed an extensive dataset of fish mercury levels from across northern Canada and compared the results to the two fish consumption guidelines. The review included data from 111 lake trout populations, 24, 61, and 25 in each of Yukon, Northwest Territories and Nunavut respectively. Results showed that 50%, 79% and 88% of the lakes in Yukon, Northwest Territories and Nunavut respectively exceed the guideline for subsistence consumers (0.2 mg/kg). The percentage of lakes exceeding the guideline for commercial sale (0.5 mg/kg) was 12.5%, 21% and 44% for Yukon, Northwest Territories and Nunavut respectively. Lockhart et al. (2005a) also investigated associations between mercury fish concentrations and geological make up of lake

surroundings. While no statistical associations were made, the authors noted that a larger proportion of the lakes situated in metamorphic, intrusive or volcanic rock had fish that exceeded guidelines.
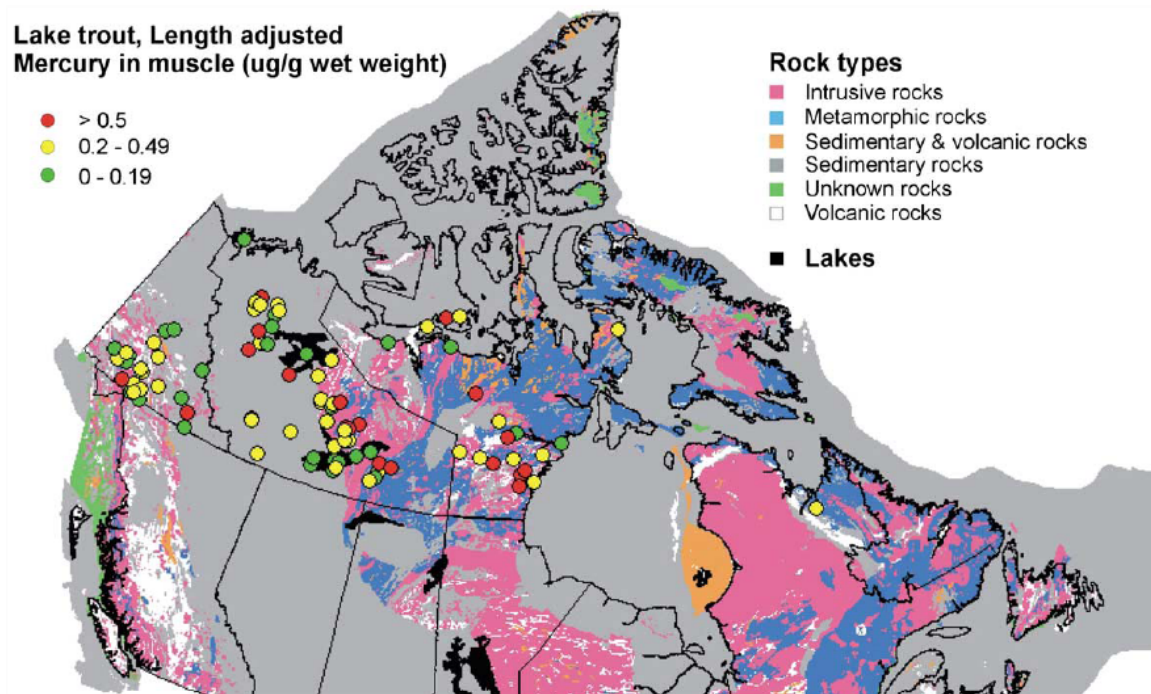
Figure 2.22. Ranges of mercury in muscle of lake trout (mg/kg wet weight). Green dots, mercury in the range below 0.2 mg/kg; yellow dots, mercury in the range between 0.2 and 0.5 mg/kg; red dots, mercury greater than 0.5 mg/kg. (Lockhart et al., 2005a)

Evans et al. (2005) did a detailed evaluation of mercury data in fish from the Mackenzie river basin and found that both fish length and lake size were moderately good predictors of mercury concentrations. Specifically, the authors predict fish to exceed the guideline for commercial sale (0.5 mg/kg) in 600 mm lake trout living in lakes smaller than 65 km^2, 450 mm walleye living in lakes smaller than 20 km^2, and 600 mm northern pike living in lakes less than 1 km^2. The authors also concluded that mercury levels tended to be quite high compared to other regions (e.g. Alberta and Saskatchewan) in part because there is very little fishing pressure which in turn increases the average age of fish in the lakes.

Another large survey of mercury in fish was carried out for the northeastern US and Eastern Canada (Kamman et al., 2005). The authors claim that, while government agencies generate extensive datasets for mercury in sport fish, this data is rarely published. The survey covers over 15,000 data records, 24 different studies and 40 species.
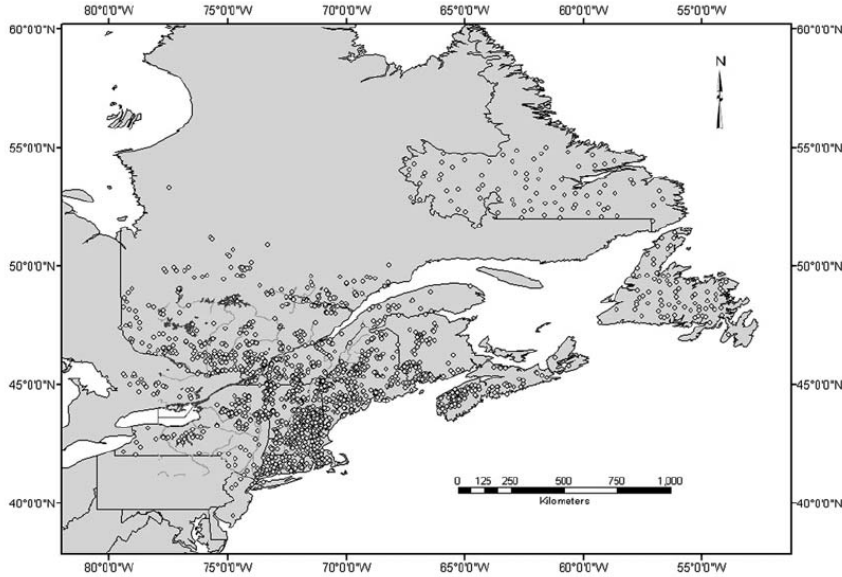
Figure 2.23. Distribution of fish tissue sampling locations across northeastern North America. Symbols vary by individual project contributing data to the Northeast States Research Consortium (NSRC) mercury project. (Kamman et al., 2005)

The four species displaying the highest concentrations of mercury were muskellunge, walleye, white perch and northern pike all of which had mean mercury concentrations over 0.6 mg/kg ww. The authors compared results from individual water bodies to the USEPA recommended guideline of 0.3 mg/kg and found that the proportion of water bodies that exceeded the guideline ranged from 14% for brook trout to 42% for yellow perch.
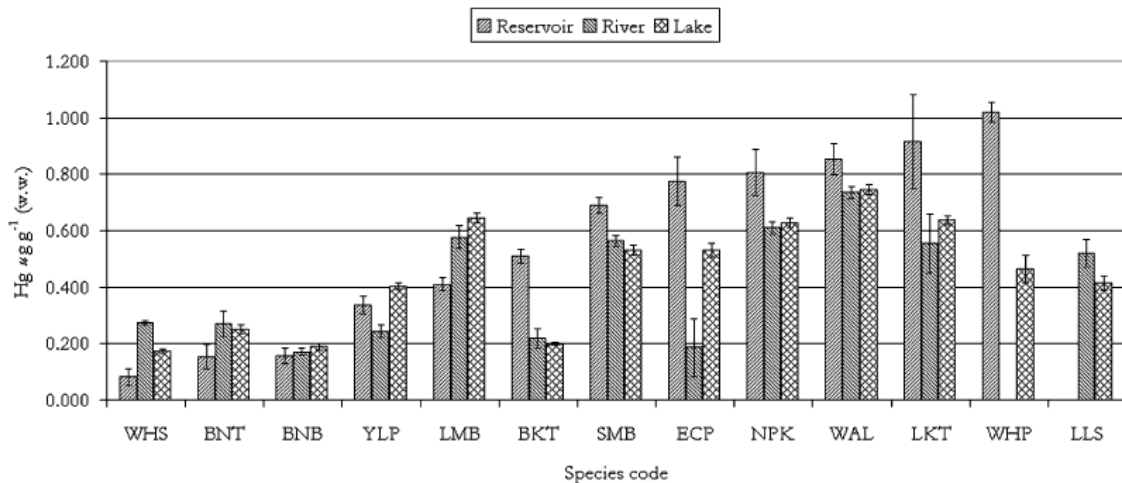
Figure 2.24. Mean mercury concentrations in fillets of 13 standard-length freshwater fish species across northeastern North America, in order of increasing mean for reservoir. Bars are ±1 standard error. Abbreviations: BKT, brook trout; BNB, brown bullhead;

BNT, brown trout; ECP, eastern chain pickerel; LKT, lake trout; LLS, landlocked salmon; LMB, largemouth bass; NPK, northern pike; SMB, smallmouth bass; WAL, walleye; WHP, white perch; WHS, white sucker; YLP, yellow perch.

EPA's National Assessment of Mercury in Lake Fish Tissue

U.S. EPA is conducting the largest freshwater fish contamination survey undertaken by EPA, the National Lake Fish Tissue Study. This survey is a national screening-level study of chemical residues in fish tissue from lakes and reservoirs in the lower 48 states. This study is the first national freshwater fish survey to have sampling sites selected according to a statistical (random) design. The design will allow EPA to estimate the percentage of lakes and reservoirs across the country with fish tissue concentrations above levels of concern for human or ecosystem health. Whole fish and fillets were analyzed for 268 persistent, bioaccumulative, and toxic chemicals, including mercury.

EPA collaborated with 47 states, 3 tribes, and 2 other federal agencies for 4 years (2000-2003) to collect fish from 500 lakes and reservoirs. Field sampling teams applied consistent methods nationwide to collect composite samples of a predator and bottom-dwelling species from each lake or reservoir. Composite samples consisted of 5 adult fish of the same species and similar size. EPA analyzed fillets for the predators and whole bodies for the bottom dwellers.
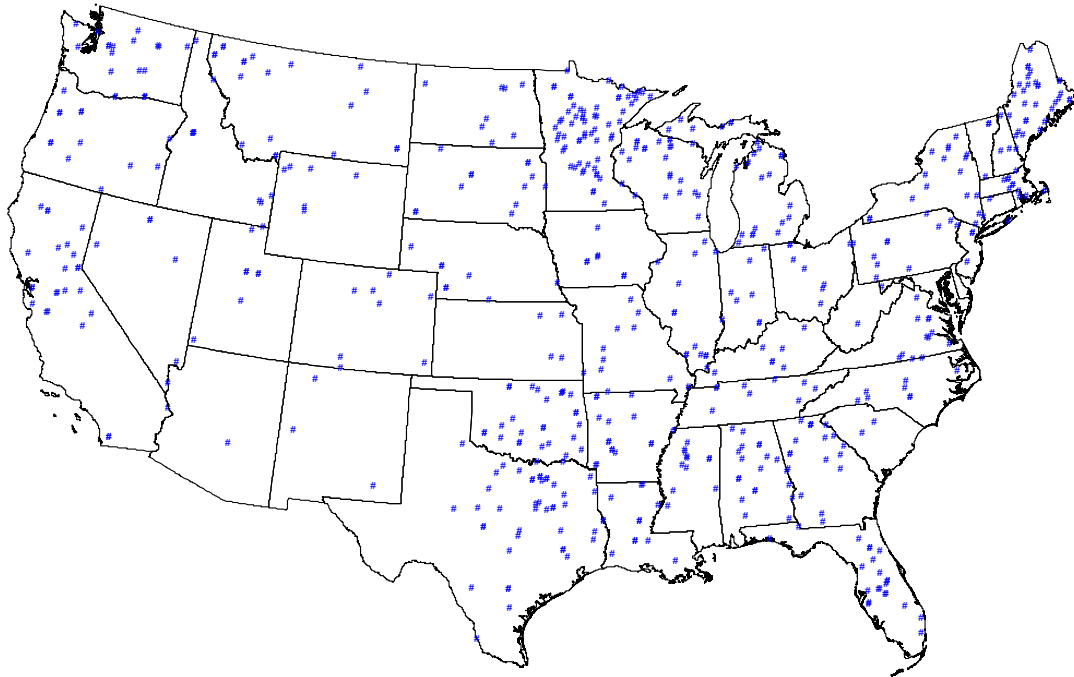
Figure 2.25. Location of lakes that were sampled as part of the US EPA's National Lake Fish Tissue Study.

Total mercury concentrations were measured in the fish tissue. The results indicate that mercury is widely distributed in lakes and reservoirs across the 48 states. Mercury was detected in all the fish samples collected from the 500 sampling sites, and the mercury

concentrations ranged from 0.005 mg/kg to 6.6 mg/kg . EPA has released all 4 years of mercury data to the public. Prior to public release, these data underwent a rigorous review by EPA, the states, and other study participants.

Preliminary Study Results

- Predator fish distribution:
    - 10th percentile= 0.089 mg/kg
    - 25th percentile= 0.177 mg/kg
    - Median (50th) = 0.285 mg/kg
    - 75th percentile= 0.432 mg/kg
    - 90th percentile= 0.562 mg/kg

- Bottom Dwellers: 95th percentile is below 0.3 mg/kg

Mercury in Fish and wildlife of the Florida Everglades has declined by about 75% to date. This decline is associated with a 90% decline in industrial emissions from sources in Florida, of which incinerators have traditionally been the most important (Florida Department of Environment Protection. 2005. South Florida Mercury Science Program, available at: www.dep.state.fl.us/labs/mercury/).

Temporal trends of mercury in Arctic fish have been assessed in data for land-locked Arctic Char from the Canadian high Arctic; lake trout, pike and burbot from the Mackenzie river basin (Figure 2.26) and Yukon; and pike from northern Sweden. While some of these data sets may suggest a slight trend, e.g. burbot from the Mackenzie river, there is little evidence of any temporal trends over the past 15-30 years (AMAP 2005; Evans et al., 2005). Possibly the best time trend data for heavy metals in fish is from a Swedish study that monitored contaminant concentrations in pike between 1968 and 1999. Though the dataset was statistically robust there was no discernable trend (AMAP 2005).
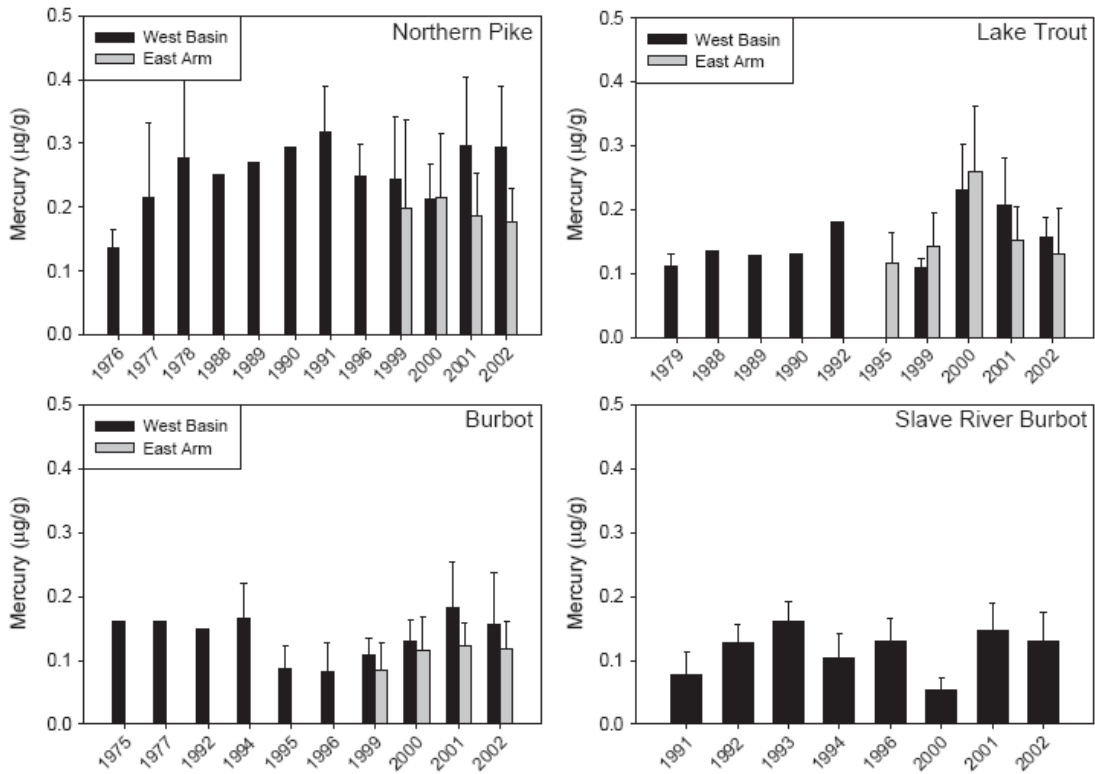
Figure 2.26. Mean (+1 standard deviation) mercury levels in Great Slave Lake and Slave River fish by sample year. (Evans et al., 2005)

2.4.2   Freshwater birds

Mercury concentrations in breast muscle from Canadian waterfowl were generally less than 0.4 mg/kg ww for non-fish eaters and up to 2 mg/kg ww for fish eaters. Liver concentrations in surface feeding ducks ranged from 0.1 to 0.7 mg/kg ww whereas diving ducks had liver mercury levels ranging up to 3.8 mg/kg (AMAP 2005).

Evers et al. (2005) published a broad survey of mercury concentrations in bird tissues that covered over 4700 records from studies carried out in the northeastern US and Eastern Canada between 1969 and 2003 (Figure 2.27).
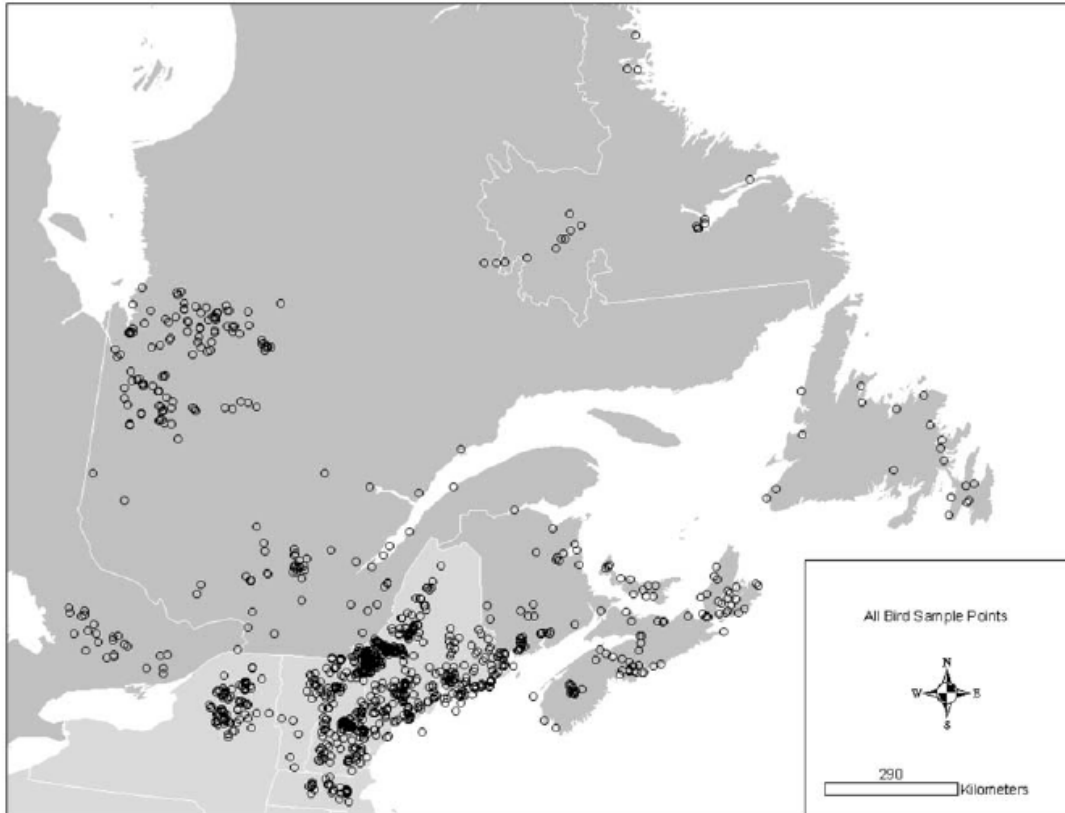
Figure 2.27. Distribution of Hg sampling effort for all bird species, 1969–2003. (Evers et al., 2005)

The survey revealed broad differences between species and location. Species differences were based primarily on trophic position while geographic variability was based primarily on waterbody characteristics. For example, common loons nesting on acidic oligotrophic lakes had some of the highest mercury levels. Mean blood concentrations by species ranged from 0.01 mg/kg ww in American goldfinch to 2 mg/kg ww in common loon. In common loons individual blood concentrations ranged from 0.05 to 8.6 mg/kg ww. The geographic distribution of loon blood mercury concentrations (Figure 2.28) did not reveal any particular spatial trends.

Burgess et al. (2005) conducted a survey of common loons at four sites in eastern Canada during the late 1990s. The authors reported mean levels of mercury in adult loon blood ranging from 2.1 to 5.5 mg/kg ww. The highest levels of mercury reported in the study were in loons from a remote park in Nova Scotia, Kejimkujik National Park. Blood concentrations reported for the Kejimkujik loons are also the highest ever reported for loons in North America.
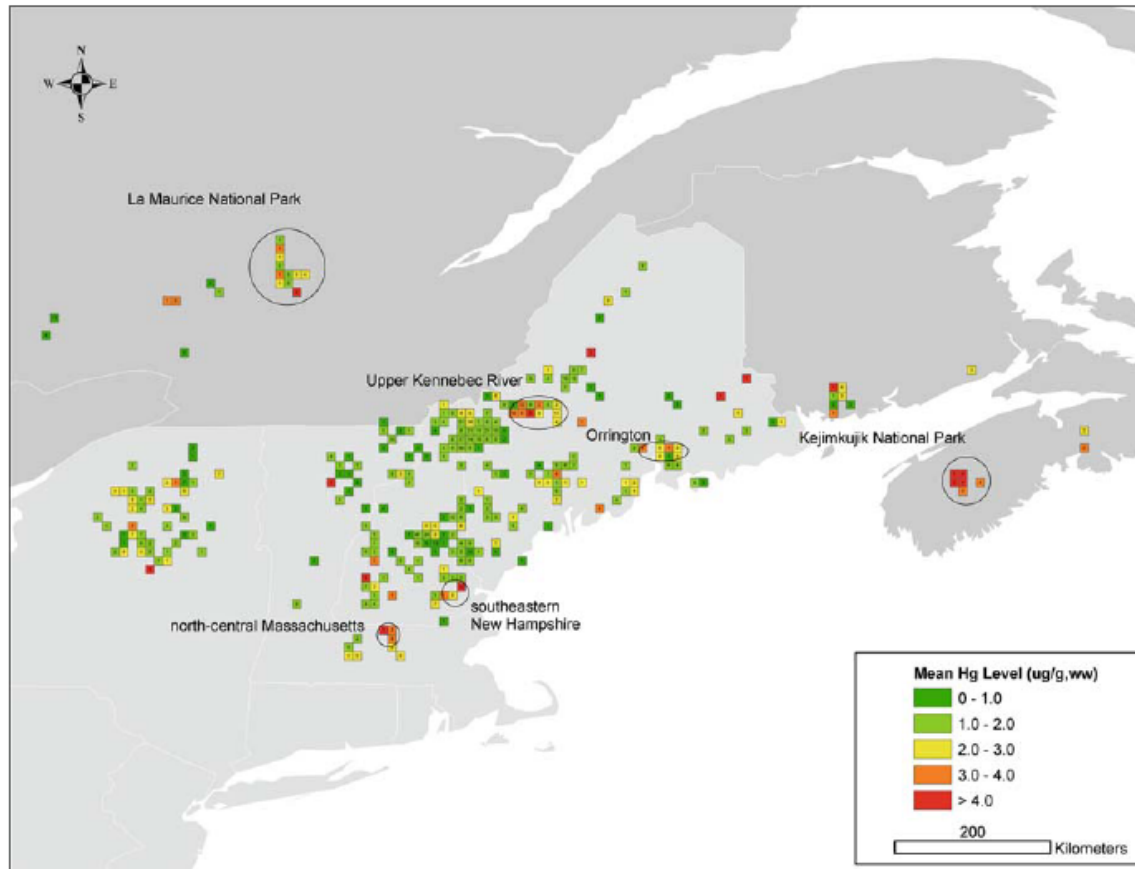
Figure 2.28. Geographic distribution of mercury levels in adult common loon blood and blood equivalents based on eggs, 1993–2003. (Evers et al., 2005)

The North American Great Lakes herring gull monitoring program has been measuring mercury in egg collections that date back to 1973 (Pekarik et al., 2005). Results from this program indicate that mercury concentrations in herring gull eggs have decreased significantly among most of the monitored colonies. The magnitude of the statistically significant decreases (11 out of 15 colonies) observed since 1982 ranges from 32% for the Detroit river colony to 86% for a colony in eastern Lake Erie. The 2002 colony mean egg mercury concentrations ranged from 0.08 – 0.21 μg/g, whereas the 1982 levels ranged from 0.21 – 0.84 μg/g. The declining trend observed in the herring gull eggs corroborates quite nicely with reports of declining trends beginning in the 1980s that were observed in lake sediment cores from eastern North America.

2.4.3 Freshwater mammals

The mean concentrations of total mercury and methylmercury in mink from Yukon, Canada, were 0.92±0.90 mg/kg ww and 0.85±0.57 mg/kg respectively (n=98) (Gamberg et al., 2005b). Another relatively large survey reported mercury concentrations in mink and otter collected from New York, New England and Nova Scotia between 1982 and 2003 (Yates et al., 2005). Mink from various locations reported in Yates et al. (2005) had mean liver mercury concentrations ranging from 2.35 to 7.84 mg/kg ww and 1.65 to 3.77

mg/kg ww in river otter. Yates et al. (2005) was also able to compare results from mink and otter collected in the early 1980s with those from the late 1990s. Based on this comparison the authors concluded that mercury levels had decreased between the early 1980s and the late 1990s. This seems consistent with the declines in atmospheric mercury deposition that have been suggested based on sediment records from the same region (Perry et al., 2005).

2.5 Levels and Trends of Mercury in Marine Ecosystems

In a marine ecosystem mercury, primarily as methylmercury, biomagnifies through trophic levels of the food web, similar to persistent organic pollutants. Fisk et al. (2005) describe food web accumulation of mercury and other metals in an Arctic marine food web of Northern Baffin Bay. Mercury concentrations in ice algae, considered the base of the food web, had barely detectable concentrations of total mercury (0.003 mg/kg ww). Invertebrate species, including copepods, amphipods and mysids, had mean total mercury concentrations in the range of 0.006 – 0.025 mg/kg ww. The only fish species included in the study was arctic cod with mean total mercury concentration of 0.04 mg/kg ww. Dovekie, a lower trophic level seabird, had liver mercury concentrations of 0.27 mg/kg ww, where as higher trophic level scavenging species, northern fulmar and glaucous gulls had liver mercury concentrations of 2.9 and 3.4 mg/kg ww respectively. By far the highest concentrations of mercury were measured in ringed seal liver (22 mg/kg ww), while the mean concentration of mercury in ringed seal muscle was 0.68 mg/kg ww. These levels are quite significant since ringed seal muscle and liver are very important and nutritious traditional foods for Inuit.

2.5.1   Invertebrates

Levels of mercury in marine invertebrates are generally quite low as illustrated by the result of Fisk et al. (2005). The exception may be for larger species like prawns and lobsters that feed at higher trophic levels. AMAP (1998) reported a range of 0.023 to 0.26 mg/kg ww for decapods collected in waters off Greenland, where the lower values were for small Bikini prawns and the high values for large deep sea prawns. Concentrations measured in bivalves tend be lower with levels reported in AMAP (1998) ranging from about 0.01 to 0.03 mg/kg ww. AMAP (2005) reported on a large survey of mercury concentrations in blue mussels. Mean total mercury concentrations in mussels ranged from about 0.005 to 0.03 mg/kg ww. No geographic trend was identified from these data.

2.5.2   Fish

Arctic marine fish generally have lower levels of mercury compared to freshwater fish. For example, sea-run Arctic char collected in Labrador and northern Quebec, Canada, had mean muscle mercury concentrations of 0.03 – 0.07 mg/kg ww (AMAP 2005) which is about three times lower than levels reported for landlocked char and an order of

magnitude lower than levels reported for lake trout. Atlantic cod collected in the Faroe Islands, Norway and Iceland had muscle mercury concentrations in the range of 0.011 – 0.128 mg/kg ww. AMAP (1998) suggests that most Arctic fish species have muscle mercury levels that fall in the range of 0.01 -0.2 mg/g ww.

AMAP (2005) reports concentrations of mercury in five species of Pacific salmon studied off the coast of Alaska where salmon are an important commercial and subsistence species. Mean mercury concentrations in salmon muscle were low and ranged from 0.034 to 0.096 mg/kg ww. Mercury concentrations differed between species based on trophic level with chinook salmon displaying the highest levels.

Large long-lived predatory marine fish species such as shark, marlin, blue-fin tuna, and swordfish can have relatively high levels of mercury. In a study by Adams (2004), total mercury was measured in muscle of three important recreational and commercial fishes landed in Florida: yellowfin tuna, blackfin tuna, and little tunny. Yellowfin tuna had a mean mercury concentration of 0.25 mg/kg ww, and 3.6% of individuals exceeded the FDA guidance level of 0.5 mg/kg. Among the blackfin tuna, the mean mercury concentration was 1.07 mg/kg ww and 81% of individuals exceeded the FDA 0.5 mg/kg guideline, while 19% of blackfin tuna exceeded the Florida state department of health "no consumption level" of 1.5 mg/kg ww. The mean mercury concentration in little tunny was 0.94 mg/kg ww and 75% of individuals exceeded the FDA 0.5 mg/kg guideline, while 18% exceeded the Florida state department of health "no consumption level.

Swordfish and bluefin tuna from the Mediterranean Sea had mean muscle mercury concentrations of 0.07 and 0.20 mg/kg ww respectively (Storelli et al., 2005). It should be noted however that the individual collected for this study were very small (<5 kg). As described in section 2.6.1, levels are generally found to be higher in swordfish, and some other large predatory species, than the levels reported in this study. Mercury has been shown to bioaccumulate with fish age and length (Adams 2004) and the fish that were analyzed in the Storelli et al (2005) study were clearly young fish. Kraepiel et al (2003) reported on levels of total mercury in yellowfin tuna landed on Hawaii in 1971 and 1998. The mean and range of mercury concentrations measured in 1971 and 1998 were 0.274 and 0.210 mg/kg ww respectively, which did not differ significantly, particularly when fish of comparable weights were compared.

In general the temporal records for marine fish reported to AMAP were insufficient for the assessment of temporal trends. Some temporal comparisons were made, though none were statistically robust, and there was little agreement between studies. Higher liver mercury levels were measured in sculpin from Greenland in the mid 1990s than in the mid 1980s. In liver of Arctic cod, however, lower mercury levels were measured in the mid 1990s than in the mid 1980s. In the Baltic Sea, both herring and cod had increasing mercury concentrations between 1979/80 and 1999.

2.5.3 Seabirds

Mercury concentrations measured in seabirds from the circumpolar Arctic varied somewhat between regions and species. In general the highest levels of liver mercury were measured in birds from Svalbard and the lowest levels were measured in birds from the Barents Sea. Northern Fulmar and razorbill had the highest levels of all seabird species reported, with liver mercury concentrations in the range of 1.7 – 3.03 mg/kg dw. In eiders, a species of sea duck, mercury liver concentrations were in a similar range (1.18 – 4.27 mg/kg dw) (AMAP 2005).

Seabird feathers from museum collections have been analyzed for mercury and compared to measurements from modern specimens. One such study did not detect any appreciable difference in mercury concentrations of thick billed murre from Greenland between the 1880s and 1980s, however, a slight increase was noted for black guillemot feathers. Another study on black guillemot feathers, comparing levels in 1897 to those of 1885, found a near 2-fold increase. Finally, white tailed sea eagles from Norway displayed modern feather mercury concentrations that were also about 2-fold higher than levels from 1850 (AMAP 2005).

Archived seabird eggs have been particularly useful for the assessment of more recent temporal trends of mercury in the Canadian High Arctic (Figure 2.29). Braune et al. (2005) reported a doubling in egg mercury levels of thick-billed murre between 1975 and 1998, and a 50% increase in northern fulmar over the same time period.
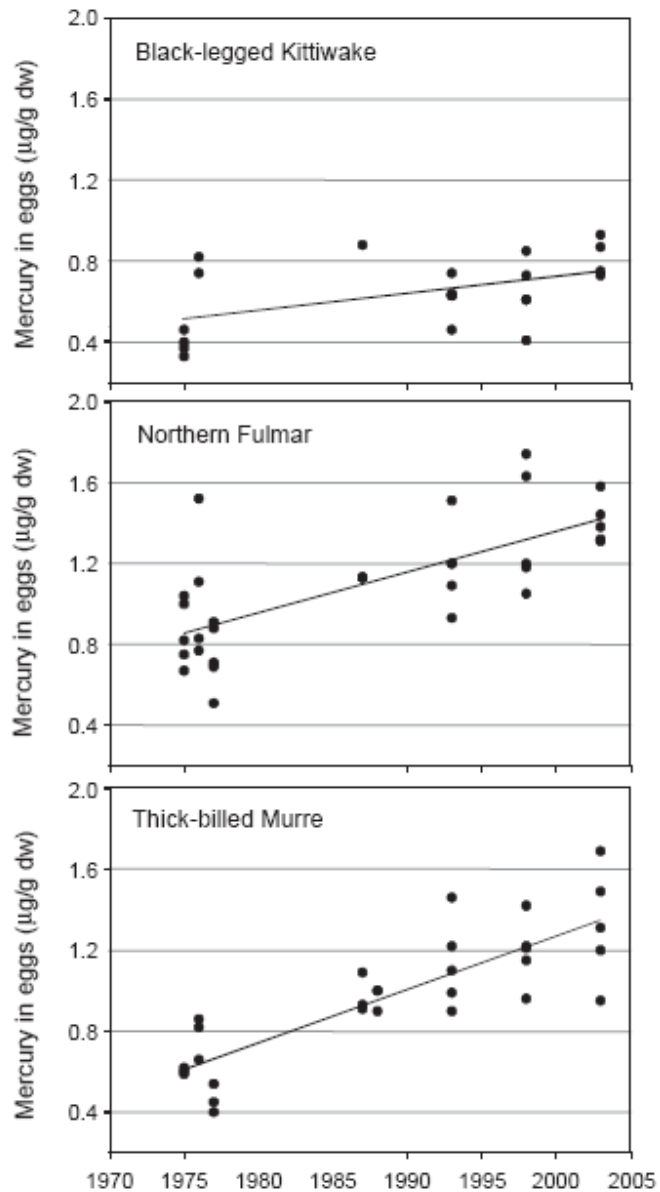
Figure 2.29. Concentrations of total mercury in seabird eggs collected between 1975 and 2003 from Prince Leopold Island (Braune et al., 2005).

2.5.4 Marine mammals

Concentrations of mercury in ringed seal liver ranged from 1.19 mg/kg ww in adults from Svalbard to 29.9 mg/kg ww in adults from Holman Island Canada. In general the highest concentrations of mercury were measured in ringed seal from the Beaufort Sea region and North Baffin Bay, while lower levels were measured in liver from other regions including Alaska, south east and west Greenland, Svalbard and White Sea (Riget et al., 2005). In ringed seal muscle, generally range from about 0.1mg/kg ww in juveniles to about 1.0 mg/kg in older animals (i.e. >15yrs) (AMAP 1998). Methyl mercury can make up between 80% and 100% of the total in ringed seal muscle.

Temporal trends data for ringed seal are not very extensive. The best temporal record is from Holman Island, Canada, and does not reveal any discernable trends. Year to year mercury concentrations in ringed seals collected from other locations in the Canadian Arctic are quite variable.
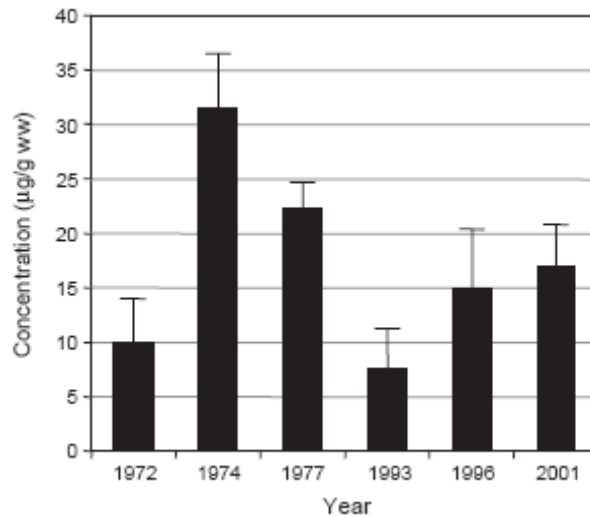
Figure 2.30. Temporal trends of mercury in ringed seals aged 5–15 years from Holman, NWT (1972–2001). Bars represent geometric means and vertical lines represent upper 95% confidence intervals. (Braune et al., 2005)

Beluga whales have been well studied in the Canadian Arctic. Levels of mercury for beluga collected from several communities in the Canadian Arctic are represented in Figure 2.31. Concentrations of mercury in liver vary quite a bit between locations and year of collection, but generally range from 5 to 16 mg/kg ww in mature animals, although levels in the 30 to 40 mg/kg ww range have been recorded in the Beaufort Sea (Lockhart et al., 2005b; AMAP 1998). Lockhart et al. (2005b) also reported mercury concentrations in muscle in the general range of 0.5 and 3.0 mg/kg ww, and muktuk (skin) ranging from 0.2 and 2 mg/kg ww. Mean concentrations of mercury in muktuk, a popular Inuit food, exceeded the Canadian guideline of 0.5 mg/kg for commercial sale of fish.
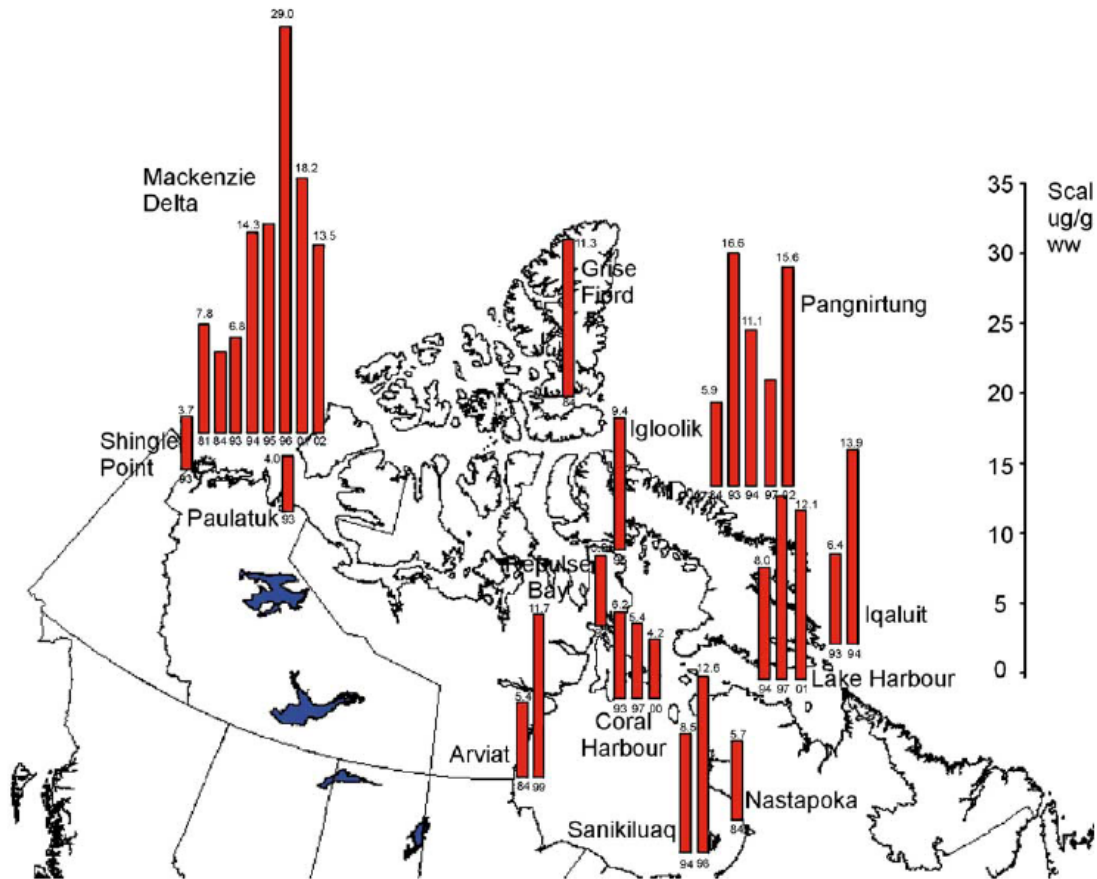
Figure 2.31. Calculated age-related levels of mercury in liver (μg/g ww) of beluga whales at age 13.1 years. (Lockhart et al., 2005b)

As with ringed seal, temporal trends in beluga liver mercury concentrations were difficult to assess. A statistically significant trend indicates that mercury concentrations have increased since the early 1980s in western Hudson Bay. Data sets from other locations are too variable and too small to enable the determination of trends. Concentrations of mercury measured in brain were similar to thresholds for toxic effects in laboratory animals (Lockhart et al., 2005b).

The analysis of dated beluga teeth recovered from archaeological sites in the Arctic has enabled the evaluation of long-term trends in beluga mercury levels. By using teeth, researchers are also able to determine the age of the beluga and can thereby evaluate mercury accumulation over the lifetime of the whales for both present and past time periods. In beluga from the Mackenzie delta region of the Beaufort Sea, modern levels of mercury for 10 year old and 30 year old whales were 7- and 17-fold higher than in whales that lived in the period of 1450 – 1650. A similar comparison, on teeth collected from Somerset Island, indicated that mercury concentrations in 30-year old beluga were 7.7 times higher now than in similar whales that lived prior to 1947. Increased anthropogenic emissions of mercury was suggested as the most likely cause of the increase, however, the authors could not rule out other potential changes in whale

behaviour or ecosystem structure that could also lead to increased mercury uptake (Outridge et al., 2005b).

AMAP (2005) also reported mercury concentrations in walrus, narwhal, Minke whale, bearded seal, spotted seal, grey whale, bowheaded whale, pilot whale, white sided dolphin and polar bear.
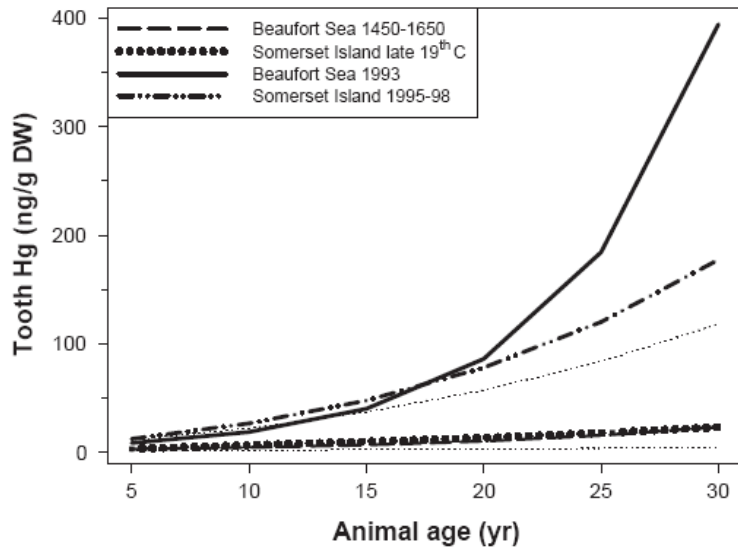
Figure 2.32. Long-term changes in geometric mean tooth Hg concentrations in beluga near Somerset Island and from the Beaufort Sea. The finely dotted lines represent ±1 S.E. around the geometric means for the Somerset beluga. (Outridge et al., 2005b)

2.6 Levels and Trends of Mercury in Human Populations

2.6.1 Levels and Trends in Food

The greatest source of dietary methylmercury comes from the consumption of both freshwater and marine fishes. In certain populations, like Inuit and Faroese, marine mammals also represent a significant source of dietary mercury.

A number of countries have established guideline levels of mercury in edible fish tissues for the protection of human health. These guidelines have been developed based largely on the toxicological data generated from epidemiological studies such as those carried out in the Faroe Islands. These studies are discussed further in section 2.7.4. The most comprehensive set of guidelines probably comes from the United States, which has adopted a risk assessment approach for the development of monthly fish consumption limits for methylmercury (Table 2.1). Limits are based on a consumer adult body weight of 70 kg, an average fish meal size of 8 oz (0.227 kg), time-averaging period of 1 month (30.44 d), and EPA's reference dose for methylmercury (1x10-4 mg/kg/day) from EPA's Water Quality Criterion for the Protection of Human Health : Methylmercury (U.S. EPA, 2001c). A general national advisory suggests the safe consumption of one meal of fish per week based on average fish mercury concentrations in the United States which generally fall in the range of 0.12 - 0.24 mg/kg ww of methylmercury. In Canada the federal department of health has adopted a guideline of 0.5 mg/kg total mercury for the commercial sale of fish and 0.2 mg/kg for subsistence consumption.

Table 2.1. Risk based guidelines for consumption of fish containing mercury (http://www.epa.gov/mercury/advisories.htm)

Monthly Fish Consumption Limits for Methylmercury	
Risk-based consumption limit	Noncancer health endpoints
Fish meals/month	Fish tissue concentrations (ppm, wet weight)
16	> 0.03–0.06
12	> 0.06–0.08
8	> 0.08–0.12
4	> 0.12–0.24
3	> 0.24–0.32
2	> 0.32–0.48
1	> 0.48–0.97
0.5	> 0.97–1.9
None (<0.5)[a]	> 1.9

[a] None = No consumption recommended.
NOTE: In cases where >16 meals per month are consumed, refer to EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, Volume 2, Section 3 for methods to determine safe consumption limits.

Many States and other organizations have collected data on mercury levels in recreationally caught freshwater fish for various reasons, including as input to the development of fish consumption advisories. Much of these data are included in EPA's National Listings of Fish Advisory (NLFA) database. In addition to listing advisories on fish consumption (Figure 2.33), the NLFA also includes state issued advisories for the consumption aquatic wildlife including turtles (MN and RI) and waterfowl (UT) (Bigler pers comm.).
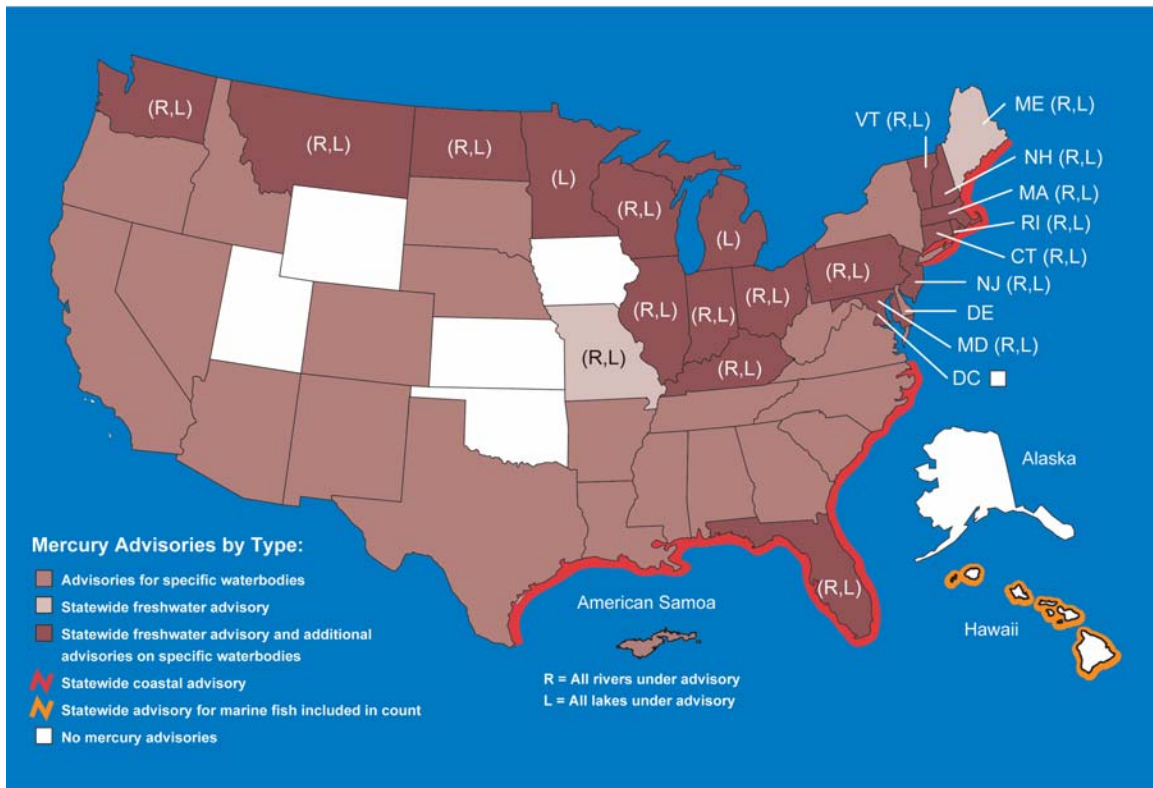
 Figure 2.33. Fish consumption advisories for mercury in the United States. Note: This map depicts the presence and type of fish advisories issued by the states for mercury as of December 2004. Because only selected waterbodies are monitored, this map does not reflect the full extent of chemical contamination of fish tissues in each state or province. (Source: USEPA, Office of the National Listing of Fish Advisories)

National Mean Mercury Concentration in Tissues of Selected Fish Species (all sample types)

*N=Number of samples, and number of states with 10 or more samples.

Legend:
- Bowfin *N=888, 5
- Chain pickerel N=317, 6
- Spotted sea trout N=139, 2
- White bass N=404, 9
- Largemouth bass N=9740, 36
- Flathead catfish N=289, 11
- Walleye N=7402, 11
- Northern pike N=5404, 6
- Smallmouth bass N=1537, 15
- Lake trout N=1120, 6
- Yellow perch N=2094, 13
- Freshwater drum N=346, 7
- Black crappie N=1286, 13
- Channel catfish N=2550, 28
- Brown trout N=494, 9
- Bluegill sunfish N=1773, 17
- Brown bullhead N=471, 14
- Common carp N=2789, 24
- White sucker N=1334, 11
- Striped bass N=230, 8
- Coho salmon N=100, 1
- Lake herring N=180, 3
- Lake whitefish N=313, 2
- Gizzard shad N=144, 2

Species (y-axis)

Mercury concentration (ppm): 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1

EPA U.S. Fish and Wildlife Contamination Program

Source: NLFWA July 2000, data from 1987-2000

Figure 2.34. Mean concentrations of mercury in various fish species based on data from 1987 - 2000 from the NLFA database.

The United States food and drug administration has published monitoring results for a large number of fish species on their website (http://www.cfsan.fda.gov/~frf/sea-mehg.html). The four most contaminated fish listed on the web site are king mackerel, shark, swordfish and tilefish, which had mean mercury concentration of 0.73, 0.99, 0.99 and 1.45 mg/kg respectively. On their website, updated March 2004, the FDA recommends that pregnant women and women planning to become pregnant do not eat any of these four most contaminated species. (http://www.cfsan.fda.gov/~dms/admehg3.html)

Burger and Gochfeld (2004) reported mercury concentration in canned tuna collected between 1998 and 2003. A total of 163 cans of albacore, marketed as white tuna, and skipjack, marketed as light tuna, were analyzed for total mercury. Mean total mercury concentrations were 0.407 and 0.118 mg/kg ww for albacore and skipjack tuna respectively. At least 89% of the measured mercury was methylmercury. These results suggest that an average can of albacore tuna would exceed the USEPA national advisory level of 0.12 – 0.24 mg/kg and the Canadian 0.2 mg/kg guideline for subsistence consumption. The authors compared results of the tuna collected between 1998 and 2003 against results from tuna collected in 1991 and suggested that levels had increased slightly.

Freshwater fish have traditionally been an important part of the Swedish and Finnish diets. Based on extensive surveys of mercury levels in fish from the late 1980s, it was estimated that pike over 1kg in size contained mercury concentrations in excess of 0.5 mg/kg ww in approximately 50% of Sweden's 100,000 lakes. The pike in 10% of the Swedish lakes were estimated to contain over 1 mg/kg ww mercury. As a result, it was recommended that women of childbearing age eat none of these fish from Swedish lakes. In Finland it was estimated that pike exceed the 0.5 mg/kg ww level in about 85% of the 22 000 lakes of southern Finland (UNEP 2002).

2.6.2   Levels and Trends in Humans

Almost all people have at least trace amounts of mercury (e.g., methylmercury) in their tissues. Generally, these low exposures are not likely to cause adverse health effects (U.S. EPA, 2005, Mercury website, available at: http://www.epa.gov/mercury/). However, as described below, some subpopulations are exposed to higher levels.

Levels of mercury in humans are typically measured in blood, hair, or urine. Urine mercury levels are often used to evaluate exposures to elemental mercury or inorganic mercury. Blood and hair are often used as indicators of exposures to methylmercury (ATSDR 1999a).

While blood represents a snapshot of mercury exposure, mercury is incorporated into hair as it grows thus integrating exposure over a long period of time. Hair samples can be used to evaluate mercury exposure over time by analyzing mercury at various intervals along the hair's length.

Levels of mercury in hair were measured in some subpopulations in the United States during various surveys between 1978 and 1995 with mean concentrations for the different study groups (different communities etc.) ranging from 0.47 – 3.8 mg/kg in adults and 0.46 – 0.77 in children (ATSDR 1999a). However, most of these studies were conducted from 15 to 28 years ago (between 1978 to 1991), and they may not represent general U.S. population exposures during that timeframe. Nonetheless, these results appear to be generally consistent with hair levels prior to 1990 in other countries based on a review of existing data by WHO (WHO 1990, as cited in ATSDR 1999a). These results were consistent with hair mercury levels reported for other countries, with a mean of 2.0 mg/kg, and below the WHO maximum tolerable level of 6 mg/kg. The mean hair mercury level from the other countries was 2 mg/kg, which is a hair level associated with exposures slightly lower than the current WHO provisional tolerable weekly intake (PTWI) of 1.6 µg/kg/week (JECFA, 2003).

However, more recent data on exposures for random samples of general U.S. population from the National Health and Nutrition Examination Survey (NHANES) found lower exposure levels than those found in these earlier studies. The NHANES is conducted once per year by the U.S. Centers for Disease Control and Prevention (CDC). It includes a representative sample of about 5,000 people in the United States. The sample is chosen

using a stratified, multistage selection process. The study includes medical exam, health and dietary survey, and blood measurements for many chemicals (including mercury, lead, and cadmium) and metabolites. In 1999-2001, hair and blood mercury measurements were taken for women of childbearing age and young children. The NHANES uses standardized methods and regular reporting (CDC, 2001).

The NHANES study for years 1999-2000, which included 1,709 women (ages 16 to 49 years) and 705 children (ages 1 to 5 years) in the U.S. showed that most women and children in U.S.A. have blood mercury levels below a level associated with possible health effects (Schober et al., 2003). For example, the mean blood level for women of childbearing age was about 1 µg/L (which corresponds with a hair level of about 0.2 mg/kg). However, about 6 to 8 percent of these women had mercury concentrations in blood exceeding about 5 µg/L, which is about the level corresponding to the US EPA's reference dose. Also, more recent data from the U.S. CDC, for years 1999-2002, showed similar results (U.S. CDC 2005).

The highest concentrations of mercury measured in the blood of Arctic residents come from Inuit of Greenland, Canada and Alaska. The source of mercury among these populations is the consumption of muscle, organs and muktuk (fatty skin) of marine mammals. Maternal blood mercury concentrations in these populations range from 5.5 to 50 µg/L (Figure 2.35). Some Inuit populations, Dene and Metis from Canada, and indigenous people from Arctic Russia have intermediate levels of mercury (1.3-2.9 µg/L). In the Faroe Islands maternal blood mercury concentrations have decreased by almost ten-fold since the government issued advice to women of child bearing age suggesting they not eat pilot whale blubber or meat. The mean concentration of mercury in maternal blood collected in 2000-2001 was 1.3 µg/L as opposed to 12.1 µg/L measured in the 1980s (AMAP 2003).

While there are few recent temporal comparisons of mercury levels in humans, comparison of modern and ancient teeth and hair from Canadian Inuit, Greenlanders and Norwegians indicate that human mercury levels in modern times are several times higher than they were pre-industrialization (Figure 2.36) (AMAP 2003). Similar results have been found for archived animal hair and archaeologically derived whale teeth (see Figure 2.32, Section 2.5.4).
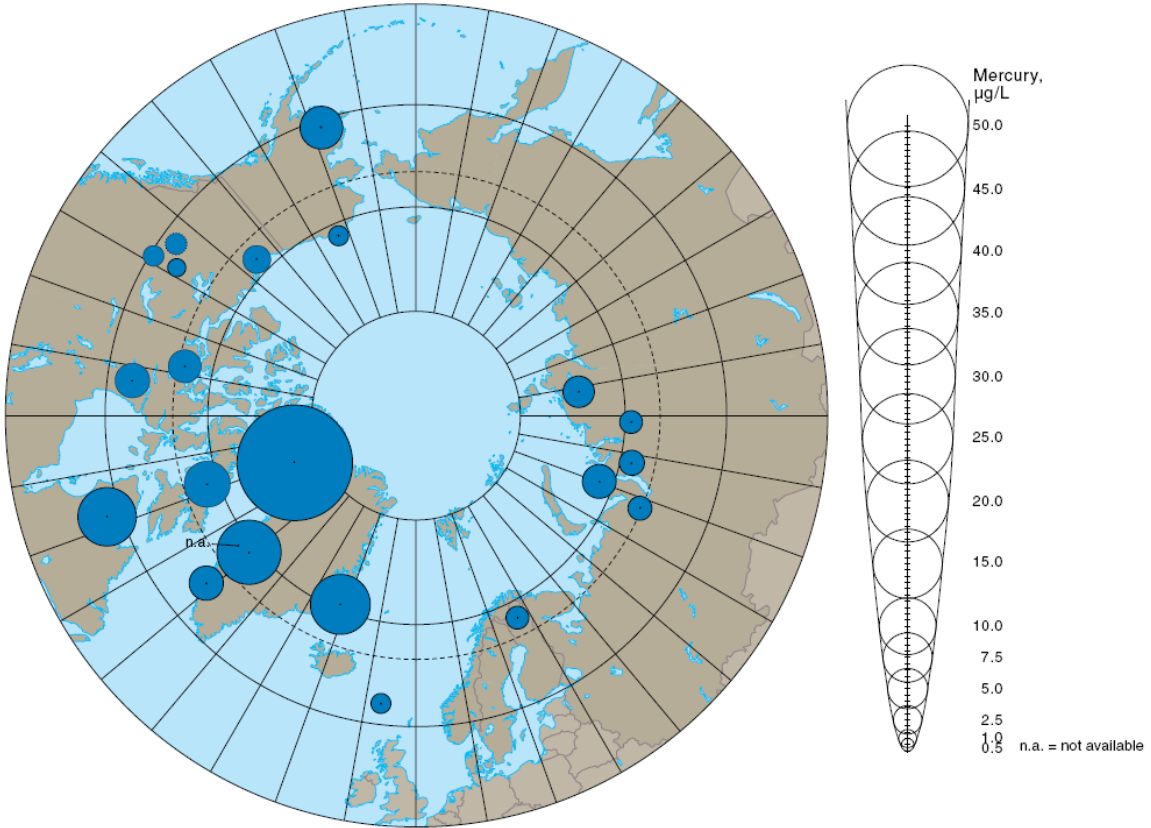
Figure 2.35. Recently measured concentrations of mercury in maternal blood (AMAP 2003)
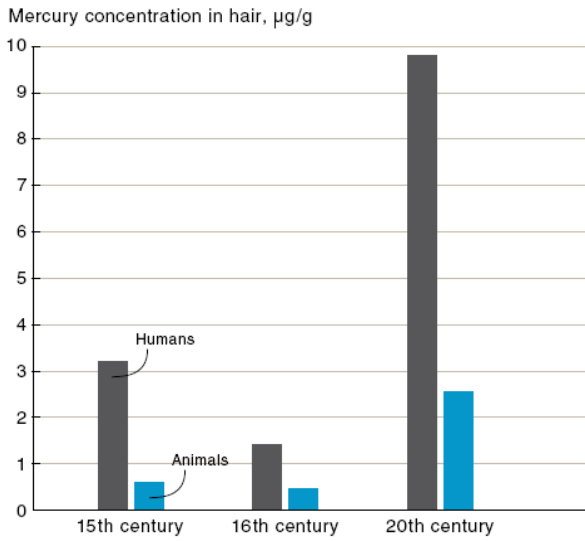
Figure 2.36. Changes in mercury concentrations in human and animal hair from Greenland (AMAP 2003).

2.7 Ecosystem and Human Health Effects

2.7.1 Terrestrial ecosystems

The ICP-IM Forest program monitors forest conditions at two types of monitoring plots. Level I plots, of which there are 6000, are widely dispersed throughout Europe and are designed to provide broad scale temporal and spatial information. Some select sites (860) are designated Level II plots and are more intensively studies to investigate the relationship between forest conditions and stressors. Rademacher (2001) conducted a comprehensive review of data from ICP Forest measurements networks and literature on concentration levels of metals in forest ecosystems and effect thresholds. Data on Hg in humus layers was available only from 8 ICP Forests Level II plots ranging from 0.6 to 0.9 mg/kg. Tyler (1992) found with respect to soil-biological processes a lowest effect level of 0.75 mg/kg.

Effects thresholds of Hg on microbiota from several studies (Zelles et al. 1989, Bringmark et al. 1998, Bringmark & Bringmark 2001 a, b) have a range of $0.3 – 5.0$ µg/g. The lower boundary of this span emanated from a field study in South Swedish forest sites in which Hg showed a covariance with Pb (Bringmark & Bringmark 2001a). A related critical limit for mercury in organic layers of forest soils aiming at the protection of microbiological processes was set to 0.5 mg kg$(OM)^{-1}$ (Meili et al. 2003), with OM being the organic matter content. This critical limit was used in critical loads calculations related to effects on microbiota in the humus layer of forest soils (ICP Modelling and Mapping, 2004, CCE-MSCE 2005). Measured Hg concentrations in humus layers of forest soils ranged between 0.6 and 0.9 mg/kg (level II data of ICP Forest, n = 8, reported in Rademacher 2001). The comparison with the reported effect thresholds shows that currently effects on soil biology cannot be excluded. By further accumulation due to atmospheric deposition as assessed by ICP Integrated Monitoring (see 2.1.1) the risk of effects will increase.

Terrestrial mammals do not appear to accumulate levels of mercury that have been associated with toxic effects. AMAP (2005) provides a good comparison of tissue concentrations measured in Arctic terrestrial biota to toxicity thresholds (Figure 2.37). This comparison showed that none of the reported mammalian liver concentrations exceed the estimated threshold for toxic effects in free ranging wildlife of 30 mg/kg. Most thresholds for toxic effects of mercury in mammals have been developed for fish eating mammals such as mink and otter. Effects of mercury, and more specifically methyl mercury, are discussed in further detail under Section 2.7.2.

Terrestrial birds also do not appear to accumulate levels of mercury that are sufficiently high to cause adverse effects. One exception may be in the case of raptors. In a study of American peregrine falcons from Alaska, it was found that levels of mercury, as well as copper and iron, were higher in eggs from unsuccessful nests than they were in successful nests. In this study a successful nest was one that had chick(s) surviving at one to three weeks. It was reported that, 13% and 9% of American peregrine eggs exceeded the estimated threshold for egg survival of (0.5 mg/kg) in 1988 and 1990 respectively.

Similarly, Arctic peregrine eggs examined in a separate study exceeded the threshold 30% of the time in separate collections made in 1988 - 1990, and 1991-1995 (AMAP 2005). Levels of exposure are higher in fish eating birds such as loons which are more likely to experience adverse effects as a result of deposition from long-range atmospheric transport (see Section 2.7.2)

2.7.2 Freshwater ecosystems

The risk of toxic effects from mercury exposure among freshwater invertebrates and fish appears to be quite low. The levels of mercury and methylmercury measured in water bodies of North America and Northern Europe are typically two to three orders of magnitude lower than the levels expected to cause effects. Most studies on the effects of mercury in freshwater ecosystems have examined acute toxicity, however some studies have looked at the effects of chronic exposure. Chronic exposure to relatively high levels of methylmercury (0.93 µg/L in water) was found to cause deformity and death in second generation larvae of brook trout with no-observable-effect concentration (NOEC) of 0.29µg/L (Wren et al., 1995). Other studies have also document effects on growth and reproduction at similar concentrations (Wren et al., 1995).

Waterfowl, particularly those that biomagnify mercury through a fish based diet, can accumulate levels of mercury associated with developmental, behavioural and reproductive effects. A blood mercury level of 4 mg/kg ww has been established as the lower threshold for "extra-high risk" in loons. Above this threshold there is increased risk of impaired reproduction, elevated corticosterone levels, asymmetry in plumage development, and altered breeding behaviour (Burgess et al., 2005). A study in Kejimkujik park, Canada, demonstrated that 92% of the resident loons exceed the 4 mg/kg threshold. In the latest USGS Status Assessment and Conservation Plan for the Common Loon in North America (Evers, 2005), mercury toxicity is cited as a leading factor impacting the sustainability of North American loon populations.

The toxic effects of mercury and methylmercury on mink, and to a lesser extent otters, have been fairly well studied. Mink and otter occupy a position at the top of aquatic food chains and are therefore expected to be most susceptible to toxic effects. Some of these studies demonstrate the relative toxicity of methylmercury compared to inorganic mercury. For example a diet containing 5 mg/kg methylmercury was lethal to adult mink within 30 days, whereas a diet containing 10 mg/kg mercuric chloride produced no adverse effect after 5 months. Signs of methylmercury intoxication, which includes anorexia, weight loss, and splaying of hind legs, followed by irregular vocalization, salivation and convulsions, have been observed at dietary concentrations as low as 1.8 µg/g administered over a 70 day period. Yet another study found that dietary mercury of 1.0 µg/g was lethal when combined with an environmental stressor, which in this case was cold winter temperatures (Wren et al., 1995). Similar feeding studies have also been conducted on river otters where dietary levels as low as 2 µg/g were found to be lethal over a period of about 6 months. At the time of death all of the otters in the study had very similar residues of total mercury, which in the case of liver was 33 µg/g. In their summary, Wren et al. (1995) conclude that dietary levels of 1-2 µg/g methylmercury are lethal to mink and otter. Tissues residues greater than 30 µg/g in liver and 10 µg/g in

brain are associated with methylmercury poisoning and could be considered indicative of mercury toxicity. In at least one case of mercury poisoning in wild mink, total mercury concentrations in fur were 34.9 µg/g.

The concentrations of mercury reported in Yukon mink were considered quite low and did not represent a toxic threat to the mink. In the Yates et al. (2005) study, however, otters from Maine and Vermont had maximum mercury fur concentrations (73.7 and 46.5 mg/kg ww, for adults and juveniles, respectively) that nearly equalled or exceeded a concentration associated with death. Similarly, maximum liver mercury concentrations in mink from Massachusetts/Connecticut (31.0 mg/kg ww) and the maximum fur mercury concentrations in mink from Maine and Nova Scotia (68.5 and 45.4 mg/kg ww, respectively) exceeded concentrations associated with acute mortality. The authors concluded that mercury was accumulating to critical toxicological thresholds in mink and otter from only a few regions, but suggest that the occurrence of sub-lethal effects could be more widespread (Yates et al., 2005).

Mercury concentrations have also been reported for European otters. Concentrations reported for studies carried out in Britain, Denmark and Ireland were 0.2–4.3, 0.3–12.4 and 0.15–17 mg/kg ww respectively. With the exception of the results from Britain, the North American results appear to be a bit lower (Yates et al., 2005). All of these results, however, suggest that some river otters and mink are likely suffering adverse effects as a result of mercury exposure in eastern North America and Europe.

2.7.3 Marine ecosystems

Concentrations of mercury in lower trophic level invertebrates and fish species are generally lower than levels measured in freshwater ecosystems. Only long lived predatory fish species such as shark and swordfish would have higher concentrations than predatory freshwater species. As in freshwater ecosystems, the levels of mercury found in marine ecosystems do not appear to represent risk of adverse effects for marine invertebrates and fish.

Seabirds can accumulate relatively high levels of mercury, for example results as high as 300 mg/kg ww in some individual albatross (Wren et al., 1995). While these results suggest a high degree of biomagnification, there does not appear to be any documented cases of adverse effects arising from mercury exposure in seabirds. It has been suggested that some species of seabird, including albatross, have the ability to detoxify mercury, transforming it from organic to inorganic forms (Ikamoto et al., 2004). This could be one of the reasons why seabirds are considered to be an order of magnitude less sensitive to mercury toxicity than freshwater birds (AMAP 2005).

Thresholds of adverse effects in pinnipeds have been developed based on controlled studies and suggest a benchmark for subclinical effects on the liver of 65 mg/kg dw in liver. This threshold, however, is thought to be very conservative. AMAP (2005) noted that some individual seals, walrus and toothed whales could exceed this threshold (Figure 2.37). Marine mammals have consistently demonstrated a high resistance to mercury toxicity that is attributed to their ability to store mercury in the non-toxic from of

mercuric selenide. Striped dolphins from the Tyrrhenian Sea and various pinnipeds with liver mercury concentrations as high as 3800 mg/kg ww for the dolphins and 420 mg/kg for the pinnipeds, show no sign of adverse effects (AMAP 2005).
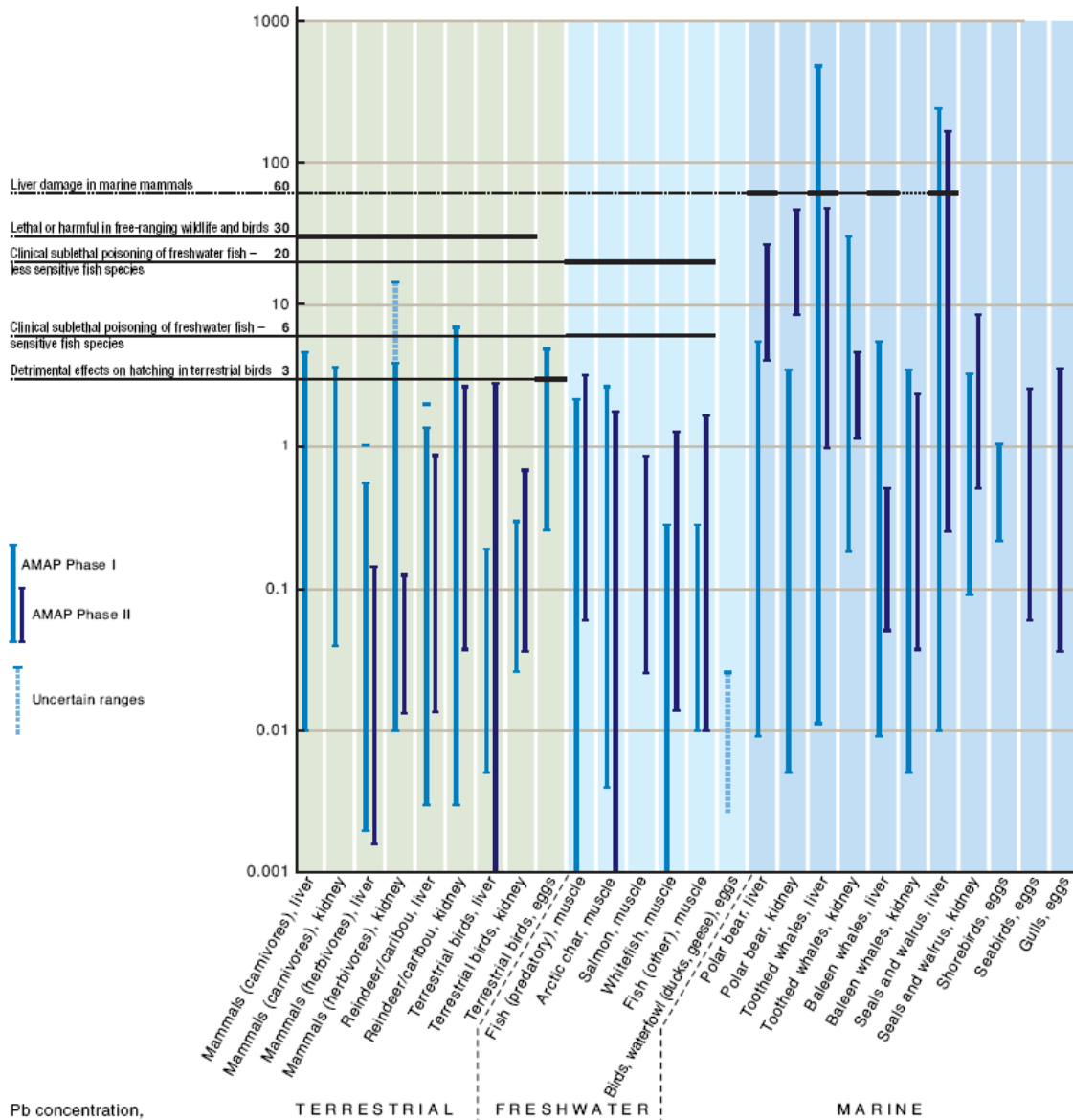

Figure 2.37. Ranges in mercury concentrations that were reported during the last two AMAP assessments are displayed as vertical bars and compared to estimated toxicity thresholds represented by horizontal lines. Toxicity thresholds are taken from ecotoxicology literature and reviewed in AMAP (2005).

2.7.4   Human health effects

The primary source of human methylmercury exposure is from the consumption of fish, particularly larger and older predatory freshwater and marine species. It is recognized however, that fish is an important, beneficial food for many populations, providing protein, omega 3 fatty acids, and other essential nutrients. Moderate consumption of a variety of fish (following established consumption guidelines) is not likely to result in exposures of concern. Guidelines consider factors such as species, fish size, and waterbody as well as age and gender of human consumers. For example, guidelines are generally more restrictive for women of childbearing age because of potential adverse effects to fetuses. Nonetheless, people who consume high amounts of contaminated fish or marine mammals may be highly exposed to methylmercury, and therefore may be at risk.

The effects of high level pre-natal exposure to methylmercury are fairly well known from publicized cased in Japan and Iraq where children born to exposed women displayed a range of symptoms including mental retardation, severe sensory impairment, seizures and general paralysis. More recently there have been three well-designed studies that have examined the effects of low-level prenatal exposure to mercury; in the Faroe Islands, New Zealand and the Seychelles (Van Oostdam et al., 2005). In each of these studies the source of mercury was the consumption of marine foods, however, marine mammals were only consumed in the Faroe Islands. Unlike the severe cases that were documented in Japan and Iraq, none of the children demonstrated any obvious signs of neurological impairment. In both the Faroe Islands and New Zealand studies, however, pre-natal mercury exposure was correlated with subtle neurobehavioral effects. The Seychelles study did not find any neurobehavioural effects related to prenatal exposure. Table 2.3 provides a comparison of maternal mercury levels for various studies, including the three cohort studies mentioned.

In the Faroe Islands study mercury concentrations in maternal hair and cord blood were correlated with pregnancy period, and performance on neurobehavioral tests of fine motor function, concentration, language, visual-spatial abilities and verbal memory. It was calculated that a doubling in prenatal mercury exposure corresponded to a one to two month delay in child development over the first seven years of life. The long-term significance of these effects (ie. as the child grows up), however, are unknown. A second major cohort study examining prenatal exposure to POPs and mercury has been undertaken in Nunavik, Canada. Since the publication of the AMAP assessment (2003) some preliminary results have been reported in Nunavik indicating subtle neurobehavioral effects associated with mercury (Després et al., 2005). The interpretation of these results is ongoing and should be published in the very near future (Van Oostdam et al., 2005).

Table 2.3. Comparison of total mercury concentrations measured in various cohort studies (Van Oostdam et al., 2005).

Cohort (reference)	Medium	Years	N	Geometric mean	Range	Interquartile range
Canada						
Nunavik Inuit	Cord blood (µg/L)	1996–2000	95	18.5	2.8–97.0	12.0–27.2
	Maternal blood (µg/L)	1993–1995	130	10.4	2.6–44.2	6.6–17.0
	Maternal hair (µg/g)	1992	123	3.7	0.3–14.0	2.5–6.2
Southern Quebec	Cord blood (µg/L)[a]	1977–1978	1108	1.0	0.9–1.0[b]	
James Bay Cree	Women hair, not pregnant (µg/g)[c]	1981	70	2.5	Max = 19.0	
Northern Quebec Cree	Maternal hair (µg/g)		215	6.0[d]	5.2[e]	
USA	Women hair, not pregnant (µg/g)	1981	1274	0.36[f]	0.14–0.90	
			1546	0.24[g]	0.09–0.62	
Faroe Islands						
First cohort	Cord blood (µg/L)	1986–1987	894	22.9		13.4–41.3
	Maternal hair (µg/g)	1994–1995	914	4.3		2.6–7.7
Second cohort	Cord blood (µg/L)		163	20.4	1.9–102.0	11.8–40.0
	Maternal hair (µg/g)		144	4.1	0.4–16.3	2.5–7.4
Seychelles Island						
Main study	Maternal hair (µg/g)	1989–1990	740	5.9	0–25	6.0
Pilot study	Maternal hair (µg/g)		789	6.6	0.6–36.4	6.1
New Zealand	Maternal hair (µg/g)	1978–1984	935	8.3[d]	6.0–86.0	
Greenland, Disko Bay	Cord blood (µg/L)	1994–1996	178	25.3	2.4–181.0	
	Maternal blood (µg/L)	1994–1996	180	12.8	1.9–75.6	

A Finnish study found the risk of coronary heart disease in men who consumed freshwater fish was significantly associated with mercury concentrations in hair. Mercury has been found to promote lipid peroxidation resulting in the formation of low-density lipoproteins which have been implicated as initiators of arteriosclerosis. Previous observations in the same population also associated increased risk of death from coronary heart disease to low serum concentrations of selenium, an antioxidant that can block the mercury induced lipid peroxidation process. Like the Finnish men, Inuit consume high concentrations of mercury in fish and marine mammals yet mortality from coronary heart disease is extremely low. It is possible that Inuit are protected by the high levels of selenium and polyunsaturated fatty acids that are also contained in the marine foods. The Faroe Islands cohort study examined potential associations between pre-natal mercury exposure and cardiovascular development. The study showed that pre-natal mercury exposure was associated with increased blood pressure and reduced heart rate variability in seven year old children (AMAP 2003).

The most stringent guidelines for human dietary exposure are largely based on the aforementioned epidemiological studies that have found neurodevelopmental effects in infants. A fairly conservative guideline for dietary intake is the reference dose (RfD) of the USEPA at 0.0001 mg/kg/day. The RfD is defined as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime" (U.S. EPA, IRIS, 1997 July 2001, available at: http://www.epa.gov/iris/subst/0073.htm). This level of dietary exposure (0.0001 mg/kg/day) can be associated with hair mercury concentrations of about 1.0 mg/kg, cord blood levels of about 5 to 6 µg/L and maternal blood mercury concentrations of about 4-5 µg/L (UNEP 2002).

In 2003, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a new PTWI of 1.6 µg/kg body weight/week for methylmercury. The Committee based

the PTWI on the evaluation of the Faroe Islands and Seychelles Islands studies and used the average from the two studies of the estimated maternal hair concentrations associated with the no observed effect level/benchmark dose level (NOEL/BMDL) for neurotoxicity associated with in utero exposure. The Committee determined that a steady-state daily ingestion of methylmercury of 1.5 µg/kg body weight/day would result in the concentration in maternal blood estimated to be without appreciable adverse effects in the offspring in the Faroe and Seychelles Islands studies. This dose level was divided by a factor of 6.4 (to account for inter-individual variability and human inter-individual variability for dose reconstruction [converting maternal blood concentration to a steady-state dietary intake]), which results in a daily dose of 0.23 µg/kg body weight/day. This daily dose was then multiplied by 7 to convert to a weekly dose level to derive a PTWI of 1.6 µg/kg body weight/week (JECFA, 2003). This level corresponds with a hair level of about 2.3 ppm, and blood levels of about 10 micrograms per Litre.

The greatest source of methylmercury exposure to human populations is from dietary intake, and the consumption of fish is by far the most important source of methylmercury for the general population. Another important dietary source of methylmercury is marine mammals, which are frequently consumed among certain populations, including Inuit and Faroese.

Table 2.4. Guidelines and benchmark dose related to human mercury exposure

US ATSDR (1999)*	MRL acute exposure (<14 days) – 0.007 mg/kg/day MRL medium term exposure (15-364 days) – 0.002 mg/kg/day MRL chronic exposure (>364 days) – 0.0003 mg/kg/day
US EPA**	RfD for MeHg – 0.0001 mg/kg/day >4.42 µg/L based on BMDL of 44 µg/L (58 µg/L in cord blood) and uncertainty factor of 10
WHO PTWI *** (JECFA 2003)	0.0016 mg/kg/week (MeHg)
US NRC	Benchmark dose – 58 µg/L totalHg in cord blood Or 10 mg/kg total Hg in maternal hair
Health Canada****	pTDI – 0.00047 mg/kg/day general population pTDI – 0.0002 mg/kg/day women of child bearing age and young children 20 µg/L blood: Normal acceptable range 20–100 µg/L blood: Increasing risk >100 µg/L blood: At risk

*Agency for Toxic Substances and Disease Registry (ASTDR) minimum risk levels (MRL)
** United States Environmental Protection Agency Reference doses (USEPA RfD)
***World Health Organization provisional tolerable weekly intake (PTWI).
****Health Canada provisional daily intakes (pTDI)

ATSDR (1999a) refers to two estimates of dietary mercury intake in the US that were based on Food and Drug Administration total diet studies from 1982-1984 and from 1986-1991. In the first study the mean intake for all people with the exception of 2-year

old children was 0.000050 mg/kg/day. In two year-olds the intake was 0.0001 mg/kg/day. In the second study, which was based on 120 000 US adults, estimated mercury intake for females ranged from 0.000006 – 0.003 mg/kg/day (mean of 0.0001 mg/kg/day) and for males ranged from 0.000003 – 0.002 mg/kg/day (mean of 0.0001 mg/kg/day) for males. Based on these results an average two year-old would be right at the US EPA guideline, as would average adults from the second study. The people at the higher end of the range reported in the second study (1986-1991) exceed the guideline by over an order of magnitude.

The USEPA guideline, as well as the WHO PTWI and Health Canada pTDI, listed in table 2.4, are all fairly easily exceeded by consuming moderate quantities of common fish species, e.g. lake trout and walleye in Canada.

In the 1970s the WHO estimated that the daily absorption of methylmercury as a result of average fish consumption was between 2 and 4.7 ug. Converted for a 60kg person, this would be 0.00003 – 0.00008 mg/kg/day. Another estimate calculated by the US FDA in 1984-1986 estimated daily mercury intake to be 2-3 µg/day for adults. In Belgium studies published in 1978 and 1983 estimated intake between 6.5 and 13 µg/day, which converts to 0.0001 – 0.00022 µg/kg/day for a 60kg person and exceeds the US EPA guideline (UNEP 2002).

The UNEP Global mercury assessment (UNEP 2002) presents information which suggests that there are other populations that also have high levels of dietary mercury intake. Examples of groups that have higher exposures to methylmercury includes some fish consumers from Greenland, Japan, Sweden, Finland, and U.S.A., and Arctic populations that consume marine mammals.

Estimates of dietary intake for Inuit from Greenland and Canada were both 850 µg/week, which is approximately four times greater than the 1988 WHO PTWI of 200 µg/week (or 3.3 µg/kg/day), and eight times higher than the 2003 PTWI of 1.6 µg/kg body weight/week for methylmercury.   The most important source is meat and muktuk of marine mammals. Seal liver also contributes a substantial amount of mercury to the diet, however, seal liver mercury is in an inorganic form and is not very bioavailable. Comparable estimates from other Northern populations in Canada, Denmark and Finland were much lower (26-42 µg/week) (AMAP 2003).

Based on the results of blood mercury concentrations reported in Figure 2.38., a large number of Inuit from Alaska, Canada and Greenland would exceed US EPA guidelines for mercury in blood. Over 10% of Inuit women from the Baffin and Nunavik regions in Canada exceed the Health Canada guideline for increased risk, as do Inuit from Illullissat and Ittoqqortoormiit, Greenland.
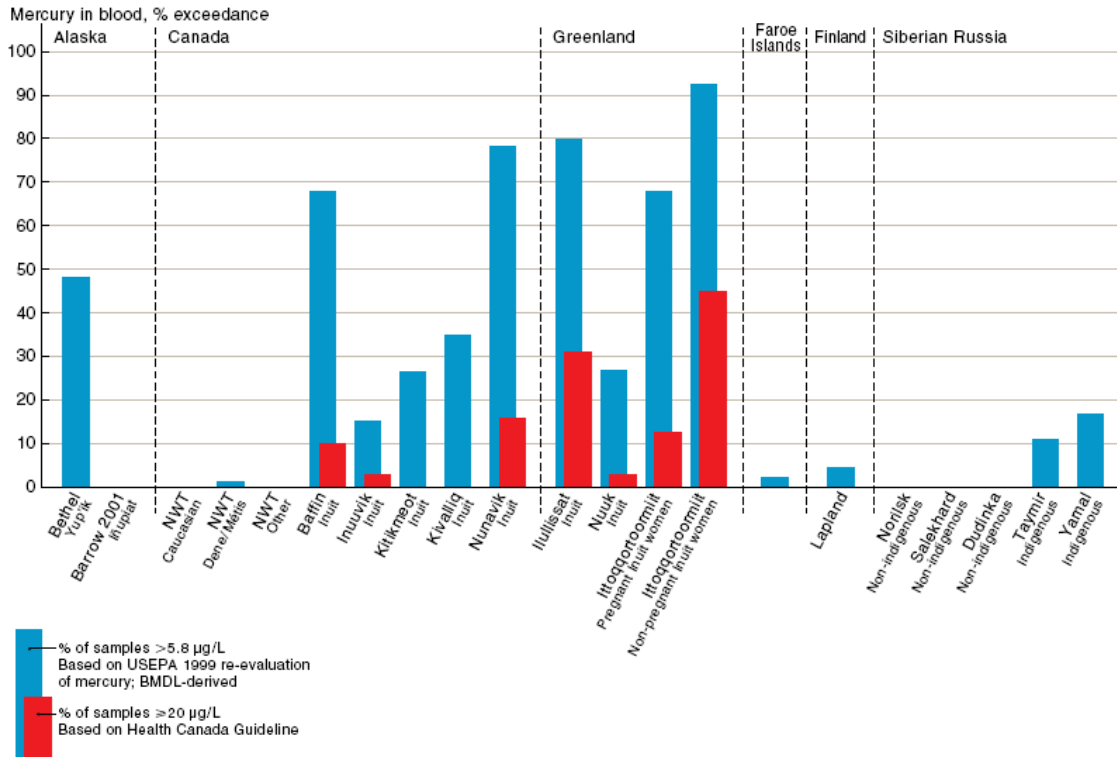
Figure 2.38. Mercury levels in blood of indigenous and non-indigenous women of reproductive age. Percentage of samples exceeding U.S. EPA and Health Canada guidelines for increasing risk (AMAP 2003).

3 Cadmium

3.1 Background

Cadmium, like other heavy metals, is a naturally occurring element that can be found in virtually all environmental compartments. Natural sources of cadmium to the atmosphere include volcanoes and windblown dust, while in aquatic ecosystems it is mobilized by biogenic processes. As described in the chapter on emissions, cadmium is emitted by various sources (e.g., fossil fuel combustion, metal production, and others). Cadmium is primarily emitted and transported through the atmosphere in the particulate phase and only the very fine particulate are susceptible to long-range transport, with the majority of larger diameter particles falling out relatively close to the source.

Once deposited onto terrestrial or aquatic ecosystems, the fate of cadmium depends in large part to the conditions of the soil or water to which it is deposited. Under acidic conditions, with low organic carbon cadmium is generally more bioavailable than otherwise. Cadmium can be taken up by plants and primary consumers and accumulates in the liver and kidneys of wildlife. In aquatic ecosystems cadmium bioconcentrates in invertebrates and to a lesser degree in fish. Cadmium does not biomagnify in terrestrial and freshwater ecosystems, however it does appear to biomagnify in marine food webs.

High levels of cadmium can have adverse effects on the liver and kidneys of mammals. Humans are most sensitive to kidney damage from cadmium exposure, which manifests in the form of renal tubular damage. The most important exposure pathway for humans is dietary intake, with grains, cereals, leafy vegetables and potatoes being the most important sources. Smoking can double a person's intake of cadmium.

3.2 Atmospheric Transport, Distribution and Deposition

In the atmosphere cadmium exists primarily in the particulate bound state as cadmium oxide and to a lesser extent cadmium chloride (ATSDR 1999b). The atmospheric residence time of fine cadmium containing particulate is one to ten days, which is long enough to allow dispersion over long distances, i.e. on a continental and hemispheric scale. A large proportion of emitted cadmium, particularly that associated with larger particles, is deposited close to the emission sources, which in the United States results in urban deposition rates being about ten times higher than deposition rates in rural areas. Particulate bound cadmium can be deposited onto receiving environments by wet or dry deposition (ATSDR 1999b).

3.2.1 Modelled cadmium levels

As in the case of lead, the use of official, country submitted, emissions data for cadmium leads to significant (around 3 times) underestimation of modelled concentrations and depositions compared to measured values. This was noted by the Executive Body of the Convention which in turn encouraged Parties to improve emission estimates

(EB.AIR/WG.5/8). It's also possible, however, that some of this underestimation may be due to re-emissions of historic anthropogenic cadmium emissions and natural sources.

The modelling of cadmium pollution levels for 1990 -2003 was based on expert emission estimates, developed by MSC-E. These estimates include anthropogenic emissions, natural emission and re-emission of historic depositions. Detailed description of the approach used to derive these emission estimates is described in (Ilyin and Travnikov, 2005).

In 1990 modelled atmospheric cadmium concentrations over most of Europe exceeded 0.3 ng/m^3 (Figure 3.1a). By the end of the considered period (1990 - 2003) concentrations over western and central parts of Europe declined and ranged from 0.1 to 0.3 ng/m^3 (Figure 3.1b). Total modelled depositions of cadmium in 1990 typically ranged from 50 to 300 g/km^2/y (Figure 3.2a). By 2003, depositions were reduced in most regions of Europe. The typical range of modelled depositions was 15 – 150 g/km^2/y (Figure 3.2b).
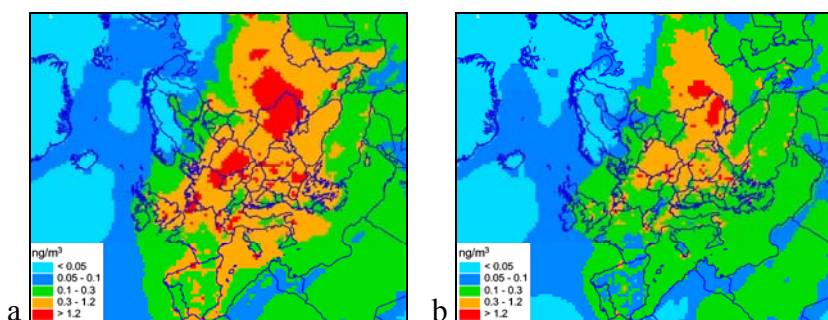
Figure 3.1. Spatial distributions of modelled air concentrations of cadmium over EMEP region in 1990 (a) and 2003 (b)
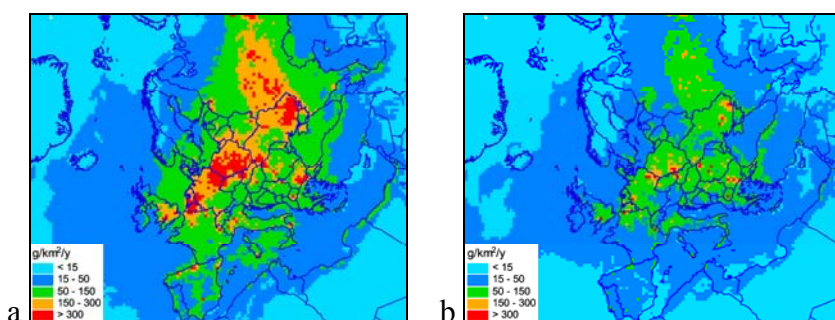
Figure 3.2. Spatial distributions of modelled total depositions of cadmium over EMEP region in 1990 (a) and 2003(b)

For Europe as a whole, based on these analyses, atmospheric concentrations of cadmium have decreased by about two-fold. In individual countries the highest estimated decline of concentrations took place in Monaco (3.4 times) and the Netherlands (3.3 times) (Figure 3.3). As many as 13 countries are characterized by a decrease greater than 2.5 times. In 16 countries the decrease was between 2 – 2.5 times.

Similar magnitudes of estimated decrease were obtained for depositions to countries. For Europe as a whole the decrease was 2.3 times, and in individual countries (Monaco, the Netherlands) it reaches 3.3 times. As many as 27 countries are characterized by at least a 2-fold decrease in cadmium deposition.

The contribution of transboundary transport from anthropogenic sources in Europe to depositions of cadmium in European countries varies from about 83% in Republic of Moldova to around 7% in Spain (Figure 3.4). In sixteen countries this estimated contribution exceeds 50%, and in 27 countries – 30%.

For each country in Europe, the main contributors of transboundary cadmium pollution were evaluated by the model. An example of these estimates is presented for Hungary (Figure 3.5). External European anthropogenic sources contribute 54% of depositions to the country as a whole. National sources make up 25%, and natural/global sources and re-emission – 22%.
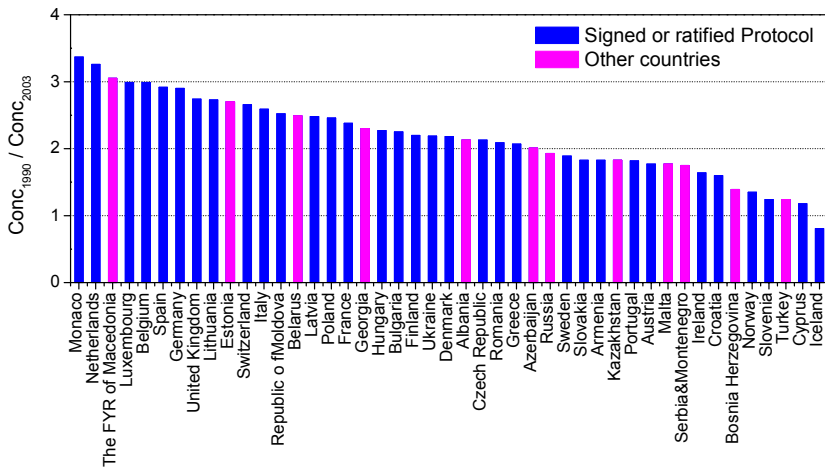
Figure 3.3. Ratio of the modelled country-averaged air concentrations of cadmium in 1990 to those in 2003 in countries of Europe.
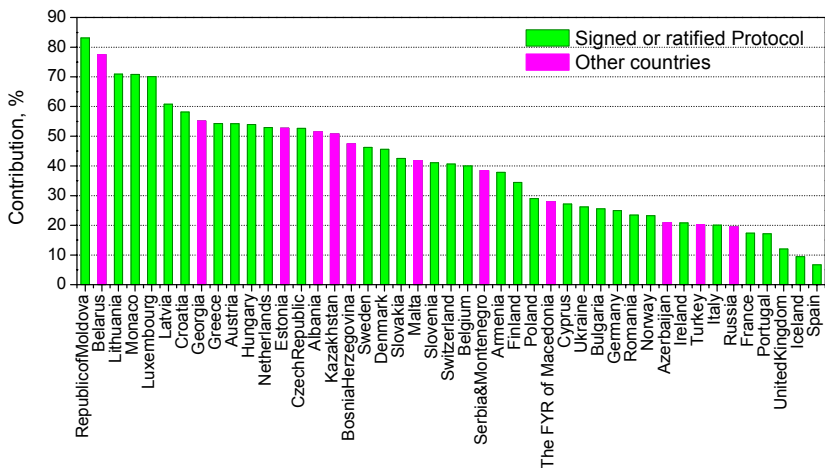
Figure 3.4. Contribution of external European anthropogenic sources to depositions of cadmium in Europe in 2003.

Contribution of external European sources to Hungary is uneven across the country (Figure 3.5). In the central part it amounts to about 40%, while near state borders it exceeds 70%.

Unlike long-living atmospheric pollutants, such as mercury or some POPs, the atmosphere lifetime of cadmium is relatively short and its potential for intercontinental transport is relatively low. However, the contribution of intercontinental transport of cadmium to pollution in Europe and North America requires more research.

a   b
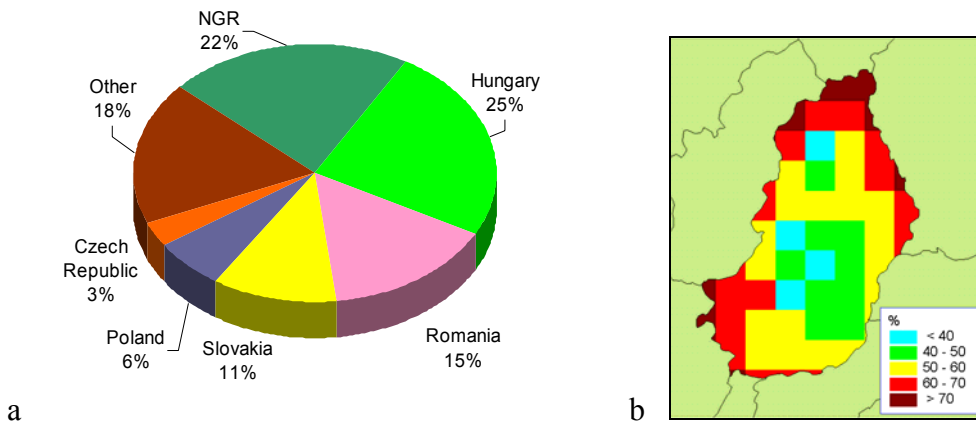
Figure 3.5. Main contributors to deposition of lead in Hungary. NGR: Natural, Global sources and Re-emission (a). Spatial distribution of contribution of external anthropogenic sources to depositions of lead in Hungary(b)

In the U.S.A., the National-Scale Air Toxics Assessment (NATA) is conducted by U.S. EPA to assess air quality, human exposures and risks for a range of chemicals. NATA includes modeling ambient air concentrations of 33 air toxics (including cadmium). The available NATA results for cadmium (Figures 3.6 and 3.7) are based on 1996 and 1999 emissions data. The ASPEN air dispersion model was used to first model air concentrations for individual census tracts (i.e., geographical units smaller than counties). The median tract-level annual average cadmium concentration was then selected to represent each county. The modelled concentrations for 1996 were generally between about 0.0016 and 0.18 ng/m^3 (U.S. EPA 2002). The concentrations for 1999 appear to be slightly lower based on these maps.
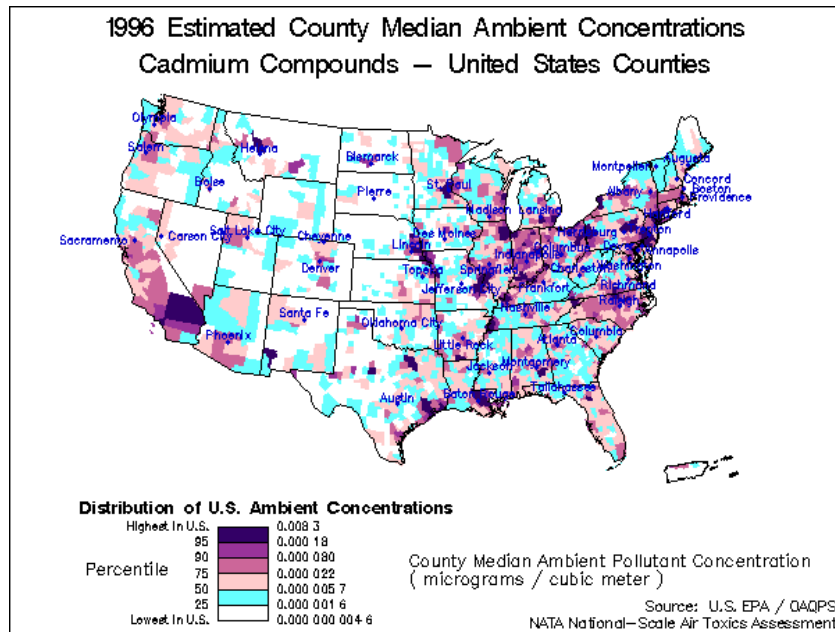
Figure 3.6. Median County-Level (annual-averaged) Ambient Air Concentrations in the U.S.A. for cadmium for 1996 (U.S. EPA, 2002)
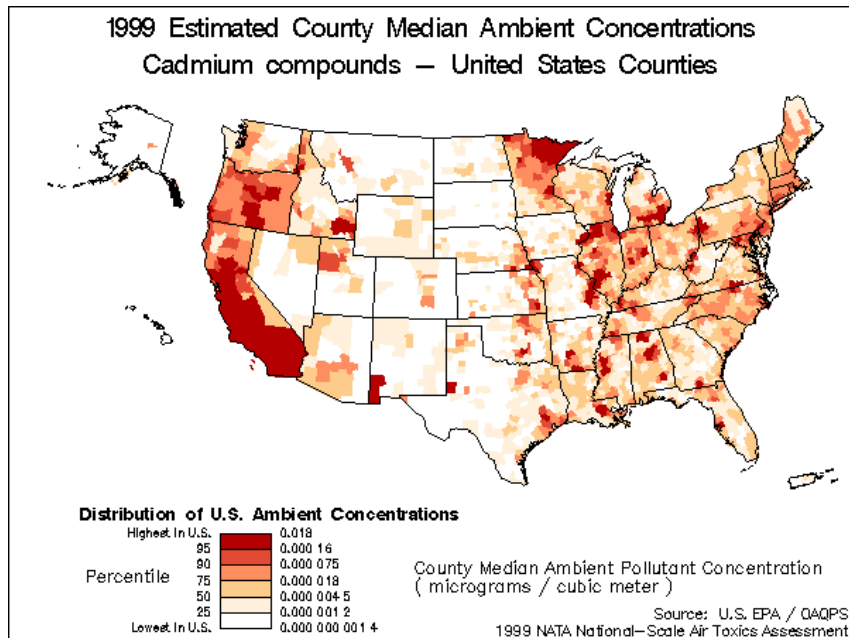
Figure 3.7. Median County-Level (annual-averaged) Ambient Air Concentrations in the U.S.A. for cadmium for 1999 (U.S. EPA, 2006)

3.2.2   Evaluation of modelling results

Analysis of the model uncertainties shows that the intrinsic model uncertainty (uncertainty of the model without emission data) varies across Europe from 20 to 60% for

concentrations in air, in precipitation and for total depositions (Travnikov and Ilyin, 2005). Intercomparison of atmospheric transport models of cadmium demonstrated that air concentrations and depositions computed by MSCE-HM model agree well with other transport models (TFMM Workshop Minutes, 2005).

Comparison of modelling results based on official emissions data, against measured results indicates an underprediction of observed (about 3 times) values by the model. Cadmium concentrations in air predicted by the model for 1990 – 2003 on the base of emission expert estimates are in good agreement with available monitoring data in aggregate (Ilyin and Travnikov, 2005). The correlation is high (the coefficient is 0.8) and for more than 70% of compared values the difference between modelled and measured concentrations does not exceed ±50%. The observed cadmium concentrations in precipitation are commonly underestimated by the model. However, the correlation between modelled and measured values is high (almost 0.8) and almost 80% of model/measurement pairs of concentrations in precipitation agree within the range ±50% of measured value. Discrepancies between modelling results, based on official emissions, and observed levels of cadmium could be mainly caused by uncertainties of official emission data, natural emissions and re-emission of historic deposition of cadmium.

The U.S. EPA compared modeled ambient concentrations from NATA for 1996 to available ambient monitoring data (from 20 sites) to evaluate the modeling results. This evaluation indicates that NATA underpredicted ambient concentrations of cadmium for 1996 by an average of about 4-5 times. A combination of several factors may be responsible for these discrepancies, including: missing emissions from the inventory (e.g., re-emissions of historic cadmium emissions, possibly some point sources); spatial uncertainty in emission locations for sources: spatial uncertainty of nearby impacts from elevated point sources and local terrain; and high coarse particle deposition velocities.

3.2.3   Atmospheric monitoring

Observed background values of cadmium concentrations in the atmosphere in 1990 were available from 40 stations located in 11 countries in Europe. In 2003 there were 61 stations (in 18 countries of Europe) that provided measurement data.

In 1990 concentrations of cadmium in air were measured at stations located in central Europe and along the North Sea coast. The concentrations ranged between 0.2 and 1 ng/m^3. In 2003 typical ranges of concentrations in air were 0.05 – 0.2 ng/m^3 (northern Europe), 0.2 – 0.5 ng/m^3 (central Europe) and 0.06 – 0.12 ng/m^3 (southern Europe).

Measurements of concentrations in precipitation in the early 1990s took place in Scandinavian countries and along the North Sea coast. Annual mean concentrations ranged between 0.03 and 0.35 μg/L. By 2003 data on measured levels became available from central Europe and from stations of the Baltic Sea region. In northern Europe the concentrations typically range from 0.02 to 0.07 μg/L, and in central Europe – from 0.04 to 0.2 μg/L.

From the early 1990s to 2003, the country-averaged concentrations of cadmium in air decreased around 2 times in central and north-western Europe (Figure 3.8a). Measured concentrations in precipitation decreased 3 - 4 times in central and north-western Europe (Figure 3.8b). In the northern part of Europe, trends of concentrations in precipitation are not evident during this time period (1990 to 2003).

a   b
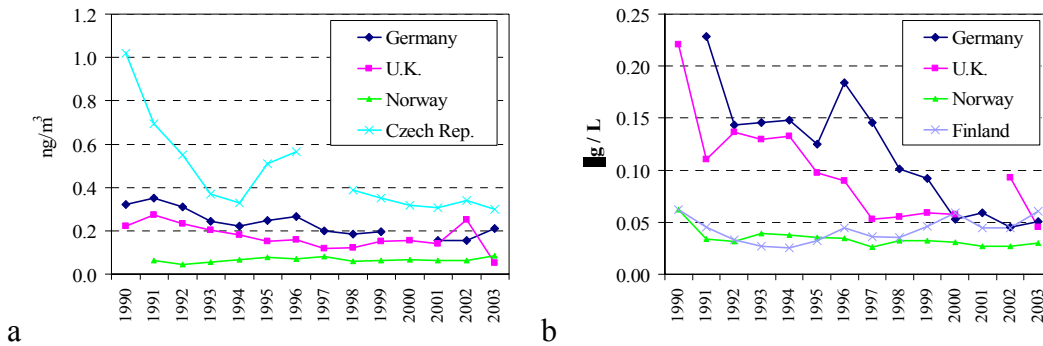
Figure 3.8. Long-term variations of measured concentrations of cadmium in air (a) and in precipitation (b) in different parts of Europe.

Analysis of observed cadmium wet depositions revealed that the total mass of cadmium deposited annually in Europe is approximately twice the mass emitted from European countries (based on official emissions estimates) (Figure 3.9) (Ilyin and Travnikov, 2005). Since this comparison did not account for dry depositions of emitted cadmium, the discrepancy between measurements and emissions could be significantly higher.
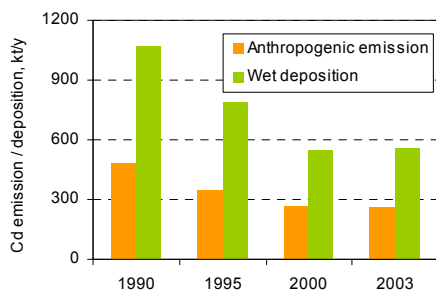
Figure 3.9. Comparison of cadmium total official anthropogenic emissions for Europe with total wet deposition to EMEP countries based on measurement data.

The inconsistencies between the official emissions and observed cadmium wet depositions could be explained by either underestimation of official data, or significant contribution of natural emissions and re-emissions of historical depositions to total European emissions, or by both reasons. These inconsistencies should be further investigated.

In remote areas of the USA atmospheric cadmium concentrations are generally less than 1 ng/m^3 (ATSDR 1999b). Levels in urban air, however, are significantly higher (3-40 ng/m^3). Over the Great Lakes, annual atmospheric cadmium concentrations ranged from

0.6 ng/m^3 in air over lake Erie, 0.2 ng/m^3 over lake Michigan and less than 0.2 ng/m^3 over lake Superior.

A few Arctic monitoring stations, including one in each of Finland, Iceland and Svalbard (Norway), reported cadmium in atmospheric aerosols within a fairly narrow range of 0.02 – 0.1 ng/m^3 (AMAP 2005). Cadmium concentrations in precipitation were measured at locations in Iceland, Norway, and Finland between the early 1990s and 2000. Concentrations were relatively uniform and mostly below 0.2 mg/L. Significant and slightly declining trends were observed at one station in each of Norway and Finland. Concentrations at Svanvik, Norway were slightly elevated and may be influenced by smelters on the nearby Kola Peninsula, as was suggested for lead (AMAP 2005).

Cores of ice extracted from the Greenland Summit glacier contain a well preserved record of atmospheric metal deposition dating back several hundred years. When comparing pre- and post-industrial (i.e. before and since 1800) depositional fluxes of cadmium, the record demonstrates an eight-fold increase that peaked between the 1960s and 1970s and then displays a steady decline thereafter (AMAP 2005).

In Europe there have been several studies that have assessed temporal records of atmospheric cadmium deposition by examination of ombrotrophic peat and lake sediments. In a recent assessment of peat cores from Ireland, Coggins et al. (2006) found peak deposition of cadmium occurred sometime between 1950 and the 1970s.

3.3 Levels and Trends of Cadmium in Terrestrial Ecosystems

Atmospheric deposition of particulate bound cadmium to terrestrial ecosystems is an important source of cadmium to these ecosystems. On agricultural lands, the use of sewage sludge and phosphate fertilizers are also important source of cadmium that can have a more direct impact on animal feed and human food.

The mobility and bioavailability of cadmium in soil is largely a function of solubility. In soils with high organic content and high pH, much of the cadmium is insoluble and therefore relatively unavailable for uptake by vegetation. The proportion of soluble cadmium in low organic content soils with low pH is much higher and the cadmium is more readily taken up by plants grown in these soils (ATSDR 1999b). Acidification of soil, by acid rain for example, can result in greater cadmium uptake by plants. Soils with natural buffering characteristics, like calcareous soils, and soils with high clay content generally reduce the mobility and bioavailability of cadmium.

In forest ecosystems of Europe, atmospheric deposition appears to be the main source of anthropogenically derived metal input representing approximately 80-95% of cadmium loading in forest soils. This is to a large extent allocated to the upper soil and humus layers. European forest soils have been accumulating atmospherically deposited cadmium over a long period of time and it is thought that a similarly long period of time (i.e.

centuries) may be required before concentrations are reduced to natural levels (Bringmark and Lundin 2004).

Retention of cadmium in various European forest catchments was estimated at a number of ICP Integrated Monitoring sites by comparing output fluxes resulting from runoff (RW) to input fluxes from deposition. Total deposition was assumed to be the sum of throughfall (TF) and litterfall (LF). A ratio of RW/(LF+TF) that is greater than 1 implies that the catchment is actually giving up cadmium, whereas a ratio less than 1 implies the catchment is accumulating cadmium. In three Swedish catchments (ICP Integrated Monitoring (ICP IM) sites: Aneboda, Kindla, Gramtratten) output fluxes were lower than input fluxes in the late 1990s and the early 2000s, with ratios(RW/(LF+TF)) of 0.1; 0.83; 0.18, respectively, indicating retention of cadmium in these catchments (Bringmark and Lundin 2004). Similar results were obtained for catchments of five out of seven other monitoring sites in Northern Europe (ICP IM sites Zobelboden (AT), Anenske Povodi (CZ), Lysina (CZ), Rucava (LV), Zoseni (LV), Bavarian Forest (DE) and Gramtatten (SE)), implying that most forests in the region continue to retain atmospherically deposited cadmium (Bringmark and Lundin 2005; Bringmark et al. 2005). In acidic soils of Northern coniferous forests cadmium is leached while retention of cadmium was associated with soils with higher pH (Bergvist 2001).

The concentration of cadmium in natural background soils is highly variable depending on the geological nature of soil minerals. ATSDR (1999b) refers to levels ranging from 0.01 – 1.0 mg/kg in non-volcanic soils and up to 4.5 mg/kg in soil of volcanic origin. The suggested mean cadmium concentration for unpolluted US topsoil is 0.25 mg/kg.

Bioavailable cadmium is taken up by plant root systems and redistributed throughout the plant. Other uptake pathways include direct foliar uptake and deposition of cadmium particulate onto plant surfaces. Accumulation generally occurs in the leaves. Food crops accumulate levels of cadmium in the following decreasing order: leafy vegetables > root vegetables > grains (ATSDR 1999b).

Atmospheric deposition appears to be an important source of cadmium to Arctic terrestrial ecosystems. Enrichment factors for cadmium measured in Arctic mosses were consistently >25 and often in the 100s (AMAP 2005).

Cadmium concentrations in mosses which are used as an indicator of the spatial distribution of atmospheric deposition (WGE 2004) ranged from < 0.1 mg/kg to 0.3 mg/kg over much of Central and Northern Europe. Some locations had higher concentrations, up to > 0.8 mg/kg, and were found with a higher frequency in East Europe. Cadmium in soil and mosses of northern Europe display spatial gradients that seem to reflect proximity to source regions, for example a decreasing south to north gradient is evident in Scandinavian countries (Figure 3.10), which corresponds to increasing distance from industrial centres of Northern Europe. Mosses, monitored in Scandinavia since the 1970s, indicate that levels have decreased up to 2000, the last year for which data was available (AMAP 2005).

A large amount of literature data on cadmium concentrations in crops and forest trees was evaluated (Alrikson et al. 2002, De Vries and Bakker 1998, Nagel et al. 2000, Jacobsen et al. 2002, Schütze and Nagel 1998) in order to enable the calculation of cadmium removal by harvest of biomass as a part of critical loads calculations. Almost exclusively data from background sites were included. The concentration ranges in harvestable parts were 0.05 – 0.25 mg/kg (dw) for mixed grassland species; 0.02 – 0.08 mg/kg (dw) for cereals; 0.2 – 0.25 mg/kg (dw) for potato, sugar beet and maize. The wood of coniferous trees contains 0.1 – 0.5 mg/kg (dw) in Central Europe and 0.02 – 0.04 mg/kg (dw) in Northern Europe. The wood of deciduous forest trees in Central Europe has a cadmium content of 0.05 to 0.5 mg/kg (dw). For details see ICP Modelling and Mapping Manual (2004).
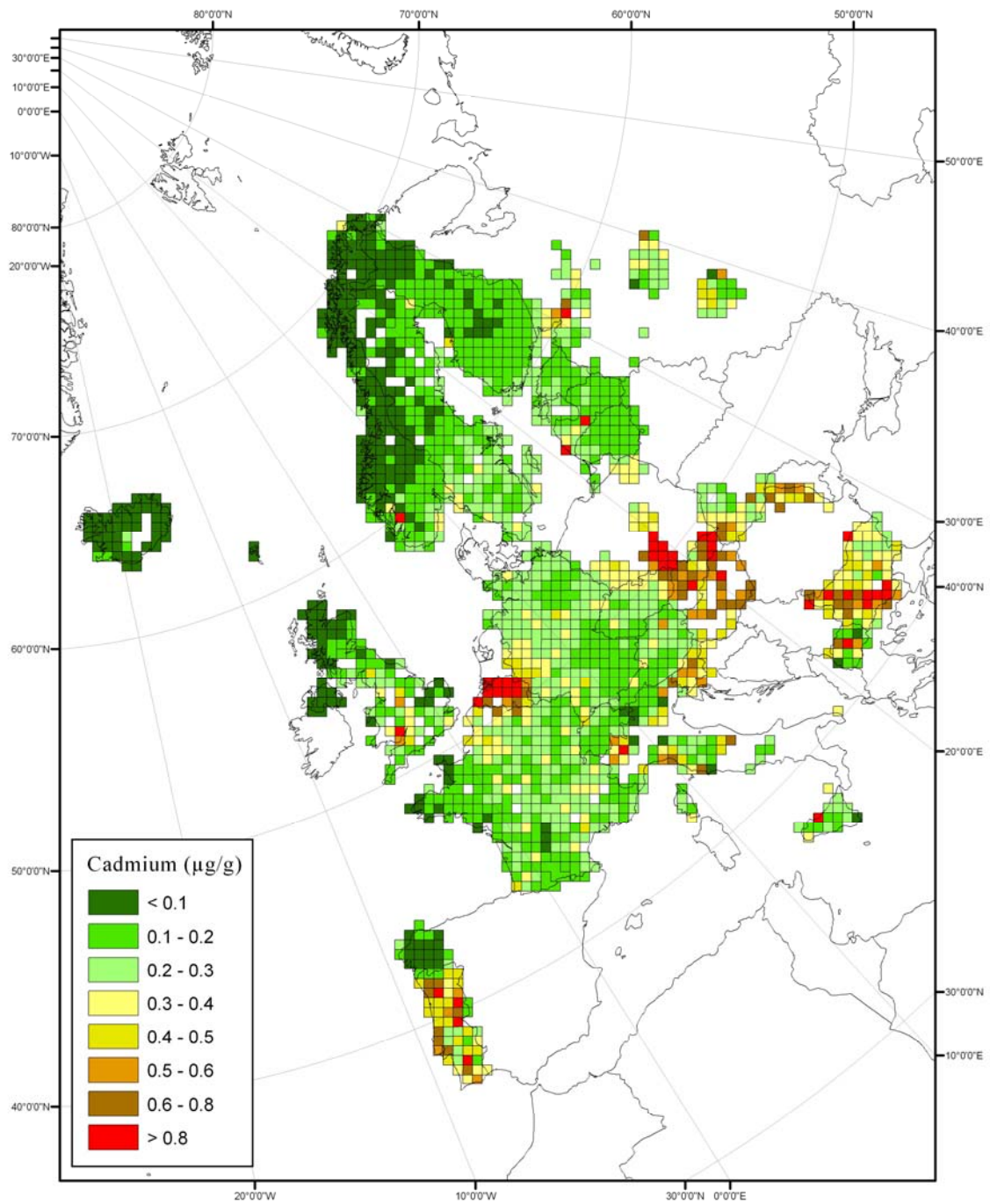
Figure 3.10. Distribution of cadmium in European mosses, 2000/2001 survey (WGE 2004).
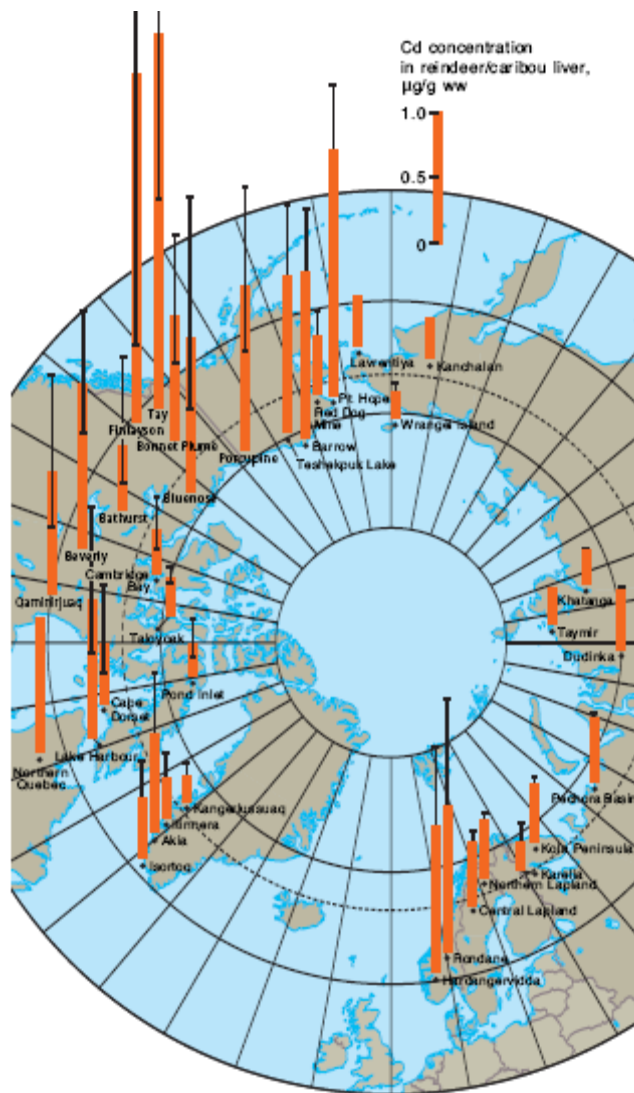
Figure 3.11. Cadmium concentrations in reindeer and caribou liver (AMAP 2005).

Cadmium is accumulated in the liver and kidneys of terrestrial herbivores. Biomagnification of cadmium up the food chain, however, does not seem to occur. This is likely do to the fact that cadmium does not accumulate to a great degree in muscle, nor is it very easily absorbed through the intestinal wall (ATSDR 1999b). The greatest source of exposure to carnivores therefore is through consumption of liver and kidneys.

In long lived herbivores cadmium can accumulate to fairly high levels in kidneys and liver. Generally levels in kidney are higher than levels in liver. Deer livers collected from Connecticut, New Jersey, Illinois and Maine, U.S.A. had mean cadmium concentrations ranging from 0.4 – 4 mg/kg ww.

Cadmium concentrations in reindeer and caribou liver are generally in the range of 0.2-2.0 mg/kg, however, higher levels (mean of 3.8 mg/kg) have been detected in Yukon where they are naturally elevated due to local geology (AMAP 2005). Cadmium levels

in reindeer liver from Scandinavia reflected the same geographic pattern seen in mosses where levels decreased from South to North, apparently reflecting decreased input from Northern Europe with increasing latitude (Figure 3.11). High levels of cadmium measured in Yukon Canada, have been attributed to naturally high levels of cadmium in the soil of the region. It was noted in the AMAP (2005) report that cadmium concentrations in caribou and other herbivores that graze on metal accumulating vegetation like willows often reflect natural geologic sources (AMAP 2005).

Temporal trends data for caribou and reindeer generally did not reveal any significant trends over the last 10-15 years, although one study from northwestern Sweden did detect a significant increase between 1982 and 1998 in reindeer (AMAP 2005).

3.4 Levels and Trends of Cadmium Freshwater Ecosystems

Cadmium is relatively mobile in aquatic systems where it exists in the dissolved phases as hydrated cadmium (2+) ions. The amount of dissolved cadmium in water tends to increase with lower pH and is also inversely associated with the humic content of the water body. Once deposited to freshwater systems cadmium can reside in the water column for long periods of time, e.g. 4-10 years as calculated for Lake Michigan, before it is deposited to the sediment. Cadmium may be permanently sequestered in sediment, however, it can also be re-mobilized and introduced back into the water column. Sorption to organic matter is the most important removal mechanism. Re-emission of cadmium to the atmosphere from surface waters does not occur (ATSDR 1999b).

Data on heavy metals in surface waters are available from a survey in Nordic lakes (about 3000 lakes in Finland, Denmark, Norway, Sweden and Russian Kola). Weighted 50- and 99.5-percentiles of the cadmium concentration were < 0.05 µg/L or < 0.28 µg/L, respectively (with no cadmium data for Kola). Cadmium showed a distinct gradient from the South of Norway and Sweden to the North. This pattern resembles that of deposition of these elements as shown by the moss survey. Multivariate statistical analysis also showed that cadmium concentrations in the lakes were elevated in regions of high long-range transport both of acidifying pollutants and metals.

In the North American Great Lakes, background concentrations of cadmium in water ranged from less than 0.02 µg/L to 0.10 µg/L. It was also noted that measured concentrations differed substantially between samples that were filtered and unfiltered samples. When background Great Lakes water was filtered, the concentrations of cadmium ranged from 0.001 to 0.068 µg/L (Wren et al., 1995).

Analysis of sediment cores from Norway was used to derive enrichment factors, which are calculated by dividing the concentration in surface sediments by the concentration in core layers that pre-date anthropogenic input. This study found that cadmium was among the most enriched elements in the surface sediments and, consistent with other spatial patters for cadmium, was more enriched in sediments from southern parts of the country (AMAP 2005).

Mean concentrations of cadmium in lakes and streams at ICP Waters sites in the period 1999 – 2001 are published in ICP Waters (2003). The number of sites per country varied from 1 to 20. In Finland, Sweden and Latvia all means were lower than or equal to 0.06 µg/L. Mean values up to 1.05 µg/L occurred at sites in the Czech Republic, Germany, Hungary, Ireland and Poland. A high value of 2.4 µg/L was found at a site in Belarus.

Cadmium is readily accumulated in freshwater organisms. Bioconcentrations factors, the ratio of cadmium in a given organism to the concentration of cadmium in water, are reported to vary over several orders of magnitude from 3 to 4190. Cadmium is not known to biomagnify in freshwater ecosystems (Wren et al., 1995). As such, freshwater invertebrates tend to have higher concentrations of cadmium than fish. Invertebrate species from Ontario, Canada, including various species of zooplankton and molluscs, had cadmium concentrations ranging between about 1 and 50 mg/kg dw. By comparison, Canadian freshwater fish generally had cadmium concentrations below 0.4 mg/kg dw (Wren et al., 1995). Reported results for Arctic fish suggest that typical levels are <0.005 mg/kg ww. Cadmium levels in anadromous char were higher due to their time spent in the ocean, and ranged from <0.5 mg/kg dw in Iceland to 2.0-2.5 mg/kg dw in Chukotka, Russia. The best time trend data for cadmium in fish is from a Swedish study that monitored contaminant concentrations in pike between 1968 and 1999. Though the dataset was statistically robust there was no discernable trend (AMAP 2005).

3.5 Levels and Trends of Cadmium in Marine Ecosystems

Cadmium in the free ionic form (Cd (II)) is also the most bioavailable form of cadmium. Compared to lead, cadmium is relatively bioavailable in the marine environment and is subject to bioaccumulation in marine biota. Cadmium also appears to biomagnify between some marine species as illustrated in Figure 3.12. Cadmium accumulates in internal organs rather than in muscle and fat. Over time the kidneys accumulate the highest concentrations of cadmium followed by the liver. Cadmium does bioaccumulate over time and therefore concentrations increase with age.

Little is known about what factors influence the distribution of cadmium in the Arctic seas, however, it appears that natural geochemical distribution and processes play a more important role than anthropogenic sources. In an effort to determine if long-range transport of cadmium is important (for the Arctic seas), Macdonald et al. (2000) developed a cadmium budget for the Arctic Ocean. Of a total estimated input of 4855 ± 1300 t/yr, they estimated 27 ± 9 t/yr to have come from atmospheric transport. While less than 1% of the cadmium came from atmospheric sources, the vast majority was imported via inflowing ocean currents. The authors concluded, following a review of corroborating evidence from other studies, that atmospheric deposition of cadmium was unlikely to have much impact on the natural cycles in the Arctic ocean.
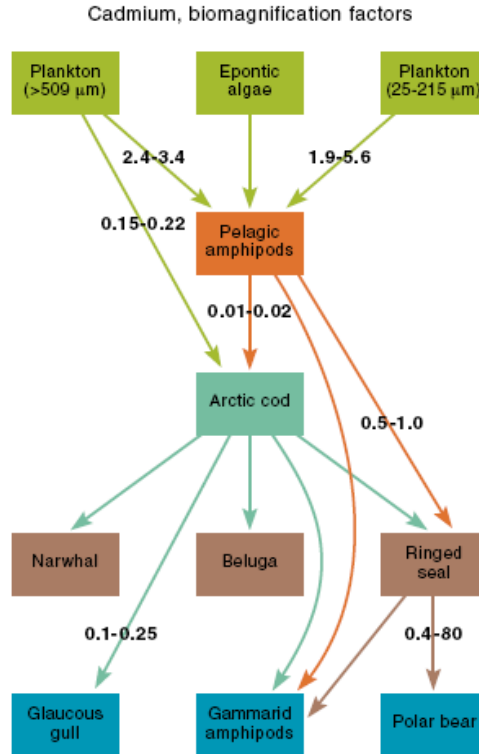
Figure 3.12. Pathways and biomagnification factors for cadmium in the Arctic marine food web. Biomagnification factors are based on dry weight concentrations in whole organisms for biomagnification to invertebrates and fish, and on wet weight concentrations for fish to muscle in top predators (for polar bear, liver was used instead of muscle) (from Muir et al., 1999). In the case of the biomagnification factors from ringed seal to polar bear, the lower value is for seal blubber to polar bear liver, and the higher value is for ringed seal liver to polar bear liver. (Source: Macdonald et al., 2003)

The conclusions of Macdonald et al. (2000) seem to be supported by results of biological monitoring. The spatial distribution of cadmium in marine biota appears to be driven by regional geology or biochemistry (Figures 3.13, 3.14, and 3.15) and not atmospheric deposition (AMAP 2005). Monitoring of Arctic marine biota has not revealed any discernable temporal trends in biotic cadmium levels. Walrus, sediment and mollusks from the Canadian Arctic suggest that levels of cadmium have not changed over the past few centuries, supporting the notion that natural sources are responsible for observed levels in marine biota. More recent trends also do not indicate any significant changes in levels in beluga and narwhal from the Canadian Arctic, mussels from Alaska, Greenland, Iceland and Norway, or sculpin from Greenland (AMAP 2005).
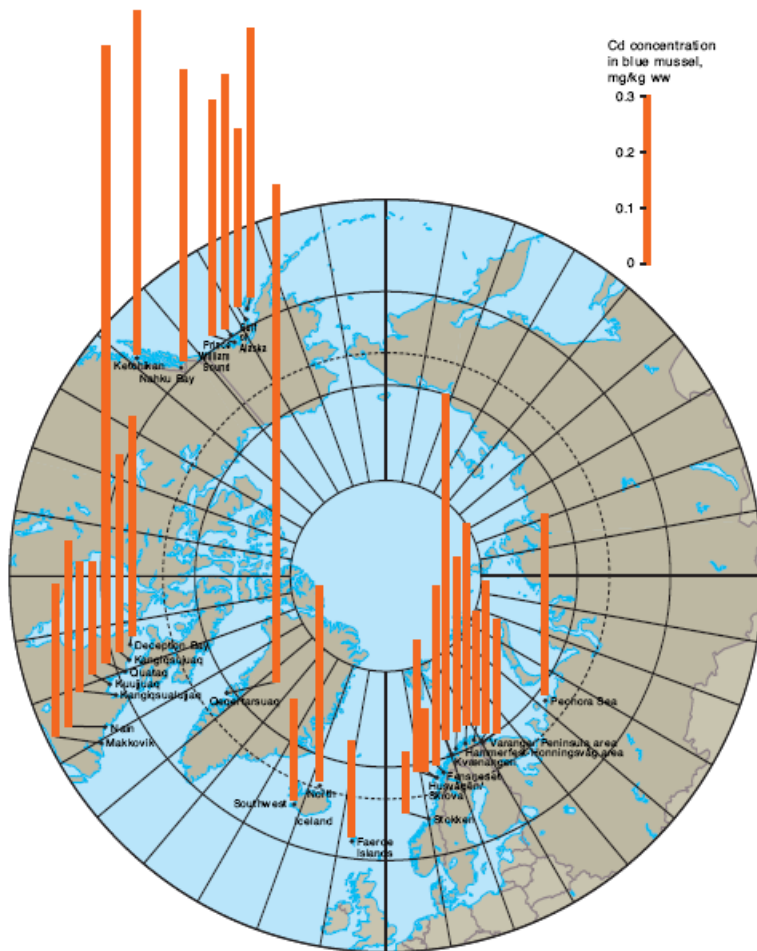
Figure 3.13. Cadmium concentrations in blue mussels (AMAP 2005).
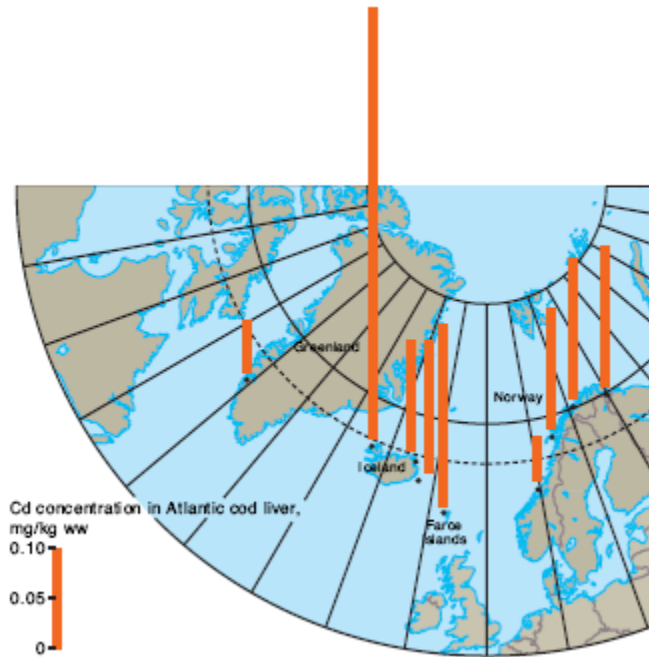
Figure 3.14. Cadmium concentrations in Atlantic cod liver (AMAP 2005)
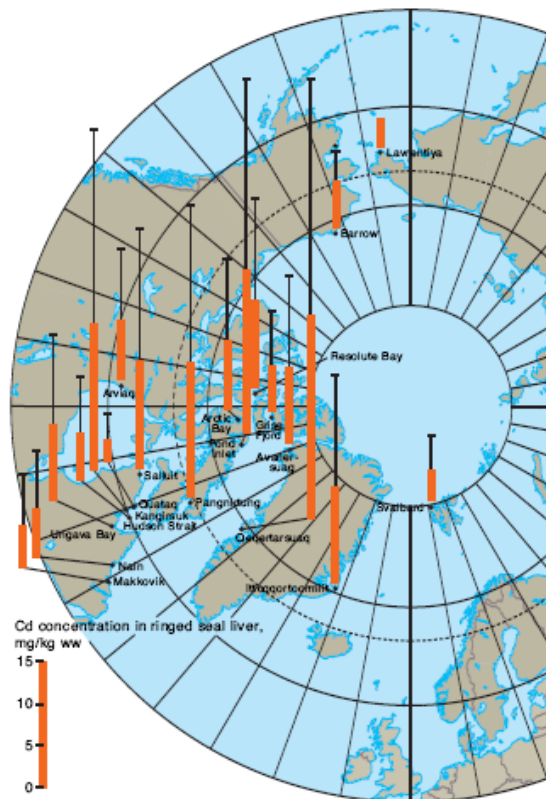
Figure 3.15. Cadmium concentrations in ringed seal liver (AMAP 2005)

3.6 Levels and Trends of Cadmium in Human Populations

3.6.1 Levels of cadmium in food

After smoking, food is the greatest source of human cadmium exposure, accounting for 99% of cadmium intake in non-smokers. The average daily intake of a non-smoking U.S. citizen is 0.03 mg/day. Smoking is considered to double cadmium intake (ATSDR 1999b). Tobacco plants, like other crops, can accumulate atmospherically deposited cadmium which is concentrated in cigarette smoke and absorbed through the lungs. The greatest dietary sources of cadmium to the general population include grain and cereal products, potatoes, leafy vegetables, and root vegetables. Organ meats, such as liver and kidney, and shellfish are also significant dietary sources of cadmium when consumed in large amounts.

The cadmium content of higher plants is in large part caused by uptake from the soil. Exceptions might occur in heavily air polluted areas. The concentration of cadmium in white clover from pot experiments at ICP Vegetation field sites away from local pollution sources and roads was analysed and plotted against bulk deposition rates. A background concentration of cadmium in the clover foliage was determined to be 0.065μg/g. Up to a bulk deposition rate of 2.5 μg/m^2/d the cadmium concentration in clover did not differ significantly from the background concentration. A similar result was obtained for leafy vegetables (De Temmerman and Hoenig 2004). Tolerable bulk deposition rates to meet the critical limits (EU 2001) for cadmium in unwashed vegetables (spinach, lettuce, endive, lamb's lettuce) on soils with low available cadmium contents ranged between 25 and 75 μg/m^2/d. There is also a correlation between deposition and the cadmium content in green fodder at relatively high cadmium deposition rates. The maximum tolerable deposition rate to not exceed a cadmium concentration of 0.57 μg/g in clover or grass was 15 μg/m^2/d and 9 μg/m^2/d, respectively (ICP Vegetation 2005). Deposition rates of cadmium caused by long-range transport are much lower than these rates, and are not expected to cause a considerable increase of cadmium concentrations in food and fodder crops by direct uptake and to critical limit exceedance.

Food items in the USA typically have concentrations of cadmium that are less than 0.1 mg/kg ww. As a general rule, cadmium concentrations in dairy products, eggs, beef and fish are less than 0.01 mg/kg ww, while levels in fruits and vegetables and grains concentrations are generally between 0.01 and 0.1 mg/kg ww (ATSDR 1999b).

Higher levels of cadmium have been found in shellfish, however, it is not clear if these concentrations are reflective of atmospheric deposition. In a 1985-1986 survey of samples from commercially harvested regions of the USA, levels were 0.09±0.06 mg/kg (ppm) (n=75) in hardshell clams, 0.05±0.04 mg/kg (n=59) in softshell clams, 0.5l±0.31 mg/kg (n=104) in Eastern oysters, and l.l±0.6 mg/kg (n=40) in Pacific oysters (ATSDR 1999b). In another survey of market fish (marine) in the US, cadmium levels ranged from 0.00013 mg/kg ww for small shrimp to 0.03 mg/kg ww for yellow fin tuna (Burger and Gotchfeld., 2005). The highest concentrations of cadmium found in shellfish are usually associated with organs, e.g. hepatopancreas of crabs, however, it has been

demonstrated that cadmium in shellfish is not readily absorbed by consumers (ATSDR 1999b).

Table 3.1. Guidelines for cadmium in edible fish tissues

Country	Guideline
UN FAO – CODEX Alimentus	mollusks (1.0 ppm) and crustacea (0.5 ppm)
Joint Monitoring Programme of Oslo and Paris commissions	0.2 ppm in fish and below 2 ppm in mussels

3.6.2   Levels of cadmium in humans

There does not appear to be very much data on cadmium in human tissues that are representative of the general population. ATSDR (1999b) for example, does not report any data for the general population, although it does report some results for high exposure groups. However, there are some data on general population exposures to cadmium in U.S.A. from the NHANES study (U.S. CDC, 2005). For years 1999-2000, based on data from 7,970 people, the CDC found that the mean blood concentration was 0.412 micrograms cadmium per liter of blood (μg/L). For data from 1999-2002, with sample size of about 17,000 people, the 95th percentile exposure level was 1.3 μg/L (U.S. CDC, 2005). In addition, an anlaysis of food intake rates and food-cadmium concentrations for the U.S. population estimated a geometric mean intake of 18.9 μg/day, or 0.4 μg/kg/day (Choudhury et al, 2001, as cited in U.S. CDC, 2005).

In one instance, maternal and cord blood levels are reported for a highly contaminated industrial region of Poland. In the study, which was investigating the placenta as a barrier to in-utero cadmium exposure, measured mean cadmium maternal blood levels of 5 μg/L and cord blood concentrations of 1 μg/L (ATSDR 1999b). Another study examining cadmium exposure in non-smoking men and women living on farms in southern Sweden found median blood cadmium concentrations ranging from 0.38–18 nmol/L (median 1.8 nmol/L) (Olsson et al., 2002). Based on a molecular weight of 112.4 g/mol, this translates to a range and median of 0.04 – 2.0 μg/L and 0.20 μg/L respectively. While smoking can double a persons intake of cadmium, it can result in blood cadmium levels that are four to five times higher than in non-smokers owing to the fact that about 10-50% of inhaled cadmium is absorbed through the lungs, while only 1-5% is absorbed through the gastrointestinal tract (Jarup et al., 1998).

Maternal blood levels were reported in AMAP (2003) for Canada, Greenland, Alaska, Russia and Finland. Inuit mothers from Canada had the highest mean levels of cadmium (1.0 to 1.9 μg/L) which was attributed to high rates of smoking and relatively high levels of cadmium in Canadian cigarettes. Intermediate levels of cadmium were measured in blood from Inuit mothers in Greenland, indigenous and non-indigenous Russian mothers and Caucasian, Dene and Metis mothers in northern Canada (0.36 to 0.65 μg/L). The

lowest blood cadmium levels were measured in Finish mothers. The highest levels of cadmium were attributed to high rates of smoking among indigenous populations, although the consumption of marine mammals was also thought to be a contributing factor. A study comparing the influence of smoking on blood cadmium levels, found cadmium levels of 0.27 µg/L in non-smokers compared to 5.3 µg/L in smokers.

3.7 Ecosystem and Human Health Effects of Cadmium

3.7.1   Terrestrial Ecosystems

Cadmium in soils can affect microorganisms and soil fauna as well as plant roots. Risks due to high concentrations in above-ground vegetation and for terrestrial food chains are less probable (Bringmark and Lundin 2004).

Rademacher (2001) conducted a comprehensive review of data from ICP Forest measurements networks and literature on concentration levels of metals in forest ecosystems and effect thresholds. Based on empirical data the Foliar Expert Panel of ICP Forests (EC-UNECE 1995a, 1998 b) discussed an evaluation guide for macro and micro nutrients as well as heavy metals. For cadmium a concentration in foliage of >1 to > 3 µg/g (depending on tree species, the high value is for beech) was suggested to indicate excess not having necessarily a damaging effect. The following effect thresholds for cadmium in plant tissues are reported:

- Balsberg Påhlson (1989):   NOEC (effects on forest) < 2 µg/g;
- Sauerbeck (1983):   NOEC (yield loss for agricultural crops) 5 - 10 µg/g;
- Balsberg Påhlson (1989):   decrease of physiological parameters and yield (forest) >3 – 10 µg/g (dw).

Results from ICP Forests Level I and Level II plots showed that cadmium was retained in upper layers of forest soils of most sites, though not necessarily in background areas (Rademacher 2001). The median cadmium concentration in the humus layer of 1513 Level I plots was 0.5 mg/kg, while 0.1 mg/kg in the upper mineral soil (50 cm, n= 1632)). The related 95-percentiles were 1.7 mg/kg (humus) and 2.5 mg/kg (mineral), respectively. At Level II plots the median cadmium concentration in the humus layer was 0.4 mg/kg, and 0.2 mg/kg in the mineral soil. Rademacher (2001) reported a series of critical limits (Bååth 1989, Wilson 1977, Atanassov et al. 1999, Tyler et al 1989, Bengtsson and Tranvik 1989, Tyler 1992, Inman and Parker 1978, Coughtrey et al 1979). Those limits for cadmium in soils showed a very wide range of 0.3 mg/kg up to 32 mg/kg depending on the effect and endpoint considered. The lower value of 0.3 mg/kg is based on the NOEC (nitrification, Wilson 1977)

Most surveys of cadmium in soils provide total contents (or in exchange aqua regia extractable concentrations). Also almost exclusively all toxicological studies provide thresholds for total cadmium contents or total added amounts. However, because

cadmium effects on soil organisms and plants are caused by the soluble proportion or even the free metal ions, effects evaluation based on total contents is rather limited. Based on a pH dependent critical limit function related to free metal ion concentrations (Lofts et al. 2004) and using a chemical speciation model (based on Tipping et al. 1998) ICP Modelling and Mapping Manual (2004) provides ranges of critical limits expressed a total concentrations of soil drainage water for use in critical loads calculations. These critical limits range from 0.4 µg/L to 5.1 µg/L depending on soil conditions. Chronic exposure to mammals at elevated concentrations can effect the functioning of liver and kidneys. In some Arctic locations cadmium concentrations measured in liver of terrestrial wildlife, e.g. caribou from Yukon, Canada, approach the threshold for adverse effects on liver (40 µg/g ww) (Figure 3.15). The cases of high exposure, like that of Yukon caribou, however, were all attributed to natural conditions, not deposition from long-range atmospheric transport (AMAP 2005).

3.7.2 Freshwater Ecosystems

In the European Commission (2003) the $PNEC_{water}$ of Cd is derived from the median HC_5 value (Aldenberg and Slob, 1993) from 44 chronic NOEC values, some of which are geometric species means. These data are derived from 19 tests with fish/amphibians, 22 tests with aquatic invertebrates and 8 tests with primary producers, and represent 28 species in total. The NOEC values were obtained from laboratory based, single species studies and refer to the dissolved fraction. It is concluded in European Commission (2003) that the "NOEC and LOEC distributions overlap in the lower concentration range and that an additional assessment factor may be necessary". Therefore, an assessment factor of 2 is applied on the HC5 and the $PNEC_{water}$ is hence 0.19 µg Cd/L.

In addition the European Commission (2003) concludes that for the aquatic compartment there is a need for better information regarding the toxic effects of cadmium to aquatic organisms under low water hardness conditions. In particular, information is required on Cd toxicity testing in very soft waters (Hardness below about 10mg $CaCO_3$/L). Current data suggest that a significant number of freshwaters in Norway, Finland and Sweden have water hardness below this threshold. There are no data for the very soft waters and these areas may be unprotected by the proposed $PNEC_{water}$ for soft water (0.08 µg Cd/L).

In the calculation of critical loads of cadmium for surface waters a PNEC of 0.38 µg/L was used as critical limit without implementing the assessment factor of 2 (Modelling and Mapping Manual 2004). This is in line with the general approach in the critical loads methodology to refuse the use of "safety factors" due to their mostly arbitrary nature and weak scientific basis. The decision is supported by the opinion of the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 2004) stating that "there is neither scientific rationale nor evidence which allows an objective selection of the factor magnitudes". The renunciation of an assessment factor leads to a less conservative risk evaluation.

Effect thresholds of cadmium in surface waters vary depending on water chemistry (Skjelkvåle and Ulstein 2002). In particular soft waters are sensitive to Cd inputs and are

not sufficiently considered in the limit recommended within the Risk Assessment of Cd (European Commission 2003) A limit of 0.1 µg/L (Lowest Biological Risk Level) considering sensitive chemical conditions in Swedish freshwaters was set by SEPA (2000). A similar limit has been set for Norway (Andersen et al. 1997). The Workshop on Heavy Metals (Pb, Cd, Hg) in Surface Waters (March 2002, Lillehammer, Norway) recommended a span of critical limits for cadmium of 0.1 – 1.0 µg/L depending on sensitivity of the water bodies. (Skjelkvåle and Ulstein 2002). A method to consider freshwater chemistry in the setting of limits for cadmium and lead is provided in De Vries et al. (2005). Comparison of present concentration and critical limits reveal that in general, European surface waters receiving pollution only from atmospheric deposition have cadmium concentrations in water below critical limits, but exceedances cannot be completely excluded.

In conclusion cadmium pollution was considered a minor problem for aquatic ecosystems in the Nordic region. However, ongoing accumulation of toxic metals in catchments combined with leaching from acidified soils might increase stresses on aquatic biota in the future (Skjelkvåle et al. 2001).

Toxic effects on fish exposed to elevated cadmium concentrations over long periods of time are generally indicated by reduced growth and survival of juvenile fish. The concentration of cadmium in water required to induce toxic effects depends greatly on factors such as species sensitivity, life stage, pH, water hardness, and diet. In a review of several laboratory studies that derived effects thresholds for sensitive fish species, Wren et al. (1995), reported that effects of chronic exposure to cadmium could be induced at water concentrations as low as 0.5 – 1.0 µg/L. Most water bodies in the UNECE region appear to have cadmium levels below this threshold range, however, ICP-Waters did note some waters in this range.

3.7.3   Marine Ecosystems

In general, the levels of cadmium that have been measured in Arctic marine species do not appear to be above toxicity thresholds. Some seabird species may exceed thresholds for terrestrial birds, however, seabirds are known to be adapted to higher levels of cadmium found naturally in the marine environment and are therefore not considered to be as sensitive as terrestrial birds. Similarly, some marine mammals approach and even exceed the threshold for terrestrial mammals, however, they are generally an order of magnitude below thresholds derived for marine mammals (Figure 3.16). Ringed seals from Greenland that display relatively high concentrations of cadmium in their kidneys did not display any signs of related adverse effects (AMAP 1998). As was noted earlier, the overwhelming majority of cadmium in the worlds oceans is naturally occurring.
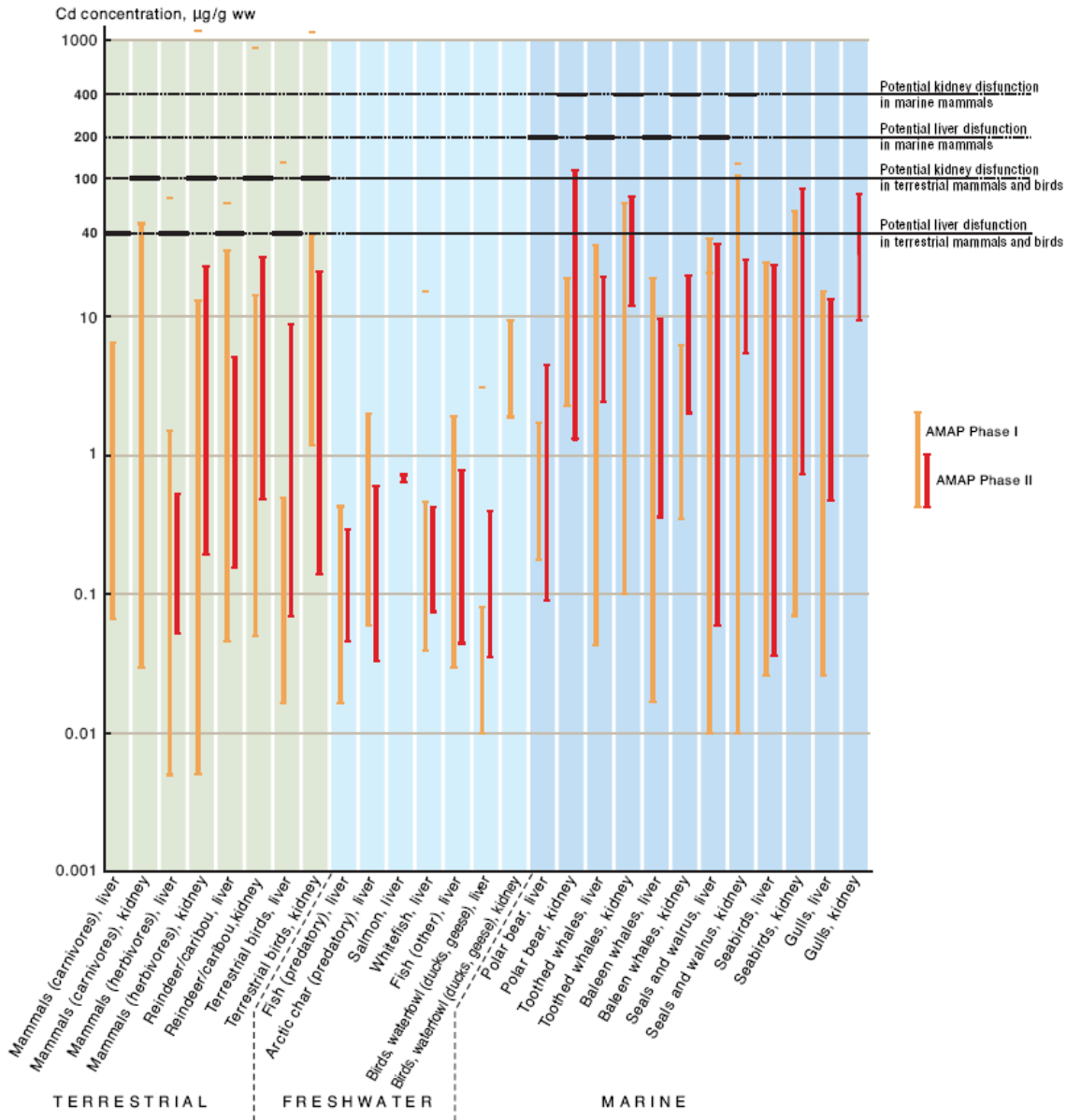
Figure 3.16. Ranges in cadmium concentrations that were reported during the last two AMAP assessments are displayed as vertical bars and compared to toxicity thresholds represented by horizontal lines. Toxicity thresholds are taken from ecotoxicology literature and reviewed in AMAP (2005).

3.7.4 **Human Health Effects**

Cadmium is a non-essential element for human biological function. At relatively low levels of exposure, cadmium can build up in the kidneys to the point where it can adversely effect kidney function and even cause kidney disease. High levels of inhalation exposure have been shown to cause lung damage and there is some evidence to suggest that prolonged exposure to elevated levels of cadmium may contribute to the onset of osteoporosis (ATSDR 1999b). U.S. EPA has classified cadmium as a "probable human

carcinogen" through inhalation exposure because some human studies and animal studies indicate an increase risk of cancer due to inhalation exposure to cadmium. However, studies of ingestion exposure do not provide evidence of cancer. Thus, available data suggest that cadmium is not likely to cause cancer through ingestion exposures (U.S. EPA, IRIS, 1992, available at: http://www.epa.gov/iris/index.html).

The contribution of LRTAP to the actual cadmium content in the topsoil may reach the contribution due to the use of phosphate fertilizers. Present data on the concentration of cadmium in the air and daily intake of cadmium with food suggest a decreasing trend in Europe. Present average concentrations of cadmium in the renal cortex in the general population in Europe at the age of $40 - 60$ years are in the range $15 - 40$ mg/kg. These values are only $4 - 12$ times lower than the critical levels estimated in cadmium workers for the induction of tubular dysfunctions (180 mg/kg) and very close to the critical level of 50 mg/kg estimated by a study in Belgium. Any further increase in the dietary intake of cadmium owing to an accumulation of the metal in agricultural soils will further narrow the gap to these critical levels and should therefore be avoided (WGE 2004).

Critical limits aiming at the protection of human health were used in the calculation of critical loads of cadmium. The basis for the critical limits are the WHO guideline value for drinking water quality (3 µg/L) and a cadmium concentration in wheat grains for food consumption of 0.1 mg/kg (Modelling and Mapping Manual 2004). The latter is based on the Acceptable Daily Intake (ADI) for adult non-smokers of $37 - 47$ µg (European Commission 2003) and on information on food consumption behaviour of the population in Germany and other European countries. It corresponds to a critical total concentration of cadmium in the soil solution of 0.8 µg/L (De Vries et al. 2005).

Mean cadmium concentrations in vegetation and crops found in background regions are in general lower than critical limits for food and fodder as well as for phytotoxic effects, concentrations in cereals are frequently close to the limit used in the critical loads calculation for cadmium but not necessarily caused by long-range atmospheric transport (Modelling and Mapping Manual 2004).

The onset of cadmium related effects on the kidney is associated with renal tubular damage. Several studies have found that an excess prevalence of renal tubular damage of 4% was related to urinary cadmium excretion of 2.5 µg/g creatine. It is estimated that this level of urinary excretion would result from cadmium intake of 50 µg/day sustained over decades, or 350 µg/week (Jarup et al., 1998), which is equal to the WHO tolerable weekly intake (TWI).

Levels of cadmium exposure among the Swedish population were reviewed by Jarup et al. (1998). In their review, the average intake of cadmium among the general, non-smoking populations was estimated at 15 µg/day (or 105 µg/week), however, there was a great deal of variation depending on dietary habits. For example, diets high in fibre and or shellfish are known to result in elevated levels of cadmium intake. The review also reported higher levels of cadmium in the blood and urine of women. This observation was associated with iron deficiencies which are generally more common in women than

in men. Low levels of iron are known to increase gastrointestinal absorption of cadmium. People with low levels of iron, particularly women, and people who consume a diet rich in cadmium (i.e. containing large amounts of shellfish, high fibre and organ meats) are expected to have the highest exposure levels among non-occupationally exposed, non-smoking population.

The Swedish review (Jarup et al., 1998) concluded that about 1% of women with low body iron stores and smokers may experience adverse renal effects given the level of cadmium intake at the time of the survey (15 µg/day). A doubling in the daily intake, to a level of 30 µg/day was expected to put about 1% of the general population at risk of renal effects and boost the rate to 5% among high exposure groups.

ATSDR (1999b) refers to two studies that estimated average intake of cadmium in the US based on dietary surveys: one conducted in the 1980s estimated an average daily intake of 30 µg/day (210 µg/week); and a study published in the early 1990s estimated a similar intake of 230 µg/week. Another study, however, which estimated intake based on measured concentrations in fecal material derived an estimate that was an order of magnitude lower. Using the value of 230 µg/week, a 50 kg person would have a weekly intake of 4.6 µg/kg/week. This level of exposure is below the WHO TWI of 7 µg/kg/week, but not by much, and it more than doubles the US ATSDR chronic dose MRL of 0.3 µg/kg/day (or 2.1 µg/kg/week). Assuming a similar distribution in cadmium intake among the U.S. population as was used in the Swedish review, would imply that 1% of the population may be experiencing cadmium related effects on the kidney.

Based on estimated consumption of traditional foods and existing contaminant databases, AMAP (2003) estimated weekly intake for Inuit from Greenland and Canada was 1000 µg/week. Similar estimates for non-Inuit populations in Canada, Denmark and Finland ranged from 32 – 100 µg/week. The relatively high level of intake among Inuit is associated with the consumption of marine mammals and particularly marine mammal organs. As was noted previously, the cadmium in marine mammals is associated with naturally occurring cadmium in the marine environment. A more detailed study, which focussed on a single Inuit community in Arctic Canada, calculated mean cadmium intakes of only 0.6 µg/kg bw/day, or 4.2 µg/kg bw/week. The upper 95 percentile of the community, however, did exceed the WHO TWI (7 µg/kg bw/week), with an estimated daily intake of 2.3 µg/kg bw/day, or 16.1 µg/kg bw/week (Van Oostdam et al., 2005). This study highlighted the difficulty with extrapolating short term dietary surveys over long periods of time to estimate chronic intake. This implies that the upper range of estimated dietary intake may be overestimated due to the overestimated frequency with which some foods are consumed.

Van Oostdam et al. (2005) also compared levels of cadmium in blood of Arctic women to a guideline of 5 µg/L set by Health Canada for limiting occupational exposure. Depending on the region, 7-18% of Inuit women exceeded the guideline, while 6% of Caucasian women in the Canadian Arctic exceeded the guideline. Marine mammal consumption was considered to be a factor in the elevated blood cadmium concentrations

among Inuit. The most important determinant of cadmium concentrations, however, was cigarette smoking.

Since exposure to elevated levels of cadmium among Arctic people is principally attributed to cigarette smoking, and not related to Arctic wide contamination, AMAP does not consider cadmium arising from long-range atmospheric sources, or other distant sources, to be a significant health risk (AMAP 2003).

4 Lead

4.1 Background

Lead is a naturally occurring element in the earth's crust and is emitted to the atmosphere from both natural (e.g. volcanoes) and anthropogenic sources. Anthropogenic sources include industrial fossil fuel combustion and metal smelting. Atmospheric lead exists primarily in the particulate form and settles fairly quickly following emission, which limits the potential for long-range atmospheric transport. As a result, concentrations of lead in environmental media are much higher in the vicinity of emission sources and decrease rapidly with increasing distance from the source. Fine particles, however, can be transported to remote regions of the earth and have been measured in places like the Arctic.

Once deposited, the uptake of lead into terrestrial and aquatic foodchains is governed largely by the biogeochemical properties of the soil and water. Most notably, the other minerals and organic matter in the soil or water as well as acidity play a large role in determining the bioavailability of lead. While plants are relatively resistant to lead, terrestrial and aquatic wildlife can suffer a number of effects as a result of elevated lead exposure, most of which are related to impaired development of the central nervous system. At high levels plants can also be adversely affected. Lead bioaccumulates in biota, however, unlike many other contaminants, lead does not biomagnify and therefore higher trophic level organisms do not tend to contain high concentrations of lead as a result of deposition from long-range atmospheric transport. Fish and wildlife can however accumulate lead over time through trophic transfer and from direct ingestion of particulate, like soil and sediment. Ingestion of lead fragments, from spent ammunition and fishing equipment for example, is a significant source of lead exposure and can be lethal to wildlife. Humans also accumulate lead from a variety of exposure pathways, including urban and household particulate, and food, which is the most important pathway for exposure to lead deposited from long-range transport. Humans, particularly young children and infants are very sensitive to the toxic effects of lead on the central nervous system. The current blood lead level used by public health officials as a screening guideline in Canada and the U.S. is 10μg/dL. This level is associated with risk for subtle neurodevelopmental impairments (U.S. CDC 2005).

4.2 Atmospheric Transport, Distribution and Deposition

Lead is emitted to the atmosphere primarily in particulate form. The atmospheric residence time, and the potential for long-range atmospheric transport depends on particle size. The median particle size emitted from smelters, which are currently among the largest sources of lead emissions, is about 1.5 um. For particles with aerodynamic diameters of 0.06 – 2.0 um, the estimated net deposition velocity is 0.6 cm/s, which, according to the U.S. National Academy of Science, translates into an atmospheric residence time of 10-days (ATSDR 2005). While most of the emitted lead is deposited

close to emission sources, the finer particles are capable of long-range atmospheric transport. The dominant lead species found in the atmosphere are $PbSO_4$ and $PbCO_3$. Organic alkyl-leads, such as tetraethyl- and tetramethyl lead, used to be widely used as additives in gasoline. Alkyl lead compounds are sufficiently volatile to exist in the atmosphere in vapour form, although they are degraded fairly quickly in reactions with hydroxyl radicals. Half-lives for tetraethyl and tetramethyl lead are 5.7 and 65 hours respectively during the summer but in the winter half lives for both compounds is several days (ATSDR 2005). Tetra alkyl lead compounds degrade to tri-alkyl compounds with half-lives that are three times that of the tetra-alkyl compounds. Overall, it would seem that atmospheric residence times for organic lead compounds would allow for long-range atmospheric transport.

4.2.1 Modelled lead pollution levels

The use of official reported emissions estimates in modelling in the EMEP region resulted in significant (2-3 times) underestimation compared to measurements. The Executive Body of the Convention raised the concern about quality of the official emission data and called upon Parties to improve it (EB.AIR/WG.5/8). Evaluation of transboundary transport of lead for the period 1990 - 2003 was performed on the base of emission expert estimates, prepared by MSC-E (Ilyin and Tranvikov, 2005). These expert estimates include anthropogenic emissions, and preliminary estimates of natural emission and re-emission.

Figure 4.1a shows spatial distribution of estimated annual mean concentrations of lead in air in 1990 and 2003. In 1990 over significant parts of Europe concentrations varied between 15 and 40 ng/m^3, and in some areas exceeded 40 ng/m^3. By 2003 the concentrations in air markedly decreased and were within 2 - 15 ng/m^3 over most of Europe (Figure 4.1b). Spatial distribution of depositions is similar to that of concentrations. In 1990 over most parts of Europe modelled depositions ranged within 2 - 8 kg/km^2/y (Figure 4.2a). By 2003 depositions decreased and their values were mainly within 0.5 - 4 kg/km^2/y range (Figure 4.2b).
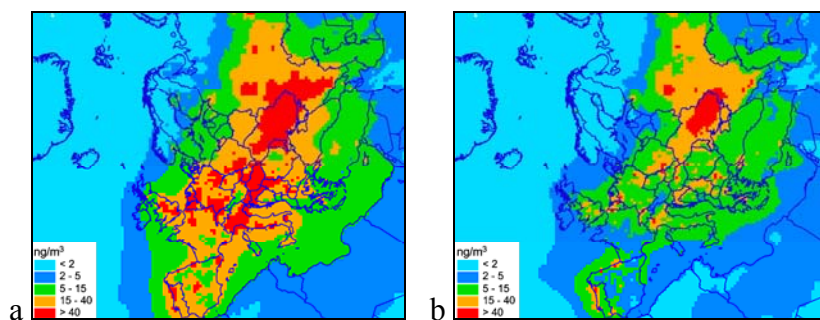
Figure 4.1. Spatial distributions of modelled air concentrations of lead in EMEP region in 1990 (a) and 2003 (b)
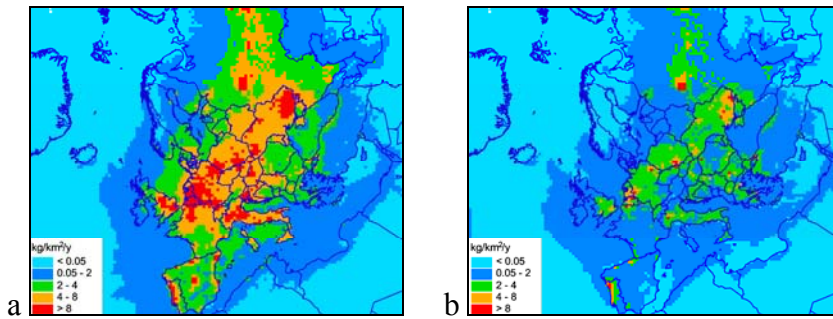
Figure 4.2. Spatial distributions of modelled total depositions of lead in EMEP region in 1990 (a) and 2003(b)

The largest decrease of air concentrations, averaged over country's territory, (Figure 4.3) took place in Slovenia (7 times). In 18 countries the concentrations decreased at least 3 times, and in 16 countries – between 2 and 3 times.

Similar decreases took place for air depositions: from 6 times in Slovenia to minor changes (within 10%) in Iceland and Greece. In 16 countries the decrease exceeded 3 times. In 17 countries the decrease ranges from 2 to 3 times. For the considered period modelled depositions of lead to Europe as a whole reduced from about 40,000 to 17,500 tonnes (2.3 times).
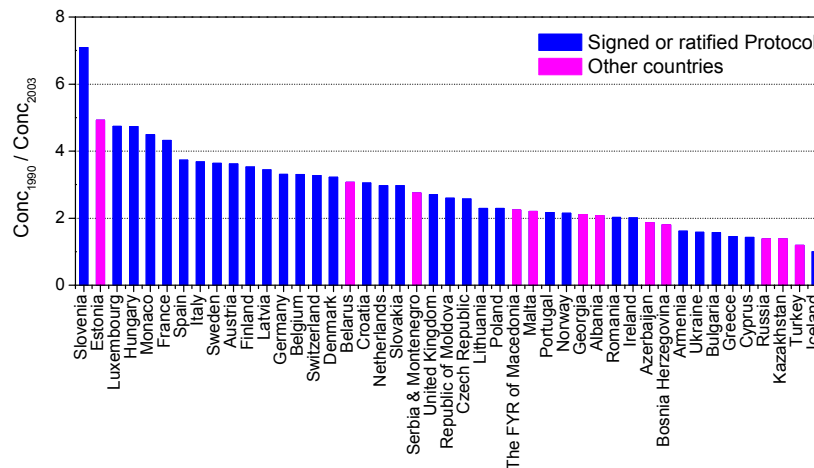
Figure 4.3. Ratio of the modelled country-averaged air concentrations of lead in 1990 to those in 2003 in countries of Europe

The contribution of lead depositions to country's territory caused by transboundary transport varies significantly (10 – 90%) between countries (Figure 4.4). The highest contribution took place for Republic of Moldova, Luxembourg, Monaco and Belarus. In 20 countries the contribution exceeds 50%, in 36 countries exceeds 30%.
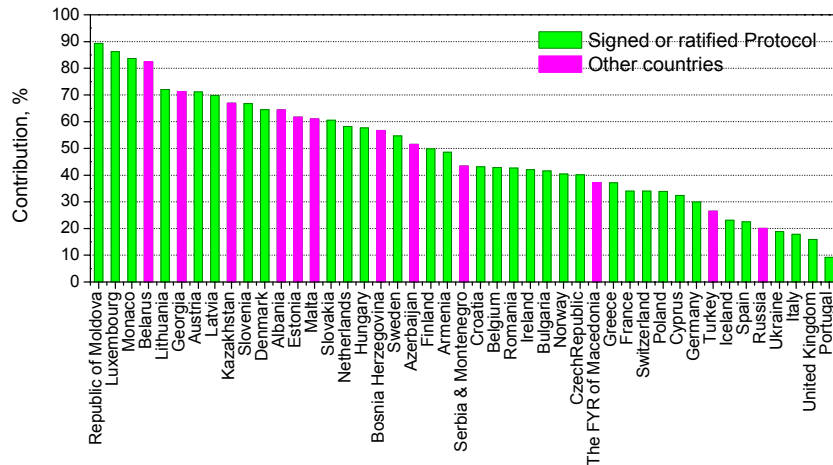
Figure 4.4. Contribution of external European anthropogenic sources to depositions of lead in Europe in 2003.

The contribution of external sources to depositions is distributed nonhomogeneously over countries territories. For example, this contribution for entire Germany is about 30% (Figure 4.5a). However, in regions close to national borders this contribution can exceed 50%, whereas in the central part it can be less than 15% (Figure 4.5b).
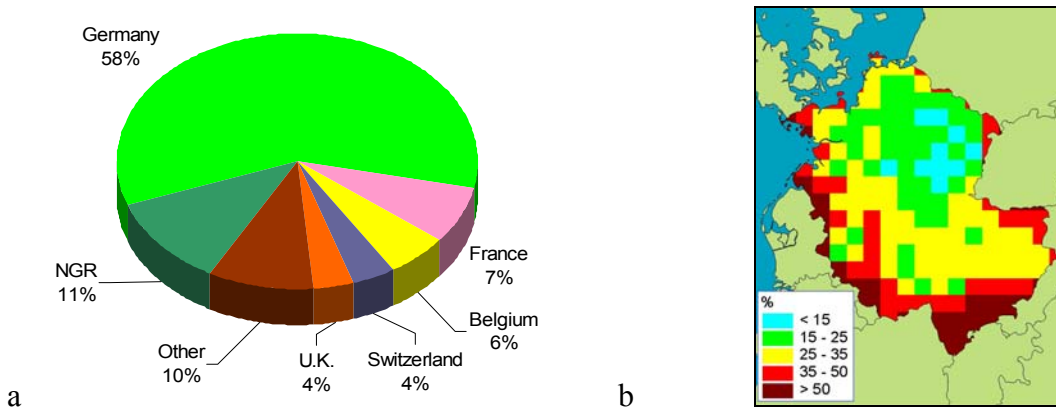
Figure 4.5. Main contributors to deposition of lead in Germany. NGR: Natural, Global sources and Re-emission (a). Spatial distribution of contribution of external anthropogenic sources to depositions of lead in Germany(b)

Potential of lead to intercontinental transport is lower compared to e.g., mercury or some POPs. However, the role of intercontinental transport of lead in pollution of Europe and North America needs further investigation.

In the U.S., the national scale assessment component of the National Air Toxics Assessment (NATA) activities has been conducted by U.S. EPA to assess air quality for a range of chemicals. NATA includes modeling ambient air concentrations of lead. The available NATA results for lead (shown in Figures 4.6 and 4.7) are based on 1996 and

1999 emissions data. The EPA used the ASPEN air dispersion model to first model air concentrations for individual census tracts (i.e., geographical units smaller than counties). The median tract-level annual average lead concentration was then selected to represent each county. As shown in Figure 4.6, the modelled concentrations for 1996 were generally between about 0.05 ng/m^3 (or lower) to 4.4 ng/m^3 (U.S. EPA, 2002). The results for 1999 were generally similar (Figure 4.7).

4.2.2   Evaluation of modelling results

Model evaluation included analysis of model uncertainties, and comparison of modelled results with observations and with results computed by other models. Analysis of the model uncertainties demonstrates that intrinsic model uncertainty (uncertainty of model without emission data) varies across Europe from 20 to 60% for concentrations in air, in precipitation and for total depositions (Travnikov and Ilyin, 2005). Intercomparison of atmospheric transport models of lead shows that air concentrations and depositions estimated by MSCE-HM model are in good agreement with other transport models (TFMM Workshop Minutes, 2005).
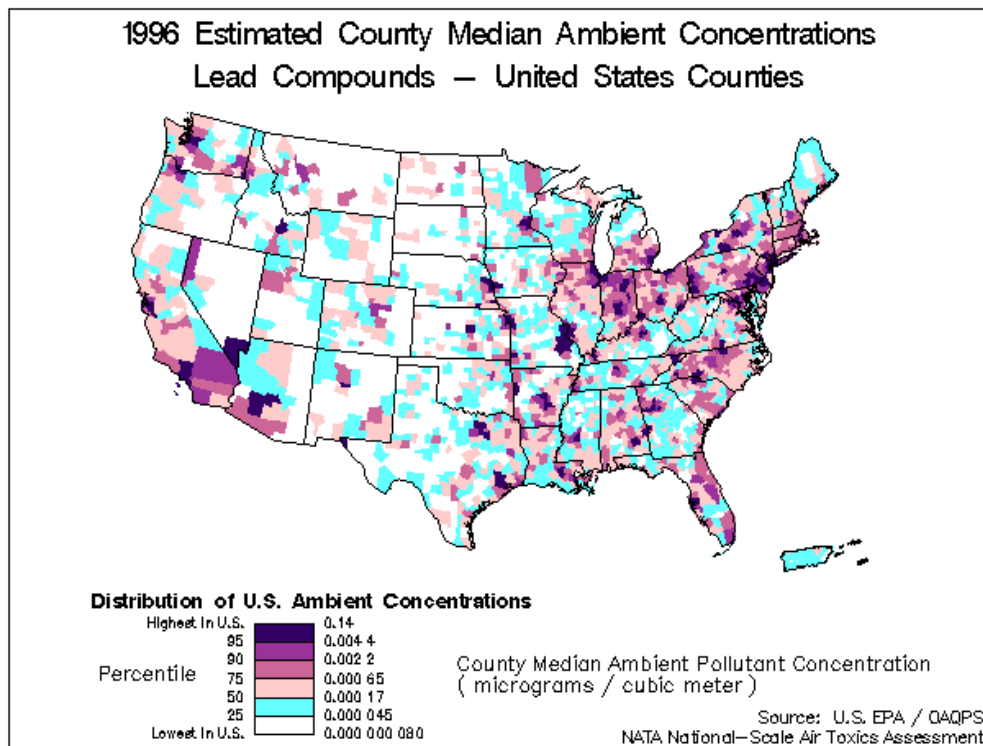
Figure 4.6. Modeled Median County-Level (annual-averaged) Ambient Air Concentrations for Lead in the U.S.A. for 1996 (U.S. EPA, 2002)
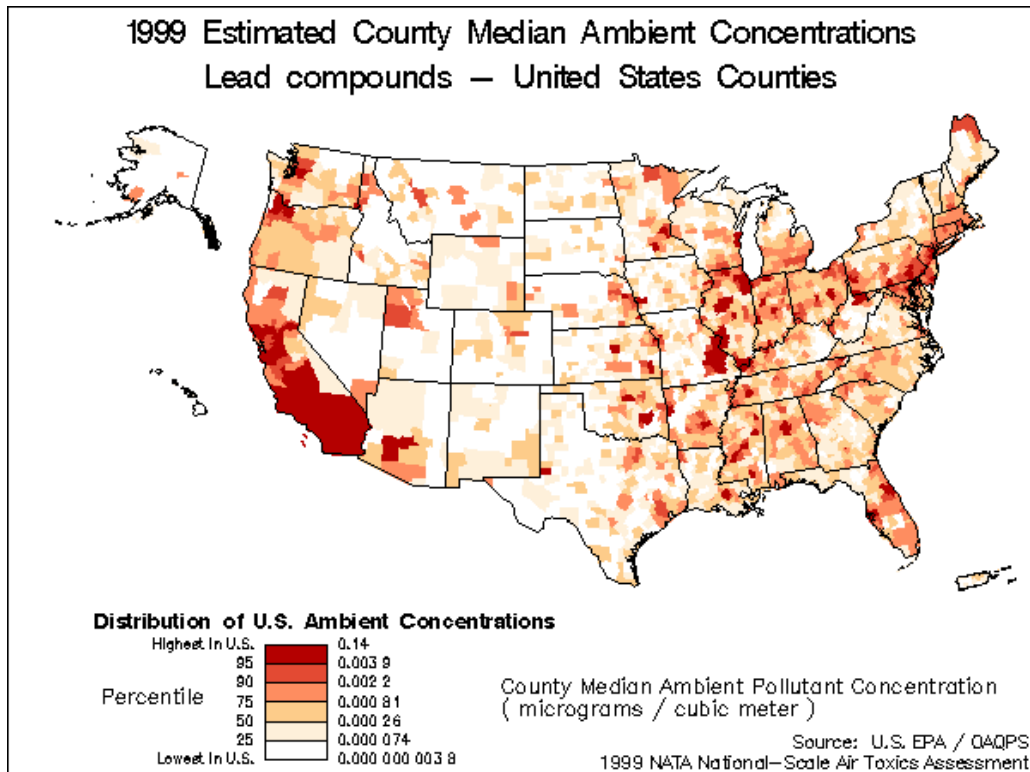
Figure 4.7. Modeled Median County-Level (annual-averaged) Ambient Air Concentrations for Lead in the U.S.A. for 1999 (U.S. EPA, 2006)

Comparison of modelling results based on official emission data, against measurements suggests an essential (2-3 times) underprediction of observed values by the model. Modelling results, based on emission expert estimates, for 1990 - 2003 (Ilyin and Travnikov, 2005) demonstrates that the modelled concentrations of lead in air and in precipitation agree well with the measurements. The correlation coefficient for annual lead concentrations in air is almost 0.9, and for concentrations in precipitation – 0.7. About 90% of modelled lead concentrations in air and 70% of concentrations in precipitation agree with measurements with accuracy better than ±50% of measured value. Discrepancies between model output, based on official emissions, and measurements could be mainly connected with uncertainties of official emission data, natural emissions and re-emission of historic deposition of lead.

The U.S. EPA compared modelled ambient concentrations from NATA to available ambient monitoring data (from 242 sites for 1996 and 181 sites for 1999) to evaluate the modelling results. This evaluation indicates that NATA underpredicted ambient concentrations of lead for 1996 by about 4-8 times, and an average of about 3 times for 1999. A combination of several factors may be responsible for these discrepancies, including: missing emissions from the inventory (e.g., especially re-emissions of historic lead emissions and natural emissions); spatial uncertainty in locations for sources: and high coarse particle deposition velocities. However, the primary factor is likely that re-entrainment (i.e., re-emissions of historic lead emissions) is not included in the modelling (U.S. EPA, 2002 and U.S. EPA, 2006).

4.2.3 Atmospheric monitoring

Europe

In 1990 measurement data collected by MSC-E on background atmospheric concentrations of lead were available from 30 stations in Europe, located in 9 countries. In 2003 measurement data were generated at 63 stations in Europe, situated in 20 countries. There are still large areas, however, where measurement data are not available, e. g. southern, south–eastern and eastern parts of Europe.

In 1990 the concentrations of lead in air were measured at stations located in the central part of Europe and along the coast of the North Sea. Measured background concentrations were mainly within 10 - 30 ng/m^3 range. In 2003 the concentrations mainly ranged between 5 and 15 ng/m^3. Concentrations in precipitation in central Europe in 1990 were around 2 – 5 µg/L. In 2003 these concentrations typically ranged from 1 to 3 µg/L.

In order to estimate long-term trends for different parts of Europe, measurement data were averaged over different countries. The long-term changes of air concentrations and concentrations in precipitation vary considerably across Europe. In central and north-western Europe the decrease was about 2 – 3 times from 1990 to 2003 based on these data (Figure 4.8a, b). In northern Europe the decrease of concentrations in precipitation was 1.5 – 3 times.

a   b
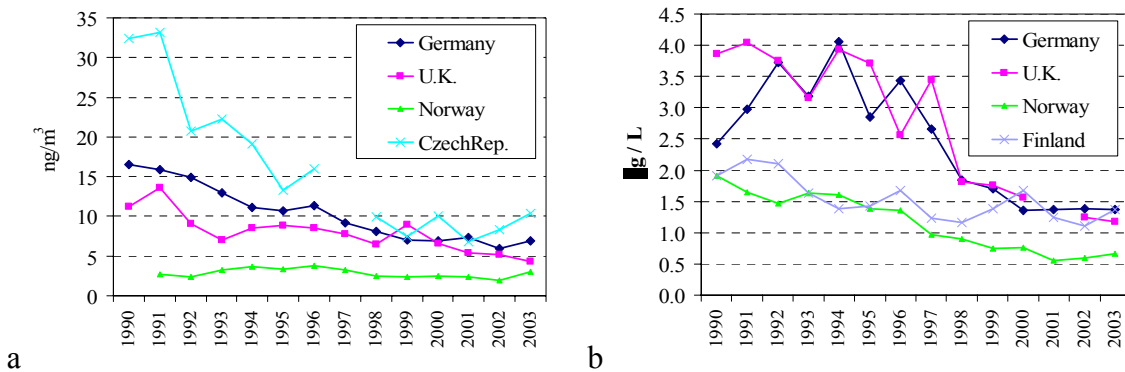
Figure 4.8. Long-term variations of concentrations of lead in air (a) and in precipitation (b) in different parts of Europe

Long-term changes in European emissions of lead are likely reflected in monitoring trends. In order to evaluate consistency between official European emissions and monitoring data, emission and measurement trends were compared (Ilyin and Tranvikov, 2005). These trends differ significantly between individual countries. In some countries the reduction of emissions for 1990 – 2003 was more than 10 times, but the decline of observed lead levels in air and in precipitation is much lower (2-3 times). This

observation is demonstrated by examples of the United Kingdom and Norway, shown in Figure 4.9 a,b. Lead pollution levels in the United Kingdom are mainly influenced by national emission sources. Lead pollution in Norway, however, is considerably influenced by long-range transport. With this in mind trends in official emissions for Norway are presented with official emission trends for France and the United Kingdom (Figure 4.9 b). These countries are considered to be main contributors of transboundary atmospheric lead pollution in Norway.
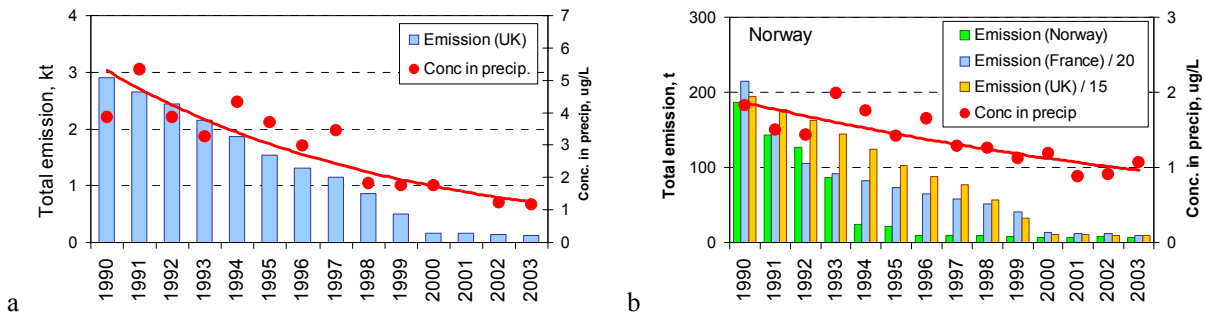
Figure 4.9. Long-term trends of lead total anthropogenic emissions in some countries and mean concentration in precipitation in the United Kingdom (a) and Norway (b). Red circles show annual measurements, red line – exponential approximation

The inconsistency between trends in measured levels of lead and official country emissions data is also apparent when examined for Europe as a whole. Comparison of total official anthropogenic emissions of lead in Europe with total wet deposition to EMEP countries based on measurement data only, demonstrates that observed deposition rates were higher than emission rates in 1995 – 2003 (Figure 4.10). The exception is 1990, when measured depositions were available only from Scandinavian stations, and hence, probably underestimate European-mean depositions.
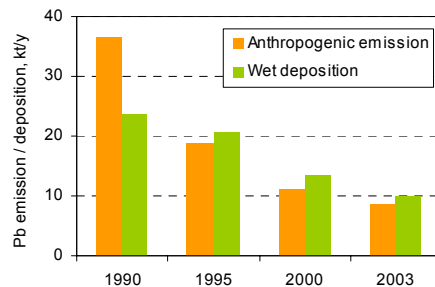
Figure 4.10. Comparison of lead total official anthropogenic emissions with total wet deposition to EMEP countries based on measurement data

The inconsistencies between official emissions and observed lead concentrations and depositions could be explained by either underestimation of official data, or significant unaccounted influence of natural emissions and re-emissions of historic depositions, or by both reasons. These inconsistencies should be further investigated.

United States

In the United States (U.S.A.), there were a total of 454 monitoring stations for lead in 1990 and 196 stations in 2003. Each year the U.S. Environmental Protection Agency (U.S. EPA) evaluates lead in ambient air. Trends analyses of lead air concentrations are based on actual measurements of lead in the ambient air at monitoring sites across the country. Trends are derived from measurements from these monitoring stations which used the Federal Reference Monitoring method on a yearly basis. Because the National Ambient Air Quality standard (NAAQS) for lead is based on a maximum quarterly (90 day) average of lead in Total Suspended Particulate (TSP), assessed each year, these trend data are typically summarized using this measure.

Figure 4.11 presents trend data for ambient lead concentrations for rural, suburban and urban sites in the U.S. for the years 1982 to 2001. These estimates are based on 38 monitoring stations which are not point-source-oriented. These stations measure TSP and therefore likely reflect lead from local sources (bound to larger coarse particles) and lead transported over longer distances on fine particulate matter (PM2.5). Figure 4.11 shows that urban and suburban sites have had the greatest decrease in ambient lead concentrations. However, the figure also shows that rural sites have also experienced significant reductions. Overall, lead air concentrations across the U.S. have decreased more than 94% since 1983 based on these data. Furthermore, this trend has continued, although at a reduced rate throughout the 1990's with lead concentrations decreasing 57% between 1993 and 2002.
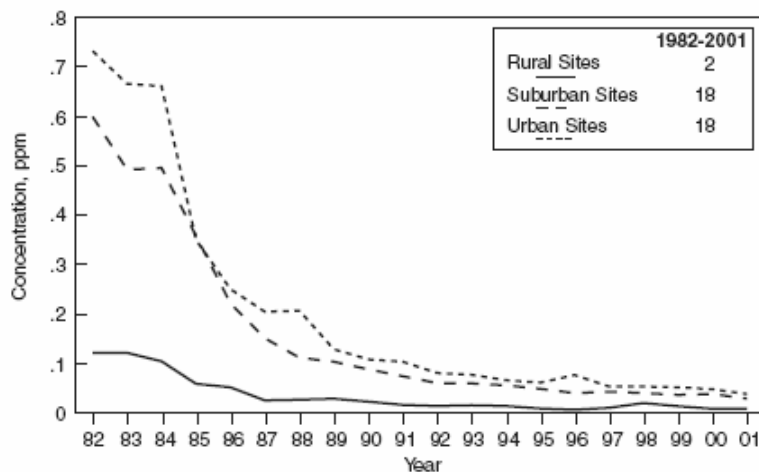
Figure 4.11. Temporal trends in maximum quarterly mean lead concentration in the U.S.A. by location (excluding sites designated as point-source oriented) 1982-2001(U.S. EPA, 2003)

The U.S. also has the Interagency Monitoring of Protected Visual Environments (IMPROVE) program, which is an effort to track visibility changes in rural and remote locations, including national parks and wilderness areas. This effort, which was initiated

in 1985, uses monitors that measure PM2.5 and lead. Because these lead measurements are based on PM2.5, they are likely to represent lead transported over longer distances. The network currently comprises 170 sites. According to the IMPROVE data, the concentrations of lead in air averaged from 1995-1998 are $5 - 10$ ng/m^3 in the north-east, $3 - 5$ ng/m^3 in the east of the USA, and about $2 - 3$ ng/m^3 in the central regions of the country (Malm and Sisler, 2000).

Arctic

The longest Arctic monitoring record of concentrations of metals in aerosols has been collected at Alert in Arctic Canada. The data series, which dates back to 1981 showed a distinct seasonal trend in anthropogenically derived metals, including lead, zinc, and copper which all displayed winter maxima and summer minima. While no long-term trend was observed for annual mean lead concentrations, an examination of winter means alone did reveal a decline. Further analysis of the data demonstrated that the winter peaks were associated with combustion sources and implied that these sources must also have decreased over the period of analysis. One potential explanation for the trend is the industrial decline in the late 1980s and 1990s that was associated with the collapse of the Soviet Union. Lead isotope analysis on aerosol samples collected at Alert were used to identify source regions. This work concluded that the low concentrations observed in the fall originated largely from natural sources in the Canadian Arctic, whereas the higher concentrations measured in the late fall and winter originated from Europe and Eurasia. Finally, in late spring and early summer a pulse of anthropogenic lead was detected that had originated from industrial sources in Asia (AMAP 2005).

An alternative explanation to the apparent decreasing trend in atmospheric lead measured at Alert, suggests the influence of a meteorological phenomenon described by the Arctic Oscillation index, which around 1989 shifted from its historically negative state to an extreme positive state and remained that way throughout the 1990s. In short, this shift was associated with, among other things, increased precipitation over the Northern Seas and Southern Eurasian Basins, which could have removed a greater amount metal containing aerosol from the atmosphere before they reached monitoring stations at sites like Alert (AMAP 2005).

Lead and other metals were also measured at a number of other circumpolar sites (Figure 4.12), however, none of the records are as long as the record for Alert. In general the data from all sites seem to indicate decreasing trends for lead between the late 1980s and 2000, although some regional and latitudinal differences were noted. For example, levels of lead measured at the Alaskan stations were generally higher and the slope of the decreasing trend was greater at the more southerly stations (62°N) compared to high Arctic stations (82°N). Data collected after the mid 1990s in Greenland did not show any trends. Since the primary source of anthropogenic lead to the atmosphere was due to combustion of leaded gasoline, the use of which was drastically reduced in the 1970s and 1980s, it is possible that the major decline in atmospheric levels happened prior to the onset of data collection (AMAP 2005). This is supported by data from glacial cores (see section 4.2.2).
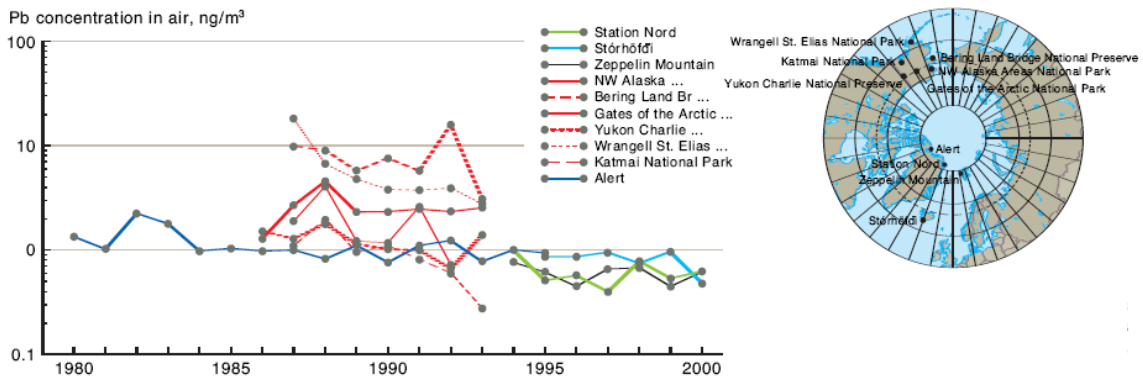
Figure 4.12. Annual mean concentrations of lead in air at AMAP monitoring stations (AMAP Atmospheric Data Centre, NILU). (AMAP 2005)

Lead concentrations in precipitation have been measured at a number of AMAP monitoring stations since the early 1990s (Figure 4.13). Only one site, Pesosjärvi, Finland reported a statistically significant slightly decreasing trend. No other trends were evident at the other sites. The highest concentrations were recorded at Sanvik, Norway, a site that might be influenced by nearby smelters on the Kola Peninsula, otherwise concentrations appear to be similar between sites (AMAP 2005).
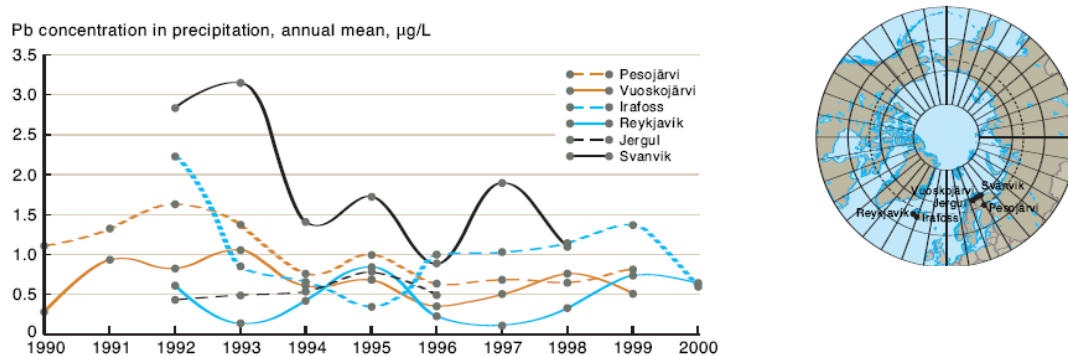
Figure 4.13. Annual mean concentrations of lead in precipitation at AMAP monitoring sites (AMAP Atmospheric Data Centre, NILU). (AMAP 2005)

4.2.4 Atmospheric deposition of lead as measured in ice cores.

Cores of ice extracted from the Greenland Summit glacier contain a well preserved record of atmospheric metal deposition dating back several hundred years (Figure 4.14). When comparing pre- and post-industrial (i.e. before and since 1800) depositional fluxes of lead the record demonstrates a 12-fold increase that peaked in the 1970s. Lead was however, used quite extensively before 1800 at which time deposition rates were already elevated. It is estimated that the peak in the 1970s represented a 200-fold increase over

natural background deposition rates. Rates of lead deposition had declined by 6.5-fold by the early 1990s reflecting the introduction of unleaded gasoline (AMAP 2005).
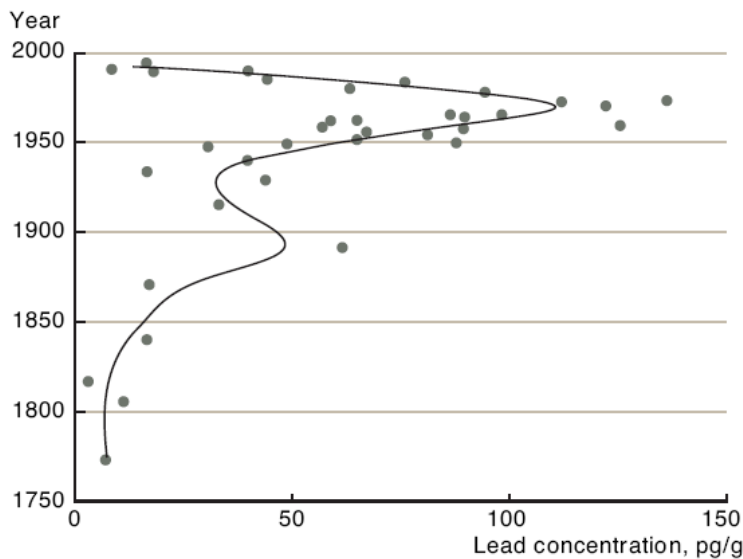
Figure 4.14. Lead concentrations in a Greenland ice core showing increases during the industrial period, but decreases since the early- 1970s when unleaded gasoline was introduced in North America. (AMAP 2005)

4.2.5   Atmospheric deposition of lead as measured in lake sediments.

In recent layers of Canadian high Arctic lake sediment cores, lead concentrations and stable isotopes of lead were similar to those from pre-industrial layers. Anthropogenic lead accounted for no more than 19% of acid leachable lead in recent sediments. By contrast, in the more southerly Hudson Bay lowlands, the anthropogenic fraction of lead measured in the core sediments increased throughout the 19th century to 70-90% by the 1980s and 1990s, representing a three- to five-fold increase in atmospheric lead deposition.   A similar result was found in sediment from a lake in Northern Quebec. It is thought that low rates of precipitation in the high Arctic compared to the Hudson Bay region and the influence of the polar front over Hudson Bay may explain some of the differences (Outridge et al., 2002; AMAP 2005). More recently, Muir et al. (2004) presented lead data for a large collection of sediment cores collected from lakes in the north eastern U.S., Easter Canada and the Canadian Arctic (Figure 4.15). Lead enrichment factors for the high Arctic were generally around 1, but increased substantially to the south and east, implying high levels of recent anthropogenic input to remote regions of Quebec and Labrador. It was also noted in the work by Muir et al. (2004) that most of the lead was from alkyl-sources.

Lakes cores collected from southwest Greenland also showed post-industrial increases in lead concentrations. The Greenland cores showed increases beginning during the eighteenth and nineteenth centuries and peaking around 1970. Recent layers of sediment

had lead concentrations about 2.5-fold higher than the estimated background concentration. Lead isotope ratios, which reflect sources, indicate recent increases in European influence relative to the historically dominant influence of Russian sources. Sediment cores from the remote Taymir Peninsula, in central Siberia, did not show any signs of recent lead increases, suggesting the region was not impacted by anthropogenic sources of lead (AMAP 2005).

In a recent assessment of peat cores from Ireland, Coggins et al. (2006) found peak accumulation rates of anthropogenic lead occurred sometime between 1950 and the 1970s. Lead accumulations in the surface peat sediments (1993–1996) were between 1.5–3.0 mg/m^2 yr and 4–5 mg/m^2/ yr which was slightly lower than rates measured in remote regions of Europe.
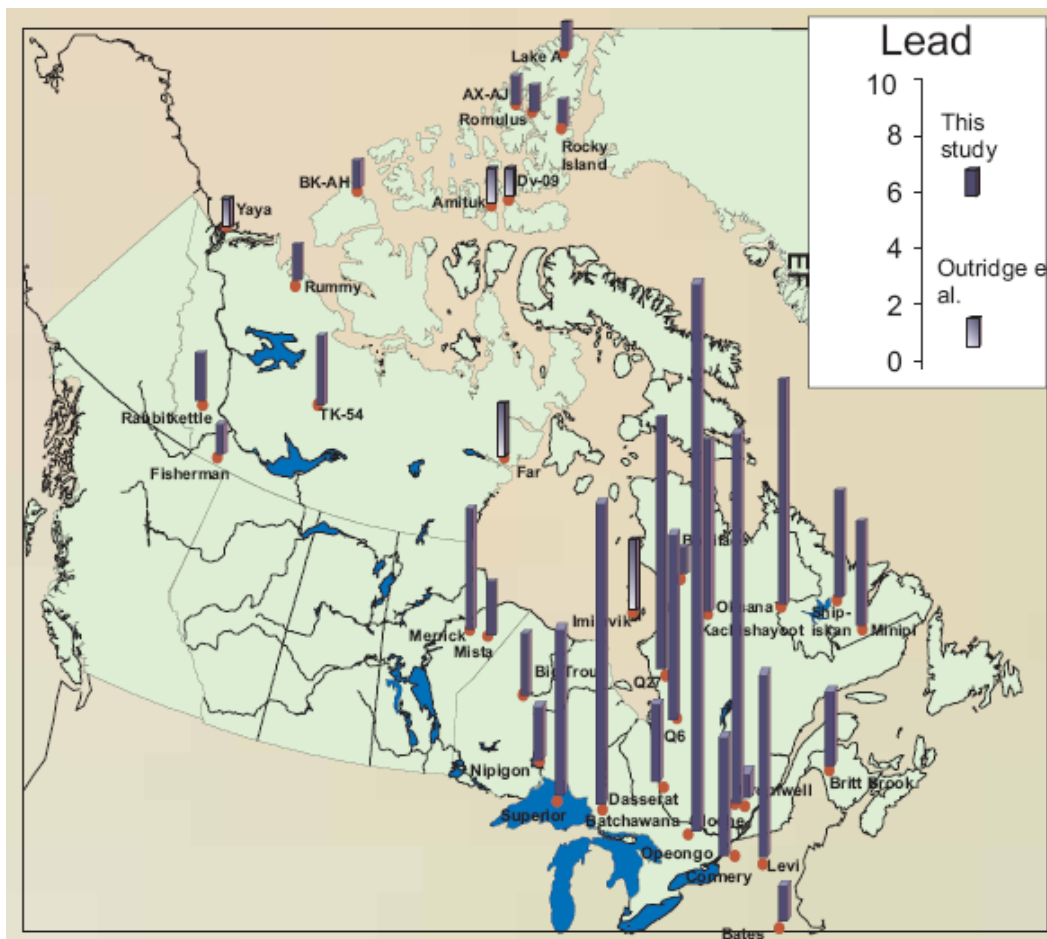
Figure 4.15. Enrichment factors for lead measured in sediment cores from Canada and the northeastern USA. (source Muir et al., 2004).

4.3 Levels and Trends of Lead in Terrestrial Ecosystems

4.3.1 Soil

The primary source of anthropogenic lead to background soils is atmospheric deposition of particulate lead arising from industrial emission sources. Once deposited on the soil there are numerous factors that influence the mobility and potential bioavailability of lead to vegetation. Within the soil matrix there are many particles to which lead can be adsorbed, or with which lead can form insoluble precipitates, thereby limiting bioavailability. The acidity of the soil also plays a large role in determining the solubility and by extension the bioavailability of lead. In general, sandy soils with low organic carbon and low pH can increase the bioavailability of lead to vegetation. On the other hand, recent results of effects research showed that other cations including H^+ compete with the heavy metals at binding places of biotic ligands. In consequence high concentrations of H^+ and other cations can have a "protective" effect with respect to effects of heavy metals on soil and water biota. (Lofts et al. 2003). This is considered in pH dependent critical limit functions as a part of the critical loads model. Direct ingestion of particulate bound lead and absorption through the gut and can be a significant source of lead to terrestrial biota and humans, independent of uptake by vegetation.

Retention of lead in various European forest catchments was estimated at a number of sites under the International Cooperative Programme on Integrated Monitoring (ICP-IM) by comparing output fluxes resulting from runoff (RW) to input fluxes from deposition. Total deposition was assumed to be the sum of throughfall (TF) and litterfall (LF). A ratio of RW/(LF+TF) that is greater than 1 implies that the catchment is actually giving up lead, whereas a ratio less than 1 implies the catchment is accumulating lead. At three Swedish (Aneboda, Kindla, Gramtratten) and two Finnish (Valkea-Kotinen, Hietajarvi) ICP IM sites output fluxes were much lower than input fluxes in the late 1990s and the early 2000s, with ratios(RW/(LF+TF)) of 0.095; 0.11; 0.13; 0.02; 0.03, respectively, indicating retention of lead in these catchments (Bringmark and Lundin 2004). Similar results were obtained for catchments of five out of six other monitoring sites in Northern and Central Europe (ICP IM sites Zobelboden (AT), Anenske Povodi (CZ), Lysina (CZ), Rucava (LV), Zoseni (LV) and Gramtatten (SE), Bavarian Forest (DE)), implying that most forests in the region continue to retain atmospherically deposited lead (Bringmark and Lundin 2005, Bringmark et al. 2005).

Results from ICP Forests Level I and Level II plots showed that lead was retained in upper layers of forest soils of most sites (Rademacher 2001). The median lead concentration in the humus layer of 1658 Level I plots was 37 mg/kg, while 20 mg/kg in the upper mineral soil (50 cm, n=1998). The related 95-percentiles were 180 mg/kg (humus) and 70 mg/kg (mineral), respectively. At Level II plots the median Lead concentration in the humus layer was 61 mg/kg, and 8 mg/kg in the mineral soil.

Under a "European Union Voluntary Environmental Risk Assessment" for lead, estimates of lead deposition and predicted environmental concentrations of lead were

made on local, regional and continental scales (LDA International (2006): Lead Development Association: Voluntary risk assessment for Pb, draft report, status 2006). A box model was used to predict environmental concentrations for lead and to apportion input from various sources. Modelling results demonstrated how atmospheric deposition that resulted from industrial emission sources was most intense within the local area around the source (i.e. within a few kilometres). The model predictions that best capture potential deposition following long-range atmospheric transport were those related to the continental scale. Predicted soil lead concentrations on the continental scale were intended to estimate the contribution of atmospherically deposited lead to natural background soils. Model output predicted background soil lead concentrations of 28.1 mg/kg, which agrees well with the mean soil lead concentrations reported by ICP-Forest plots. Only 1.02 mg/kg was attributed to input from atmospheric deposition.

The European Union Voluntary Environmental Risk Assessment also contains a detailed compilation of background soil lead concentrations for European countries, including Germany, Netherlands, Belgium, Denmark, France, United Kingdom and Sweden. The average soil Lead concentrations measured away from point sources ranged from 16 to 41 mg/kg dry weight. The average of all the reported means from the various surveys included in the review was 27.6 mg/kg dw, while the mean 90th percentile value was 50.6 mg/kg dw and the mean 10th percentile value was 18 mg/kg dw.

The ATSDR (2005) profile of lead also identifies background levels of lead in soil to be in the range of 10 – 30 mg/kg. There is no indication that remote background levels are even impacted by long-range atmospheric transport in the U.S., however, evidence from the sediment cores throughout North America suggest that even background soils are likely enriched in lead as a result of atmospheric deposition. Soil lead concentrations in urban areas of the U.S. are generally an order of magnitude higher than background concentrations. In areas that have historically seen high volumes of vehicular traffic and in the vicinity of smelters, soil lead concentrations can be several orders of magnitude greater than background concentrations. Clearly these elevated levels are not related to long-range atmospheric transport. Elevated lead concentrations in urban and residential settings are, however, thought to be an important source of human lead exposure.

4.3.2 Vegetation

Atmospheric deposition of lead onto plant surfaces and uptake through root systems can be an important source of lead to the overall contaminant burden of the plant (ATSDR 2005). The uptake of lead through plant root systems is affected by numerous soil characteristics, but in general is enhanced in soil with low organic content and low pH (i.e. acidic). A survey of fruits and vegetables grown in private U.S. gardens with high levels of lead in soil (27-4580 mg/kg) demonstrated that virtually none of the fruit accumulated lead above the detection limit of 10 mg/kg, however, 39% of leafy vegetables exceeded10 mg/kg (ATSDR 2005). Uptake of lead by plants has been successfully reduced with the addition of lime to the soil, which raises the pH.

Lead concentrations in mosses are used as an indicator of the spatial distribution of atmospheric deposition and ranged from < 2.0 mg/kg to 8.0 mg/kg over much of Central

and Northern Europe (WGE 2004). In so-called hotspots located primarily in eastern Europe, moss samples had lead concentrations up to and exceeding 24.0 mg/kg. Lead in mosses of northern Europe display spatial gradients that seem to reflect proximity to source regions, for example a decreasing south to north gradient is evident in Scandinavian countries (Figure 4.16), which corresponds to increasing distance from industrial centres of Northern Europe. This is consistent with the observed distribution of cadmium in mosses, which is likely derived from similar source regions. Concentrations of lead in mosses decreased dramatically in Scandinavia after the early 1980s, with the greatest decreases occurring in the south. Results presented in AMAP (1998) show how concentrations of lead in moss from southern Norway went from over 100 mg/kg dw to less than 30 mg/kg dw between 1975 and 1995.

Concentrations of lead measured in mosses from Arctic Alaska were quite low compared to the levels measured in Europe (0.35-2.33 mg/kg dw). Enrichment factors for these samples were also quite low (<10), which suggests that the lead was soil derived, and did not come from atmospheric transport (AMAP 2005).

A large amount of literature data on Lead concentrations in crops and forest trees was evaluated (Alrikson et al. 2002, De Vries and Bakker 1998, Nagel et al. 2000, Jacobsen et al. 2002, Schütze and Nagel 1998) in order to enable the calculation of Lead removal by harvest of biomass as a step within critical loads calculations. Almost exclusively data from background sites were included. The concentration ranges in harvestable parts were 1 - 3 mg/kg (dw) for mixed grassland species; 0.1 – 0.3 mg/kg (dw) for cereals; 0.7 – 1.0 mg/kg (dw) for potato and sugar beet and 3.8 mg/kg (dw) for maize. The wood of coniferous trees contains 0.5 – 10 mg/kg (dw) in Central Europe and 0.1 – 0.2 mg/kg (dw) in Northern Europe (Modelling and Mapping Manual 2004).
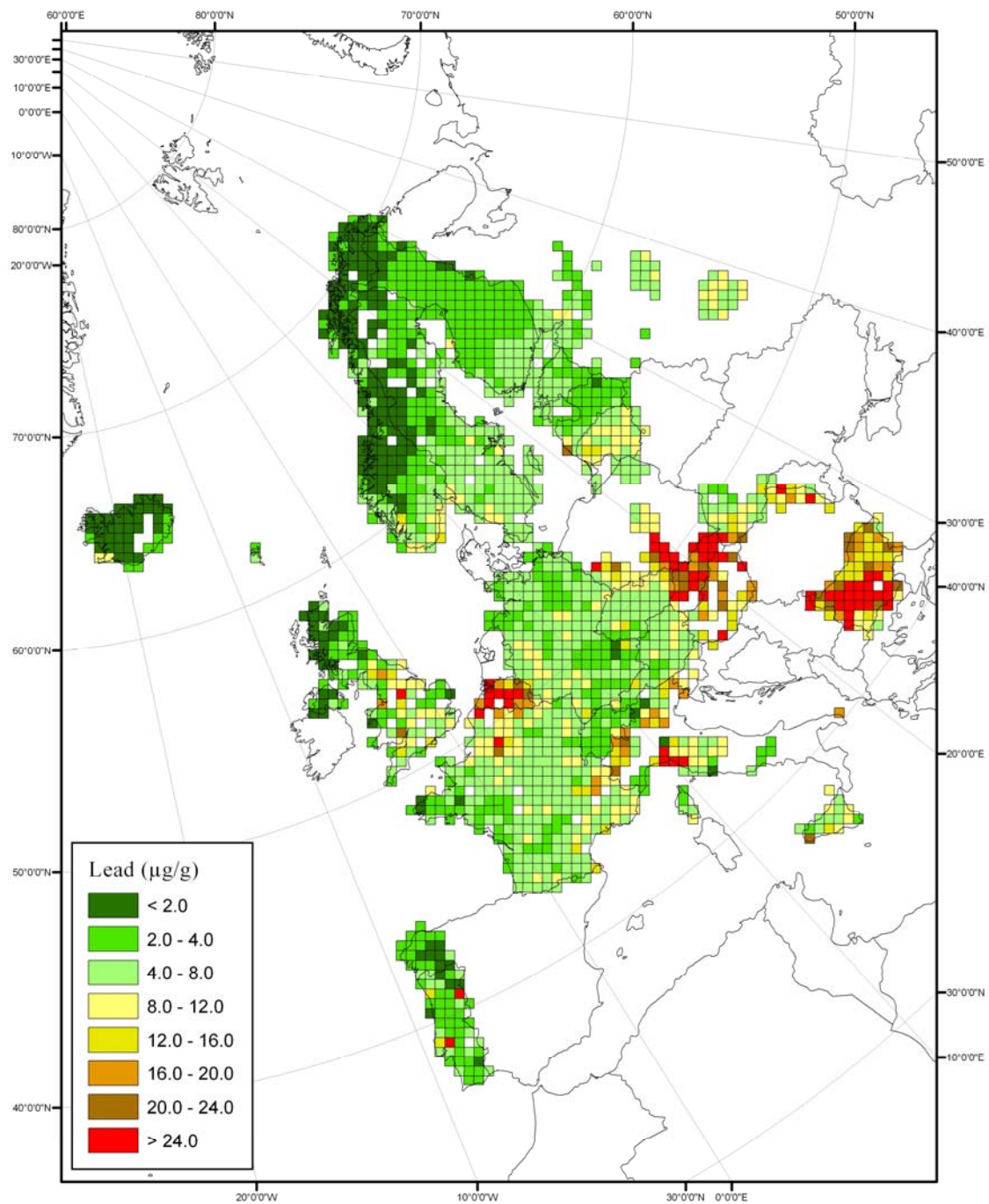
Figure 4.16. Distribution of lead in European mosses (WGE 2004).

4.3.3   Wildlife

Terrestrial wildlife is exposed to lead through consumption of vegetation and ingestion of associated soil particles. This includes lead that has been taken up from soil through the root system and stored in the plant tissues, as well as lead that is deposited directly on plant surfaces. Lead can be passed from prey to predator but lead does not biomagnify as it is passed up the food chain (ATSDR 2005). As a result the greatest levels of wildlife exposure in terrestrial ecosystems occur at lower trophic levels.

Recent information concerning wildlife exposure to lead is largely focussed on exposure pathways and sources that are not related to long-range atmospheric transport. These studies focus on exposure pathways related to things like local sources or lead shot and fishing tackle.

The most reliable information related to potential exposure from long-range atmospheric transport comes from AMAP assessment reports (AMAP 1998 and 2005). AMAP reports information on levels of lead in terrestrial birds, voles, hare, caribou, and moose.

Concentrations of lead in ptarmigan were reported for Canada, Alaska, Scandinavia and Russia. The highest levels were found in ptarmigan livers from southern Scandinavia, which were as high as 5 mg/kg dw, with lower levels reported in the north. This spatial pattern is consistent with results for mosses. Ptarmigan livers from eastern Siberia had lead concentrations of 1.6-2.3 mg/kg dw, which was similar to the results from northern Scandinavia. Canadian ptarmigan from the western Arctic had higher concentrations of lead than ptarmigan from the eastern Canadian Arctic, which is thought to reflect differences in geology and diet, not atmospheric deposition (AMAP 1998 and 2005).

AMAP (2005) presented a circumpolar survey of lead concentrations in caribou and reindeer liver (Figure 4.17). Mean concentrations for the caribou populations surveyed varied over an order of magnitude between about 0.1 and 1.0 mg/kg ww with a couple of populations approaching 2 mg/kg ww. It's difficult to speculate what might be driving the spatial trends but in most cases a combination of factors such as local geology, dietary habits and perhaps atmospheric deposition could play a role. In Scandinavia it was noted that reindeer liver lead concentrations were significantly higher in the south than they were in the north, which is consistent with results for moss and ptarmigan. Data from other terrestrial herbivores, including hare, moose and voles also displayed the decrease south to north concentrations gradient.

There are very little temporal trends data for lead in terrestrial biota. In western Canada results for lead in moose and caribou liver measured over 9 year period have not revealed any significant change. In Swedish reindeer monitored between 1982 and 2000, lead was shown to decrease in liver samples. This, however, appears to the only set of data that showed a significant trend. While not statistically significant, comparisons between concentrations of lead in Norwegian voles between 1981 and 1995 indicated a 70% decrease. The suggested declines in lead concentrations in terrestrial herbivores of Scandinavian countries combined with the changing south-north gradient of lead concentrations in various media, implies that the atmospheric deposition from emission

sources in Northern Europe has influenced the region in the past, but that deposition rates have been declining in the past 25 to 30 years.
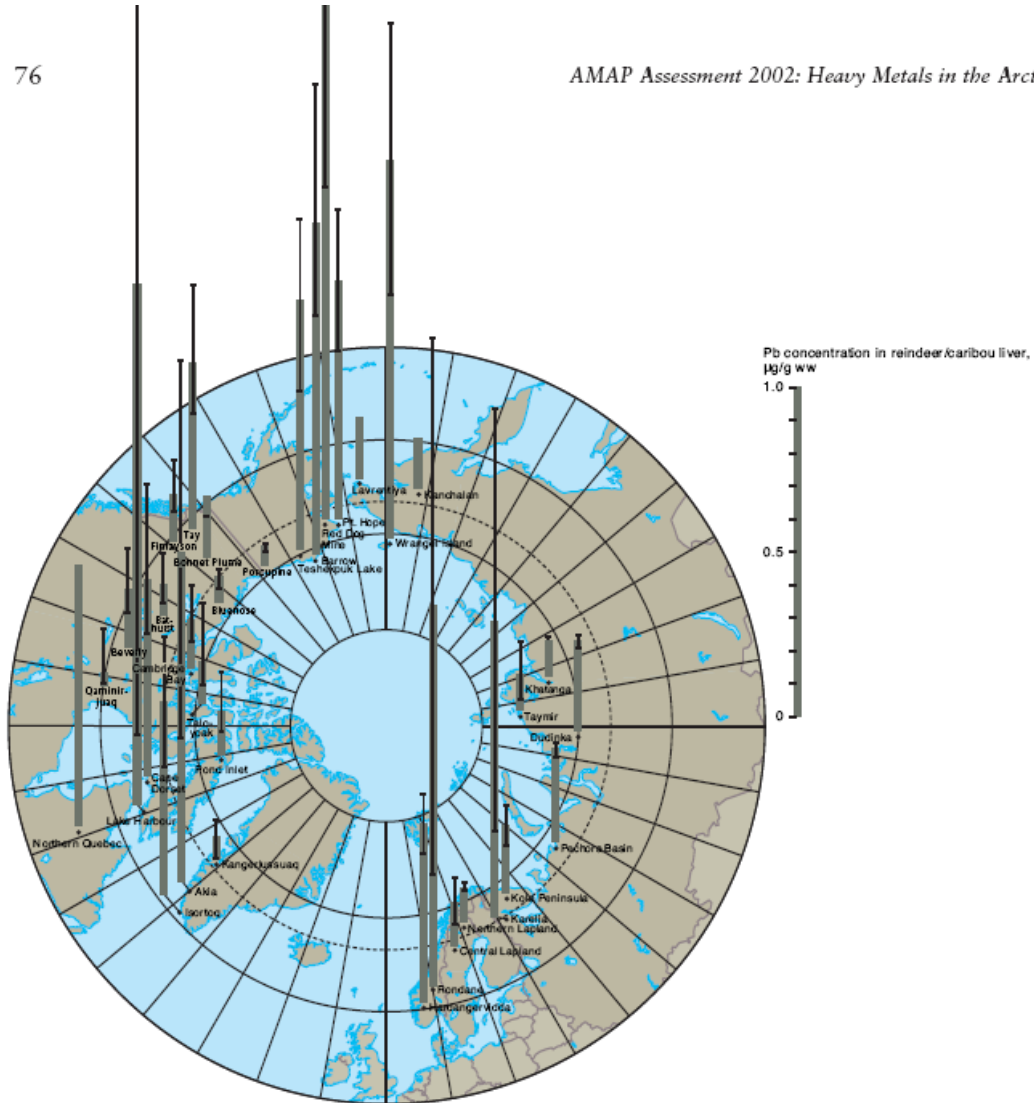
Figure 4.17. Lead concentrations in liver of reindeer and caribou (AMAP 2005).

4.4 Levels and Trends of Lead in Aquatic Ecosystems

In non-acidic freshwater ecosystems, lead tends to form precipitates with other dissolved ions, e.g. sulphate and carbonate ions. The amount of dissolved lead therefore depends on the pH of the water and the amount of other dissolved material. For example, at a pH >5.4, the solubility of lead in hard water is 30 µg/L, whereas in soft water lead solubility is approximately 500 µg/L (ATSDR 2005).

4.4.1 Water and sediment

Data on heavy metals in surface waters are available from a survey in Nordic lakes (about 3000 lakes in Finland, Denmark, Norway, Sweden and Russian Kola). Weighted 50- and 99.5-percentiles of the lead concentration were 0.14 - 0.38 µg/L or 2.07 - 7.69 µg/L, respectively (no data for Kola). Lead showed a distinct decreasing gradient from the South of Norway and Sweden to the North, which is consistent with the pattern of lead deposition inferred from a survey of moss. Multivariate statistical analysis showed that Lead concentrations in the lakes were elevated in regions of high long-range transport both of acidifying pollutants and metals. There was also the indication that small running waters may have higher levels of heavy metals than lakes (Skjelkvåle et al. 2001).

Mean concentrations of Lead in lakes and streams at ICP Waters sites in the period 1999 – 2001 are published in ICP Waters (2003). The number of sites per country varied from 1 to 20. In the Czech Republic, Finland, Latvia, Poland and Sweden all means were lower than 1.0 µg/L. Mean values up to 14 µg/L occurred at sites in Germany, Hungary, Ireland and Switzerland.

The European Union Voluntary Environmental Risk Assessment (LDA International, 2006) included a review of reported values for total lead and dissolved lead in European surface waters. In their review, the authors of the report found that for the countries surveyed, mean values for total lead ranged from 0.07 – 3.1 µg/L with a median value of 0.77 µg/L. Country means for dissolved lead ranged from 0.07 – 0.81 µg/L with a median of 0.18 µg/L. Concentrations of lead measured in Canadian Arctic rivers, most of which should not be influenced by local sources ranged from <0.7 – 1.3 µg/L.

Analysis of sediment cores from Norway was used to derive enrichment factors, which are calculated by dividing the concentration in surface sediments by the concentration in core layers that pre-date anthropogenic input. This study found that lead was the most enriched metal in the surface sediments and, consistent with other spatial patterns for lead, was more enriched in sediments from southern parts of the country (AMAP 2005).

In their conclusion, Skjelkvåle et al. (2001) considered lead pollution to be a minor problem for aquatic ecosystems in Northern Europe. However, ongoing accumulation of toxic metals in catchments, combined with leaching from acidified soils could increase stresses on aquatic biota in the future.

4.4.2 Aquatic organisms

Uptake and accumulation of lead by aquatic organisms is highly dependent on the biogeochemical characteristics of the water body. Lead bioavailability can change by two orders of magnitude simply through variation in water hardness, pH and dissolved organic matter (EU voluntary risk assessment), which can change the amount of dissolved lead ion in the water column. Lead in the particulate form is also bioavailable when ingested by aquatic organisms and can also be a substantial source of exposure in aquatic biota. Lead concentrations in aquatic biota can vary widely from one region to another depending on a number of factors, including input from anthropogenic sources.

Much of the recent literature on the accumulation and effects of lead in aquatic ecosystems focuses on water bodies impacted by local sources of contamination, such mine sites, or the impact of lead shot and sinkers. Most of the current data on lead concentrations in aquatic ecosystems from remote locations is reported in AMAP assessment reports.

Some results for lead in freshwater invertebrates from Artic lakes and rivers are reported in AMAP 1998, however, most of these are either at or below detection limits. Lead concentrations in freshwater fish from Arctic lakes are also relatively low. Land locked arctic char from Nunavut, Canada, had levels of 0.007 – 0.03 mg/kg ww. Sea run char from Greenland had similar concentrations and levels in char from Labrador Canada had lower levels, ranging from 0.001 to 0.005 mg/kg ww AMAP (2005). AMAP (1998) reported data for a number of freshwater fish species in Northern Canada, including northern pike, lake trout, burbot and whitefish. Many of the results were below detection limits and where lead was detected levels generally ranged from 0.1 to 1.0 mg/kg ww, with results at the upper end of the range reported for liver. The best temporal data set available indicated no significant change of lead concentrations in Swedish char livers between 1981 and 2000 (AMAP 2005). Results from the Arctic are consistent with reported mean concentrations of lead in carp (0.035 mg/kg ww) from remote regions of the American mid-west (Goldstein and DeWeese, 1999).

Aquatic birds do not accumulate significant amounts of lead under background conditions where solely influenced by atmospheric deposition. Concentrations of lead are reported for some aquatic birds in the AMAP Assessment Report (1998) but most values were either at or near the detection limit.

4.5 Levels and Trends of Lead in Marine Ecosystems

Lead concentrations reported for surface seawater in the AMAP assessment report (1998) ranged from 5-15 ng/L in the North Pacific, 15-40 ng/L in the Arctic Ocean and 29-41 ng/L in the North Atlantic and Norwegian Sea. It is speculated that these levels represent about a ten fold increase in concentrations compared to pre-historic levels and that anthropogenic influences are the cause. Both atmospheric deposition and direct input from, for example mine tailings, is implied. Locally elevated lead concentrations have been measured in seawater near mining sites.

Lead concentrations in marine invertebrates including bivalves, amphipods and decapods were reported in the 1998 AMAP assessment report. Levels in non-bivalve invertebrates were quite low, i.e. <0.2 mg/kg. Marine fish have lead concentrations in muscle that are about the same or lower than levels reported for invertebrates. Since lead does not appear to biomagnify in the marine ecosystem, as demonstrated by low levels in marine fish compared to invertebrates, marine mammals also tend to have low levels of lead. Some data have been reported for polar bear, beluga and ringed seal most of which are below 0.1 mg/kg (AMAP 1998). The most recent AMAP report (2005) does not report concentrations of lead in marine fish or mammals.

Blue mussels are key monitoring species in AMAP and represent the bulk of marine data on lead. Lead concentrations in blue mussels from Greenland were 0.072-0.188 mg/kg, while mussels from Norway had concentrations of 0.101-0.483 mg/kg. Icelandic mussels had similar concentrations to those from Greenland. Blue mussel shells have been used to compare recent and pre-historic levels of lead in Arctic Canada. The study, which examined shells collected from raised Holocene (9000-1000 years before present) beach ridges in the Canadian high Arctic and sub-Arctic, found that recent lead levels in shells from the high Arctic were no different than the Holocene shells. At the sub-Arctic site in southeastern Hudson Bay, modern shells had significantly higher levels of lead than the Halocene shells.   Analysis of stable Lead isotope ratios suggested anthropogenic input from Eurasian and North American sources (AMAP 2005). Recent temporal data sets for lead in blue mussels from Coastal Norway, Greenland and Arctic North America do not show any discernable trends.

In the marine environment lead is typically found sorbed to particulate matter in a form that is not very bioavailable. As a result lead does not appear to accumulate in marine biota to any significant degree. Lead is also not subject to biomagnification, and is generally not considered a risk to ecosystem health. Exceptions may exist in areas close to local sources of lead contamination (AMAP 2005).

4.6 Levels and Trends of Lead in Human Populations

Among the general population, the most significant source of lead exposure that may be attributed to long-range atmospheric sources is dietary intake of contaminated food (primarily agricultural products like fruits, vegetables and grains), and to a lesser extent drinking water and inhalation of lead particulate in air (ATSDR 2005, WGE 2004). In most cases, however, other sources of exposure that are not associated with long-range atmospheric transport may be dominant, particularly in cases of high exposure (ATSDR 2005, AMAP 2005). Examples of these sources include dust from contaminated urban and suburban soil, older homes where there may be residues of lead based paint and associated dust, old corroding pipes that contribute lead to drinking water, and residues from lead shot used to hunt. Contaminated outdoor and indoor dust can be a particular concern for young children who tend to ingest more dust that adults. Soil bound lead that may not be bioavailable for plant uptake, can be bioavailable to humans when digested in the gut. Lead bioaccumulates in humans and can induce neurodevelopmental effects at low levels of exposure in infants, as such human lead exposure represents a serious concern to health authorities. In human soft tissues the half life of lead is about 1-2 months, and in bones the half life may be years to decades (Leggett, 1993; O'Flaherty, 1993, as cited in CDC, 2005).

4.6.1 Levels in food

In the United States, the Food and Drug Administration (FDA) Total Diet Study (TDS) conducted a food basket survey in 1991-1996 and measured concentrations of lead in about 260 food items from three US cities (ATSDR 2005). Concentrations of lead in milk and cheese, eggs, meat, poultry, fish, legumes and nuts, grain and cereal products, vegetables, mixed dishes and meals, desserts, snacks, fats and dressings, and infant and junior food. Only five products had quantifiable concentrations of lead (detection limit for the study was 0.008 mg/kg), namely: canned peaches (0.032 mg/kg), canned pineapple (0.013 mg/kg), canned fruit cocktail (0.031 mg/kg), sweet cucumber pickles (0.036 mg/kg), and dry table wine (0.023 mg/kg). Typical concentrations measured in the TDS for 1991-1996 along with results from a similar study conducted in 1980-1983 are presented in Table 4.1. By comparing the two sets of results, it would appear that levels of lead in US market foods have decreased since the early 1980s.

A similar study was conducted in five Canadian cities from 1986-1988 (Dabeka and Mackenzie, 1995). Lead concentrations were determined in 756 composite samples of market foods representing 11 categories (Table 4.2). Lead concentrations ranged from below detection limit (0.0004 mg/kg) to 0.5 mg/kg with a mean of 0.023 mg/kg for all food categories. The food groups with the highest concentrations of lead, 0.123-0.163 mg/kg, were all canned foods owing to the use of lead containing solder, which is was phased out of use by the late 1980s. The use of lead solder was likely behind the high concentrations measured in canned food during the FDA TDS as well.

As was stated above, the greatest dietary source of lead derived from long-range atmospheric transport and deposition lead is agricultural products. The lead content of higher plants is in large part caused by direct uptake from the atmosphere. The concentration of lead in white clover from pot experiments at ICP Vegetation field sites that were away from local pollution sources and roads was analysed and plotted against bulk deposition rates. A background concentration of lead in the clover foliage was determined to be 0.15 mg/kg (dw). Tolerable bulk deposition rates to meet the critical limits (EU 2001) for lead in unwashed vegetables (spinach, lettuce, endive, lamb's lettuce) ranged between 40 and 140 µg/m^2/day (ICP Vegetation 2005). There is also a correlation between deposition and the Lead content in green fodder. When only a small degree of contamination of green fodder by soil particles is taken into account, the tolerable deposition rates to meet a plant concentration of 40 mg/kg at 12 % moisture content (a frequent official limit in European countries) can be higher than 1000 µg/m^2/day (ICP Vegetation 2005). From this information it can be concluded that long-range transport is not a reason for critical lead limit exceedance in European food and fodder crops.

Table 4.1. Concentration of lead measured in various food categories during FDA Total Diet Studies (nd = below detection limit of 0.008 mg/kg) (ATSDR 2005).

Food category	Mean concentration (µg/g)	
	TDS 1980–1982[a]	TDS 1991–1996[b]
Dairy products	0.006	
Milk and cheese		<0.02–<0.05
Eggs		<0.03
Meat, fish, and poultry	0.016	nd–<0.05
Grain and cereal products	0.023	nd–<0.05
Vegetables	0.010–0.041	nd–<0.05
Legumes and nuts	0.124	nd–<0.05
Fruits	0.046–0.060	nd–0.032
Mixed dishes and meals		nd–<0.04
Desserts		nd–<0.04
Snacks		<0.05
Oils, fats, shortenings, and dressings	0.017	nd–<0.04
Sugar, adjuncts, condiments, and sweeteners	0.028	<0.03–0.036
Infant and junior foods		nd–<0.04
Beverages	0.010	nd–0.0.023

Table 4.2. Concentration of lead measured in various food during a survey of Canadian market foods (Dabeka and Mackenzie, 2005).

Food category	Number of samples	Concentration (ng/g)		
		Mean	Median	Maximum
Milk and milk products	64	7.7	3.9	44.7
Meat and poultry	89	20.2	8.2	523.2
Fish	28	19.3	13.7	72.8
Soups	20	15.5	8.7	48.7
Bakery goods and cereals	120	13.7	10.5	66.4
Vegetables	190	24.4	8.7	331.7
Fruits and fruit juices	127	44.4	15.9	372.7
Fats and oils	15	9.6	<8.8	19.7
Sugar and candies	35	18.3	10.3	111.6
Beverages	35	9.9	<3.1	88.8
Miscellaneous	33	41.7	23.4	178.9
All categories	756	23.2	9.2	523.4

Based on the US FDA Total Diet Studies, average daily intake of lead was determined for various demographic groups for the years 1980 – 1990 (Table 4.3). During the time, the daily intake for all groups appeared to decrease by a factor of ten. For example the estimated daily lead intake of 6-11 month old infants went from 34 µg/day to 3.8 µg/day and the daily intake of 25-30 year old men went from 84 µg/day to 8.5 µg/day. The study authors attribute the dramatic decrease almost entirely to the elimination of lead in solder of canned foods and the introduction of unleaded gasoline (ATSDR 2005).

Table 4.3. Average daily intake of lead (µg/day) estimated from the results of the US FDA Total Diet Studies (1980-1990) (ATSDR 2005).

Age	Sex	1980	1982	1984	1986	1988	1990
6–11 months	Male/female	≈34	20	16.7	10	5	3.8
2 years	Male	≈45	25.1	23.0	12.8	5.0	4.3
	Female	No data	No data	No data	No data	No data	No data
14–16 years	Female	No data	No data	28.7	15.2	6.1	6.1
14–16 years	Male	No data	No data	40.9	21.8	8.2	8.5
25–30 years	Female	No data	32.0	28.7	14.8	7.9	6.7
25–30 years	Male	84	45.2	40.9	21.2	10.0	8.5
60–65 years	Female	No data	No data	30.4	15.6	No data	2.2
60–65 years	Male	No data	No data	37.6	19.1	No data	8.1

A number of other studies discussed in ATSDR (2005) report have estimated intake of lead among the American and Canadian populations. In general the results show that daily intakes of lead resulting from food consumption are about 5-20 µg/day. When other sources of intake are considered, e.g. dust, intake estimates can be as high as 100 µg/day.

4.6.2 Levels of lead in human blood

In the United States, the National Health and Nutrition Examination Survey (NHANES) has measured blood lead levels since 1976. Between 1976 and 1991 NHANES reported a drop in mean blood lead levels among the general population (age 1 – 74 years) from 12.8 to 2.8 µg/dL (ATSDR 2005). The percentage of people with blood levels over 10 µg/dL also dropped from 77.8% in 1976 to 4.3% in 1991. The likely causes of the decline are considered to be the removal of lead solder from cans and lead additives from gasoline. By 1999-2002 the overall percentage of blood levels exceeding 10 µg/dL was down to 0.7%. Between 1999 and 2002 1.6% of children aged 1-5 exceeded blood lead levels of 10 µg/dL, the highest percentage of any age group.

Concentrations of lead in maternal blood are moderately elevated in Inuit, Dene and Metis mothers from Arctic Canada (3.1-5.0 µg/dL) (AMAP 2003). The most plausible explanation for the elevated levels is the use of lead shot when hunting. Similar levels were reported for Greenland Inuit, also thought to result from the use of lead shot, particularly for hunting seabirds. By comparison, maternal blood lead levels among other groups from Arctic Canada were significantly lower (1.9-2.2 µg/dL). Similarly low levels of lead were measured in blood from mothers in Alaska, Russia and Finland.

4.7 Ecosystem and Human Health Effects

4.7.1 Terrestrial Ecosystems

Plants, invertebrates and microbiota
The toxicity of lead in terrestrial ecosystems is highly dependent on the physicochemical properties of the soil and specific biological characteristics of species in the ecosystem. Most plants appear to be unaffected by relatively high levels of lead in soil which may be do to their apparent ability to store lead in an insoluble form and to limit translocation in the plant (Pain, 1995). At high enough levels of exposure lead has been experimentally shown to have a wide range of effects in plants, including disruption of cell membranes and mitosis, inhibition of plant growth, ATP (adenosine triphosphate) synthesis and structural protein formation, reduction of photosynthesis, water absorption and transportation rates, increase in generation time, and decrease in pollen germination and seed viability (Pain 2005). The author also notes, however, that "little lead is generally available for uptake by plants in soils and sediments, and very high soil/sediment lead concentrations are often required before toxic effects upon plants are observed". In the review Pain (2005) cites a study on European spruce forests and the possible role of atmospheric lead in their decline. AMAP (2005) provides a review of lead toxicity values and cites a soil lead benchmark value of 50 mg/kg for the protection of plants and

500 mg/kg for the protection of soil organisms. Rademacher (2001) reported a range of lower effects thresholds (7-50 mg/kg) for the protection of more sensitive receptors.

Rademacher (2001) conducted a comprehensive review of data from ICP Forest measurements networks and literature on concentration levels of metals in forest ecosystems and effect thresholds. Median values of Lead in needles and leaves of beech, oak, pine, spruce and other tree species at Level I plots ranged between 1.3 µg/g (dw) and 3.4 µg/g (dw), the medium value for all species was 2.1 µg/g (dw). Median Lead concentrations in needles and leafs of the same tree species, but from Level II plots, varied from 0.8 µg/g (dw) to 1.8 µg/g (dw) with a median for all species together of 1.2 µg/g (dw). These concentrations are lower than effect levels for plant tissues reported in:

Balsberg Påhlson (1989):   NOEC (effects on forest) < 15 µg/g;
Sauerbeck (1983):   NOEC (yield loss for agricultural crops) 10 – 20 µg/g;
Balsberg Påhlson (1989):   decrease of physiological parameters and yield (forests) >20 – 70 µg/g (dw).

Based on empirical data, the Foliar Expert Panel of ICP Forests (EC-UNECE 1995a, 1998 b) discussed an evaluation guide for macro and micro nutrients as well as heavy metals. For Lead a concentration in foliage of >4 to > 30 µg/g (depending on tree species, the high value is for oak) was suggested to indicate excess not having necessarily a damaging effect. A differentiated examination of the various tree species (groups) showed excessive toxic threshold values in some cases. Pine, especially the older needle years, showed the highest median value for lead of 5 mg/kg. Excess concentrations were detected in 13 % of the spruce samples and 7 % of the beech samples (see ICP Forest contribution, March 2006).

Results from ICP Forests Level I and Level II plots showed that lead was retained in upper layers of forest soils of most sites (Rademacher 2001). The median Lead concentration in the humus layer of 1658 Level I plots was 37 mg/kg, while 20 mg/kg in the upper mineral soil (50 cm, n=1998). The related 95-percentiles were 180 mg/kg (humus) and 70 mg/kg (mineral), respectively. At Level II plots the median Lead concentration in the humus layer was 61 mg/kg, and 8 mg/kg in the mineral soil. Rademacher (2001) reported a series of critical limits (Bååth 1989, Wilson 1977, Sloof et al. 1999, Atanassov et al. 1999, Tyler et al 1989 Bengtsson and Tranvik 1989, Tyler 1992, Inman and Parker 1978, Coughtrey et al 1979). Those limits for Lead in soils showed a very wide range of 7 mg/kg up to 1052 mg/kg depending on the effect and endpoint considered. The very low value of 7 mg/kg is based on the NOEC (nitrification, Wilson 1977). Next higher limits are in the range of 25 to 50 mg/kg and are related to observed effects on nitrification (Wilson 1977), effects on soil invertebrates (Tyler et al. 1989). In another study effects on soil biota were observed due to concentrations of lead and perhaps also mercury in South Swedish moor layers (Bringmark et al. 1998). Field investigations have indicated effects on microbiota (C-mineralisation) at 74 µg/g (dw) (Bringmark & Bringmark 2001a).

Most surveys of Lead in soils provide total contents (or in exchange aqua regia extractable concentrations). Also, almost exclusively, all toxicological studies provide thresholds for total Lead contents or total added amounts. However, because Lead effects on soil organisms and plants are caused by the soluble proportion or even the free metal ions, effects evaluation based on total contents is of limited value. Based on a pH dependent critical limit function related to free metal ion concentrations (Lofts et al. 2004) and using a chemical speciation model (based on Tipping et al. 1998) ICP Modelling and Mapping (2004) provides ranges of critical limits expressed as total concentrations of soil drainage water for use in critical loads calculations. These critical Lead limits vary widely from 0.08 µg/L to 71 µg/L depending on soil conditions.

Mean Lead concentrations found in background regions are in general lower than critical limits for food and fodder as well as for phytotoxic effects.

Wildlife

In wildlife lead effects biological function at the molecular level and can inhibit the activities of many enzymes necessary for biological function. Lead can have adverse effects on the haematological system, the brain and nervous system, learning and behaviour, and reproduction and survival. Research has suggested that young animals in particular are sensitive to certain neurological and behavioural effects that arise from effects of lead on the developing brain and nervous system. By acting on the structure and function of the nervous system, exposure to lead can result in impairment of intellectual, sensory, neuromuscular, and psychological functions (Pain 1995).

In their review of toxicity thresholds for lead, AMAP (2005) outlines tissue concentrations at which effects may occur. Table 4.4 lists general tissue concentrations and ranges at which various levels of poisoning have occurred in various animal studies. Subclinical poisoning refers to instances were no effects were observed, clinical poisoning involves obvious illness, and severe clinical poisoning suggests lethality. These thresholds have been derived from studies on animals that have been exposed to lead from contaminated sites or ingestion of lead fragments. The levels of lead observed in terrestrial wildlife that may be attributed in part to deposition from long-range atmospheric transport do not exceed these thresholds and are not expected to suffer adverse effects from lead toxicity.

Table 4.4. Threshold concentrations for lead in biota (AMAP 2005).

	Normal	Subclinical poisoning	Clinical poisoning	Severe clinical poisoning
Blood (µg/dl)	<20	20-<50	50-100	>100
Liver (mg/kg ww)	<2	2-<6	6-15	>15
Bone (mg/kg dw)	<10	10-20	>20	

4.7.2 Freshwater Ecosystems

The toxicity of lead in aquatic ecosystems depends largely on speciation and solubility. Organic forms of lead tend to produce toxic effects at lower concentrations than inorganic species. The most sensitive sublethal effects can occur at water lead concentration as low as 7 µg/L and about 10 µg/L the activity of some hematopoietic enzymes can be inhibited (Pain 1995). The type of effects that may be seen at elevated water lead concentrations include anemia, reduced egg hatching, darkening of the dorsal tail region and degeneration of the caudal fin, and scoliosis (lateral curvature of the spine) (Pain 1995).

Critical limits in calculations of critical loads to protect aquatic ecosystems were set to 11 µg/L (ICP Modelling and Mapping 2004). This limit is based on Crommentuijn (1997). The effects of lead concentrations in surface waters vary, however, in dependence of water chemistry (Skjelkvåle and Ulstein 2002). A limit of 1.0 µg/L (Lowest Biological Risk Level) considering sensitive chemical conditions in Swedish freshwaters was set by SEPA (2000). A similar limit has been set for Norway (Andersen et al. 1997). The Workshop on Heavy Metals (Pb, Cd, Hg) in Surface Waters (March 2002, Lillehammer, Norway) recommended a span of critical limits for Lead of 1.0 – 10 µg/L depending on sensitivity of the water bodies. (Skjelkvåle and Ulstein 2002). A method to consider freshwater chemistry in the setting of limits for Cadmium and Lead is provided in De Vries et al. (2005). In general the comparison of present lead concentrations in European freshwaters that receive lead input exlusively from atmospheric deposition with critical limits, shows that there is only a minor risk of effects in biota. However, such effects cannot be completely excluded in several water bodies.

4.7.3 Marine Ecosystems

Concentrations of lead in marine biota are very low and well below toxicity thresholds derived for other biota. For example, marine fish species have significantly lower levels of lead than freshwater fish. Lead in marine ecosystems, particularly at locations away from point sources, does not appear pose a toxicological threat. In general, AMAP (2005) does not consider levels of lead in the marine environment to be a concern.

4.7.4 Human Health Effects

Lead is a highly toxic metal that is known to bioaccumulate in humans. At high levels of exposure, such as those seen in some occupational scenarios, lead can affect nervous system function, increase blood pressure and cause anaemia. At extremely high levels, lead can cause severe damage to the brain and kidneys and ultimately can be lethal. Lead can also cause reproductive effects such as miscarriages and impaired sperm production (ATSDR 2005). The greatest risks from low levels of lead exposure are to the developing nervous system of infants. Research has shown that children exposed even

slightly elevated levels of lead in utero perform more poorly on tests of infant intelligence than children with lower levels of exposure. The current blood lead screening guideline, or level of concern, set by the United States Centers for Disease Control and Prevention (CDC) is 0.48 umol/L, or 10 μg/dL. This same value has been adopted by Health Canada as an "action level". Resent research, however, has demonstrated associations between maternal blood levels and scores of infant intelligence at concentrations that were less than 0.16 umol/L (Tserekos and Buka, 2005). Results such as these have led some experts to suggest that there is no threshold for adverse effects on the developing central nervous system.

In their report of 2004, the Working Group on Effects reported that the geometric mean of lead concentrations in blood in European adults is much lower than levels that have been associated with the most sensitive effects (WGE 2004). It was therefore concluded that the present environmental exposure to lead could be considered as rather safe to adults. Present data on the concentration of lead in air, daily intake of lead with food and lead in blood levels suggest a decreasing trend of environmental lead exposure, in particular in countries where lead has been eliminated from gasoline (WGE 2004).

Blood lead concentrations in the majority of the human population are below the CDC level of concern of 10 μg/dL, however, a small percentage of people still exceed this level. According to 1999-2002 surveys in the US, 1.6% of 1-5 year old children exceed the CDC level of concern. In Canada a study of umbilical cord blood lead levels revealed that 0.9% of infants exceed the health Canada10 μg/dL action level. Among First Nations people in Quebec 3% of cord blood samples exceeded the action level and 6% of cord blood samples exceeded the action level among Inuit of northern Quebec.

Blood lead concentrations have been more broadly studied in Arctic residents and reported in the AMAP (2003) report on human health. The results of these surveys showed that among aboriginal populations in the western Canadian Arctic 2-5% of women exceeded the health Canada action level (Figure 4.18). Among Inuit women of the eastern Canadian Arctic and Greenland 10-12% exceeded the action level.

It is evident, however, that deposition of lead from long-range atmospheric transport is not the most important source of lead exposure to the human population. Past use of lead, and in some cases current use of lead (Tsekrekos and Buka, 2005), have resulted in the elevated levels of lead exposure seen in the surveys noted above. Contaminated urban soils and household dust are likely the most important source of lead exposure to the general population, particularly children. Among more remote populations, including aboriginal peoples of the Arctic, the use of lead shot to harvest country foods is thought to be the dominant source of dietary lead exposure (AMAP 2003).
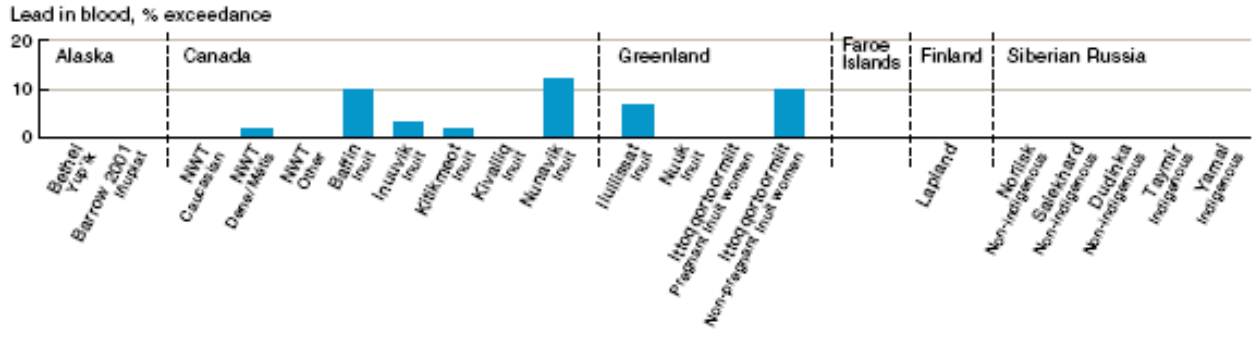
Figure 4.18. lead levels in blood of aboriginal and non-aboriginal women of reproductive age. Percentage exceeding the US CDC level of concern and the Health Canada action level, both of which are 10 µg/dL (AMAP 2003).

5 Other Metals in the Environment

In addition to the three metals discussed in chapters 2, 3 and 4 of this review, the Task Force on Heavy Metals was asked to present relevant information on other metals related to effects of deposition from long-range transboundary air pollution. The main group of metals that were considered in this review were those for which Parties to the Protocol have collected and reported emissions data including: arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se) and zinc (Zn). Other metals, though not reported on by Parties, for which new information on long-range transportation exists include platinum group metals: platinum (Pt), palladium(Pd) and rhodium(Rh); and antimony (Sb).

In order to assess deposition from long-range atmospheric transport, the most logical places to begin is with an examination of Arctic data. The first AMAP assessment report (AMAP 1998) reviewed many of the other metals mentioned in the previous paragraph and assessed possible anthropogenic enrichment of these metals in the environment. In a cursory review aimed at identifying metals to be considered in a more detailed assessment, the degree to which the natural elemental cycles was perturbed by anthropogenic influences was reviewed. The main line of evidence in determining perturbation was the enrichment factor of a metal, defined as an increase in concentrations in a given reference material, like surface soils, in relation to a reference metal like aluminum. Based on a review of literature, AMAP (1998) listed each of, As, Cu, Se, Sb, and Zn as being enriched on a global scale, whereas Cr and Ni were considered to be enriched only up to a regional scale (1000-2000kms). The lines of evidence used in this determination included measurements in air, sediment, soil, and surface waters. With the exception of As and Sb, all of these metals are considered micronutrients essential to biological function, however, in excess and generally dependent on chemical speciation they can each be toxic. For example the trivalent form of Cr is essential, but the hexavalent from is quite toxic. The most toxic form of As is inorganic trivalent As compounds such as arsenic trioxide, whereas organic forms of arsenic (e.g. methylated) are generally considered to be non-toxic. At the time of publication, there was not very much information about the platinum group metals and the degree to which they might be enriched on global or regional scales.

Results of atmospheric modeling were reviewed in AMAP (1998) to assess the degree to which metals were transported to the Arctic from regions of industrial emissions. The findings of various model simulations and comparison with limited atmospheric measurements indicated that during the winter 60 to 70% of metal input (in general) to the Arctic atmosphere were from the former Soviet Union, with remainder originating in Europe and North America. In the summer, the contribution from Europe increased to as much as 75%. It was estimated that up to 6% of total As, Zn, and Sb emissions in all of Eurasia were deposited in the Arctic. There remained some question, however, as to the degree of deposition in the Arctic, given that conditions in the Arctic atmosphere do not favour deposition of fine particulate, the predominant form taken by metals in the atmosphere.

The lack of precipitation, and otherwise limited potential for wet deposition in the high Arctic has been suggested as an explanation for the lack of some enrichment in high Arctic environments. For example, no temporal trend in deposition of Cu and Zn was found over the 1300 yr history captured in a sediment core from a lake in the Canadian high Arctic, suggesting that deposition had not been influenced by anthropogenic emissions in the lake basin (Outridge et al. 2005).

Glacial evidence of long-range transport

Some of the evidence for long-range transport and deposition of heavy metals in the Arctic has come from the analysis of glacial snow and ice cores. The most recent results of this type of study were presented by Krachler et al. (2005), and demonstrate historic increases in deposition of Sb to the ice cap. The increased Sb deposition to the Devon ice cap, in the Canadian high Arctic, that mirrors various phases of industrial activity over the last 160 years. This includes a dramatic increase in atmospheric Sb enrichment that occurred just after world war II, as well as a substantial decrease that occurred in the 1970s with the introduction of flue gas filters. More recently however, the authors noticed that Sb enrichment in Arctic air had increased by 50% over the last thirty years. This increase was attributed primarily to the increasing growth in use of Sb compounds in automotive brake pads, and as flame retardants in various products. The greatest source of Sb to the Arctic appears to be from Asia, as indicated by high winter maxima in deposition.

The platinum group metals (PGM), platinum, palladium and rhodium are the principle elements used in catalytic converters to reduce automobile emissions of hydrocarbon, carbon monoxide, nitrogen oxides. Catalytic converters employing various mixtures of PGM have been in use since the mid 1970s in North America, and more recently (early 1990s) in Europe as well (Barbante et al., 2001). Due to the increasing use of catalytic converters, and the increasing number of automobiles in the world, researchers have recently begun to assess the potential for PGMs to become global dispersed contaminants. It has been well demonstrated that vehicle exhaust emissions contain these metals in particulate form resulting in elevated levels of PGM in urban air, roadside dust, roadside soil and roadside vegetation (as reviewed in Rauch et al., 2005). It was believed, however, that the distribution of PGM was confined to roadside environments but recent studies are demonstrating that PGM is indeed being distributed worldwide.

A review of PGM dispersion and source attribution by Rauch et al. (2005) reported evidence of both regional and long-range atmospheric transport. Evidence for regional impacts included a core from a bog in Massachusetts, USA, where recent rates of deposition were over an order of magnitude higher than the estimated natural deposition rates. The bog, however, was only 250m from a highway. Evidence of more distant transport is starting to build. Ice cores collected in the Alps have demonstrated late 20th century increases in the deposition of these metals to the Alpine glaciers. While some of the increase is attributed to automobile exhaust, there is evidence of other sources as well. Perhaps the most compelling evidence for long-range atmospheric transport comes from historic profiles recorded in snow and ice at Summit Greenland (Figure 5.1). In this

study Barbante et al. (2001) reported increases of 40 to 120 times the rate of deposition recorded 7000 years ago. Increases at Summit appeared to begin in the 1970s and then spiked dramatically in the 1990s. The increased deposition of PGM at Summit is attributed to a combination of sources including automobile emissions and metal smelters in Russia. In their review, Rauch et al. (2005) conclude that automobile exhaust accounts for a substantial portion of the PGM distributed throughout the northern hemisphere. Contrary to former beliefs, over 90% of the PGM emitted from automobile exhaust appears to be distributed outside of the immediate roadside environment. The conclusion of the review, purported to be the first review of PGM contamination in the northern hemisphere, was that "a relatively large fraction of PGE emitted from catalysts is transported at both regional and global scales, resulting in a widespread contamination".

While anthropogenic emissions of platinum, palladium and rhodium are clearly resulting in increased deposition to remote environments, it is not clear what the impact of this contamination might be.
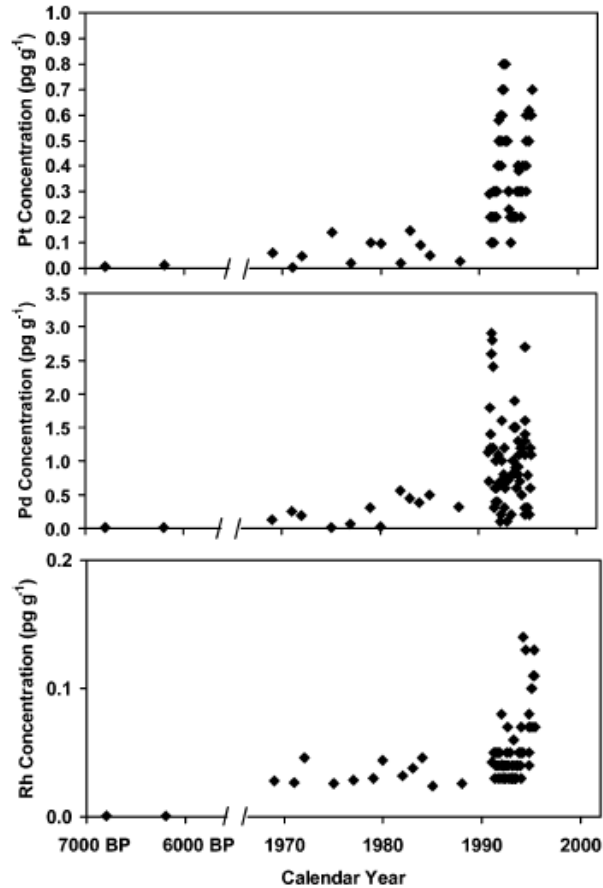
Figure 5.1. Platinum group element concentrations in ice and snow from Summit in central Greenland (Barbante et al., 2001).

5.1 Atmospheric Monitoring

One of the longest and most complete records of metal concentrations in Arctic airborne aerosols has been collected at Alert, Canada (Gong and Barrie, 2005). At Alert concentrations of metals associated with anthropogenic sources were measured as weekly means in aerosols between 1980 and 2000. Results are reported for a variety of elements attributed to both natural and anthropogenic sources. Included among the metals associated with anthropogenic sources, and relevant to this chapter, were Cu, Zn, and Ni. Season trends demonstrated maxima in winter and minima in the summer (Figure 5.2). The long-term trends were fairly subtle but when only winter concentrations were analyzed the data indicated a decrease in concentrations from 1980s to about 1995 and then an apparent increase thereafter (Figure 5.3).
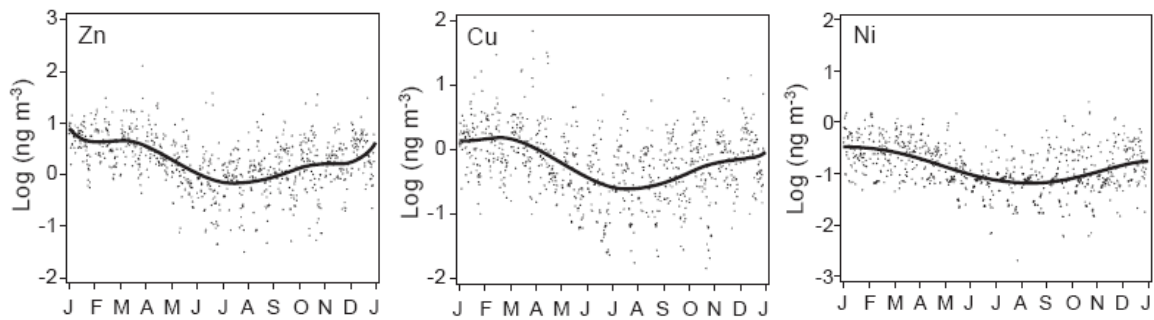
Figure 5.2. Seasonal trends in heavy metal concentrations measured in aerosols at Alert Canada (Gong and Barrie, 2005).
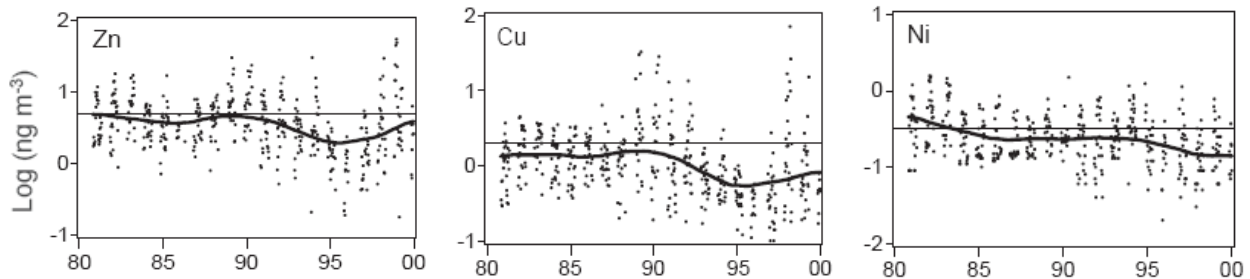
Figure 5.3. Temporal trends in winter time heavy metal concentrations in aerosols at Alert Canada (Gong and Barrie, 2005).

5.2 Terrestrial Ecosystems

Zinc and particularly Cu are considered to be less connected to long-range atmospheric transport than Pb, Cd, and Hg. Concentrations of copper (Cu) and zinc (Zn) in aqueous

input to mostly forested catchments and stream water running out of them have been assessed within the ICP Integrated Monitoring Programme. In general concentrations of Cu as well as Zn were lower in the runoff streams from catchments (ICP IM sites in Austria, Czech Republic, Finland, Latvia, Sweden) indicating that these metals were accumulating in the catchments (Bringmark and Lundin 2005).

Higher concentrations of both metals in throughfall than in precipitation at stations in AT, CZ, LV, SE and FI indicated substantial interception of dry particles in the forest canopy. Consistent with Cu and Zn being considered to be local pollutants, their concentrations in precipitation at the selected IM sites followed a increasing North to South gradients (Cu: 0.8 – 1.3 µg/L in FI, 9.3 µg/L in AT; Zn: 2.1 – 4.0 µg/L in FI, 20.7 – 21.6 µg/L in CZ). Lower Cu concentrations in streamwater (Cu: 0.1 – 3.1 µg/L) than in precipitation at 8 IM stations in 4 countries indicate accumulation in the catchments. For Zn the same was true at 6 ICP IM stations in 4 countries (Zn in streamwater: 0.7 – 15.1 µg/L), but at 3 stations the concentrations on outflow were equal or higher than in precipitation.
In addition concentrations of As, Cr, Ni, and V are measured at ICP IM stations in some countries.

The concentration of Cu in white clover from pot experiments at ICP Vegetation field sites away from local pollution sources and roads was analysed and plotted against bulk deposition rates. A background concentration of Cu in the clover foliage was determined to be 3.5 µg/g. An indication of atmospheric Cu pollution was assumed, if concentrations in the foliage exceeded 4.15 µg/g (ICP Vegetation 2005).

Concentrations of 10 metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium, zinc) in mosses have been surveyed in 2000/2001 (ICP Vegetation 2003). In general there was a clear east/west decrease in the concentrations of metals in mosses.

- The As concentration in mosses ranged from < 0.2 to > 0.6 µg/g in the largest part of Europe. Elevated concentrations up to > 14 µg/g occurred in the vicinity of industries and power plants.
- The Cr concentration in mosses ranged from < 1.0 to >3.0 µg/g in the largest part of Europe. Elevated concentrations up to > 15 µg/g occurred in areas influenced by industry, smelters or high bedrock concentrations. Partly the influence of transboundary Cr pollution could be identified.
- The Cu concentration in mosses ranged from < 4.0 to >12.0 µg/g in the largest part of Europe. Elevated concentrations up to > 28 µg/g occurred in the vicinity of smelters, copper mines, coal combustion and vineyards. Partly the influence of transboundary Cu pollution could be identified.
- The Fe concentration in mosses ranged from < 500 to >1500 µg/g in the largest part of Europe. Elevated concentrations up to > 4000 µg/g occurred areas influenced by iron and steel industries and mines. Dust and contaminated soil were also identified sources of Fe in mosses.
- The Ni concentration in mosses ranged from < 1.0 to >4.0 µg/g in the largest part of Europe. Elevated concentrations up to > 20 µg/g occurred in the vicinity of oil

and lignite combustion and industries. Partly geologic and soils sources of Ni could be identified. Transboundary Ni pollution was not reported.

- The V concentration in mosses ranged from < 2.0 to >6.0 µg/g in the largest part of Europe. Elevated concentrations up to > 14 µg/g occurred in the vicinity of oil and coal combustion and smelters. Contaminated soils were identified to be a possible source of V deposition in some areas.
- The Zn concentration in mosses ranges from < 40.0 to >80.0 µg/g in the largest part of Europe. Elevated concentrations up to > 160 µg/g occurred in the vicinity of metal and other industries and combustion. Contaminated soil was a possible source of Zn deposition in some regions. In Finland a decreasing gradient from south to north was identified, although there was no significant single emission source.

5.3 Freshwater Ecosystems

Data on heavy metals other than Pb, Cd, Hg in surface waters are available from a survey in Nordic lakes Skjelkvale et al. (2001). Direct and indirect influence of long-range transported air pollution is the major important factor for distribution of Zn and Co. These two metals showed a gradient of higher concentrations in lakes in the south than in the north. This pattern resembles that of the deposition of these elements as shown by the moss survey. Total organic carbon in lakes is important for Fe and Mn but also for a certain degree for As, Cr and V. Bedrock geology is the major controlling factor for Cu and Ni with the exception of areas around the smelters in the Kola peninsula, where Cu and Ni concentrations in lakes are very high due to local airborne pollution. Bedrock and surficial geology is also important for the concentrations of As, Co, Cr, and V. The weighted 99,5 percentiles of the concentrations in the total lake population in Finland, Norway and Sweden were for V: 2.23 – 3.13 µg/L; Cr: 1.35 – 2.11 µg/L; Fe: 1542 – 7663 µg/L; Mn: 101 – 474 µg/L ; Co: 0.96 – 2.4 µg/L ; Ni: 3.17 – 5.74 µg/L ; Cu: 2.73 – 4.6 µg/L ; As: 2.02 – 4.95 µg/L. For Zn 50 percentiles are reported that ranged between 1.1 – 2.2 µg/L for these lakes. The methods of stratification and statistical evaluation of the data from about 3000 Nordic lakes are described in Skjelkvale (2001). The results of the study indicated that pollution with these heavy metals is a minor ecological problem on a regional scale in the Nordic countries (Hg concentrations were not reported in this study).

Mean concentrations of Cu, Zn and Ni in lakes and streams at ICP Waters sites in the period 1999 – 2001 are published in ICP Waters (2003). The number of sites per metal and country varied from 1 to 24. The ICP Waters database is not considered to be representative with respect to general heavy metal concentration levels in surface waters. Tables 5.1 to 5.3 give an overview of mean values of measured concentrations of Cu, Zn and Ni, respectively, at ICP Waters sites. ICP Waters limited its investigations to those sites, where atmospheric deposition is the only source of pollution.

Table 5.1 Mean concentrations of copper at ICP Waters sites in the period of 1999 – 2001.

Country	Number of sites included	Range of mean values (µg/L)
Canada	1	1.2
Czech Republic	6	0.33 – 1.4
Finland	4	0.21 – 0.37
Germany	18	0.66 – 2.4
Hungary	1	4.0
Ireland	10	0.02 – 1.4
Latvia	4	0.7 – 1.2
Poland	2	1.7 – 1.8
Sweden	6	0.38 – 2.0
Switzerland	24	2.0 – 16.0
United Kingdom	6	20.0

Table 5.2. Mean concentrations of zinc at ICP Waters sites in the period of 1999 – 2001.

Country	Number of sites included	Range of mean values (µg/L)
Canada	5	3.8 – 10.0
Czech Republic	6	4.0 – 15.0
Finland	4	0.8 – 4.4
Germany	20	3.0 – 98.0
Hungary	1	12.0
Ireland	10	3.1 – 101.0
Latvia	4	2.5 – 4.1
Poland	2	5.7 – 7.3
Sweden	6	1.1 – 7.5
Switzerland	24	2.5 – 14.0
United Kingdom	6	20 - 48

Table 5.3. Mean concentrations of nickel at ICP Waters sites in the period of 1999 – 2001.

Country	Number of sites included	Range of mean values (µg/L)
Finland	4	0.1 – 0.3
Germany	18	0.44 – 31.0
Hungary	1	4.0
Ireland	10	0.02 - 3.6
Sweden	6	0.2 – 0.9

5.4 Effects on terrestrial ecosystems

Forest condition in Europe has been monitored for more than 20 years by ICP Forests in close collaboration with the European Union (EU). Large-scale variations of forest condition are assessed at 6 000 so-called Level I plots systematically spread across Europe. At a number of Level I plots, soil and foliar condition has been monitored once in addition to annual crown condition assessments. Causal relationships are studied in detail on 860 Intensive Monitoring Plots, called Level II. With respect to heavy metals, chemical soil and foliar condition is analysed as well, but in addition to deposition, soil solution and litterfall measurements are carried out.

Soil sampling plots at ICP Forests Level I plots yielded around 4000 single heavy metal samples each for the elements Zn and Mn, 3500 each for Fe and Cu, and about 2500 each for Cr and Ni. Samples were taken at various depths, in the humus (O and H layers) as well as in the mineral soil. Slightly more than half of the analyses come from the humus, slightly less than half from the mineral soil.

Rademacher (2001) related measured concentrations of Zn, Cu, Ni, Cr, in forest ecosystems to critical levels that were chosen from available literature (see Table 5.4). Heavy metal pollution of soils was uncritical at most of the observed Level I plots. Exceedances at Level I plots vary between 1 and 15% for different soil layers and elements.

Table 5.4. Critical levels of Cr, Ni, Zn and Cu compiled from literature and their exceedances for major heavy metals at Level I plots. hu: humus layer; min: mineral soil.

		Cr	Ni	Zn	Cu
	Critical level (mg/kg)	100	50	200	60
hu	number samples	1206	1153	1840	1608
	exceedances	**3%**	**<1%**	**3%**	**3%**
min	number samples	1302	1302	242	2087
	exceedances	**3%**	**10%**	**2%**	**2%**

At Level I, there are 2000 foliar analyses available for Zn, Mn and Fe, and 1200 analyses for Cu (Rademacher, 2001). Species specific levels of an excess supply have been defined by the ICP Forests Expert Panel on Foliar Analysis (see Table 5.5).

The measured values mostly lie within pollution limits that are regarded as harmless and which show that the nutrient supply is also within safe limits, especially for important micronutrients such as Cu and Zn. A differentiated examination of the various tree species (groups) shows a surplus of nutrients and excessive toxic threshold values in some cases. Copper supply was very high in 45% of the beech samples and was regarded as critical in 8% of the samples.

Table 2: Excess levels of Zn, Mn, Fe and Cu as compiled from literature (see Rademacher 2001) and their exceedances for major heavy metals in current year needles and leaves of spruce and beech at Level I plots. spr: spruce; be: beech.

		Zn	Mn	Fe	Cu
	Excess level (mg/kg)	60	2000	200	7
spr	number samples	974	974	926	360
	exceedances	**3%**	**6%**	**<1%**	**5%**
	Excess level (mg/kg)	50	2500	200	10
be	number samples	160	160	160	141
	exceedances	**6%**	**6%**	**18%**	**45%**

5.5 Freshwater Ecosystems

In the study of Nordic lakes, the levels of contamination by heavy metals (not including mercury), were not considered to be of ecological concern.

5.6 Effects on human health

ICP Vegetation (2005) reported on heavy metal deposition and potential contamination of crops as a potential cause for concern related to human health. In their evaluation, arsenic (As) was included along with Pb, Cd, and Hg. Arsenic is a toxic element. Inorganic As, present as arsenite As(III) and arsenate As(V) found in food are the most toxic forms. Problems with arsenic poisoning are also related to inorganic forms in groundwater. These elevated concentrations origin from geologic sources. There is a Provisional Tolerable Weekly Intake (PTWI) for arsenic in drinking water (15µg/kg body weight) in the form of inorganic arsenic, but not for food (WHO 1993). The intake by the mean adult population in Europe is 880 µg week^{-1} (SCOOP 2004). About 87 % of the weekly arsenic intake (adults) in the EU is from fish and seafood, mostly in less toxic organic forms. Half of the remaining 13 % is originating from fruits, vegetables and cereal products, mainly in inorganic form (SCOOP 2004). The contribution of atmospheric deposition to the contamination of plants at rural sites is rather low. This is mainly caused by very low deposition rates in areas not directly influenced by local sources. At deposition rates < 5 µg m^{-2} d^{-1}, which is typical for rural areas, the arsenic concentration in leafy vegetables is less than 0.02 mg/kg. The concentration in unwashed vegetables increases to about 0.55 mg/kg at deposition rates in the range of 20 – 100 µg m^{-2} d^{-1}. A deposition rate of about 120 µg m^{-2} d^{-1} would be necessary to reach a level of As concentration in fodder (lucerne or clover meal) of 4 mg/kg at 12 % moisture content, that is the maximum tolerated value for fodder in some countries.

In general, the non-essential metals, like As and Sb, are considered to have greater toxic potential that the essential metals like Cu, Zn and Se. The essential metals are required for biological function and play important roles in many biochemical reactions without which life would not exist. Animals have developed fine tuned mechanisms to maintain the right level of these metals in their bodies and preventing potentially toxic accumulation. Selenium plays a big role in detoxifying other heavy metals, such as Cd, Hg and As, by forming non-toxic selenide compounds which are either harmlessly stored or excreted from the body. Despite the potential for long-range transportation, there is little risk of adverse effects resulting from the essential metals (i.e. Cu, Zn, Se, Ni). Selenium levels in some marine mammals can approach toxic thresholds for other mammals, however, the applicability of these thresholds to marine species is unclear. While the non-essential metals do have the potential to cause adverse effects at relatively low concentrations, the environmental concentrations in remote regions like the Arctic that result from long-range transportation are very low and do not warrant concern at this time (eg. As, Sb, Pt, Pd, and Rh). AMAP (2005) recommended monitoring for metals, like the platinum group metals, which demonstrated increasing temporal trends in the Arctic environment.

6 References

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