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Estimation of the Long-range Transport of Mercury, Cadmium, and Lead to Northern Finland on the Basis of Moss Surveys

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Abstract

Nation-wide surveys of the accumulation of 10 heavy metals in mosses were carried out in Finland in 1985, 1990, 1995, and 2000. Separate investigations were carried out, on the basis of these surveys, into the atmospheric deposition of Hg, Cd, and Pb beyond the Arctic Circle in northern Finland. These metals are readily distributed in the form of longrange transboundary pollution, and particular concern has been raised about the transport and accumulation of these metals into Arctic areas. The Hg, Cd, and Pb concentrations in mosses in northern Finland were low. There was a clear decrease in Cd and Pb concentrations during the period 1985-2000. The Pb concentration decreased, on the average, from 8 to 2 μg g⁻¹, and the Cd concentration from 0.3 to 0.1 μg g⁻¹. Hg concentrations, which were analyzed in 1995 and 2000, decreased only slightly from 0.037 to $0.031 \mu g g^{-1}$. The slight decrease in Hg concentrations in northern Finland appears to reflect the decreasing Hg emissions and the high mobility of this metal. Factors leading to the decrease in Pb and Cd concentrations in mosses in northern Finland include a decrease in local emissions and a decrease in transboundary air pollution. The past two decades have been characterized by decreases in heavy metal emissions of throughout Europe. The greatest reductions have been in Pb emissions, due to the introduction of unleaded fuels.

Introduction

Of the heavy metals released into the atmosphere, the most attention has been focused in recent years on Hg, Cd, and Pb. Particular concern has been raised about the transport and accumulation of these readily distributed heavy metals into arctic areas, where the flora and fauna are exceptionally sensitive to a range of air pollutants (e.g., AMAP, 2002). Mercury, Cd, and Pb have been classified in the most hazardous category of heavy metals, because they accumulate in the food chain and are toxic to most organisms at relatively low concentrations. Much of these heavy metals are produced as a result of anthropogenic activities. In aquatic ecosystems, Hg is converted into highly toxic methyl mercury. Mercury, Pb, and Cd also occur naturally, e.g., in bedrock and in small quantities everywhere in nature.

Almost half of the Hg that is released into the atmosphere is derived from natural emission sources, such as volcanoes, forest fires, and volatilization from surface water and soil, whereas the majority of Pb and Cd emissions are of anthropogenic origin (Pacyna and Pacyna, 2001). The most important anthropogenic source of Hg is the burning of fossil fuels, especially coal, which has been estimated to account for more than one half of total anthropogenic emissions (Mukherjee et al., 2000; Pacyna et al., 2001). Other significant emission sources include waste incineration, the metal industry and cement production. Most of the Cd that is released into the atmosphere originates from the processing of iron ore and, in smaller quantities, from the burning of fossil materials and waste. The most important emission source of Pb is vehicle traffic, other emission sources including the metal industry and mining activities. During the last two decades, lead emissions from traffic have decreased considerably, especially in Europe and North America. This has been due to the introduction of unleaded petrol (Pacyna and Pacyna, 2001; Ilyin et al., 2003). Cadmium and Hg emissions have also decreased in Europe along with the reduction in coal burning and improvements in scrubbing technology (Pacyna and Pacyna, 2001; Ilyin et al., 2003). However, there has been no corresponding global reduction in Hg emissions.

Mercury, Pb and to some extent also Cd are metals that are readily transported over long distances in the atmosphere. Mercury differs from other heavy metals in that it occurs primarily in gaseous form in the atmosphere, usually as Hg^0 and small amounts of $\mathrm{Hg}(\mathrm{II})$ (Schroeder and Munthe, 1998). It can also occur in the atmosphere in solid form (pHg) attached to particles. Elemental gaseous mercury (Hg⁰) can be transported by circulating air masses for thousands of kilometers from the emission source and remain in the atmosphere for ca. 1 yr (Ilyin et al., 2003). The other forms of mercury are more readily deposited on the ground than elemental mercury (Hg⁰). Mercury is deposited from the atmosphere onto the ground as both dry and wet deposition, primarily in oxygenated form into the vegetation, soil, and water systems. Under suitable conditions, however, it can be revolatilized and return into the atmosphere. Lead occurs primarily in the atmosphere in elemental form as aerosol particles or as a number of chemical compounds. In the atmosphere Cd is also primarily attached to aerosol particles, but little is known about its forms of occurrence.

In this study we have investigated the deposition of Hg, Cd, and Pb in northern Finland in 1985, 1990, 1995, and 2000, based on the national, heavy-metal moss surveys (Poikolainen et al., 2004). We have compared furthermore these results in northern Finland to the results in all Finland. The surveys are carried out as a part of the Nordic and pan-European heavy-metal surveys on mosses (Rühling et al., 1987; Buse et al., 2003). Mosses are excellent heavy-metal biomonitors because they obtain most of their nutrition from wet and dry deposition. The fact that mosses lack a cuticle, the presence of which is characteristic of all other higher forms of vegetation, promotes the accumulation of heavy metals and other air pollutants in mosses. The same moss species can be used as biomonitors in nationwide surveys owing to their broad distribution.

Materials and Methods

Changes in Hg, Pb, and Cd concentrations in mosses were studied in the region located north of the Arctic Circle in northern Finland.

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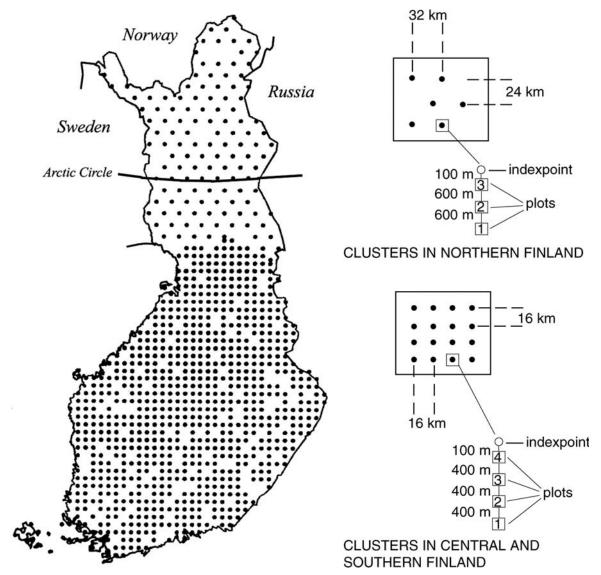


FIGURE 1. Permanent sample plots of the National Forest Inventory in Finland.

These results were compared to the concentrations in all Finland. The study was based on the nationwide heavy metal surveys carried out on the permanent sample plots of the National Forest Inventory (NFI) in 1985, 1990, 1995 and 2000 (Poikolainen et al., 2004). The sample plot network consisted of sample plot clusters located 16 km apart in southern and central Finland, and 24 to 32 km apart in northern Finland (Fig. 1). Each cluster had four sample plots in southern and central Finland, and three in northern Finland. The moss samples were collected each survey year from 950 clusters throughout the country, ca. 80 of which were located to the north of the Arctic Circle. The samples were collected on at least two of the sample plots in each cluster.

The samples were collected in accordance with the Nordic instructions (Rühling et al., 1987). Glittering feather moss (*Hylocomium splendens*) was primarily sampled, but red-stemmed feather (*Pleurozium schreberi*) was sampled if glittering feather moss was not present. The moss samples were cleaned and dried (+35°C), and the three annual growth sections (weighing ca. 2 g/plot) were removed for analysis. The samples were homogenized in a ceramic mill.

The Cd and Pb concentrations were determined on samples from every survey year, and the Hg concentration on samples taken in 1995 and 2000. The Hg concentration was determined on samples from approximately 1/3 of the sample plot clusters in 2000. The Cd and Pb concentrations were determined, after wet digestion with HNO₃/

HClO₄, by inductively coupled plasma atomic emission spectrometry (ICP-AES). For the determination of Hg, the samples were digested (HNO₃/H₂O₂) in sealed digestion tubes in a microwave oven. The Hg concentration was determined by the cold vapor method (CV-AFS; Lippo et al., 1997). The preparation, digestion, and Hg determinations were carried out at the Muhos Research Station (Metla), and the determination of Cd and Pb at the Central Laboratory (Metla) in Vantaa. The quality of the analysis was controlled by means of reference moss samples (Steinnes et al., 1997) and commercial reference samples (NIST SRM 1572, NIST SRM 1573a).

The statistical significance of changes in the Hg, Cd, and Pb concentrations in the study area and in all Finland were determined using Tukey's test. The occurrence of heavy metals on the area to the north of the Arctic Circle was analyzed using Principal Component Analysis, PCA. The variables used were all of the heavy metals included in the national heavy metal surveys: Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn, and As, which behaves in the same way as a heavy-metal but is a nonmetal.

Results

The Hg, Cd, and Pb concentrations were relatively low at the beginning of the study period in the region to the north of the Arctic Circle. In 1995 the average Hg concentration was $0.037 \mu g g^{-1}$, and in

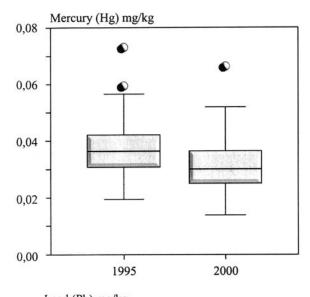
Lead, cadmium, and mercury concentrations (mg kg⁻¹) in mosses (Hylocomium splendens or Pleurozium schreberi) beyond the Arctic Circle in northern Finland and in all Finland in 1985, 1990, 1995, and 2000 (mean, median, standard deviation, minimum, maximum)

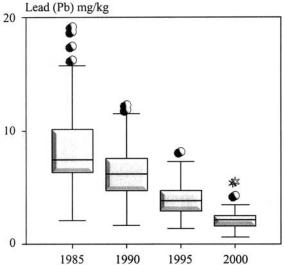
	Pb		Cd		Hg	
Year	Northern Finland	All Finland	Northern Finland	All Finland	Northern Finland	All Finland
1985						
Mean	8.31	15.5	0.17	0.37	_	_
Median	7.43	14.2	0.16	0.36	_	_
S.D.	3.34	6.42	0.07	0.14	_	_
Min	2.07	2.07	0.03	0.03	_	_
Max	19.0	49.9	0.41	1.46	_	_
1990						
Mean	6.28	10.2	0.15	0.28	_	_
Median	6.15	9.40	0.15	0.27	_	_
S.D.	2.20	4.19	0.05	0.11	_	_
Min	1.70	1.70	0.04	0.04	_	_
Max	12.3	31.8	0.32	0.97	_	_
1995						
Mean	3.97	6.22	0.14	0.18	0.037	0.053
Median	3.85	5.64	0.13	0.17	0.036	0.047
S.D.	1.39	2.62	0.04	0.06	0.009	0.022
Min	1.40	1.07	0.07	0.03	0.019	0.017
Max	8.12	19.3	0.25	0.67	0.073	0.150
2000						
Mean	2.13	3.37	0.08	0.12	0.031	0.048
Median	2.12	2.96	0.08	0.12	0.030	0.042
S.D.	0.72	1.42	0.04	0.04	0.010	0.023
Min	0.65	0.65	0.01	0.01	0.014	0.014
Max	5.50	10.0	0.18	0.42	0.066	0.180

1985 Cd $0.17~\mu g~g^{-1}$, and Pb $8.3~\mu g~g^{-1}$ (Table 1, Fig. 2). In PCA the two main components explained 53% of the variation in the data. The first principal component identified Pb, V, Fe, Cr, and Cd, and the second Cu and Ni. In the southwestern part of northern Finland, the Cd and Pb concentrations were obviously higher to the south than to the north of the Arctic Circle. The differences in the Hg concentrations between the different parts of northern Finland were relatively small.

During the study period, the average Cd and Pb concentrations clearly decreased at the same time as the concentration differences within northern Finland decreased (Figs. 3, 4, 5). The decrease in the Pb concentrations was statistically highly significant (P < 0.001). In 2000, the average Pb concentration was only ca. 2 $\mu g \, g^{-1}$. The change in the Cd concentrations did not become statistically significant until 1995 and 2000. The average Cd concentration in 2000 was 0.10 $\mu g \, g^{-1}$. In the northernmost part of Finland, the Pb and Cd concentrations were in general the average values given above. The Hg concentrations decreased slightly in the area to the north of the Arctic Circle between 1995 and 2000, but the change was not statistically significant.

At the beginning of the survey period in 1985, the Cd and Pb concentrations were clearly the highest in the southernmost part of Finland, and they followed a decreasing trend on moving northwards; the lowest concentrations occurred in the area to the north of the Arctic Circle. The Cd concentrations in Finland decreased from 1985 to 2000 by an average of ca. 67%, and the Pb concentration by 78%. The concentrations of both heavy metals decreased, in relative terms, the most in southern Finland. The Cd concentration in southern Finland in 1985 were ca. 0.50 $\mu g \ g^{-1}$ and the Pb concentration 25 $\mu g \ g^{-1}$. In contrast, their concentrations in 2000 were ca. 0.18 $\mu g \ g^{-1}$ and





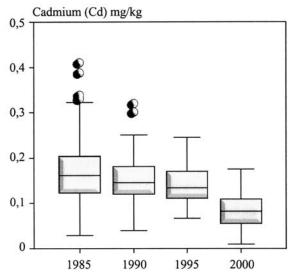


FIGURE 2. Mercury, cadmium, and lead concentrations presented by boxplots in the region to the north of the Arctic Circle (* decreasing statistically significant).

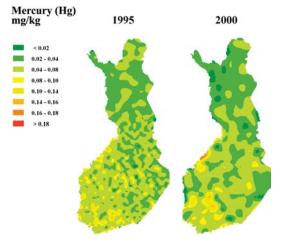


FIGURE 3. Mercury concentration in mosses in Finland in 1995 and 2000.

 $5.0 \ \mu g \ g^{-1}$. The average Hg concentration decreased from 1995 to 2000 by ca. 10%. The concentrations were highest in southern and western Finland. In certain areas they increased to above $0.10 \ \mu g / \ g^{-1}$, but in most areas the concentrations were between 0.04– $0.08 \ \mu g \ g^{-1}$. These

concentration values however, remained in average twice as high compared to the samples from the northernmost parts of Finland.

Discussion

The Cd and Pb concentrations on the northern side of the Arctic Circle in northern Finland are the lowest in the whole of Europe, and at the same level as in neighboring areas in northern Sweden and northern Norway (Steinnes et al., 2001; Buse et al., 2003). Low concentrations indicate a low level of deposition because the Pb and Cd concentrations in mosses have proved to correlate well with the concentrations measured in wet deposition (Berg et al., 1995). The concentrations in mosses in northern Finland are in good agreement with the concentrations measured in wet deposition and in the air in the same areas (Leinonen, 2001).

The decrease in Pb and Cd concentrations in northern Finland is due to the reduction of local emissions and the decrease in long-range transboundary deposition. There are very few anthropogenic emission sources of Pb and Cd on the northern side of the Arctic Circle in northern Finland; most of the sources are small district heating plants and traffic. Along the coast of the Gulf of Bothnia on the southern side of the Arctic Circle there are a number of metal- and wood-processing plants that emit Cd and Pb. There are also large smelters on the neighboring Kola Peninsula in northwestern Russia, but their Cd and Pb emissions are low compared to the Cu and Ni emissions. The local environmental conditions, as the nutrient conditions on the site and

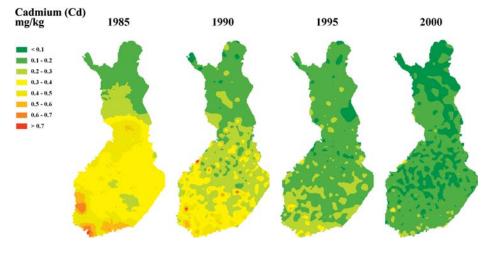


FIGURE 4. Cadmium concentration in mosses in Finland in 1985, 1990, 1995, and 2000.

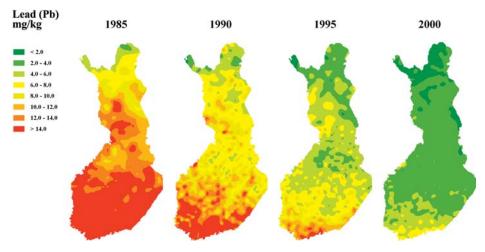


FIGURE 5. Lead concentration in mosses in Finland in 1985, 1990, 1995, and 2000.

"local dust" have also effects on the concentrations of cadmium in mosses (Økland et al., 1999).

Based on principal component analysis, Pb, Cd together with V, Cr, and Fe formed a distinct group. Their occurrence together suggests long-range transport. Chromium mainly originates from the stainless steel plant at Tornio on the coast of the Gulf of Bothnia. A considerable part of the Pb and Cd most probably originates also from industrial plants and traffic in the coastal area of the Gulf of Bothnia. A part of the Pb and Cd deposition in Finland originates from abroad (Ilyin et al., 2003). According to model calculations, most of the Pb and Cd deposited in Finland comes from Russia and Poland (Ilyin et al., 2002). The proportion of long-range transboundary deposition out of total deposition decreases on moving from south to north, and a corresponding trend has also been observed in Cd and Pb concentrations in Fennoscandia (Berg et al., 1995). The importance of long-range transboundary transport in deposition in northern Finland has decreased during the last two decades because especially Pb emissions have decreased throughout almost all parts of Europe. Lead deposition has been estimated to have decreased in Europe between 1990 and 2001 on the average 2.7-fold and Cd deposition 1.5-fold (Ilyin et al., 2003). During the same period the Cd and Pb concentrations in mosses have decreased in Western and Northern Europe especially (Buse et al., 2003). Although the Pb and Cd deposition in northern Finland is low, and the concentrations in mosses and herbaceous plants have decreased, considerable amounts of Cd and Pb have accumulated over the decades in the soil and sediments in arctic areas, and they will continue to have an influence on the ecosystems for a considerable period of time.

The Hg concentrations in mosses in northern Finland are also relatively low compared to the highest measured concentrations in Europe (Buse et al., 2003). It is worth noting that, although the Hg concentrations in Finland and Norway (Steinnes et al., 2003) are the highest in the southern parts of the two countries, there are no significant differences between the different parts of the countries. A similar situation has been reported for the Hg concentrations the epiphytic lichen Hypogymnia physodes in Finland (Lodenius, 1981). No large differences have been recorded in Hg concentrations in the air between 1996 and 2001 between the southern and northern parts of Fennoscandia; the concentrations have varied between 1.3 and 1.6 ng m⁻³. In contrast, the Hg concentrations in wet deposition in the southern parts of Fennoscandia have been significantly higher than those in the northern parts (Wängberg et al., 2002). The Hg concentrations measured in mosses are likely to provide more accurate information about the total deposition of Hg than the mercury concentrations in wet deposition (Steinnes et al., 2003). It has even been proposed that, in the cool climate of the northern parts of Fennoscandia where the wet deposition of Hg is low, mosses can retain larger quantities of gaseous mercury, and that the volatilization of Hg back into the air is smaller than that in the south (Steinnes et al., 2003).

In northern Finland, and in other northern parts of Fennoscandia, anthropogenic emissions of Hg are small. According to model calculations, Hg spreads into arctic areas primarily from Central Europe, Southeast Asia, the east coast of North America, and from natural sources in the oceans (Ilyin et al., 2003). It has been estimated that one half of the Hg deposition in arctic areas originates from outside the area. Anthropogenic emissions and total deposition of Hg decreased during the 1990s throughout the whole of Europe (Ilyin et al., 2003). Mercury emissions in Finland decreased during the 1990s from 1100 to 650 kg (Mukherjee et al., 2000). However, the decrease in emissions has not had any significant decreasing effect on Hg concentrations in mosses in the northernmost parts of Finland. This can be caused by the transporting of mercury to the north from the emission sources outside Europe or that mercury deposit easier in cold climate.

Considerable conversion of elemental mercury (Hg⁰) into reactive mercury [Hg(II) and pHg] occurs via number of chemical reactions in arctic marine areas during the arctic spring. Reactive mercury then readily passes into the snow and vegetation (Schroeder et al., 1998, Steffen et al., 2002). The bromine (Br) and chlorine (Cl) compounds evaporating from the sea apparently act as catalysts for these chemical reactions. These changes in Hg species in arctic areas are apparently related to the global circulation of Hg. These processes are responsible for the movement of Hg from the air into different food chains. The Hg concentrations measured in mosses do not indicate that the accumulation of Hg in snow and vegetation would occur in significant quantities in northern Finland. Little is known about the capacity of mosses to accumulate Hg. More information is needed especially about the mechanisms involved in the scavenging of gaseous mercury, and about the variation in Hg concentrations in mosses at different times of the year. It is likely that the binding of Hg and its volatilization back into the atmosphere is affected by the properties of mosses, the air temperature, amount of light, rain, and the air currents in these areas.

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