The fate of airborne lead pollution in boreal forest soils

by

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AKADEMISK AVHANDLING

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Examinator: Professor Ingemar Renberg, Umeå universitet
Opponent: Professor John G. Farmer, University of Edinburgh, Scotland
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Abstract
Lead has a more than three-millennia-long pollution history in Europe. Metal production, burning of coal and use of leaded petrol resulted in a significant pollution of the atmosphere. As a consequence of atmospheric fallout, the Swedish boreal forest is strongly contaminated by airborne lead pollution. High levels of lead in the soil and soil pore water are of concern because the soil fauna, plants and aquatic biota may respond negatively to this toxic element. The fate of the accumulated pool of pollution in the soil is not well known.

In this thesis, I determine four variables of importance for increasing our knowledge about the past, present and future lead levels in the boreal forest soil: 1) the pre-pollution atmospheric deposition rate of lead; 2) the upward flux of lead from deeper soil layers to near-surface horizons as a result of plant uptake; 3) the mean residence time of lead in the mor layer (the organic horizon at the surface of forest soils); and 4) the vertical and lateral transport of pollution lead within the mineral soil and to streams. Lead concentration measurements and stable lead isotope analyses were used for distinguishing pollution lead from natural lead in cores from ombrotrophic bogs, forest soil profiles, forest mosses, soil-water and stream-water samples.

The results clearly stress that the boreal forest ecosystem is totally dominated by pollution lead. This is proved by low \( \frac{^{206}\text{Pb}}{^{207}\text{Pb}} \) ratios (mainly between 1.14 and 1.20) in the mor layer, forest plants and stream water, while the local geogenic lead of the mineral soil (C-horizon) has high ratios (> 1.30). The dominance of pollution in the mor layer is caused by high deposition rates of airborne lead pollution, minute transport rates of lead from the mineral soil by forest plants (about 0.02 mg lead m\(^{-2}\) year\(^{-1}\)) and a long mean residence time of the deposited lead (~250 years for mature forest). In the pristine pre-pollution environment, lead was a rare element due to low atmospheric deposition rates (0.001 to 0.01 mg m\(^{-2}\) year\(^{-1}\)). It is estimated that the present lead inventory in the mor layer is up to 100 times higher than in the pristine environment where \( \leq 8 \) mg m\(^{-2}\) was present in the mor. The levels in this biologically important horizon will decrease at a very slow rate and it will take centuries for the deeper part of the mor layer to fully respond to decreasing atmospheric inputs. In a hypothetic scenario with a ceased atmospheric lead deposition, the pool of pollution lead will ultimately be redistributed to deeper water-saturated soil layers from where a lateral transport to surface waters occurs. In the studied catchment, the export of pollution lead from the soil to the stream is estimated to peak slightly about one thousand years from now.

Key words: Air pollution, lead, lead isotopes, peat, forest soil, forest plants
List of papers
This thesis is based on the following papers, which will be addressed in the text according to their Roman numerals


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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>OBJECTIVE</td>
<td>3</td>
</tr>
<tr>
<td>MATERIAL AND METHODS</td>
<td>4</td>
</tr>
<tr>
<td>Lead isotopes</td>
<td>4</td>
</tr>
<tr>
<td>Study material and study sites</td>
<td>4</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>4</td>
</tr>
<tr>
<td>Pre-pollution atmospheric deposition rates of lead</td>
<td>4</td>
</tr>
<tr>
<td>Fluxes of lead as a result of plant uptake</td>
<td>6</td>
</tr>
<tr>
<td>Mean residence time of lead in the mor layer</td>
<td>7</td>
</tr>
<tr>
<td>Vertical and lateral transport rates of pollution lead in the mineral soil</td>
<td>8</td>
</tr>
<tr>
<td>Background concentrations of lead in the mor layer</td>
<td>9</td>
</tr>
<tr>
<td>CONCLUDING REMARKS</td>
<td>9</td>
</tr>
<tr>
<td>FUTURE PERSPECTIVES</td>
<td>10</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>11</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>12</td>
</tr>
<tr>
<td>APPLÅDEN!</td>
<td>17</td>
</tr>
</tbody>
</table>
INTRODUCTION

Lead is probably the most dispersed metal pollutant in the environment. This toxic element has been emitted into the atmosphere since the birth of metallurgy in ancient times and with increasing intensity since the establishment of medieval and modern industries (SETTLE and PATTERSON, 1980; RENBERG et al., 1994). The first pollution in Europe came from small local smelting facilities around the Mediterranean Sea and Asia Minor (NRIAGU, 1983) and the emission increased later along with the onset of large-scale mining activities, burning of fossil fuel and, in the past century, the combustion of lead-containing fuel (BRÄNNVALL et al., 1999). This long-term atmospheric lead pollution has resulted in an extensive contamination of the Northern Hemisphere.

The enrichment of lead in the environment following atmospheric fallout was noticed by scientists in the 1960s (WARREN and DELAVAUT, 1960; CANNON and BOWLES, 1962). High lead concentrations were found adjacent to roads and urban areas, which caused increasing concerns about human health and environmental effects (HARDY et al., 1971). Analyses of the lead content of forest mosses became an important tool for biomonitoring of the atmospheric deposition in Scandinavia (TYLER, 1970), and a national survey in Sweden, re-occurring every fifth year since 1970, found a strong south-north pollution gradient where the northern parts of Sweden appeared unaffected (RÜHLING and TYLER, 1971). A similar south-north gradient was also discovered in Norway (ALLEN and STEINNES, 1980). Higher lead concentrations in the south suggested influence of long-range transported air pollution from heavily industrialised areas in continental Europe. Increased environmental concern in Sweden and elsewhere in the western world resulted in the implementation of stronger environmental policies and a phase out of lead as an anti-knock additive in petrol. Decreased emission as a consequence of the harder restrictions resulted in decreasing lead concentrations in forest mosses, and in 1995 the concentration in mosses from all over Sweden had reached levels only found previously at the most remote sites in northern Sweden (RÜHLING and TYLER, 2001). However, even though the historic lead production rates were known quite early (SETTLE and PATTERSON, 1980) and local pollution in the vicinity of historical mining and processing sites in Britain had been demonstrated (LEE and TALLIS, 1973), it was not until recently that the importance of the atmospheric deposition of long-range transported lead in pre-industrial times was recognized.

Using lead concentration measurements of lake sediments from Sweden, Renberg et al. (1994) showed that the variation in the lead content of the sediment could be explained by long-range transported pollution from early mining activities starting as early as 2600 years ago. This evidence from Swedish lakes was backed up by data from the Greenland ice record (HONG et al., 1994; ROSMAN et al., 1997) and lead isotope analyses of peat (BRÄNNVALL et al., 1997; SHOTYK et al., 1998) and lake sediment records (BRÄNNVALL et al., 1999). In Europe, the pre-industrial pollution was substantial; estimates from the sediment records in Sweden show that about half of the cumulative load of atmospheric lead was deposited prior to AD 1800 and that the present deposition is similar to that of the medieval era (BRÄNNVALL et al., 1997; BRÄNNVALL et al., 2001b).

Until the 1990s investigations of lead pollution of forest soils only applied concentration analyses. Most studies found that lead concentrations of soil samples and vegetation were generally much lower in northern Sweden and northern Norway than in continental Europe (RÜHLING and TYLER, 1971; ALLEN and STEINNES, 1980; ANDERSSON et al., 1992; RÜHLING et al., 1996). From the lower lead concentrations in the north spawned a belief that northern Scandinavia was a ‘refuge’ from air pollution and, thus, a good representative of ‘natural’ or ‘background’ conditions. A belief that still seems deeply rooted among the general public, and among some
scientist’s too. However, the introduction of stable isotope analyses of forest soils and lake sediments, a technique that allows differentiation between natural and pollution derived lead, showed extensive spatial pollution of the Swedish forest and suggested that the soil has accumulated about 0.7 g m$^{-2}$ in northern Sweden and as much as 3.1 g m$^{-2}$ of atmospheric lead in the southern part (BINDLER et al., 1999; BRÄNNVALL et al., 2001a). The fate of this pool of pollution lead stored in the soil is not well known. Will it stay in near-surface soil horizons until the next ice age? Will it migrate down into deeper soil layers leading to a self-cleaning process of the surface? Will it pollute our forest streams in the future?

Another gap in our knowledge is the limited understanding of past lead levels in the pre-pollution environment. Assessment of the contemporary pollution status of the environment requires knowledge about natural conditions. The Swedish Environmental Protection Agency defines the natural background concentration of a metal as: “the concentration existing in the environment before anthropogenic impact occurred, i.e. the concentration in an unaffected ecosystem” (NOTTER, 1993). Determining the natural concentration in the organic layer of forest soils — the main habitat for soil animals and plant roots — has been the focus of several previous studies. Estimates have been made using the lowest concentration found in remote regions (ALLEN and STEINNES, 1980; ANDERSSON et al., 1992) and the lower percentiles of distribution functions from large data sets (MATSCHULAT et al., 2000). The limitations with these two approaches are that they can only identify the lowest levels in an already polluted world. To overcome the fact that there is no place within the forest today where natural levels of lead can be measured, Johansson et al. (1995) estimated the background concentration of lead in the organic horizon (from here on refer to as the mor or mor layer) by combining present levels in the mor with pollution time trends from lake sediments. They found that lake sediments in northern Sweden had experienced a two-fold relative increase in the lead concentration and argued that the natural background concentration of lead would be half the present concentration of about 15 mg lead kg$^{-1}$ found in remote areas in northern Sweden. However, the analyzed sediment cores were only 25-30 cm long and represented only the relative increase during the last hundred years in the lakes. This estimated background was, therefore, suggested to be an overestimation (BINDLER et al., 1999), due to the several-thousand-year-long atmospheric pollution history in Sweden (BRÄNNVALL et al., 1999). In the study by Bindler et al. (1999), the natural background value of lead in the mor layer was calculated using the estimated pre-pollution atmospheric deposition and the residence time of atmospheric lead in the mor layer. The estimate of the pre-pollution atmospheric deposition rate was derived from ombrotrophic peat archives, i.e. peat that receives elements solely from the atmosphere, and residence time of lead was derived from organic horizons in North America (MILLER and FRIEDLAND, 1994; JOHNSON et al., 1995; WANG and BENoit, 1997). Bindler and co-workers calculated that the natural concentration of lead in the mor layer could be as low as 0.1 mg kg$^{-1}$, which is up to 1000 times lower than the present levels (BINDLER et al., 1999). High lead levels, in comparison with levels in a pristine, pre-pollution environment, are of concern since soil microbes and soil animals respond negatively to increases in the lead burden of the soil (RÜHLING and TYLER, 1973; BRINGMARK et al., 1998; PALMBORG et al., 2001; LASKOWSKI et al., 2003).

However, the model used for calculating the background concentration in the mor layer by Bindler et al. (1999) was tentative and included two assumptions that could not be fully validated and needed further scrutinizing. First, the model assumed that the input of lead to the mor from plant uptake was insignificant. Although lead is not an essential element (MARKERT, 1992) and is considered relatively unavailable for biological uptake, it is suggested that lead can be taken up from forest soils by plants (PETERSON and FRY, 1987; GJENGEDAL and STEINNES, 1994; JOHNSON et al., 1995; BINDLER et al., 2004b) at rates sometimes comparable to the annual atmospheric deposition rates (BERGKVIST, 2001). Actually, one of the first interpretations of the
high concentrations of lead in the upper organic horizon of soil was that the lead was enriched in this layer due to plant uptake (SWAIN and MITCHELL, 1960), a theory that has persisted long and is still advocated (RASMUSSEN, 1998). The second uncertainty of the model was the application of turnover rates originally derived from sites in North America to Swedish conditions. The rationale for using literature values from America was the lack of similar estimates for Sweden. Swedish estimates of the turnover time of lead in the upper organic layer existed, but these were derived using steady-state assumptions that were strongly criticised due to the variable input of atmospheric lead over time (MILLER and FRIEDLAND, 1994; WANG and BENoit, 1997). How representative these estimates from hardwood forests in America were for Swedish conditions was difficult to evaluate. The organic layer of the Swedish podzolic forest soils, is a well-defined layer with a humus form of mor type (KLINiKA, 1997). This organic layer is by definition essentially un-mixed with the mineral soil due to the limited activity of digging soil animals. These characteristics differ from the organic horizon developed under a hardwood forest, where the litter stimulates a more active digging soil fauna, which mixes the soil and results in the development of organic layers of moder or mull humus types (METZ, 1954). The apparent biophysical differences between these organic layers stressed the need for including new Swedish estimates of the turnover rate of lead in the mor layer into the model.

**OBJECTIVE**

The main objective of this thesis was to provide better knowledge about the fate of airborne lead pollution within boreal forest soils by using stable lead isotope analyses as a tracer of lead derived from pollution and local soil minerals. It tries to determine four fundamental variables for predicting past and future changes in the soil pollution lead pool; 1) the pre-pollution atmospheric deposition rate of lead (paper I); 2) the upward flux of lead from deeper soil layers to the mor layer as a result of plant uptake (paper II); 3) the turnover time of lead in the organic horizon (paper III); and the vertical and lateral transport rates of pollution lead in the mineral soil (paper IV). A schematic model including the four variables is illustrated in Figure 1.

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Figure 1. Conceptual picture of a forest soil profile and arrows illustrating the four main variables that this thesis tries to determine.
MATERIAL AND METHODS

**Lead isotopes**

Lead isotope analysis provides a neat way to distinguish between lead derived from pollution and from natural sources within an ecosystem. The potential of the technique for environmental studies was already demonstrated in the 1970’s (AULT et al., 1970) and through some pioneer work in the 1980’s (SHIRAHATA et al., 1980). It was, however, not until the late 1990’s that the technique was applied more broadly by environmental scientists when the necessary analytical instruments became common equipment at environmental laboratories.

The theory of distinguishing pollution-derived lead from local geogenic (natural) lead is based on differences in the proportion of lead with the atomic masses 204, 206, 207 and 208. Pollution lead is derived from sulphide ore deposits or from coal, whereas the local geogenic lead originates from lead-containing minerals within the soil, commonly referred to as ‘rock-derived’ lead. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of most coal bodies and ores, from which industrial and petrol pollution lead is derived, is typically between 1.04 and 1.20 in Europe (BROWN, 1962; SUGDEN et al., 1993; MONNA et al., 1997; FARMER et al., 1999). As a result, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the Swedish atmosphere, consisting of emissions from a mixture of different pollution sources, ranges typically between 1.13 and 1.17 (HAPPER et al., 1991; ROSMAN et al., 1998; BINDLER et al., 2004a). In contrast, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the lead derived from soil minerals has a ratio above 1.30 in Sweden (BRÅNNVALL et al., 2001a). Lead with the atomic mass of 206 and 207 is produced by the radioactive decay of uranium isotopes ($^{238}\text{U}$ and $^{235}\text{U}$, respectively). More lead with the atomic mass 206 is produced over time in relation to lead with the atomic mass of 207, causing the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio to increase with increasing age if a sufficient amount of uranium is present. High $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the lead found naturally in the Swedish soil is due to the old and uranium-rich bedrock. The low ratio for lead in ores is an effect of the separation from the uranium source during the ore formation a long time ago (FAURE, 1986). Because of significant difference in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio between rock-derived and pollution-derived lead it is possible to distinguish the pollution fraction from the natural.

**Study material and study sites**

This thesis is based on stable isotope analyses (mainly the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) and lead concentration analyses of peat cores from ombrotrophic bogs, soil profiles, forest mosses from a herbarium collection (spanning the last 120 years) and of soil-water and stream water samples (Figure 2). Solid soil samples from deep mineral soil layers (50-120 cm) were used for determining the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the rock-derived lead, whereas the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the atmospheric pollution was determined from analyses of ombrotrophic peat and forest mosses.

RESULTS AND DISCUSSION

**Pre-pollution atmospheric deposition rates of lead**

Lead was one of the first metals to be produced (NRIAGU, 1998) and the method to extract lead from sulphide ores was discovered about 5500 years ago by the early cultures around the Mediterranean Sea and Asia Minor (NRIAGU, 1983). The introduction of coinage in Europe about 3500 years ago resulted in an increased exploitation of lead-containing silver ores (SETTLE and PATTERSON, 1980). Prior to 3500 BP lead production and emissions to the atmosphere were low and Brännvall et al. (1997) and Renberg et al. (2000) also found the first indications of atmospheric pollution about 3500 years ago by identifying changing lead concentrations and
$^{206}\text{Pb}/^{207}\text{Pb}$ ratios in ombrotrophic peat and lake sediments. Low atmospheric flux rates of about 3-11 µg m⁻² yr⁻¹ prior 3500 BP were calculated from three ombrotrophic bogs in Sweden (BINDLER et al., 1999) and one in Switzerland (SHOTYK et al., 1998). My calculated atmospheric deposition rates between 5900 and 3700 BP from the three studied bogs are in the range of 1-10 µg Pb m⁻² yr⁻¹ (Paper I), which confirm the findings of the previous studies that the deposition during this time was 100 to 1000 times lower than the present.

The low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the bogs also prior to about 3500 BP suggest that the atmospheric deposition of lead to the Swedish forest landscape was mainly dependent upon transport from distant sources (Figure 3). Unpolluted Swedish mineral soils (C-horizons) have much higher isotopic ratios than the lead in the bogs and this lead can not have been derived from Swedish mineral soils (Figure 3). Several samples from two periods at 5400-5000 BP (event 1, paper I) and 4100-3800 BP (event 2, paper I) have an isotopic composition that can only be explained by inputs from a source with $^{206}\text{Pb}/^{207}\text{Pb}$ ratio as low as 1.16 (Figure 3).

Even though data on the isotopic composition of different natural sources of atmospheric lead are sparse and show large heterogeneity, none of the likely natural sources have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio below 1.17. The similarity in $^{206}\text{Pb}/^{206}\text{Pb}$ ratios between samples from event 1 and event 2 and lead derived from ore deposits from early European mining districts (YENER et al., 1991; STOS-GALE et al., 1995; ROHL, 1996; SAYRE et al., 2000) suggests that these samples consist, at least partly, of pollution lead. Processing of lead ores, as mentioned earlier, has a long history and Greek mines operated well before 5000 BP (Eliot et al., 1937), which makes pollution from early metal-using civilizations fully possible. At the time of event 2 (~4000 BP), exploitation of Pb ores also occurred on the British Isles (NRIAGU, 1983). Vertical downward migration of modern pollution seems to be an unlikely explanation for the low ratios in the deeper peat as discussed in paper I. However, the later finding in paper IV suggests that also deep groundwater might be contaminated, which introduces a possibility that the peat can receive lead with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.16 through groundwater flow. It is not likely that this contamination occurred through upward groundwater flow, since basal ombrotrophic peat layers in Sweden have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios above 1.3 (BRÄNNVALL et al., 1997). Still, contamination by lateral flow...
Box-plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios found for potential local and distant sources of atmospheric Pb in comparison with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the analyzed peat. Local soil sources are represented by Swedish and Danish C-horizons (15 and 4 sites, respectively) and lake sediments older than 3000 years reflecting soils within the catchments (30 sites). Distant natural sources are represented by global soil-dust sources ($n=28$), including the Sahara desert, used for provenance determination of aeolian dust in the Greenland ice (Sun, 1980; Biscaye et al., 1997), volcanic rocks from Italy ($n=73$) (Fitchen and Upton, 1987; Ayuso et al., 1998), and volcanic rocks from Iceland ($n=36$) (Sun, 1980). Pollution sources are represented by reported $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of ores and artifacts from early active mining districts in Anatolia, the Balkans, the British Isles, Greece and the Iberian peninsula ($n=522$) (Yener et al., 1991; Sayre et al., 1992; Arribas and Tosdal, 1994; Stos-Gale et al., 1995; Rohi, 1996; Stos-Gale et al., 1998; Sayre et al., 2000) and modern aerosol data from south-east Sweden ($n=35$) (Rosman et al., 1998).

It could be a possibility. Recent studies have, however, found $^{206}\text{Pb}/^{207}\text{Pb}$ ratios around 1.17 in 4000-year-old peat in England (Le Roux and Weiss, 2004) and ratios as low as 1.14 for 5500-year-old peat in Spain (Kylander et al., 2005). $^{206}\text{Pb}/^{207}\text{Pb}$ ratios lower than known natural sources in peat bogs with different hydrology indicate that the low ratio of the peat might be a reflection of a large-scale lead atmospheric source rather than contamination by groundwater. A more precise determination of why peat with very old and similar ages from different parts of Europe has low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios needs further studies. Is it so that we have underestimated the impact on the atmosphere by early civilizations or is there an important natural source(s) of lead for Europe having a $^{206}\text{Pb}/^{207}\text{Pb}$ below 1.17? It is my belief that future studies that tries to resolve these questions have to address in depth the issue of pollution lead potentially moving laterally within the peat to deliver an answer in a convincing way.

**Fluxes of lead as a result of plant uptake**

The above-ground inventory of lead in the standing vegetation in undisturbed forests is very small in comparison to that of the soil. The estimated inventory of lead in plant biomass is about 1 mg lead m$^{-2}$, which is less than 1 % of the total amount of lead found in the mor layer and constitutes only 0.001 % of the lead found in the upper 90 cm of the soil (paper II). This clearly supports the conclusions from previous studies suggesting that the uptake of lead from the soil is small (Berthelsen et al., 1995; Reimann et al., 2001). Most of the lead taken up by plant roots originates, not surprisingly, from pollution stored in the mor layer where most of the roots are found. What is more surprising though is that a large part (about 50 %) of the lead incorporated
into the biomass of Scots pine (*Pinus sylvestris*) seems to be derived from uptake directly from the atmosphere, as indicated by lower \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios for needles, bark and apical wood in comparison to roots and basal stemwood (paper II). Previous laboratory and field experiments have indicated that trees are capable of a direct uptake of atmospheric lead (LEPP and DOLLARD, 1974; LINDBERG et al., 1982; BERTHELSEN et al., 1995; WATMOUGH and HUTCHINSON, 2003) but the extent of this process has not been demonstrated before.

The total uptake rate of lead from the mineral soil and the mor layer is estimated to be about 0.02 and 0.03 mg lead m\(^{-2}\) yr\(^{-1}\), respectively, which is small in comparison to the modern atmospheric inputs of about 0.5-3 mg lead m\(^{-2}\) yr\(^{-1}\) (RÜHLING and TYLER, 2001). Thus, the atmosphere is at present the main source of lead to the mor layer, in contrast to conditions prevailing in the pristine environment (prior to ~ 3500 BP). The small amount of lead taken up annually by plants does not support the suggestion that the enrichment of lead in organic layers of forest soils is a result of plant cycling as previously advocated (RASMUSSEN, 1998). Our single estimate from the site in Arvidsjaur gives, however, no measure of the variability in uptake rates of lead within the boreal forest. There are indications that different plant communities can have different uptake rates, since it is obvious from the study in paper II that plant species differ in their uptake of lead. For example, birch and juniper seem to accumulate lead within their tissue to a higher extent from the soil or from somewhat deeper depths than pine judging from the higher \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios for these plants. Birch is known for improving the soil quality by transporting cations from deeper mineral soil layers (STONE, 1975; REIMANN et al., 2001) and uptake of lead from deeper soil layers containing mainly local geogenic lead could explain the higher \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios for this plant. An additional explanation could be that birch and juniper take up less lead directly from the atmosphere. Higher deposition rates of atmospheric lead pollution than at our study site in Arvidsjaur will likely also result in higher uptake rates of pollution by plant roots and above ground plant compartments. Studies from hardwood forests in N. America with higher atmospheric deposition rates of lead have found 10 to 100 times higher lead inventories in biomass than in our study (JOHNSON et al., 1995; WATMOUGH and HUTCHINSON, 2004).

**Mean residence time of lead in the mor layer**

Lead is continuously transported downwards from the mor layer and lost to the mineral soil due to biogeochemical and physical migration processes, mainly through co-transport with organic particles and colloids (TYLER, 1981; DÖRR and MÜNICH, 1991; WANG and BENOIT, 1996). A limited plant uptake of lead from the mineral soil suggests that only minor proportions of the lead lost through migration processes to the mineral soil will be ‘pumped’ back to the mor layer (paper II). The low \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios of about 1.15-1.16 for the mor layer in a mature forest (> 120 years) in comparison with mineral soil layers (paper III), suggest that in-mixing of mineral grains and upward transport of lead from the mineral soil as a result of the activity of burrowing soil animals is negligible. The limited upward transport of lead will result in an intrinsic ‘self-cleaning’ of the mor layer and the lead content of the mor layer will decrease with time. The rate in which this pool of lead is removed to deeper soil layers has been the focus of several previous studies. The first predictions used the annual loss of lead, estimated from laboratory environments or field sampling with soil lysimeters, to estimate a turnover time of about 450 to 1000 years in this soil layer (TYLER, 1978; TYLER, 1981). However, studies have criticized the earlier approaches by arguing that the steady-state assumption and the short-term studies could not be justified considering the temporal variations in the atmospheric fallout of lead (MILLER and FRIEDLAND, 1994; WANG and BENOIT, 1997). Later studies calculated, based on repeated sampling at the same sites, stable isotope tracing and modelling of past atmospheric inputs, a much shorter mean residence time of 25 to 150 years for lead in organic layers in north-eastern...
USA (Miller and Friedland, 1994; Johnson et al., 1995; Wang and Benoit, 1997; Kaste et al., 2003).

My estimate of a 250-year-long mean residence time of lead in a mature boreal coniferous forest, using three independent approaches that consider the variability of past atmospheric inputs, is intermediate between the earliest estimates from Sweden and the most recent from North America (paper III). However, it is emphasized in paper III that the residence time of lead in the mor layer is a dynamic property that can vary from about 50 years in early succession stages where deciduous trees and grasses dominate to values of around 250 years in mature undisturbed stands. The shorter residence time of lead in the early succession stage is thought to be due to a more rapid decomposition of deciduous litter in comparison to coniferous litter, which would increase the migration velocity of lead (Dörr and Münnich, 1991). The about 250-year-long residence time for lead in the mor layer suggests that the response to the recent decrease in atmospheric pollution will be a more prolonged process in the boreal forest than previously predicted when using residence times of 25 to 75 years originating from estimates for North American soils (Bindler et al., 1999). However, even though the mor layer as a whole will respond slowly to decreased atmospheric lead deposition, it is important to underline that the organic matter in the upper parts of the organic horizon will be replaced by fresh litterfall and the lead in this part of the mor layer (S-layer) will reach equilibrium with the present atmospheric deposition within a few years.

**Vertical and lateral transport rates of pollution lead in the mineral soil**

As a result of the continuous downward transport, lead is redistributed very slowly from the mor layer to deeper, water-saturated mineral soil layers. Through these layers occur a lateral transport of soil water and metals to surface waters (Bishop et al., 1995; Sherrell and Ross, 1999). Slow migration rates in the soil, resulting in turnover times up to several hundred years in the unsaturated soil layers, suggest that most of the pollution deposited since medieval time has not yet reached the saturated zone (paper IV). Hence, there is good reason for expecting increasing lead levels in streams with time as the pollution pool of lead enters into deeper, water-saturated soil layers. The time it will take for the pollution lead to reach groundwater and streams has been discussed in a few studies from North America (Johnson et al., 1995; Kaste et al., 2003). These studies all have in common that they predict an increased export of lead to streams peaking within a few hundred years. According to my estimate, the maximum release of pollution lead will occur about a thousand years from now as a consequence of much slower migration rates of lead in Swedish forest soils. That the lead migration appears to be generally slower at my study sites than in the North American sites is likely a result of a longer mean residence time for the soil carbon pool due to lower mean annual temperatures in northern Sweden (Sanderman et al., 2003), which subsequently results in slower migration rates for lead (Dörr and Münnich, 1991).

It seems, however, unlikely that this build-up and subsequent release of lead will cause a drastic increase in the lateral transport of lead to forest streams; thus this process is not a ‘ticking time-bomb’ that threatens future water quality (Paper IV). Modelling of the transport of lead in a hillslope gradient indicates a maximum increase by a factor of two, which is actually less than the variation within a year. It is my belief that only a dramatic increase in the water table, as a result of climatic change, constitutes a reasonable factor that could alter the studied system towards critical levels of lead in surface waters. Still, it is important to emphasize that even though forest streams will not reach critical levels of lead in the future, it is obvious from our study that they are at present strongly affected by atmospheric pollution and will be so for a very long time.
Background concentrations of lead in the mor layer

The amount of lead in the pristine mor layer can be calculated using the background deposition (paper I), upward-transport of lead by plants (paper II) and the estimated turnover time (paper III). The turnover time ($\tau$) can be considered as the time it would take to empty the inventory of lead stored in the mor layer ($Q$) if the loss of lead ($q$) remained constant. In mathematical terms this is expressed as:

$$\tau = \frac{Q}{q}$$  \hspace{1cm} \text{Eq.1}

Over longer time-scales with a fairly constant background atmospheric deposition it is realistic to assume that the inventory of lead in the mor ($Q$) would approach a steady state, where the losses would approximate inputs from the atmosphere and plants ($q = D + P$). The inventory of lead in the mor during such circumstances could be calculated as:

$$Q = \tau \times (D + P)$$  \hspace{1cm} \text{Eq.2}

Calculations based on my estimates, i.e. a turnover time ranging from 50 to 250 years, a maximum background deposition of 0.01 mg m$^{-2}$ yr$^{-1}$ and a flux of 0.02 mg m$^{-2}$ yr$^{-1}$ from plant uptake of lead from the mineral soil, suggest that the amount of lead stored in the mor layer before large-scale atmospheric pollution was $\leq$ 8 mg m$^{-2}$ (corresponding to an average concentration of $\leq$ 1 mg kg$^{-1}$ considering that the typical dry mass of this layer is around 10 kg m$^{-2}$). This inventory is about 10 to 50 times lower than the present inventories in my study sites (paper II, III and IV) and more than 100 lower than inventories found in southern Sweden (BRÄNNVALL et al., 2001a). Bindler et al. (1999) suggested background inventories in the mor layer of $<0.1$ mg lead m$^{-2}$ (average concentrations $< 0.1$ mg kg$^{-1}$). This inventory is likely too low due to the small but significant uptake of lead from the underlying soil (paper III) and the longer residence time of lead within the Swedish mor layer in comparison to the previous used estimates from American soil.

CONCLUDING REMARKS

One of the most obvious results presented in this thesis is the low $^{206}$Pb/$^{207}$Pb ratio found for major components of the boreal forest in comparison to the lead found naturally in the soil. The mor layer, mosses, trees, shrubs, soil-water and stream water all have $^{206}$Pb/$^{207}$Pb ratios typically around 1.15-1.20, while the C-horizon or bedrock samples have ratios above 1.3 (Figure 4). The isotopic composition of these components cannot be explained without involving a dominant source with a low $^{206}$Pb/$^{207}$Pb ratio. This source is — without doubt — atmospheric pollution originating from metal production, industries and coal burning in Europe, which typically has a $^{206}$Pb/$^{207}$Pb ratio between 1.06 to 1.19 (BROWN, 1962; SUGDEN et al., 1993; FARMER et al., 1999). The majority of lead circulating within the boreal forest is, therefore, derived from atmospheric pollution transported over long and short distances, not from natural sources.

Lead has been, and still is, an important metal for society and emissions to the atmosphere will persist into the future. It is naive to strive for lead levels in the boreal forest as low as in the pristine ancient environment. Even though the suggested background value of $\sim$8 mg lead kg$^{-1}$ by Johansson et al. (1995) is much higher than my estimate (about ten times higher) and more likely represents a value typical for the medieval pollution era, it is far below critical levels (BRINGMARK and BRINGMARK, 2001) and constitutes a more realistic and more achievable environmental goal. In fact, the estimated variables in this thesis predict (Eq. 2) that the average concentration of lead
in the mor will stabilize around a quite similar value (≤ 13 mg kg⁻¹) if the present atmospheric deposition of about 0.5 mg m⁻² yr⁻¹ prevail into the future. It will, however, take several centuries to reach this level in a mature undisturbed forest given the long residence time of lead in the mor layer.

**Figure 4.** Box-plot summarizing the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of different forest compartments analyzed in paper I, II, III and IV. Shown are the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the bedrock and C-horizon in comparison to that of the plants, the mor layer, soil-water, stream water and the airborne pollution indicated by $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the herbarium mosses.

**FUTURE PERSPECTIVES**

In comparison to many other pollutants we know much about the cycle of lead in the environment, mainly due to more than four decades of environmental research on the topic and the possibility to use stable lead isotopes as tracers. Still, there are important gaps in our knowledge that remain, which restrain predictions about past and future lead levels in the boreal forest ecosystem. Below follows some gaps that I consider important for future studies.

As previously discussed, more studies are needed for determining the variability of the upward transport of lead from deeper soil layers to the near surface as a result of plant uptake. However, there are other processes that can cause a similar upward transport of lead within the soil matrix that should be addressed in future studies. Soil animals may cause some mixing of the mor layer and animals that spend parts of their life-cycle in deeper soil layers may transport downward migrated lead back up to the surface again. Even though the low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the mor layer indicates that the in-mixing of mineral grains from the mineral soil as a result of bioturbation has a low importance in the studied soil, this process might become significant in soil with a more active soil fauna. It is, therefore, most relevant to include possible effects by soil biota and other animals on the transport of lead within forest soils when improving the model presented in this thesis.

The large variability in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the C-horizon, i.e. the local geogenic lead, is limiting a more precise determination of the penetration depth of atmospheric pollution in the soil. Low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in deeper soil layers can both be a result of pollution, but also due to natural mineralogical variations as a result of weathering (HARLAN and EREL, 2002) or
processes related to till formation (paper II). To decrease the uncertainty of future studies trying to trace pollution both within the soil and within the whole forest ecosystem, it is necessary to develop a method to correct for the natural mineralogical ‘noise’.

Another matter that has not been addressed in this thesis is the implications of different external disturbances for the pool of pollution lead in the soil. It is likely that lead stored in the mor layer and near-surface soil layers is affected by forestry or natural disturbances like storm events and forest fires. More knowledge is needed for determining the effects of different disturbances on the fate of lead in the soil. To what extent is the soil pool of pollution lead affected by burning, logging, soil scarification, changes in vegetation, increased water-table and soil compactions? A recent study suggests that forestry increases the mobility and fluxes of mercury from soils to surface waters (Porvati et al., 2003). Clearly, the study by Porvati et al. indicates the relevance for increasing our understanding about forest management practices and lead pollution. However, I think that future studies focusing on the effects by forestry needs an open mind where negative effects as well as positive effects should be considered. For example, it is likely from the results presented in this thesis that faster decomposition of the organic matter as a result of clear-cutting will speed up the self-cleaning process of the mor layer.

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Det finns en tradition inom de flesta lagidrotter att efter varje färdigspelad match tacka medspelare, motståndarlag och domaren med en stor applåd. Att skriva en avhandling är ett riktigt lagarbete och ibland så svettigt att det kan ge en illusion av att vara en idrott. Jag vill därför ge det egna laget en stor applåd för all uppbackning på och utanför plan fem.


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