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Historical Cadmium and Lead Pollution Studied in Growth Rings of Oak Wood

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SUMMARY

Time-defined oak wood segments and soil samples were used as a source of information on the cadmium and lead pollution process induced by the emissions that occurred from 1726 to 1840 around a Swedish alumworks. Trees growing during the time of the emissions contained elevated levels of both cadmium and lead, probably as a result of increased metal concentrations in the atmosphere. Younger trees, which started their growth after the emissions ceased contained no elevated levels of cadmium or lead. The only exception was one tree where the lead concentration of the soil was about 1700 mg/kg in the 10-20 cm layer. A conclusion that can be drawn is that a relatively small increase in the Cd/Pb content of the atmosphere can produce a substantial increase in the Cd/Pb concentrations in the wood. On the other hand, it takes much more Cd/Pb in a soil to produce similar concentrations of Cd/Pb in wood.

The lead chronologies of some young trees in the immediate vicinity of the alumworks illustrate the dilution of lead in the environment, displaying decreasing lead concentrations over time. There are still, however, substantial amounts of lead present in the area shown both in the soil and the wood analysis, thereby again emphasising the long duration of lead pollution of an area.

INTRODUCTION

Monitoring of changes in the environment, such as changes in the metal content of various media, is an important tool in environmental management. Monitoring programmes have been developed in many countries and have implemented during recent decades. The state of the environment before they started is

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generally not included in these programmes, perhaps partly because of a lack of appropriate methods. Metallic elements present in soil, water and biota are the result of emitted amounts accumulated over time from both natural and anthropogenic sources. Thus if the aim is to assess the metal load of an area, it is not sufficient only to study present metallic emissions. Rather, metal pollution should be seen as a process with both a spatial and a temporal distribution.

Investigations of many different media that preserve earlier environmental conditions have been used in attempts to develop methods for historical monitoring. In aquatic environments sediments are often used, which cover a long time span (Renberg et al., 1994) with, in some cases, excellent time resolution. Using sediments as environmental records for metal pollution has been proven successful, at least for some metals (Alderton, 1985). A sediment analogue in terrestrial environments could be trees, which both display an annual growth and incorporate metals.

There are many well-founded objections raised to the simple assumption that a time-defined element content of a tree represents a historical environment. See for instance reviews by Burton (1985), and Cutter and Guyette (1993). Hagemeyer (1993) notes that a large number of studies have been performed without any consensus as to whether the method yields valid results, and he suggests great caution in the interpretation of the data. In both these reviews are outlined a number of conditions that improve the chances of success in reconstructing past metal loads. For instance, the method seems more useful when studying elements of low mobility in wood (lead) and when ring-porous woods (e.g. *Quercus* spp.) are employed in the study. It also seems as if this method is suitable for the study of long-term trends, and especially at sites with a high deposition of pollutants. A conclusion valid for most studies where the tree-ring method has been employed is that more attention has been given to the actual tree-ring analysis and not so much to the question, What could be expected? Or, in other words, most studies lack proper, independent estimations of emissions, which makes them difficult to interpret. A few exceptions are Sheppard and Funk (1975), Guyette et al. (1991) and Eklund (1995), where the tree-ring method is tested against estimated emissions.

The aim of this study is to investigate what kind of traces can be found in the wood of oak trees and in the soil of the substantial lead and small cadmium emissions from a Swedish alumworks that was in operation from 1726 to 1840. Since more than 150 years have passed since the emissions ceased it should also be possible to record the dilution of the metals in the environment.

THE STUDY AREA AND ITS HISTORY

Shale-based alum production was Sweden's first chemo-technical industry, featuring an advanced technology and specialisation among its workers. Alum was mainly used as a mordant when dyeing cloth but also, among many other uses, to produce a writable surface on rag paper. The economic importance of the alum trade was great and it generated a substantial income to the government as a tax on all production, a tithe. The alum era in Sweden commenced with the establishment of Andrarum in Skåne 1637 and ceased around 1900 when alum was replaced by aluminium sulphate and other substances produced from different raw materials than alum shale.

The works which is the focus of this study, Lovers alumworks, was situated south of the town of Kalmar in south-eastern Sweden (Figure 1) and has been the subject of other studies covering its environmental impact. Svidén and Eklund (1993, 1996) dealt with the changes in production and environmental impact related to the use of the alum shale as fuel in the production processes. In another paper, Eklund et al. (1995) present estimates of cadmium and lead emissions from the works' period of activity, 1726 to 1840. The emissions were calculated from estimates of the amount of shale that was used in production and recent analysis of the element content in the shale. The use of lead pans manufactured at the works contributed further to the large amounts of lead emitted to the air. The estimated cadmium and lead emissions over time are presented in Figure 2. For further details on these estimates, see Eklund et al. (1995).

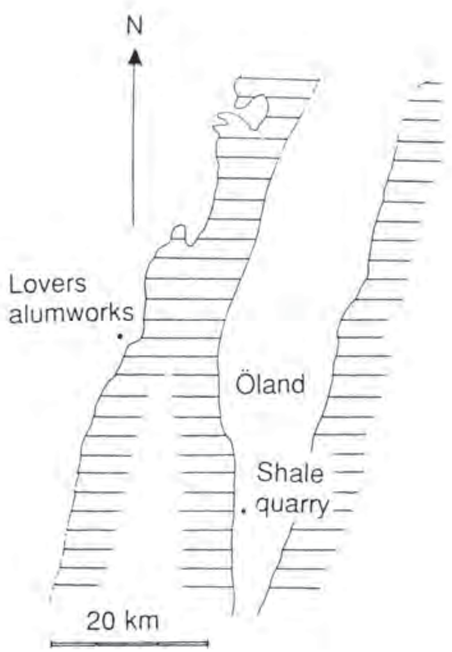

FIGURE 1. The location of Lovers alumworks and its shale deposits on Öland

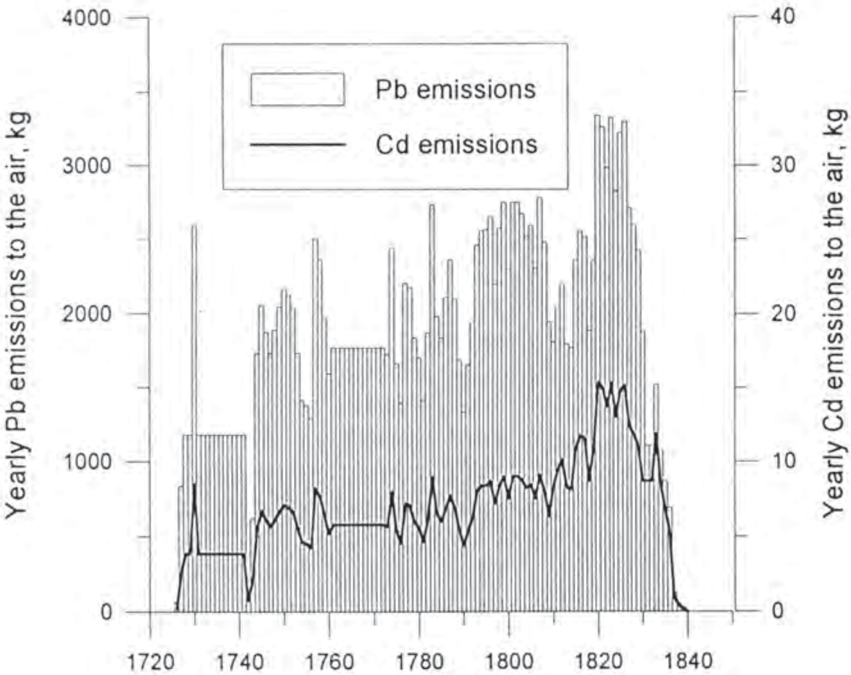

FIGURE 2. Estimated lead and cadmium emissions from Lovers alumworks, after Eklund et al. (1995)

After the close-down of the alumworks no other industrial activity was ever instituted on the premises, though a match factory was established only five hundred metres away in 1860, and closed in 1918. In the production of phosphorous matches lead dioxide (PbO_2) was used. It is not known to what extent this use gave rise to lead emissions. Cadmium is generally present as a contaminant in phosphorous and could also have been emitted from the match factory. However, it is likely that the contribution to the metal pollution of the area from the match factory was small compared to the alumworks, at least for lead.

METHODS

The procedure for sampling, preparation and analysis was generally the same as presented in earlier studies of metals in oak tree rings (Eklund, 1995 and Eklund et al., submitted). In brief, sampling was done with a steel increment corer (5 mm) and the samples were kept frozen until further preparation. The wood cores were cut into segments representing ten years growth, digested in closed vessels and analysed by AAS by the graphite-furnace technique.

Sampling was restricted to eight trees in the surroundings of the alumworks and complemented with soil sampling where eight subsamples were pooled to form a general sample representing the soil beneath each oak tree (Figure 3). One tree location (no. 5) was excluded from the soil sampling because it was in a garden. Top soil samples (0-10cm, approximately corresponding to the A-horizon) and subsoil (10-20cm) were collected with a soil auger. The fine soil fraction (< 2mm) of the samples was dried, extracted with concentrated nitric acid in digestion tubes and analysed for cadmium and lead by flame AAS. Acid strengths of standards were matched with the samples. Soil pH was determined on fresh soil samples after extraction in 0.2M potassium chloride, and loss on ignition was calculated after heating the dried soil samples at 550° C for two hours.

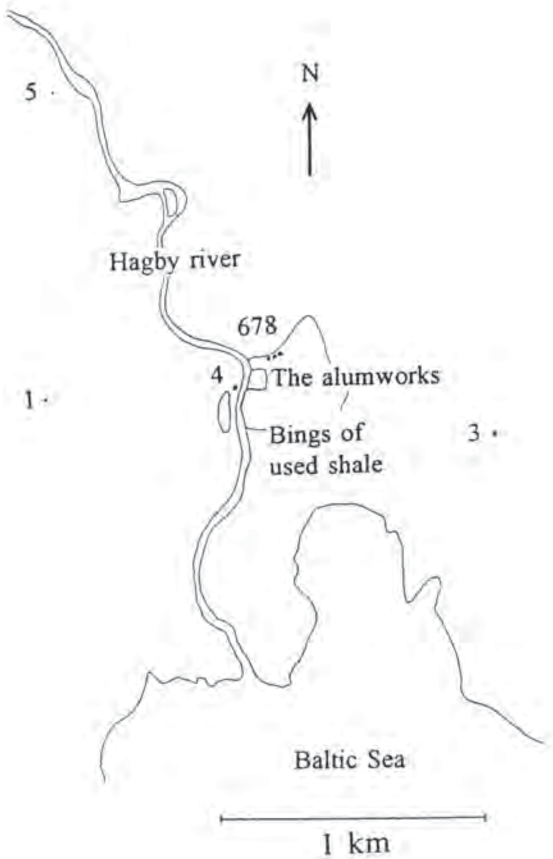

FIGURE 3. The location of the sampled oak trees around Lovers alumworks.

The estimated age of the trees generally corresponds well with the chronologies displayed in Figures 4-6 with one exception, tree no. 5 which is believed to be much older, but which was hollow due to decay. From its growth characteristics and size that tree was probably about the same age as tree no. 1 (about 260 years).

RESULTS AND DISCUSSION

The soil data on pH, loss on ignition, cadmium and lead content are presented in Table 1. Soil pH did not differ much between the different sites, except for no. 2 where values just above pH3 were recorded. This is also the only site with a podzolic soil where organic matter has accumulated to a large extent in the upper soil horizon. The cadmium concentrations are of the same levels as general background values for southern Sweden (SNV, 1993). So also are the lead contents of the soil, with one conspicuous exception, site no. 4 which contains 880 mg/kg soil in the upper 0-10 cm and 1700 mg/kg soil in the 10-20 cm layer.

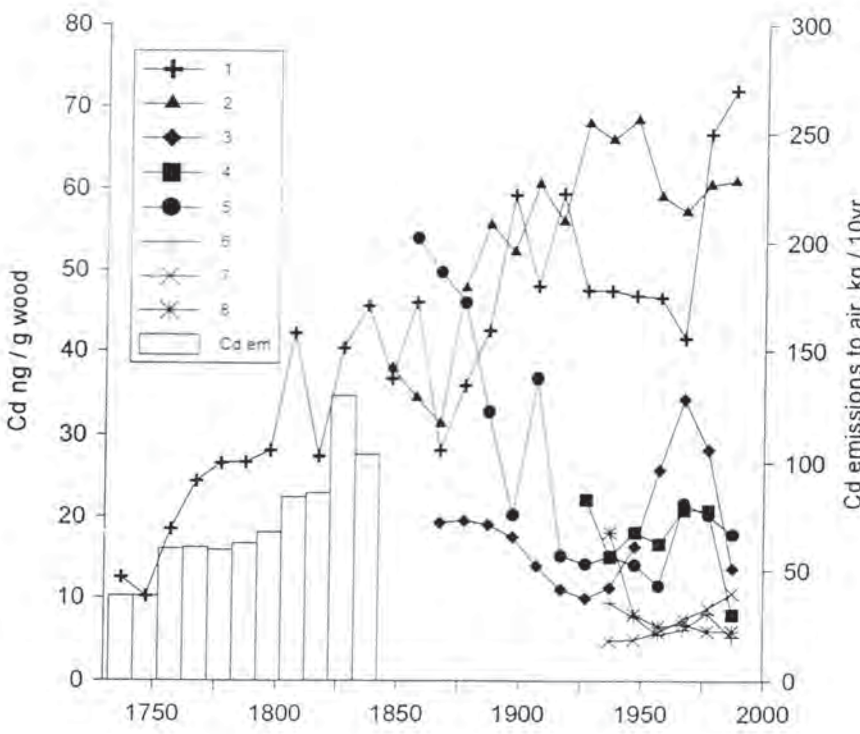

FIGURE 4. Concentrations of Cd in wood of eight oaks growing adjacent to Lovers alumworks and the estimated Cd emissions from the works. Expected background values do not normally exceed 30 ng/g wood.

The substantial emissions of lead and the small emissions of cadmium from the alumworks estimated in an earlier paper (Eklund et al, submitted) thus only reveal themselves as elevated levels of soil lead at one site. What complementary information can the tree rings provide?

Background values for cadmium and lead in oak wood, representing sites not affected by point source pollution, have been established in earlier studies (Eklund, 1995, Eklund et al, submitted and Jonsson et al, submitted). Concentrations of cadmium in oak wood from such sites generally do not exceed 30 ng/g wood and often display an increase during the 1960s and 70s followed by a decrease during the last decade. Trees 3, 4, 6, 7 and 8 do not diverge from this general cadmium chronology, but trees 1, 2 and 5 do (Figure 4). Common features for trees 1 and 5 are their great age and thus their exposure to elevated concentrations of cadmium in the atmosphere during the activity of the alumworks. Trees 1 and 5 do differ in the subsequent part of their cadmium chronology, where tree 5 displays a continuing decrease whilethe cadmium concentrations of tree 1 continue to increase after the alumworks was closed down. A possible reason for this could be differences in their growth rate.

The same explanation cannot be used for the high cadmium concentrations of tree 2, which probably commenced its life just after the alumworks closed down. Instead, the low soil pH of the site could explain the high cadmium level of the wood. It is well known that the mobility of cadmium increases drastically when the pH of the soil pore water is below a value of 5 (Christensen, 1989; Eriksson, 1989) and in this case it probably is, since the pH measured in a KCl-solution was 3.17 (A-horizon) and 3.26 (B-horizon) (Table 1).

Tree no	Soil pH[2]	L.O.I.(%)	Cd(mg/kg)	Pb(mg/kg)	Soil type
1 (A-hor.)	5.17	8.5	0.18	27	Sandy soil
1 (B-hor)	4.75	4.8	BD[1]	19	Sandy soil/ pebbles
2A	3.17	83	0.30	59	Mor layer
2B	3.26	30	0.18	21	Sandy soil
3A	5.69	6.0	0.08	16	Silty soil
3B	5.49	3.9	BD	12	Clayey soil
4A	4.98	18	0.22	880	Humus / burnt shale
4B	4.98	9.9	0.15	1700	Burnt shale
6,7,8A	5.09	10	0.15	88	Burnt shale
6,7,8B	5.07	4.3	BD	12	Burnt shale

[1] below detection limit, [2] measured in KCl.

TABLE 1. Characteristics of the soil where the sampled trees grow. No soil samples were collected beneath tree no 5.

For lead, the results from trees 2 and 3 correspond well with the background chronologies mentioned earlier (Figure 5). They show a small, general increase during the whole of the 20th century but do not exceed 200 ng Pb/g wood, with the highest concentrations in the latest formed segments. Thus, no impact from the alumworks' activities is visible in their lead chronologies even though the deposition of lead on the ground where they came to grow must have been substantial. However, trees 1 and 5, which were growing during the period of alum production, display a quite different lead chronology (Figure 5). The lead content of tree 1 is already elevated in the first segment sampled, 1732-1742, indicating a rapid response to increased levels of atmospheric lead caused by the alum production whichcommenced in 1726. The concentrations of lead in trees 1 and 5 are elevated compared to background levels for wood segments representing all times up to the present. The high lead levels in the wood segments formed after the closing of the alumworks are, at least partly, a product of outward transport which is further discussed by Jonsson et al. (submitted), who describe how high peaks in lead chronologies seem to affect the content of lead in the growing wood for at least some decades after the peak. Furthermore,

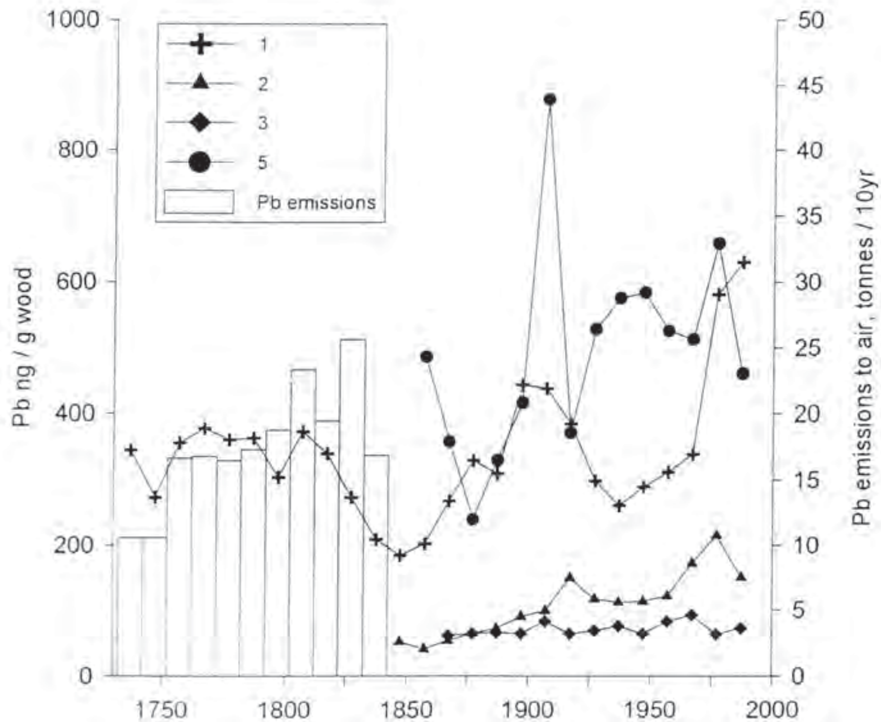

FIGURE 5. Concentrations of Pb in the wood of the four oldest oaks sampled adjacent to Lovers alumworks and the estimated Pb emissions from the works. Expected background values vary from 0 to 200 ng/g wood with an obvious increase over time.

these trees are both situated close to a small road which has probably contributed to their lead load.

The four youngest trees (4, 6, 7, 8) are all situated less than two hundred metres from the site of the alumworks. One of them (no. 4) is situated on the bank of a stream (Figure 6) and contains extremely high levels of lead with one value above 9000 ng/g wood, even though the tree was not present at the time when the lead emissions occurred. Concentration of lead in the soil of the site was also strongly elevated, with the highest value in the 10-20 cm layer, 1700 mg/kg. A possible explanation to the lead chronology of tree 4 could thus be that lead is moving through the soil profile to some extent and becomes incorporated in the tree through the roots. This is however, somewhat surprising, since the mobility of lead in soil is rather low and most of the lead in soil is unavailable to plant roots (Kabata-Pendias and Pendias, 1992). A complementary explanation could be that the tree´s roots are in contact with the bottom of the stream and thereby are exposed to a much larger volume of water compared to a tree that only experiences contact with slowly percolating water of a soil profile. The key to the high lead content of tree 4 could thus be its root contact with the flowing water of the stream, rather than the high lead content of the soil.

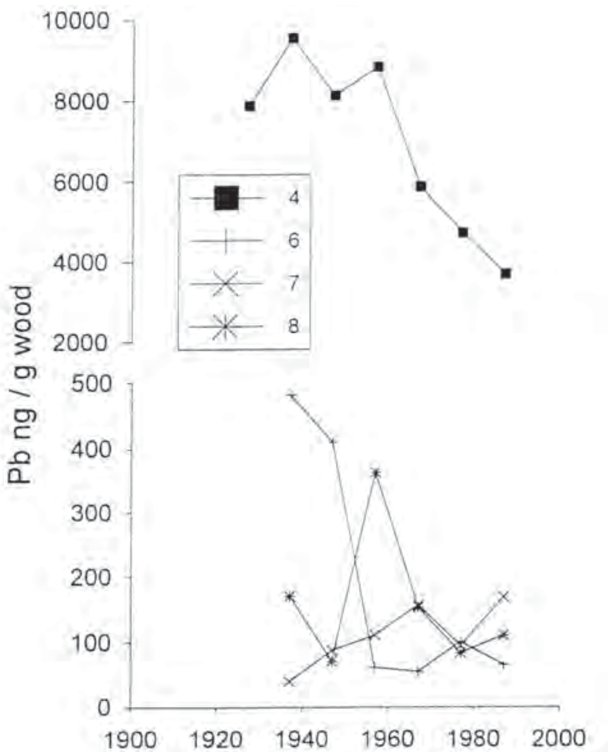

FIGURE 6. Concentrations of Pb in the wood or the four youngest trees sampled adjacent to Lovers alumworks. Expected background values vary from 0 to 200 ng/g wood with an obvious increase over time.

Since concentrations of lead in oak wood generally increase over time, the lead chronologies for these younger trees describe what could be interpreted as dilution of the lead. The element is slowly moving through the soils of the area and reaches ground and surface water on its irrevocable route to the sea sediments. Thus the lead concentrations continually decrease in the immediate surroundings of the source, as illustrated by the chronology of tree 4, and to some extent also by trees 6, 7 and 8. However, the lead content of the upper soil layer and the high levels in the most recent segments of tree 4 underline the fact that we are dealing with slow processes and that large amounts of lead are still present at the site, 150 years after the emissions ceased.

CONCLUSIONS

The crucial issue of what it is we are actually monitoring when we analyse the elemental content of oak wood is complicated. In this study, there are indications of a stronger correlation between the metal concentration of the atmosphere and the wood than between the soil and the wood. This seems valid for both cadmium and lead. However, for one tree, with very high concentrations of lead in its surrounding soil, the content of lead in the wood was also very much elevated. A conclusion that may be drawn is that a relatively small increase of the Cd/Pb content of the atmosphere can produce a substantial increase in the Cd/Pb concentrations in the wood. On the other hand, it takes much more Cd/Pb in a soil to produce similar concentrations of Cd/Pb in the wood. There is also some support for this conclusion in Eklund (1995).

The ongoing dispersal of lead in the soil and and ground water of the area is illustrated as a pulse in one of the sampled trees, where the highest load was recorded in the segment around 1930, 90 years after the emissions ceased. At present, 150 years after the works closed down, lead levels in the wood of that tree have dropped to less than 50% of the chronology's peak value. There are still, however, substantial amounts of lead present in the area, displayed both in soil and wood analysis, which emphasise the long duration of lead pollution in an area.

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