

A whole-basin study of sediment accumulation using stable lead isotopes and flyash particles in an acidified lake, Sweden

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Abstract

Using analyses of lead concentrations, lead isotopes ($^{206}\text{Pb}/^{207}\text{Pb}$), and spheroidal carbonaceous flyash particles (SCP), we studied sediment accumulation patterns in the acidified lake Härsvatten in southwest Sweden. After determining the natural background $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.5) in deeper sediments in long sediment cores from three basins in the lake, we applied an isotope mixing model to quantify pollution Pb accumulation in 46 gravity cores. The mean pollution Pb inventory in the cores was 2.6 g m^{-2} (range, $0.3\text{--}11 \text{ g m}^{-2}$). Although some variation in Pb concentrations can be explained by loss on ignition (LOI) and water depth (together, $R_{\text{adj}}^2 = 0.33$), there is no relationship between pollution Pb inventories and these variables. Contrary to the traditional model of sediment focusing, where higher accumulations of pollutants are expected in deeper waters, the highest inventories for pollution Pb and SCP are generally found at shallow sites ($<4 \text{ m}$ water depth) and not in the three deep basins of the lake (10, 12, and 24 m deep). Furthermore, the model for sediment focusing, which may be appropriate for describing the physical building of sediments in a lake basin, may be inappropriate for describing the specific processes controlling the distribution of pollutants in a lake basin of this type.

It has been understood for more than three decades that analysis of stable lead isotopes is an effective tool to distinguish between lead (Pb) derived from different sources in environmental samples and particularly to distinguish pollution Pb from natural Pb (Chow and Patterson 1962; Shirahata et al. 1980). Lead has four stable isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb); the relative amounts of these isotopes vary among different Pb-bearing minerals depending on the geological age and origin. Much of the Pb-bearing ores extracted and processed for industry, as well as Pb contained in fossil fuels, have distinct isotope signatures from the Pb more generally present in rocks, soils, and sediments. The $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio has been particularly effective in lake sediment studies to assess historical trends in Pb pollution and to assess its geographic distribution on a regional scale (Graney et al. 1995; Blais 1996; Brännvall et al. 1997, in press *a*) or within single basins (Petit et al. 1984; Farmer et al. 1996; Monna et al. 1999), as well as for studies using other environmental archives (Carignan and Gariépy 1995; Bacon et al. 1996; Rosman et al. 1998; Weiss et al. 1999). Isotope

analyses have also been used to quantify the fate and transport of atmospherically deposited Pb in soils (Erel et al. 1997; Bindler et al. 1999; Brännvall et al. in press *b*).

Although Pb isotope analyses have been applied in lake sediment studies of pollution, Pb isotopes have not been applied in whole-basin studies to examine sedimentation patterns and whole-lake inventories. Whole-basin studies typically rely on analyses of metal concentrations only to assess the accumulation and distribution of Pb originating from anthropogenic sources (Blais and Kalff 1995; Benoy and Kalff 1999). Here, we apply Pb isotope analyses to quantify pollution Pb concentrations and, subsequently, to assess the spatial distribution and the cumulative inventory of Pb pollution in a whole-lake basin. In addition, we analyze spheroidal carbonaceous flyash particles (SCP), an emission product of fossil fuel combustion (Rose and Juggins 1994; Wik and Renberg 1996), and assess their spatial distribution and cumulative inventory. Analysis of Pb isotopes and SCP in a whole-lake basin may contribute new insights into the distribution and accumulation of pollutants in small, forested lakes and, more generally, improve the understanding of the fate of pollutants in these lake systems.

Benoy and Kalff (1999) identified weaknesses in the understanding of sediment accumulation and Pb accumulation in lake basins, particularly the role of littoral zones as sources of material to the pelagic zone, as well as the role of littoral zones as sinks over long time periods. Research into lake bottom dynamics, such as how and where heavy metals accumulate in lake sediments, is typically based on large-lake systems (Håkanson and Jansson 1983), which may not

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always be appropriate for more typical forested, small-lake systems and particularly for acidified, oligotrophic clear-water lakes. Wik and Renberg (1991) previously have shown that acidification of these lake types can alter the sedimentation of pollutant indicators such as SCP.

Materials and methods

Site description—Härsvatten is located in southwestern Sweden (55°03'N, 12°02'E) and is one of 26 Swedish national reference lakes, which have been analyzed extensively since 1983. Summary reports of the physical characteristics and the chemical and biological status of these lakes are given by Persson (1996; <http://www.ma.slu.se>) and the water chemistry by Wilander (1997). Härsvatten is an acidified, clear-water, oligotrophic lake. The lake is dimictic, with a thermal stratification in the summer between 10 and 15 m deep. Approximately 80% of the lake bottom is considered to be within the epilimnion.

Härsvatten is characterized by an uninhabited forested catchment (*Picea abies* Karst. and *Pinus sylvestris* L.), uneven topography, thin or no till cover, and rocky soils (podsol). The regional bedrock is gneiss and granodiorite, which is exposed through much of the catchment, particularly along the lake's shoreline. The forest cover extends to the shoreline. Mire/wetlands comprise approximately 13% of the catchment. The lake has a surface area of 0.18 km², and the catchment area, excluding the lake, is 2.03 km². The mean depth of the lake is 5.7 m, and the estimated water turnover rate is 0.9 yr (Persson 1996). Annual precipitation is about 800 mm yr⁻¹. The outlet from the lake is at the southwestern end, and there is one very small inlet (<0.5 m across) at the north end of the lake, which drains from the headwater lake, Måkevatten, and enters Härsvatten through a small wetland. There is no evidence of active erosion where the stream crosses the small wetland or where the inlet enters the lake over exposed bedrock. Härsvatten is located 3.5 km from Gårdsjön, for which there are detailed descriptions of the regional biogeochemistry (Andersson and Olsson 1985).

The mean pH of Härsvatten during the period 1983–1993 was 4.4 (Wilander 1997), and as a consequence of acidification, the lake is fishless. Analysis of the long-term diatom record in a long sediment profile from the south basin of Härsvatten has revealed a complex pH history for the lake (Renberg et al. 1993). Following deglaciation of the region, the pH (diatom-inferred) of the lake gradually declined from 6.3 to 5.3. As a result of regional land-use changes about 1,500 yr ago, the pH of the lake increased to about 6, which generally lasted until the middle of the 20th century, when the lake's pH rapidly declined to its present acidified status.

Härsvatten has a complex morphometry (Fig. 1). The whole-lake basin can be divided into four general regions: a north basin, with a maximum depth of 12 m (sites N1–11); a central area separating the larger north and south basins, which is generally shallow (<3 m water depth), but with a small basin 8 m deep (sites M1–6); a south basin, the lake's largest basin with the lake's maximum depth of 24.3 m (sites S1–24); and an east basin, which is also generally shallow (<3 m water depth), but with a maximum depth of nearly

10 m (sites E1–6). The east basin is separated from the main north–south axis of the lake by a series of islands and very shallow sills.

Although the aquatic plant community of Härsvatten has not been specifically studied, some general inferences can be made based on studies of other clear-water acidic lakes near Härsvatten, in combination with observations made during sediment coring of Härsvatten. Because these lakes have low pH values and clear waters, (i.e., deeper light penetration), benthic vegetation is favored. Consequently, these lakes have experienced an expansion of algal mats and *Sphagnum* mosses into deeper areas of the lake bottoms. Studies in Gårdsjön, prior to liming of the lake, and nearby Stora Hästevatten (not limed) found *Sphagnum* growing on the lake bottoms as deep as 15 m (Andersson 1985; Grahn 1985). Field observations at Härsvatten indicated moss was present to at least 10 m depth in some parts of the lake, as were algae, and *Isoetes* was found to 5 m deep. The moss observed on the lake bottom was not dense enough in appearance to be considered mats; nor were *Isoetes* growing in great abundance.

Analytical methods—To establish the temporal changes in Pb concentrations and stable Pb isotopes, long sediment profiles were collected from each of the three main basins in the lake. Either a freeze-corer (Renberg 1981) (south basin, 1993 and 1997, and north basin, 1997) or a kajak gravity corer (8.4-cm internal diameter, HTH-Teknik) (east basin, 1998) was used for the unconsolidated surface sediments, and a Russian peat corer (1 m long, 8 cm diameter) was used for the consolidated, deeper sediments. The Pb profile from the south basin was originally published in Brännvall et al. (1997).

To characterize the spatial distribution of Pb and SCP in the lake basin, particularly their cumulative inventories, 46 short sediment cores (Fig. 1), typically 25 cm long (ranging from 10 to 30 cm), were collected from Härsvatten using the gravity corer. Coring took place in 1997 and 1998. The depth from the ice surface was recorded for each site. In the field, these cores were sectioned into an upper sample, from 0 to 10 cm deep, and a lower sample, which was the remainder of the sediment core. Four cores were sectioned into 5-cm intervals. Each sediment section was placed in a plastic bag or container and stored at 4°C. In the lab, the samples were weighed, freeze-dried, and reweighed to determine the water content and dry mass of the sediment.

Loss on ignition (LOI), a proxy for organic matter content, was determined by heating dried samples at 550°C for 4 h. The freeze-dried samples were analyzed for Pb concentrations and stable Pb isotopes (²⁰⁶Pb and ²⁰⁷Pb) using inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer model ELAN 5000), following a 10:1 (v/v) HNO₃:HClO₄ acid digestion. Calibration curves and isotope correction factors were made using certified standard reference material (NIST common Pb isotope standard SRM 981). Concentrations were verified against the certified standard, SPEX ICPMS-2. Relative standard error is <10% for concentration and <0.5% for isotope ratios. Concentrations are reported on a dry weight basis (μg g⁻¹).

SCP were analyzed in the freeze cores from the south

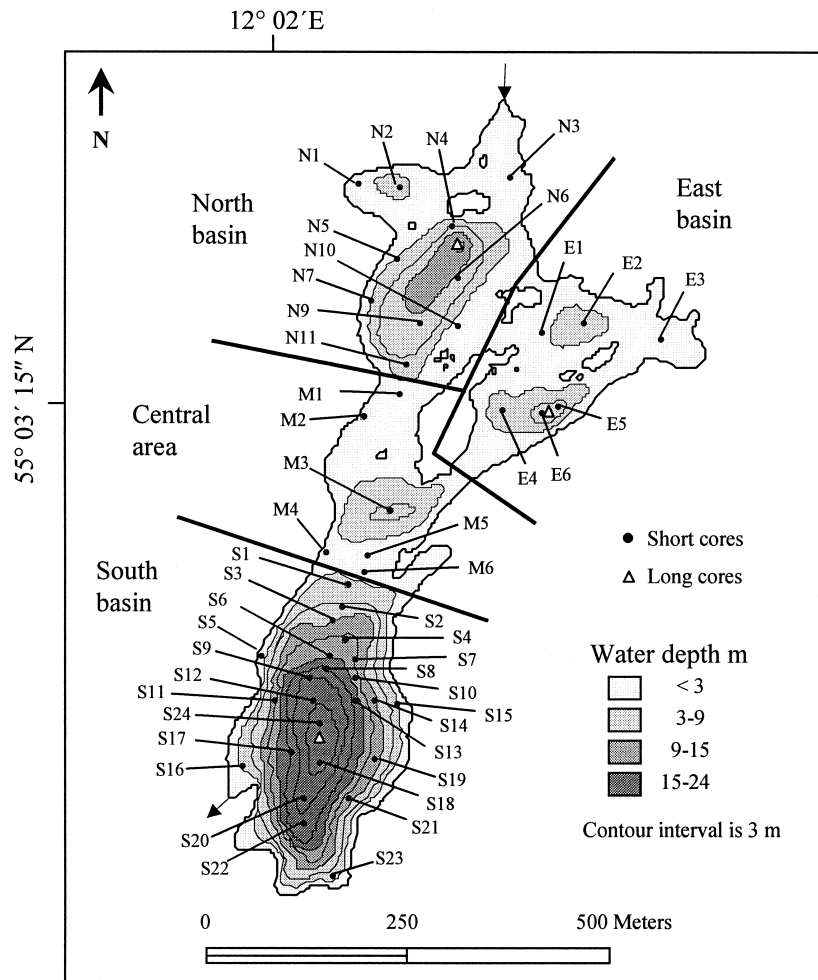


Fig. 1. Map of Härsvatten showing lake bathymetry and the sampling sites for the 46 short sediment cores (labeled with site reference name) and three long sediment cores.

basin and north basin (complete profiles), all of the upper core sections, and in a test set of 10 lower core sections (sites N1, N3, E3, E6, M1, M2, S2, S4, S16, and S24). The freeze cores were sectioned at 0.5-cm intervals. Preparation and counting of SCP followed standard methods (Wik and Renberg 1996): oxidation of a sediment subsample with hydrogen peroxide; rinsing with 5% HCl (1 time); rinsing with deionized water (4 times); homogenization of the suspension; pouring an aliquot into a glass petri dish, which is then allowed to dry slowly; and counting of the SCP under a stereomicroscope at $\times 50$ magnification.

One sediment interval in the long core from the east basin was radiocarbon dated (Tandem Laboratory, Uppsala, Sweden) using macrofossils and the date was calibrated to calendar years using Radiocarbon Calibration Program 3.0 (Stuiver and Reimer 1993). Three bulk sediment samples from the south basin long core were also radiocarbon dated. Other dates can be inferred from well-characterized features in the profiles of Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in Swedish lake sediments based on detailed Pb chronologies from a data set comprising 35 lakes and three peat bogs, which includes radiocarbon dating and a number of

annually laminated sediment cores (Renberg et al. 1994; Brännvall et al. 1997, 1999, 2000a). Well-recognized pollution Pb peaks occur at A.D. 0, 1200, and 1970. By comparison to the other dated Pb chronologies from the Swedish data set, the three radiocarbon dates of bulk sediment samples from the south basin are a few hundred years too old.

Besides describing the pollution status, SCP profiles can also be used to derive three approximate dates: that is, an inferred dating tool, with an the initial appearance of SCP at ca. 1850, a rapid post-Second World War increase ca. 1950, and a characteristic maximum ca. 1970 (Wik and Renberg 1996).

One soil profile was collected from a hill site approximately 100 m from the lake and analyzed for Pb using the same methods. The profile was collected as follows. For the humus layer, five samples were collected using a sharpened steel tube. For the mineral horizons below, samples were taken continuously down to bedrock at 75 cm deep. The sampling intervals were 5 cm for the first 10 cm, 10 cm from 10 to 70 cm deep, and the remaining 5 cm to bedrock.

The pollution Pb concentration ($\text{Pb}_{\text{pollution}}$) of the sediment samples can be estimated using a simple mixing model.

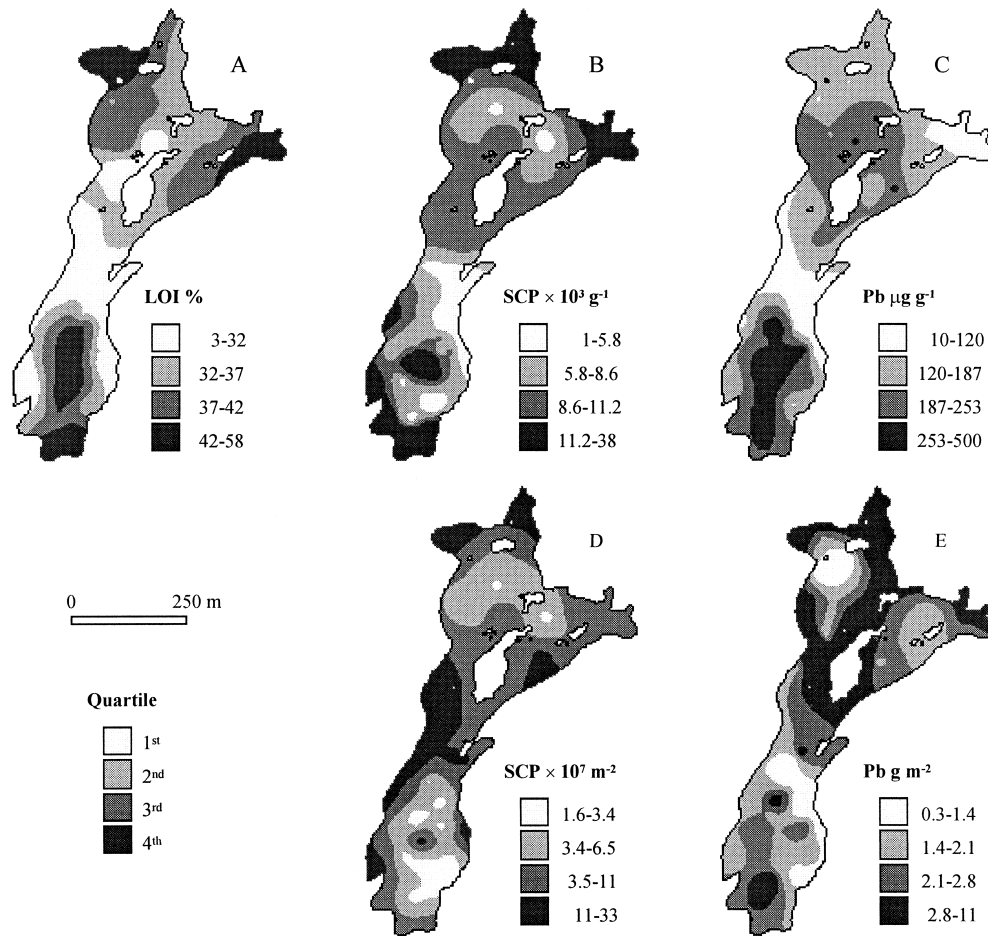


Fig. 2. (A) Organic matter content (LOI), (B) SCP concentrations (particles g^{-1} dry sediment), (C) Pb concentrations ($\mu\text{g g}^{-1}$ dry sediment), and (D) SCP inventories (particles $\times 10^7 \text{ m}^{-2}$) in the upper core sections and (E) pollution Pb inventories (g m^{-2}) in whole cores in Härsvatten. Data intervals are based on quartiles. Minimum and maximum values for each parameter are given.

$$\begin{aligned} \text{Pb}_{\text{sample}} \times \frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{sample}} &= (\text{Pb}_{\text{natural}} \times \frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{natural}}) \\ &+ (\text{Pb}_{\text{pollution}} \times \frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{pollution}}) \end{aligned} \quad (1)$$

This is reexpressed as

$$\begin{aligned} \text{Pb}_{\text{pollution}} &= \frac{(\frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{sample}} - \frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{natural}})}{(\frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{pollution}} - \frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{natural}})} \\ &\times \text{Pb}_{\text{sample}}, \end{aligned} \quad (2)$$

where $\frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{sample}}$ refers to the isotope ratio and $\text{Pb}_{\text{sample}}$ refers to the total Pb concentration of a given sample; $\frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{background}}$ refers to the mean isotope ratio in deeper, uncontaminated sediments in long sediment profiles; and $\frac{{}^{206}\text{Pb}}{{}^{207}\text{Pb}}_{\text{pollution}}$ refers to the mean isotope ratio of pollution sources. Isotope ratios for the natural Pb and pollution Pb contributions in these equations are discussed later in the text.

Total inventories of pollution Pb and SCP for each sample can be determined by multiplying the concentration of a sample ($\mu\text{g g}^{-1}$ or particles g^{-1}) with the sample dry mass.

This value can be reexpressed in terms unit area (g m^{-2} or particles m^{-2}) by dividing the total inventory by the area of the core tube.

MapInfo and ARC-View 3.1 were used for spatial analysis and to produce the map figures for the distribution of LOI, Pb, and SCP concentrations and Pb and SCP inventories. Determination of mean inventories (pollution Pb and SCP) for the four regions of the lake basin and mean inventories for the whole-lake basin were made on the basis of Thiessen polygons determined for the area represented by each coring site.

Results and discussion

Organic matter—The organic matter content of Härsvatten sediments, as inferred by LOI (Fig. 2), varies from 3% in the shallower central area (M4; 3.8 m deep) to a maximum of 58% in the deep hole of the south basin (S24; 24.3 m deep). There is a positive relationship between water depth and LOI (for upper core sections $r = 0.47$; Table 1), and in the deeper south basin, this relationship is stronger ($r = 0.72$, $P < 0.001$). Although this positive relationship exists,

Table 1. Correlation matrix for pollutant concentrations and inventories with water depth and LOI (Pearson product-moment correlation coefficients). Significance is indicated by * $P < 0.05$, ** $P < 0.01$, and *** $P < 0.001$.

	LOI (%)	SCP (g^{-1})	SCP (m^{-2})	Pb ($\mu\text{g g}^{-1}$)	Pb (g m^{-2})
Depth (m)	0.47***	-0.03	-0.43**	0.55***	-0.17
LOI (%)		0.41**	-0.51***	0.48***	-0.01
SCP (g^{-1})			0.24	0.13	0.15
SCP (m^{-2})				0.39**	0.14
Pb ($\mu\text{g g}^{-1}$)					0.33*

the greatest variation in organic matter is found in sediments from ≤ 4 meters deep, with LOI values from 3 to 57% (upper core sections). Overall, water depth can only account for about one quarter of the variation in LOI ($R_{\text{adj}}^2 = 0.26$) in the whole lake and almost half of the variation in the south basin ($R_{\text{adj}}^2 = 0.45$).

The water content of the sediments has a weak relationship with water depth. Like organic matter, the greatest variation in water content (70–96%) is found in sediments from ≤ 4 meters deep. The organic matter and water contents of sediments from the south basin are generally higher than in other parts of the lake basin.

Spheroidal carbonaceous flyash particles (SCP)—Temporal trends: Temporal changes in SCP (Fig. 3) in the south basin freeze core reflect the typical trends established for Swedish lake sediments (Wik and Renberg 1996) and are in general agreement with a profile analyzed in 1993 (Wik-Persson and Renberg unpubl. data). SCP first appear in the sediment profile at 12.5 cm depth, reach a maximum value of 95,000 SCP g^{-1} at 5.5 cm deep, and decline rapidly toward the surface with 18,000 SCP g^{-1} in the 0–0.5-cm interval. In the freeze core from the north basin, the maximum SCP concentration, 56,000 SCP g^{-1} , is in the surface interval, which suggests that the recent sediment record is either disturbed or interrupted at this site. This conclusion is confirmed by diatom analyses of this core (A. Ek unpubl. data) that show the presence of a high percentage of alkaliphilous diatom species in the surface sediment layers, such as *Cy-*

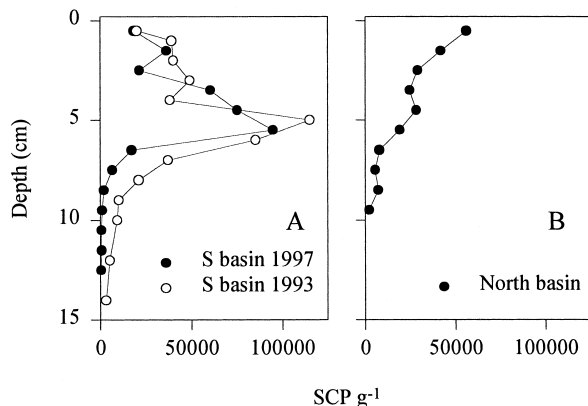


Fig. 3. SCP concentration profiles in (A) two freeze cores from the south basin, one collected in 1993 (Wik-Persson and Renberg unpubl. data) and one in 1997, and (B) one freeze core from the north basin.

clotella species, which are not present in acidified lakes (Stevenson et al. 1991). The disturbance is not an artifact of sediment coring since an undisturbed sediment–water interface was preserved in the freeze core; rather, it is assumed to be caused by sediment slumping, which has deposited older sediments at the site. Consequently, Pb was not analyzed in this freeze core.

Spatial variation: The concentration of SCP in the upper core sections ranges from 2,000 particles g^{-1} at a shallow, near-shore site (S15; 2.8 m deep) to 65,000 particles g^{-1} in the deep south basin (S24; 24.3 m deep), with an average of 12,000 g^{-1} in the 46 cores (Fig. 2). The variation in SCP concentrations is not related to depth, and only 15% of the variation can be explained by LOI (Table 1).

Analysis of SCP both in the upper and in the lower sections of 10 sediment cores selected from different depths and regions of the lake (sites N1, N3, E3, E6, M1, M2, S2, S4, S16, and S24) indicates that about 90% ($87\% \pm 5$ [mean \pm SD]; range, 78–95%) of the total number of particles is contained in the upper core sections (0–10 cm). For consistency, all discussion of SCP is confined to the upper core sections only. Among cores, SCP inventories range from 1.7×10^7 (S6; 12.5 m deep) to 33×10^7 (M4; 3.8 m deep), with an average of 8.1×10^7 SCP m^{-2} (Fig. 2). This range of values is comparable to the reported values for Gårdsjön, 5 km distant from Härsvatten (Wik and Renberg 1991). By region within the lake, the highest average inventory is found in the shallower central area, followed by the northern, eastern, and southern basins (13×10^7 , 8.1×10^7 , 8.0×10^7 , and 5.7×10^7 SCP m^{-2} , respectively). In comparison to concentrations, slightly more of the variation in inventories can be explained by either depth (15%) or LOI (25%) (Table 2).

Pollution Pb—Temporal trends in Pb pollution: The isotope composition of Pb pollution in Europe has changed slightly over time, within well-defined windows. The $^{206}\text{Pb}/$

Table 2. Variance (R_{adj}^2) in SCP and pollution Pb (concentrations and inventories) explained by water depth (m) and LOI (%).

Variable	Pb			
	SCP (g^{-1})	SCP (m^{-2})	($\mu\text{g g}^{-1}$)	Pb (g m^{-2})
Depth (m)	-0.02	0.16	0.28	0.01
LOI (%)	0.14	0.24	0.21	-0.02
Depth + LOI*	0.19	0.27	0.33	-0.01

* Due to some covariance between depth and LOI ($r = 0.47$), the figure is lower than the sum of their individual scores.

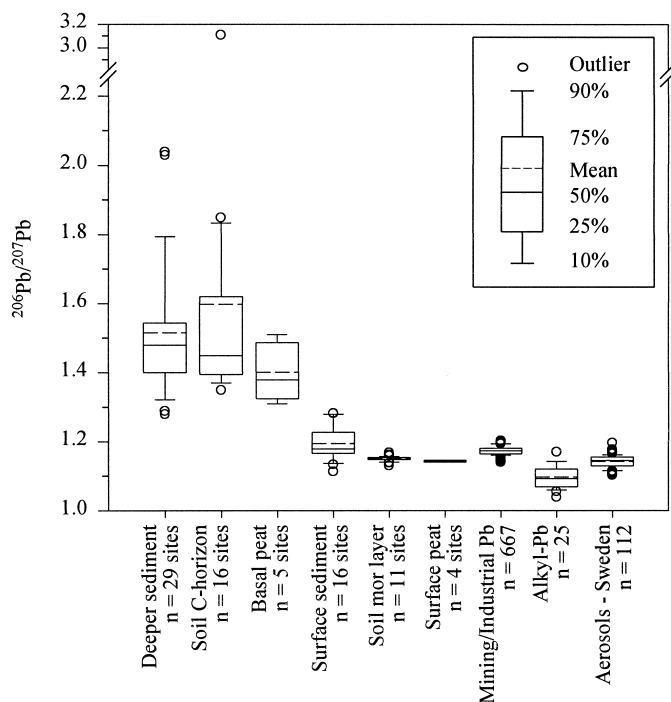


Fig. 4. Box plot showing the natural $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio in deeper, unpolluted lake sediments (>3,000 yr old), soil C horizons, and basal peat layers from Sweden; the isotope ratio of surface sediments, soil mor layers, and surface peat layers from Sweden; and the characteristic $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios of mining/industrial Pb from European ores (ancient times to the present), alkyl-Pb in gasoline, and atmospheric aerosols in Sweden, which reflects a blend of pollution Pb sources.

^{207}Pb ratio of Pb pollution from metal production in Europe from the Greek/Roman period onward has typically been about 1.17, a value based on analyses of metal artifacts and ores from old mining centers across Europe (1.174 ± 0.013 ; reported range, 1.064–1.203; $n = 667$ values) (Grögler et al. 1966; Brill and Wampler 1967; Wedepohl et al. 1978; Sugden et al. 1993; Rosman et al. 1997). Similar values are reported for coal (Sugden et al. 1993). The 1.17 isotope value is also recorded in three Swedish ombrotrophic peat bogs, which are supplied with their pollutants strictly from the atmosphere, for the period from A.D. 0 to 1900 (Bindler et al. 1999).

From about 1900, the ratio of pollution Pb has declined largely as a result of the import of Australian Pb: first for industry and more importantly later, after the Second World War, as an alkyl-Pb additive to gasoline. Leaded gasoline has a low isotope ratio—1.04 to 1.14 (Keinonen 1992; Sugden et al. 1993; Veron et al. 1999). This decline in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of pollution is also recorded in the peat bogs, with the isotope ratio declining below 1.17 about 1900 to a value of ca. 1.15 for the later half of the 20th century (up to 1996, when the bogs were cored). The ratio of 1.15 recorded in the peat bogs is also comparable to the average value of atmospheric aerosols measured in Sweden in 1988 (Hopper et al. 1991) (Fig. 4), as well as to the values for forest mosses in Norway (Rosman et al. 1998) and Finland (Keinonen 1992). Furthermore, analyses of 50 samples of

the soil mor layer (organic horizon) from 11 sites in Sweden also have an average isotope value of 1.15 (1.150 ± 0.007) (Bindler et al. 1999); this ratio should represent a time-integrated value spanning a few to several decades, depending on the turnover rate of organic matter in this organic horizon. Based on the peat archives and mor samples and on the analyses of atmospheric aerosols and forest mosses, modern Pb pollution can be characterized by an average $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of 1.15.

In the Swedish environment today, it is a common observation that older lake sediments (>3,000 yr), deeper mineral soils (C-horizon), and basal peat layers have high isotope ratios, whereas surface sediments, soil organic horizons (mor layer), and surface peat layers have low isotope ratios (Fig. 4). The temporal changes in long-range transported atmospheric Pb pollution leading to this situation in Sweden are well characterized, based on analyses of Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in 32 lakes and three bogs (Renberg et al. 1994; Brännvall et al. 1997, 1999, in press a). In summary, the Pb pollution history in Sweden is as follows: the earliest traces of Pb pollution date to about 3,000 yr ago, with a small peak during the Greek/Roman period; a decline to almost background values during the Dark Ages; a marked increase in pollution from about A.D. 1000, and again following industrialization; a further increase after the Second World War, peaking about 1970; and a marked decline since. Increases in Pb pollution are indicated by increases in Pb concentrations and sharp declines in isotope ratios. Preindustrial pollution from the Greek/Roman period to the Industrial Revolution (ca. 1800) was quite sizeable and accounts for an estimated 50% of the total pollution Pb accumulation in lake sediments in Sweden (Renberg et al. 1994; Brännvall et al. 1999, in press a).

The trends in the sediment profiles from the east and south basins of Härsvatten follow the established trends for Swedish lake sediments. In prepollution sediments (>3,000 yr old), mean Pb concentrations from the three basins are quite low— $6 \mu\text{g g}^{-1}$ in the south basin, $4 \mu\text{g g}^{-1}$ in the east basin, and $2 \mu\text{g g}^{-1}$ in the north basin—and the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios of these sediments are quite high—1.49, 1.52, and 1.47, respectively (Fig. 5). Lead concentrations increase and isotope ratios decrease generally toward the sediment surface as a consequence of increasing deposition of pollution Pb over the last ca. 3,000 yr. Traces of the Greek/Roman peak in Pb production are clearly seen in the long sediment cores from the south (85 cm deep) and east (55 cm deep) basins. This early pollution peak is reflected by a four- to fivefold increase in Pb concentrations and a pronounced decline in Pb isotope ratios. In the upper 5 cm of the long cores from the south and east basins, the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios of the sediment decline below 1.17, which reflects the modern addition of alkyl-Pb into the atmospheric mixing of Pb pollution sources.

Spatial variations: The Pb concentrations in the upper core sections range from $10 \mu\text{g g}^{-1}$ in a shallow, near-shore site in the south basin (S15; 2.9 m deep) to $500 \mu\text{g g}^{-1}$ in the south basin (S7; 15 m deep) (Fig. 2). The average Pb concentration is $200 \mu\text{g g}^{-1}$, with a corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of 1.17 (range, 1.146–1.236). In the lower sec-

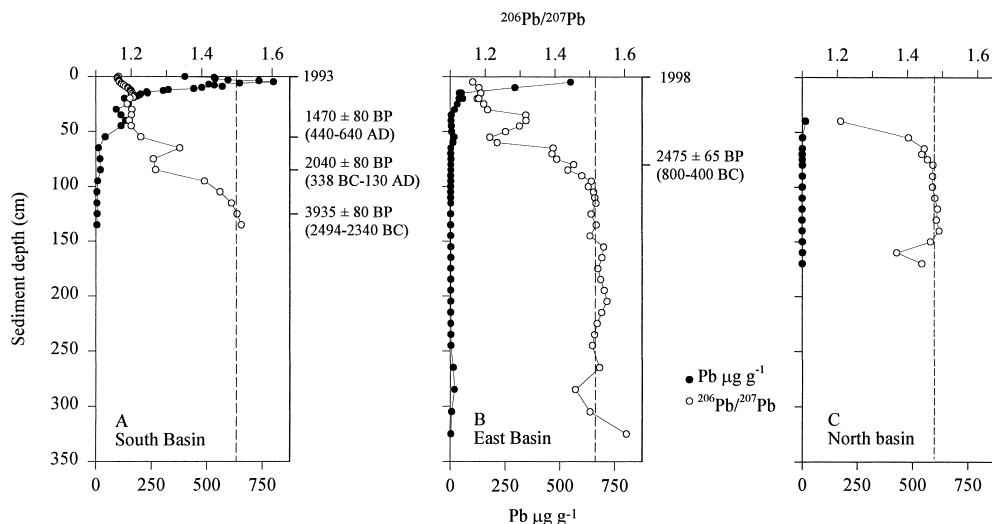


Fig. 5. Lead concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in long sediment profiles from (A) the south basin, including three ^{14}C -dated intervals (both ^{14}C and calibrated calendar years are given), (B) the east basin, with one ^{14}C -dated interval (the top 20 cm was sectioned in 5-cm sections, site E6), and (C) the north basin of Härsvatten (freeze core not analyzed for Pb). The vertical dashed line in each panel denotes the mean isotope ratios of deeper, unpolluted sediments.

tions, which are of variable length (time span), the average Pb concentration is $95 \mu\text{g g}^{-1}$, with a range from $8 \mu\text{g g}^{-1}$ at intermediate depth in the south basin (S6; 12.5-m water depth) to $490 \mu\text{g g}^{-1}$ at a shallow, near-shore site in the north basin (N3; 1.5-m water depth). The average isotope ratio of the lower sections is 1.20, with a range from 1.169 to 1.332; all values are well below the background ratios of deeper sediments in the long profiles (1.46–1.51).

Low Pb concentrations and high natural $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios are also found in a long sediment core from the upstream lake Måkevatten and in the one soil profile collected 100 m from Härsvatten. In Måkevatten, deeper sediments (78 to 400 cm deep; $n = 18$ samples) have a mean concentration of $4.4 \mu\text{g g}^{-1}$ (range, $2.5\text{--}7.5 \mu\text{g g}^{-1}$) and a mean ratio of 1.50 (range, 1.43–1.72) (Brännvall et al. in press a). For the soil profile from 30 to 75 cm deep (bedrock was encountered at 75 cm), the mean Pb concentration is $4.5 \mu\text{g g}^{-1}$ (range, $3.5\text{--}6.5 \mu\text{g g}^{-1}$; $n = 5$), and the mean ratio is 1.65 (range, 1.63–1.66).

There is a positive relationship between Pb concentrations and both water depth and LOI in the upper core sections ($r = 0.55$ and 0.48 , respectively; Table 1), and each variable can explain about 25% of the variation in Pb concentrations. Together, water depth and LOI can explain about one-third of the variation (Table 2).

Pollution Pb inventories: In the Pb isotope mixing model it is necessary to set the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of natural and pollution Pb to constant values. Although the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of pollution, as well as that of natural Pb from the lake's catchment, must have varied slightly in regard to both time and space, the ratios of each are well characterized. Based on the Pb pollution history in Sweden and the background values from deeper sediments, the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios for the mixing model (Eq. 1 and 2) can be

defined as follows. The natural isotope ratio ($^{206}\text{Pb}/^{207}\text{Pb}_{\text{natural}}$) in Härsvatten is 1.5. Although the geology and, more specifically, the mineralogy of the catchment are heterogeneous, the deeper lake sediments should represent an integrated isotope ratio for the catchment.

Given the different ages represented by sediments above and below the 10-cm depth, it is necessary to apply different $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios for pollution Pb in the upper versus the lower core sections. Based on the first appearance of SCP (ca. 1840 [Wik and Renberg 1996]) at 12.5 cm deep in the south basin freeze cores (Fig. 3) and because the majority of SCP are found in the upper core sections of the 10 test sites, the top 10 cm of sediment should represent sediments largely accumulated during the 20th century. Therefore, a value of 1.15 is applied as the average modern value for pollution Pb, a value based on the peat bog archives, analyses of the organic horizon, and analyses of atmospheric aerosols in Sweden (Fig. 4). Clearly, the time span represented in each sediment core is different, and consequently, a single ratio will not be appropriate for every site. However, raising or lowering the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of pollution Pb or natural Pb has very little effect on the calculated inventories. For example, raising or lowering the pollution Pb ratio to 1.16 or 1.14 would change the inventories by <5%.

Because the lower core sections are likely to predate the introduction of alkyl-Pb, the preindustrial $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of 1.17 is applied. Based on this ratio, an average 90% of the Pb in the lower core sections comes from pollution sources. The average calculated "natural" Pb concentration (using Eq. 2) is $4 \mu\text{g g}^{-1}$, which is comparable to the actual concentrations in the deeper, uncontaminated sediments and from the deeper mineral soils.

Traditional reliance on Pb concentration changes as a means of identifying the depth boundary for the influence of pollution Pb deposition is imprecise (Benoy and Kalff

1999). With an average background Pb concentration in the sediment of $3 \pm 3 \mu\text{g g}^{-1}$ (range, $1\text{--}19 \mu\text{g g}^{-1}$; $n = 41$ samples from the long cores), it would be difficult to assess the pollution influence on samples with low Pb concentrations. Based on concentrations only, given the natural variability and analytical errors, samples with lower Pb concentrations would likely be considered as uninfluenced by pollution. In contrast, Pb isotope ratios are effective at distinguishing the influence of pollution Pb even at lower concentrations. For example, at site S15 in Härsvatten, although the total Pb concentration is only $10 \mu\text{g g}^{-1}$ in the upper core section, Pb isotope analyses reveal a clear influence of pollution Pb on the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope signature of this sample (1.228). Based on the isotope mixing model, 80% of the Pb in this sample is noncatchment (i.e. pollution).

The short sediment cores, which are of variable length but not longer than 30 cm, are likely to underrepresent the full burden of pollution Pb deposited over the past 3,000 yr. However, most of the pollution Pb accumulated in lake sediments in Sweden has been deposited in the past 1,000 yr, with 50% deposited after 1800, especially in the 20th century (Renberg et al. 1994; Brännvall et al. 1999). In the 325-cm sediment profile from the east basin, the total inventory of pollution Pb is 3.5 g m^{-2} . Of this inventory, 90% (3.1 g m^{-2}) is contained in the uppermost 20 cm (the length of the gravity core, E6) of the sediment. Therefore, the short cores do allow, at least, for the calculation of a reasonable pollution Pb burden at each of the sites and for the lake as a whole.

The average pollution inventory for the whole-lake basin is 2.6 g m^{-2} , which is not evenly distributed in the lake; inventories range from 0.3 to 11 g m^{-2} (Fig. 2). The sites with the highest pollution Pb inventories are not found in the deeper basins of the lake, but in fairly shallow waters closer to the shore. The highest Pb pollution inventories are 11 g Pb m^{-2} in coarser grained sediment in the central area (M1; 3 m deep; 25% LOI), followed by 9.1 g m^{-2} at the northern end of the lake (N3; 1.5 m deep; 35% LOI). As is the case for SCP inventories, there are distinct regional differences in Pb inventories. The highest average inventories are found in the central area and northern basin (3.5 and 3.4 g m^{-2} , respectively) followed by the eastern and southern basins (2.1 and 1.9 g m^{-2} , respectively).

As is the case for pollution Pb inventories, El-Daoushy et al. (1999) observed higher inventories of ^{210}Pb , $^{239+240}\text{Pu}$, and ^{241}Am in the sediments from the northern half of the lake (in this case, the central, east, and north basins) versus the sediments from the southern basin. The inventories of $^{239+240}\text{Pu}$ and ^{241}Am were 1.7 times greater in the northern half than in the southern basin, whereas the ^{210}Pb inventory was 1.24 times greater in the northern part of the lake. Similarly, they also observed high inventories for these elements at shallow sites.

The pollution Pb inventory in Härsvatten sediments is about 2–3 times greater than the calculated inventories for 11 lakes in southern Québec ($0.95 \pm 0.35 \text{ g Pb m}^{-2}$), which is not so remarkable given the much longer history of atmospheric pollution in Europe compared to North America. Extrapolating the average Pb inventory to the lake's surface

area of 0.18 km^2 yields a whole-lake inventory for pollution Pb of about 500 kg.

The average pollution Pb inventory in Härsvatten sediments, 2.6 g m^{-2} , is about half that determined for the one soil profile in the catchment, where the pollution Pb inventory was 5.5 g m^{-2} . The higher inventory in the soil is logical since the scavenging effect of the forest canopy is known to enhance dry deposition (Lindberg et al. 1982). By comparison, about 2–3 g m^{-2} of pollution Pb has accumulated in the soil at inland sites in southern Sweden (seven soil profiles from three sites) (Bindler et al. 1999; Brännvall et al. in press *b*). Atmospheric deposition rates for Pb are about twofold higher in the southwest coastal region of Sweden compared to areas inland (Rühling et al. 1996)

Sedimentation patterns—The basic model for sediment distribution and accumulation in lakes is based on the concept of sediment focusing. Sediment focusing is the process by which sediments from shallower areas, through effects of slope, wind/wave action, and water currents, are redistributed to deeper areas of lake bottoms. Based on properties such as water depth, organic matter content, and water content of the sediments, lake bottoms can be subdivided into erosion, transportation, and accumulation zones (Håkanson and Jansson 1983; Blais and Kalff 1995; Rowan et al. 1995). In the model, fine-grained material with long suspension times (i.e., low sedimentation velocities), such as organic matter, will accumulate in the deep basins of lakes, along with associated strongly bound metal ions, such as Pb (Håkanson and Jansson 1983); therefore, the model of sediment focusing is applied by extension to interpret the accumulation of heavy metals in lake basins.

There is a strong indication that sediment focusing adequately describes the distribution of organic matter in the large south basin of Härsvatten. However, on a whole-lake basis, sediment focusing is not adequate to describe the distribution of organic matter, SCP, or pollution Pb. There is some relationship between Pb concentrations and the variables LOI and water depth, but there is no relationship with these variables or with the inventory of organic matter (sediment dry mass [g m^{-2}] \times LOI) when pollution Pb inventories are considered (Table 1).

There is also no significant correlation between SCP and pollution Pb concentrations or their inventories (Table 1), which is not surprising given differences in the physical and chemical properties of Pb, a metal cation, and SCP, a spherical particulate, which can be expected to result in different sedimentation velocities. Despite a lack of correlation, there is a similarity in the general distribution of their inventories in the lake basin, which suggests that factors other than sediment focusing control their distribution. It is clear that both pollution Pb and SCP accumulate throughout the lake basin, and they have a similar regional distribution in the lake. The inventories for both are highest in the central area, followed by the northern, eastern, and southern basins. Despite a basin-wide distribution, it must be pointed out that the temporal trends for SCP in the south basin and long-term trends for Pb in the east and south basin are consistent with other Swedish lakes, indicating that historical trends are well preserved in the deep basins of Härsvatten. However, al-

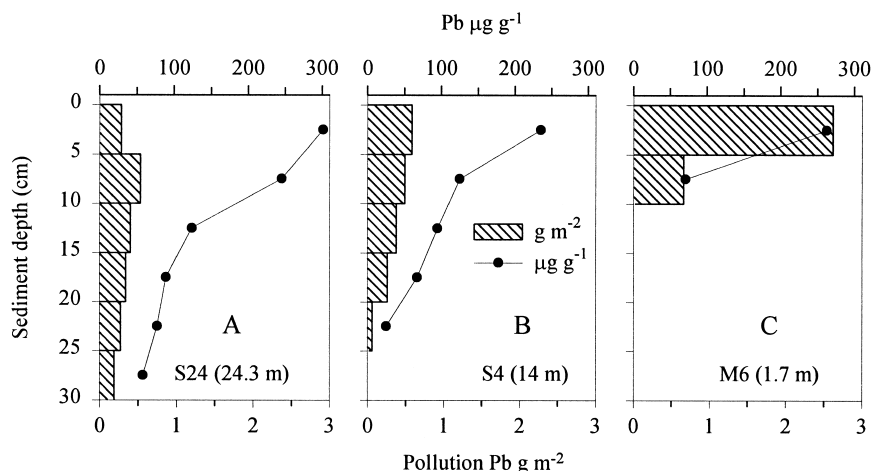


Fig. 6. Pb concentrations and pollution Pb inventories in three short sediment cores sectioned in 5-cm intervals from the southern half of Härsvatten, sites (A) S24 (24.3 m deep), (B) S4 (14 m deep), and (C) M6 (1.7 m deep).

though the timing of changes in Pb concentration is consistent between the south and east basin cores, the magnitude of those changes is not. It is understood that studies of individual lake sediment cores from deep basins of lakes only allow reconstruction of relative trends and not reconstruction of absolute fluxes of atmospheric deposition.

Two examples illustrate the inadequacy of sediment focusing to describe pollution Pb accumulation in Härsvatten. The first example is a set of three cores forming a transect in the southern half of the lake (sites M6, S4, and S24), which were sectioned in 5-cm intervals (Fig. 6). In the deep area of the south basin (S24; 24.3 m deep), the sediments have a high organic and water content (50–60% LOI; 92–98% water). The pollution Pb inventory in the 30-cm core is 2.0 g m^{-2} . At intermediate depth in the same basin (S4; 14 m deep), the organic and water contents are lower (32–45% LOI; 91–95% water), but the pollution Pb inventory is comparable (1.8 g m^{-2}). M6 is a shallow site (1.7 m deep) bordering the south basin, which has much lower organic and water contents (10% LOI; 70–80% water content); here, the pollution Pb inventory is 3.3 g m^{-2} even though only a 10-cm core could be retrieved because of the compactness of the sediment.

A second example, while not arguing against sediment focusing per se, demonstrates the importance of examining accumulation inventories in shallow water sites. This site (S15) would be classified as an erosion bottom in sediment-focusing models (2.8 m deep; 4% LOI; 50% water content). The Pb concentration in the upper core section is only $10 \mu\text{g g}^{-1}$, which is higher than the average background Pb concentration in deeper sediments ($3 \pm 3 \mu\text{g g}^{-1}$) but within the reported range ($1\text{--}19 \mu\text{g g}^{-1}$). However, the $1.23 \text{ }^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the section indicates significant mixing of pollution Pb. Based on the isotope mixing model, approximately 80% of the Pb originates from pollution. Given the high sediment density, the pollution Pb inventory is quite substantial (0.6 g m^{-2}).

The Pb isotope analyses reveal weaknesses in defining erosion, transportation, and accumulation bottoms based

only on sediment properties (depth, LOI, water content) and Pb concentrations. Even in sites traditionally considered as erosion bottoms (i.e., shallow water sites with low organic and water contents), significant amounts of pollution Pb can accumulate. Although concentrations may be quite low in these sites, substantial inventories can result because of the greater sediment mass. Following addition of Cd to a lake in the Experimental Lakes Area, Canada (Stephenson et al. 1996), high Cd inventories in shallow-water sites were observed, including one sandy site that had a fivefold higher inventory than deep-water sites. Similar to Härsvatten, the high inventory at the sandy site resulted from the greater mass of the sediments at the site (kg m^{-2}). Studies in the marine environment show that sites with coarser grain sizes can effectively trap fine-grained particulates through advective transport and/or bioturbation (Bacon et al. 1994; Huettel and Rusch 2000; Rusch and Huettel 2000). Even in relict sand areas of the continental shelf without net sediment accumulation, Bacon et al. (1994) found that excess ^{210}Pb inventories showed a near balance between accumulation and supply. The hydrodynamics at shallow-water sites can further enhance the incorporation of fine particulates and solutes into more permeable sediments (Rusch and Huettel 2000).

Because this study of Härsvatten was designed to assess the use of Pb isotope analyses to quantify pollutant inventories and their spatial distribution in the lake basin and not to examine transport mechanisms, we can only speculate on the specific mechanisms that have resulted in the observed distribution of pollutants. However, since we suggest that sediment focusing is an inadequate model to describe the pollutant distribution, it is useful to suggest potential factors. Factors that might be considered are the complex lake morphometry, the effects of acidification on sedimentation processes, and lake hydrology, such as the effects of prevailing winds. Prevailing winds will affect the circulation of the surface layer, transport of particulate material in the surface film of the lake water (Södergren 1993), and during winter, meltwater on the ice surface. The prevailing winds in south-

western Sweden are toward the northeast (Olsson et al. 1985) from the outlet toward the inlet of Härsvatten.

The complex morphometry of the lake basin is not unusual for lakes in Sweden or in other formerly glaciated regions. The lake is not defined by a single deep basin but, rather, has three definable basins. The east basin is almost isolated from the main north–south axis of the lake, and a generally shallow area <3 m deep separates the north and south basins. This morphometry can result in complex sediment transport dynamics and impede typical sediment-focusing processes.

In acidified lake systems similar to Härsvatten (e.g., Lake Gårdsjön) it is observed that *Sphagnum* and algal mats expand on the lake bottoms into deeper waters (Grahn 1985; Ek et al. 1995). The expansion of these mats is hypothesized to interrupt sediment-focusing processes because the moss and algae act as efficient sediment traps, like macrophytes (Benoy and Kalff 1999), and thus contribute to an evening-out of the sediment distribution across a lake bottom (Andersson and Olsson 1985; Wik and Renberg 1991). Implementation of liming to counteract lake acidification can greatly reduce the extent of benthic *Sphagnum* and algal mats and potentially “restore” sediment-focusing processes. For example, Wik and Renberg (1991) found no relationship between SCP inventories and depth prior to the start of the liming program in Lake Gårdsjön. After liming, they found a relationship with SCP inventories in surface sediments and depth, with some notable outliers. In the case of Härsvatten, casual observation of moss and macrophytes during coring does not suggest an abundance of bottom vegetation.

The recent acidification of the lake, to about pH 4.4, occurred in the 1950s to 1960s. Although a substantial fraction of the pollution Pb deposited over the past ca. 3,000 yr was deposited in the last 50 yr (~20% of the accumulated pollution Pb inventory estimated from ombrotrophic peat bogs [Bindler et al. 1999]), any changes in sedimentation processes that may have occurred as a consequence of acidification seem inadequate to fully describe the pollution Pb sedimentation pattern in Härsvatten, which is the product of about 3,000 yr of atmospheric Pb pollution. Nor will recent changes in sedimentation processes account for the broader, regional distributions of pollution Pb and SCP in the lake.

Hydrologic modeling of the transport of transuranic elements in Härsvatten (El-Daoushy et al. 1999), including ^{210}Pb , indicates that fine particulates (those with settling velocities $\leq 0.1 \text{ m d}^{-1}$) have pronounced transport vectors from southwest to northeast. The vectors are sufficiently long to result in transport of fine particulates from the southwestern shore northward toward the inlet. For example, fine particulates deposited on the water surface at the near-shore sites S5 (3.7 m deep) and M4 (3.8 m deep) could be transported and deposited at site N3 (1.6 m deep). The pollution Pb inventories at these sites fit this model: 1.5, 1.8, and 9.1 g Pb m^{-2} , respectively.

In lakes where there is a significant difference between the Pb isotope ratios of the natural environment and those of pollution sources, such as those in Sweden, Pb isotope analysis is an effective tool to assess pollution loads, and it can be used to examine the fate and transport of pollution Pb in lake systems. In Härsvatten, the analyses of Pb and

SCP indicate that sediment focusing is not an important factor governing the sedimentation of these pollutants, which may have important implications for the sediment accumulation and distribution of other pollutants that are more critical from an ecotoxicological perspective (i.e. Hg).

Finally, one must ask whether Härsvatten is a typical lake system or an “outlier” on account of the effects of acidification. Likewise, one must ask whether the classic model of sediment focusing is more appropriate to describe the physical building of sediment than the specific processes controlling the distribution of pollutants in lake basins. Future studies should include analysis of a similar, but not acidified, oligotrophic boreal forest lake using Pb isotope analyses to assess whether the complexity of the sedimentation patterns (not the specific patterns themselves) of pollutants in Härsvatten is representative for these lake systems and to assess the effect on sedimentation processes. Other factors should also be considered, such as the role of decomposition of organic matter in littoral zones on the accumulation of heavy metals in acidified and nonacidified systems.

References

- ANDERSSON, B. I. 1985. Properties and chemical composition of surficial sediments in the acidified Lake Gårdsjön, SW Sweden. *Ecol. Bull.* **37**: 251–262.
- ANDERSSON, F., AND B. OLSSON [EDS.]. 1985. Lake Gårdsjön: An acid forest lake and its catchment. Swedish Natural Science Research Council Ecological Bulletins 37.
- BACON, J. R., K. C. JONES, S. P. MCGRATH, AND A. E. JOHNSTON. 1996. Isotopic character of lead deposited from the atmosphere at a grassland site in the United Kingdom since 1860. *Environ. Sci. Technol.* **30**: 2511–2518.
- BACON, M. P., R. A. BELASTOCK, AND M. H. BOTHNER. 1994. ^{210}Pb balance and implications for particle transport on the continental shelf, U.S. Middle Atlantic Bight. *Deep-Sea Res. II* **41**: 511–535.
- BENOY, G. A., AND J. KALFF. 1999. Sediment accumulation and Pb burdens in submerged macrophyte beds. *Limnol. Oceanogr.* **44**: 1081–1090.
- BINDLER, R., M.-L. BRÄNNVALL, I. RENBERG, O. EMTERYD, AND H. GRIP. 1999. Natural lead concentrations in pristine boreal forest soils and past pollution trends: A reference for critical load models. *Environ. Sci. Technol.* **33**: 3362–3367.
- BLAIS, J. M. 1996. Using isotopic tracers in lake sediments to assess atmospheric transport of lead in eastern Canada. *Water, Air, Soil Pollut.* **92**: 329–342.
- , AND J. KALFF. 1995. The influence of lake morphometry on sediment focusing. *Limnol. Oceanogr.* **40**: 582–588.
- BRÄNNVALL, M.-L., R. BINDLER, O. EMTERYD, M. NILSSON, AND I. RENBERG. 1997. Stable isotope and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden. *Water, Air, Soil Pollut.* **100**: 243–252.
- , I. RENBERG, O. EMTERYD, J. BARTNICKI, AND K. BILLSTRÖM. 1999. The Medieval metal industry was the cradle of modern large-scale atmospheric lead pollution in northern Europe. *Environ. Sci. Technol.* **33**: 4391–4395.
- , ———, ———, AND I. RENBERG. In press *a*. Four thousand years of atmospheric lead pollution in northern Europe: A summary from Swedish lake sediments. *J. Paleolim.*
- , ———, ———, AND ———. In press *b*. Vertical distribution of atmospheric pollution lead in Swedish boreal forest soils. *Water, Air, Soil Pollut.*

- BRILL, R. H., AND J. M. WAMPLER. 1967. Isotope studies of ancient lead. *Am. J. Archaeol.* **71**: 63–77.
- CARIGNAN, J., AND C. GARIÉPY. 1995. Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Québec, Canada. *Geochim. Cosmochim. Acta* **59**: 4427–4433.
- CHOW, T. J., AND C. C. PATTERSON. 1962. The occurrence and significance of lead isotopes in pelagic sediments. *Geochim. Cosmochim. Acta* **26**: 263–308.
- EK, A., O. GRAHN, H. HULTBERG, AND I. RENBERG. 1995. Recovery from acidification in lake Örvattnet, Sweden. *Water, Air, Soil Pollut.* **85**: 1795–1800.
- EL-DAOUSHY, F., AND OTHERS. 1999. Large-scale and long-term environmental behaviour of transuranic elements as modelled through European surface water systems. European Commission, Nuclear Fission Safety, Final Report (Contract No. FI4P-CT96-0046), Uppsala University, Sweden.
- EREL, Y., A. VERON, AND L. HALICZ. 1997. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. *Geochim. Cosmochim. Acta* **61**: 4495–4505.
- FARMER, J. G., L. J. EADES, A. B. MACKENZIE, A. KIRIKA, AND T. E. BAILEY-WATTS. 1996. Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. *Environ. Sci. Technol.* **30**: 3080–3083.
- GRAHN, O. 1985. Macrophyte biomass and production in Lake Gårdsjön—an acidified clearwater lake in the SW Sweden. *Ecol. Bull.* **37**: 203–212.
- GRANEY, J. R., A. N. HALLIDAY, G. J. KEELER, J. O. NRIAGU, J. A. ROBBINS, AND S. A. NORTON. 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. *Geochim. Cosmochim. Acta* **59**: 1715–1728.
- GRÖGLER, N., J. GEISS, M. GRÜNENFELDER, AND F. G. HOUTERMANS. 1966. Isotopenuntersuchungen zur Bestimmung der Herkunft römischer Bleirohre und Bleibarren. *Naturforschg.* **21a**: 1167–1172.
- HÅKANSON, L., AND M. JANSSON. 1983. Principles of sedimentology. Springer-Verlag.
- HOPPER, J. F., H. B. ROSS, W. T. STURGES, AND L. A. BARRIE. 1991. Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead. *Tellus* **43B**: 45–60.
- HUETTEL, M., AND A. RUSCH. 2000. Transport and degradation of phytoplankton in permeable sediments. *Limnol. Oceanogr.* **45**: 534–549.
- KEINONEN, M. 1992. The isotopic composition of lead in man and the environment in Finland 1966–1987: Isotope source of lead as indicators of pollutant sources. *Sci. Total Environ.* **113**: 251–268.
- LINDBERG, S. E., R. C. HARRISS, AND R. R. TURNER. 1982. Atmospheric deposition of metals to forest vegetation. *Science* **215**: 1609–1611.
- MONNA, F., J. DOMINIK, J.-L. LOIZEAU, M. PARDOS, AND P. ARPAUGAS. 1999. Origin and evolution of Pb in sediments of Lake Geneva (Switzerland-France). Establishing a stable Pb record. *Environ. Sci. Technol.* **33**: 2850–2857.
- OLSSON, B., L. HALLBÄCKEN, S. JOHANSSON, P. A. MELKERUD, S. I. NILSSON, AND T. NILSSON. 1985. The Lake Gårdsjön area—physiographical and biological features. *Ecol. Bull.* **37**: 10–28.
- PERSSON, G. 1996. 26 svenska referenssjöar 1989–1993, en kemisk-biologisk statusbeskrivning. Naturvårdsverket (Swedish EPA).
- PETIT, D., J. P. MENNESSIER, AND L. LAMBERTS. 1984. Stable lead isotopes in pond sediments as tracer of past and present atmospheric lead pollution in Belgium. *Atmos. Environ.* **18**: 1189–1193.
- RENBERG, I. 1981. Improved methods for sampling, photographing and varve-counting of varved lake sediments. *Boreas* **10**: 255–258.
- , T. KORSMAN, AND H. J. B. BIRKS. 1993. Prehistoric increases in the pH of acid-sensitive Swedish lakes caused by land-use changes. *Nature* **362**: 824–826.
- , M. WIK-PERSSON, AND O. EMTERYD. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* **368**: 323–326.
- ROSE, N. L., AND S. JUGGINS. 1994. A spatial relationship between carbonaceous particles in lake sediments and sulphur deposition. *Atmos. Environ.* **28**: 177–183.
- ROSMAN, K. J. R., W. CHISHOLM, S. M. HONG, J. P. CANDELONE, AND C. F. BOUTRON. 1997. Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 BC to 300 AD. *Environ. Sci. Technol.* **31**: 3413–3416.
- , C. LY, AND E. STEINNES. 1998. Spatial and temporal variation in isotopic composition of atmospheric lead in Norwegian moss. *Environ. Sci. Technol.* **32**: 2542–2546.
- ROWAN, D. J., R. J. CORNETT, K. KING, AND B. RISTO. 1995. Sediment focusing and ^{210}Pb : A new approach. *J. Paleolimnol.* **13**: 107–118.
- RÜHLING, Å., E. STEINNES, AND T. BERG. 1996. Atmospheric heavy metal deposition in northern Europe 1995. *Nord* 1996: 37. Nordic Council of Ministers.
- RUSCH, A., AND M. HUETTEL. 2000. Advective particle transport into permeable sediments—evidence from experiments in an intertidal sandflat. *Limnol. Oceanogr.* **45**: 525–533.
- SHIRAHATA, H., R. W. ELIAS, AND C. C. PATTERSON. 1980. Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote sub-alpine pond. *Geochim. Cosmochim. Acta* **44**: 149–162.
- SÖDERGREN, A. 1993. Role of aquatic surface microlayer in the dynamics of nutrients and organic-compounds in lakes, with implications for their ecotones. *Hydrobiologia* **251**: 217–225.
- STEPHENSON, M., AND OTHERS. 1996. Sedimentation of experimentally added cadmium and ^{109}Cd in Lake 382, Experimental Lakes Area, Canada. *Can. J. Fish. Aquat. Sci.* **53**: 1888–1902.
- STEVENSON, A. C., AND OTHERS. 1991. The Surface Waters Acidification Project: Modern diatom/lake chemistry data-set. EN-SIS Publ., London.
- STUIVER, M., AND P. J. REIMER. 1993. Extended C^{14} data-base and revised Calib 3.0 C^{14} age calibration program. *Radiocarbon* **33**: 215–230.
- SUGDEN, C. L., J. G. FARMER, AND A. B. MACKENZIE. 1993. Isotopic-ratios of lead in contemporary environmental material from Scotland. *Environ. Geochem. Health* **15**: 59–65.
- VERON, A., P. FLAMENT, M. L. BERTHO, L. ALLEMAN, R. FLEGAL, AND B. HAMELIN. 1999. Isotopic evidence of pollutant lead sources in Northwestern France. *Atmos. Environ.* **33**: 3377–3388.
- WEDEPOHL, K. H., M. H. DELEVAUX, AND B. R. DOE. 1978. The potential source of lead in the Permian kupferschiefer bed of Europe and some selected Paleozoic mineral deposits in the Federal Republic of Germany. *Contrib. Mineral. Petrol.* **65**: 273–281.
- WEISS, D., W. SHOTYK, J. D. KRAMERS, AND M. GLOOR. 1999. *Sphagnum* mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmos. Environ.* **33**: 3751–3763.
- WIK, M., AND I. RENBERG. 1991. Spheroidal carbonaceous particles as a marker for recent sediment distribution. *Hydrobiologia* **214**: 85–90.
- , AND ———. 1996. Environmental records of carbonaceous fly-ash particles from fossil-fuel combustion. *J. Paleolimnol.* **15**: 193–206.
- WILANDER, A. 1997. Referenssjöarnas vattenkemi under 12 år; tillstånd och trender 1983–1994. Naturvårdsverket (Swedish EPA).

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