NATUR WISSENSCHAFTEN REVIEW ARTICLES

Archives of Atmospheric Lead Pollution

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Environmental archives such as peat bogs, sediments, corals, trees, polar ice, plant material from herbarium collections, and human tissue material have greatly helped to assess both ancient and recent atmospheric lead deposition and its sources on a regional and global scale. In Europe detectable atmospheric lead pollution began as early as 6000 years ago due to enhanced soil dust and agricultural activities, as studies of peat bogs reveal. Increased lead emissions during ancient Greek and Roman times have been recorded and identified in many long-term archives such as lake sediments in Sweden, ice cores in Greenland, and peat bogs in Spain, Switzerland, the United Kingdom, and the Netherlands. For the period since the Industrial Revolution, other archives such as corals, trees, and herbarium collections provide similar chronologies of atmospheric lead pollution, with periods of enhanced lead deposition occurring at the turn of the century and since 1950. The main sources have been industry, including coal burning, ferrous and nonferrous smelting, and open waste incineration until c .1950 and leaded gasoline use since 1950. The greatest lead emissions to the atmosphere all over Europe occurred between 1950 and 1980 due to traffic exhaust. A marked drop in atmospheric lead fluxes found in most archives since the 1980s has been attributed to the phasing out of leaded gasoline. The isotope ratios of lead in the various archives show qualitatively similar temporal changes, for example, the immediate response to the introduction and phasing out of leaded gasoline. Isotope studies largely confirm source assessments based on lead emission inventories and allow the contributions of various anthropogenic sources to be calculated.

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Introduction

Human impacts have caused dramatic changes in the geochemical cycle of many elements, and the possible effects of these changes have raised increasing concern on a regional and global scale (Fyfe 1981; Buat-Ménard 1993). Based on the most recent inventories of natural and anthropogenic source terms (Nriagu and Pacyna 1988; Nriagu 1989; Pacyna et al. 1995; Olendrzynski et al. 1996), total anthropogenic lead emissions to the atmosphere make up 332×10^9 g/year (range: 288.7–376), compared to estimated total natural emissions of 12×10^9 g/year (range: 0.9–23.5). Table 1 lists the estimated contributions of various natural and anthropogenic sources in more detail.

Of all the pollutant metals, lead yields the highest interference factor (IF; Nriagu 1978), which is calculated as:

IF = global anthropogenic emission rates/global natural emission rates.

To estimate the impact of these historical perturbations on the natural lead distribution in the biosphere, the history of worldwide lead production provides an important basis (Fig. 1). Old World technologies for smelting lead-silver alloys from sulfide ores and cupeling silver from the alloys were developed at least 5000 years ago. From 4000 until c. 2700 years ago, world lead production averaged 160 tons/year; it rose to c. 10,000 tons/year with the introduction of silver coinage and rose again to c. 80,000 tons/year during the period of the Roman Republic, 2000 years ago. Lead production declined during medieval times, but with the advent of the Industrial Revolution, production increased dramatically – from 100,000 tons/year to 1,000,000 tons 60 years ago (Fig. 1). In 1980 about 3,000,000 tons of lead were produced annually worldwide (Settle and

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Table 1. Global lead emission from natural and anthropogenic sources (from Nriagu and Pacyna 1988; Nriagu 1989)

Source		Production (in 1000 tons per year)
Natural	Windborne soil particles	0.3–7.5
	Seasalt spray	0–2.8
	Volcanoes	0.5–6.0
	Wild forest fires	0.1–3.8
	Biogenic processes	0–3.4
	Total	**0.9–23.5**
Anthropogenic	Fuel combustion	
	Coal	1.8–14.6
	Oil	0.9–3.9
	Gasoline	248
	Wood	1.2–3.0
	Nonferrous metal industry	
	Primary	30.0–68.2
	Secondary	0.1–1.4
	Other industries and use	5.1–33.8
	Waste incineration	1.6–3.1
	Total	**288.7–376.0**

Patterson 1980). The main means of dispersing this lead are atmospheric transport of (a) aerosols from smelters and gasoline exhausts and (b) reentrained dusts and smokes (Settle and Patterson 1980).

To assess the extent and the consequences of past atmospheric deposition, various archives such as ice cores, peat bogs, lake and ocean sediments, corals, and trees have been studied. These records differ from each other with respect to the temporal resolution and time period covered, and each has its own advantages and characteristics.

Seasonal resolution can be achieved by using ice cores from glaciers, which have rapid accumulation rates, reaching several centimeters per year (Haeberli and Wallén 1992; Boutron 1995). Corals can provide annual resolution due to growth rates as high as 10–20 mm/year (Shen and Boyle 1987, 1988a; Linn et al. 1990; Tudhope et al. 1998). Aquatic sediments and peat bogs are deposited at much slower rates: c. 10 mm/10^6 years in Fe-Mn crusts (von Blanckenburg et al. 1996), c. 10–100 m/10^6 years in shelf regions (Einsele 1992), c. 50–1000 m/10^6 years in lakes (Einsele 1992) and c. 1 mm/year in peats in northern Eurasia (Klimanov and Sirin 1997). Hence, these sedimentary records provide more compact but less detailed inventories.

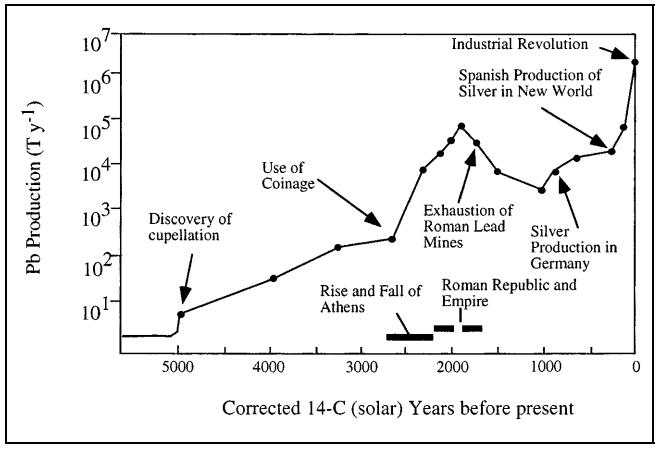

Fig. 1. Diagram showing worldwide lead production over the past 5000 years (Redrawn from Settle and Patterson 1980)

These archives also differ greatly with respect to the time period covered: deep-sea sediments and Fe-Mn crusts cover up to several millions of years (Christensen et al. 1997; von Blanckenburg et al. 1996), peat bogs reach back to the Late Glacial Period approximately 15,000 years ago (Warner et al. 1993; Shotyk et al. 1998), whereas corals and trees record only up to a few hundred years (Shen and Boyle 1987; Hagemeyer 1993).

The isotopic composition is often determined to identify the sources of lead. Of the four stable lead isotopes, only ^{204}Pb is nonradiogenic (Doe 1970; Dickin 1995). The other three are the final decay products of complex decay chains from uranium (U) and thorium (Th):

$^{238}U \rightarrow {}^{206}Pb$
($t_{1/2} = 4.5 \times 10^9$ years; $\lambda = 1.55 \times 10^{-10}$/year)
$^{235}U \rightarrow {}^{207}Pb$
($t_{1/2} = 7.1 \times 10^8$ years; $\lambda = 9.85 \times 10^{-10}$/year)
$^{232}Th \rightarrow {}^{208}Pb$
($t_{1/2} = 1.4 \times 10^{10}$ years; $\lambda = 0.49 \times 10^{-10}$/year)

where $t_{1/2}$ is the half-life and λ the decay constant. The intermediate members of each series are relatively short lived and can usually be ignored within geological time spans. Depending on the formation age, the initial uranium, thorium, and lead concentrations and the geological history, the lead isotope ratios of rocks and minerals can differ significantly from one location to another, and minerals alter their ratios continuously depending on the U/Pb and Th/Pb ratios. The natural $^{206}Pb/^{207}Pb$ ratio of atmospheric lead in central and western Europe ranges from 1.19 to 1.21 (Monna et al. 1995, 1997; Shotyk et al. 1998). Most natural aerosols in this region are derived either from Saharan dust (Grousset et al. 1994; Wagenbach et al. 1996; Chester et al. 1997) or from weathering of Variscan granites (Steinmann and Stille 1997).

Anthropogenic lead in the atmosphere is derived from high-temperature industrial processes (steel and nonferrous metal production), fuel combustion (gasoline, oil and coal), and incineration of municipal solid waste (Nriagu and Pacyna 1988; Nriagu 1989; Pacyna et al. 1995). The lead ores presently

used for industrial manufacturing and automotive fuel originate outside Europe and are characterized by $^{206}Pb/^{207}Pb$ ratios lower than 1.16 (Ault et al. 1970; Chow 1970; Chow et al. 1975). Unlike the light, stable isotopes (C, H, N, O, S), the fractionation of lead isotopes is not measurable during industrial or biological consumption processes (Ault et al. 1970; Rabinowitz and Wetherill 1972; Parkinson and Catchpole 1973).

We review some characteristics of past atmospheric lead deposition and its possible sources with emphasis on mainland Europe and Greenland; corals and marine sediments are only briefly discussed.

Ice Cores

Studies of snow and ice deposits have revealed most of our present knowledge on the history of atmospheric metal pollution (Oeschger and Langway 1989). These began with the landmark paper of Murozumi et al. (1969), who investigated ice cores from Greenland as an archive of lead pollution and its possible sources. They deduced that extensive hemispheric lead contamination of the Arctic atmosphere had begun even before the Industrial Revolution. Subsequent studies have revealed that the concentrations of lead and other heavy metals in ice deposits of Greenland between 2500 and 1600 years before the present (BP) were approximately four times higher than the background, implying a widespread pollution of the northern hemisphere by emissions from Roman mines and smelters (Hong et al. 1994, 1996a). In a recent study using lead isotope ratios, Rosman et al. (1997) showed that this lead was derived mainly from the vast mining areas in Spain. Lead concentrations decreased to background levels (approximately 0.5 pg/g) after the collapse of the Roman Empire. A steady rise began again with the mining renaissance in Europe, reaching values of 10 pg/g in 1770 and 50 pg/g in the mid-1990s (Candelone et al. 1995). Figure 2 shows the changes in lead concentrations and the calculated lead enrichments in central Greenland ice from 2960 to 470 years BP. A significant drop in the lead concentrations has been documented since the 1970s, and this is attributed to the phasing out of leaded gasoline in North America and Europe (Rosman et al. 1993).

The great potential of Greenland and Antarctic ice cores to provide the data for reconstructing reliable records of atmospheric metal deposition, however, has a major drawback in the extremely low concentrations of lead and nearly all the heavy metals of interest (picogram/g or less). Such studies have thus been severely challenged by contamination problems and, until recently (e.g. Barbante et al. 1997), inadequate analytical sensitivity. Patterson and Settle (1976) showed clearly the problem of contamination involved in trace and ultratrace analyses of remote archives. Therefore only those few laboratories with extremely ultraclean conditions can be considered for these investigations (Boutron 1990). Another limitation is the geographic location. The Greenland ice record is influenced by both European and North American sources, and thus it is not possible to reveal a pollution history exclusively for continental Europe by using the Greenland ice records (Rosman et al. 1993). An extensive review of the Greenland and Antarctic archives with respect to heavy metal deposition has been presented by Boutron and coworkers (Boutron et al. 1994; Boutron 1995).

Glaciers in Europe have generated a considerable amount of important information on recent heavy metal pollution (Wagenbach et al. 1996; Döring et al. 1997) and on changes in general aerosol chemistry (Wagenbach 1989; Baltensberg et al. 1997). Atmospheric lead deposition in snow was recorded between 1993 and 1996 in a high alpine glacier at Jungfraujoch, Switzerland, at c. 3500 m a.s.l. (Döring et

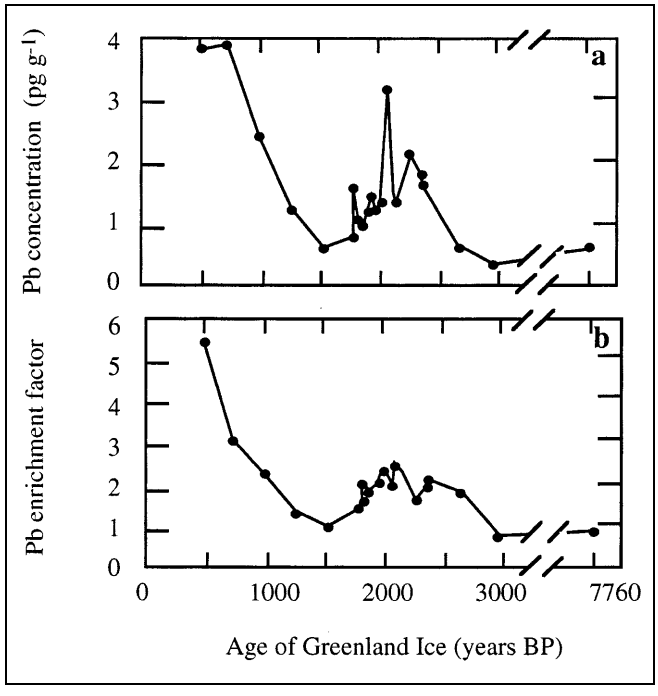

Fig. 2. Changes in lead concentration (a) and (b) lead enrichment (b) in central Greenland ice from 2960 to 470 years BP. Crustal enrichment (*EFPb*) was calculated as: $EFPb = (Pb/Al)_{sample}/(Pb/Al)_{crust}$. (Redrawn from Hong et al. 1994)

al. 1997). The concentrations varied between 0.02 ± 0.002 and 5.5 ± 0.15 ng/g and were slightly lower than concentrations from precipitation samples at similar remote sites in Europe (Atteia 1994). The $^{206}Pb/^{207}Pb$ ratios ranged from 1.156 to 1.131 and are explained by a two-source mixing between lead derived from gasoline (<1.12) and soil dust (>1.18). The ratios agree well with aerosols from western Europe (Elbaz-Poulichet et al. 1984; Grousset et al. 1994) and show that although lead emissions from traffic have decreased largely during the past 10 years, the contribution from this source in modern snow is still detectable and seems to be equal to the lead input from other sources (e.g., waste incineration). The interpretation of a long-term pollution history using European glaciers, however, is subjected to critical limitations such as periodic melting or percolation of melt-water (Oeschger and Langway 1989; Wagenbach 1989), possibly resulting in mobilization and transport of lead.

Sediments and Surface Water

Sediments used as archives range from lake sediments on different continents (e.g., Shirahata et al. 1980; Monna et al. 1995; Mogollon et al. 1996; Chiaradia et al. 1997) to various marine sediments (e.g., Chow and Patterson 1962; Hamilton and Clifton 1979; Patterson 1987; Véron et al. 1987; Gobeil and Silverberg 1989; Hamelin et al. 1990; Oehlander et al. 1993; Gobeil et al. 1995; Kersten et al. 1997; van Geen et al. 1997). Due to their low accumulation rates, Fe-Mn crusts and deep sea sediments generally cannot be used to assess short-term changes in atmospheric deposition such as recent anthropogenic perturbation. They provide long-term integrated records and changes in lead deposition found in the Pacific and Atlantic Oceans have been related to large-scale climatic modifications such as the vigor of the wind and the ocean circulation systems (Christensen et al. 1997). The isotopic composition has remained remarkably uniform over the past 30 million years, and small variations correspond to other paleoceanographic indicators of climate change including weathering and glaciation (Christensen et al. 1997). Coastal sediments with much higher accumulation rates than deep-sea sediments have been used to establish regional historical trends despite the possible complications caused by biological or geological perturbations. Significant lead pollution has been documented in surface sediments collected in the northeastern (Véron et al. 1987) and northwestern Atlantic shelf (Hamelin et al. 1990; Hamelin et al. 1997). These records suggest that about half of the atmospheric pollutant lead introduced since the beginning of the Industrial Revolution has already accumulated in North Atlantic sediments. Figure 3 gives an average inventory of the input of anthropogenic lead into the North Atlantic, derived from sediment concentrations (Véron et al. 1987). Lead isotope measurements of sediments have been used to decipher the major geographic origin of this lead and identified Europe as the dominant source for the northeast and North America for the northwest Atlantic (Hamelin et al. 1990).

Lake sediments have been widely investigated in North America (e.g., Graney et al. 1995; Blais 1996) and Europe (e.g., Keinonen 1992; Horn et al. 1993; Renberg et al. 1994; Monna et al. 1995), mostly covering periods within the past 150 years. With respect to the lead pollution sources and temporal deposition patterns, the studied sediments showed a remarkably similar and coherent picture: lead fluxes and/or isotopic composition generally shifted away from the natural background at the beginning or in the middle of the nineteenth century, for example, in Belgium (Petit et al. 1984), Switzerland (Müller 1982; Birch et al. 1996; Moor et al. 1996; von Gunten et al. 1997), Sweden (Johansson 1989; Bränvall et al. 1997), Germany (Müller 1997), Scotland (Farmer et al. 1996, 1997), and North America (Graney et al. 1995). Lead concentrations and Pb isotopes indicate a very rapid increase in industrially derived atmospheric emission until c. 1960, thereafter followed by gasoline combustion (Petit et al. 1984). Figure 4 shows the sedimentary record of Lake Zug, Switzerland. Lead concentrations reached a maximum of 110 μg/g at a depth of 8 cm, corresponding to c. 1970, the time of the greatest lead emissions in

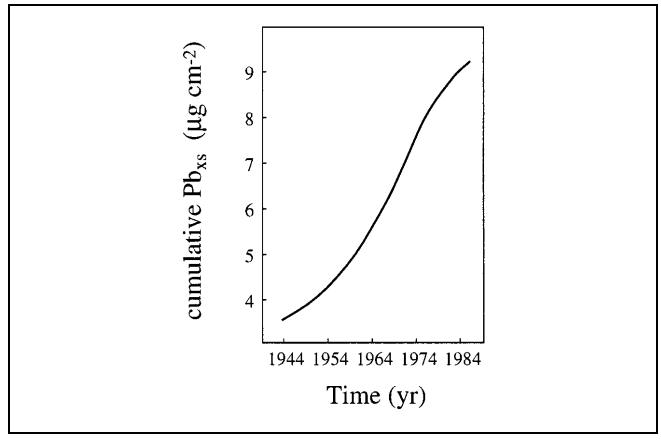

Fig. 3. Average inventory of the input of anthropogenic pollutant lead (Pb_{xs}) over the North Atlantic, derived from sediment concentrations. (Redrawn from Véron et al. 1987)

Switzerland (Moor et al. 1996). The ratios in the sediments had a minimum of 1.13 in c. 1980 and increased to 1.16 in c. 1990, attributed to the phasing out of leaded gasoline (Moor et al. 1996). Analyses of lake sediments from Sweden provide until now the only long-term records of atmospheric lead deposition, reaching back to pre-Roman times (Renberg et al. 1994; Bränvall et al. 1997). These records show lead concentrations increasing above background levels more than 2600 years ago, and small but significant lead deposition peaks occurred about 2000 years ago (Fig. 4). A more significant increase began 1000 years ago and accelerated during the nineteenth and twentieth centuries, with a deposition maximum at about 1970 (Renberg et al. 1994). Sources of lead in lake and ocean sediments, however, are not necessarily only atmospheric. Fluvial inputs and erosion of rocks, which are exposed along bluffs and surrounding shorelines add to the atmospheric lead and make the records more complicated and difficult to interpret. For example, lead concentrations in sediments of Lake Zurich increased after the beginning of industrialization in the early nineteenth century, but were correlated later with the rise and fall in local industrial production and wastewater discharge rather than with atmospheric emission inventories (von Gunten et al. 1997). Similarly, a study of lead pollution in the western Mediterranean Sea using sediments showed that metal input was dominated by river discharge coming from inland Spain with intensive mining areas and activities during the second half of the nineteenth century (van Geen et al. 1997), and any atmospheric contribution was overprinted.

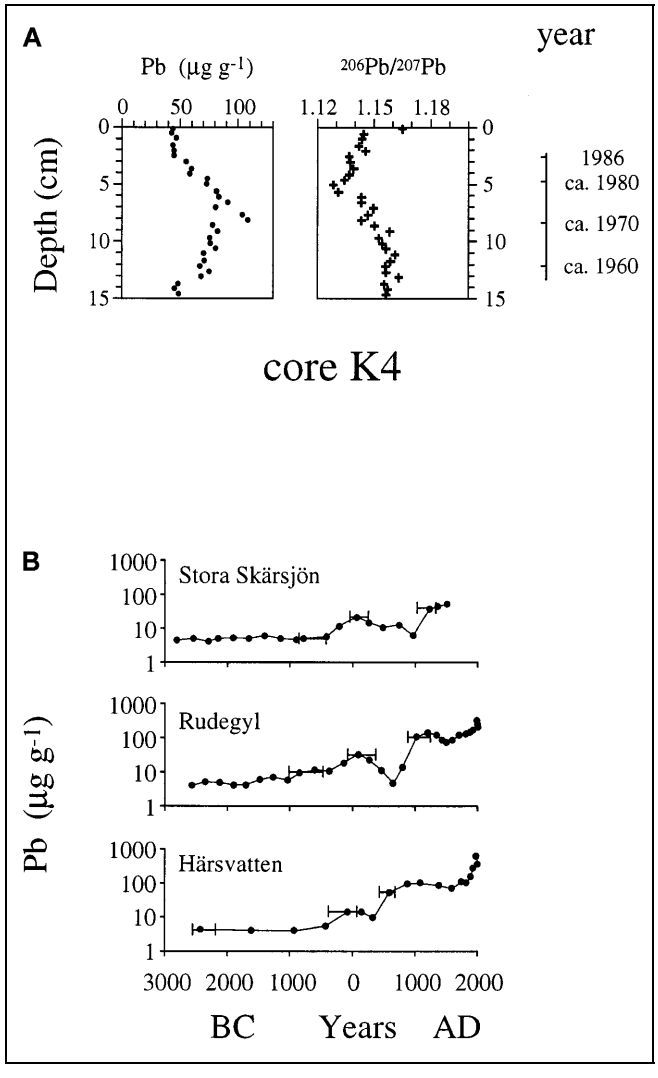

Fig. 4. a) Lead concentrations and $^{206}Pb/^{207}Pb$ ratios in a sediment core from Lake Zug, Switzerland. (Redrawn from Moor et al. 1996) b) Lead concentrations in three sediment cores from lakes in Sweden plotted against time (calibrated radiocarbon age dates). Lead deposition increased above background levels more than 2600 years ago. (Redrawn from Renberg et al. 1994)

An additional complication is associated with possible postdepositional mobility in the pore water due to (i) significant changes in pH, Eh, or other geochemical conditions and (ii) substantial release of lead during reductive dissolution of Fe and Mn oxides from sediments with seasonally anoxic bottom waters (Norton and Kahl 1987; Benoit and Hemond 1991).

Continuous monitoring of surface waters in the western Mediterranean (Nicolas et al. 1994) and eastern North Atlantic (Boyle et al. 1994; Wu and Boyle, 1997) demonstrate a decrease in lead contamination following the reduction in industrial and traffic emissions in Europe and North America. Lead isotopes have been used to document the decrease in North American lead input into the Sargasso sea (Shen and Boyle 1988b) coupled with increasing proportion of recycled European lead (Véron et al. 1993). Meanwhile, the presence of North American lead has been detected over the entire North and Central Atlantic, all along the transit of the North Atlantic gyre (Véron et al. 1994; Hamelin et al. 1997).

Peat Bogs

Ombrotrophic peat bogs receive all of their water and nutrients from the atmosphere by dry and wet deposition. As such, peat bogs have a great potential for recording the chronology and magnitude of atmospheric deposition of immobile elements. Peat bogs and ice cores are thus the only archives recording *exclusively* atmospheric lead deposition. Peat

bogs have several advantages: (a) peatlands are distributed across the globe, accounting for approximately 5% of the earth's total land area and offering thus the possibility to study local pollution histories, (b) in the northern hemisphere, peat formation began after the retreat of glacial ice, offering the possibility of records for the entire Holocene, which is not yet possible with the Greenland ice record (Hong et al. 1994, 1996b), and (c) because of their proximity to emission sources cores from bogs contain much higher metal concentrations than polar ice, i.e., in the order of 10^6–10^8 times for lead. Thus the measurement of heavy metals is much easier, a wider array of elements is potentially accessible, and contamination is less problematic. While the possible importance of post-depositional migration remains uncertain for most of the metals of interest (Damman 1978, Damman et al. 1992), recent analyses of the isotopic composition of Pb in dated peat cores indicated little if any vertical downward migration of this element (Shotyk et al. 1996a, 1997; Weiss 1998; MacKenzie et al. 1997, 1998a,b). Before using a peat core as archive of atmospheric Pb deposition, however, the ombrotrophic status of the peat bogs must be assessed by geochemical methods (Shotyk 1988, 1996).

Peat bogs have been investigated in a number of studies conducted in North America (e.g., Glooschenko et al. 1979; Glooschenko 1986; Norton and Kahl 1987; Norton et al. 1990, 1997; Urban et al. 1990), South America (Espi et al. 1997), and Europe (van Geel et al. 1989; Görres and Frenzel 1993, 1997; Shotyk 1996; Shotyk et al. 1996a; MacKenzie et al. 1998a,b). Enough data are thus available to establish a preliminary chronology of atmospheric lead fluxes in Europe for the past 2000 years using peat bogs (Shotyk et al. 1996b; Dunlop et al. 1999). In most studies the trends of fluxes are similar to the history of global lead production. For example, the decrease in lead emission following the decline in the Roman Empire and the increase in lead production since the beginning of the Industrial Revolution in the nineteenth century is clearly reflected in peat bog deposits of Sweden (Bränvall et al. 1997), the United Kingdom (Lee and Tallis 1973), Switzerland (Shotyk et al. 1996a), and the Netherlands (van Geel et al. 1989).

European peat bogs, affected more strongly by local pollution sources, show slightly different patterns. Peat bogs in the Harz mountains of Germany have highest lead concentrations in samples dating from medieval times, resulting from local mining (Müller and Lambersdorf 1995; Kempter et al. 1997). Changing lead input due to the varying mining activities at that time is correlated with local economic rises and falls (Müller and Lambersdorf 1995). In northwestern Spain a distinct lead peak at 2800 years BP is attributed to the metal trade of the Phoenicians that predated Roman culture by several centuries (Martinez-Cortizas et al. 1997). Pollution case studies from peat bogs near Sheffield, United Kingdom (Gilbertson et al. 1997), and southwestern England (West et al. 1997) reflect clearly local mining histories.

A continuous record since 12,370 ^{14}C years BP is documented from the Etang de la Gruère in the Jura Mountains of Switzerland (Shotyk et al. 1998; Weiss 1997). Enhanced fluxes caused by climate changes reached their maxima 10,590 ^{14}C years BP (Younger Dryas), and 8230 ^{14}C years BP. Soil erosion caused by forest clearing and agricultural tillage increased lead deposition after 5320 ^{14}C years BP (Weiss et al. 1997), documented by enhanced Pb and Sc concentrations in the peat bog profile. Increasing Pb/Sc and decreasing ^{206}Pb/^{207}Pb ratios beginning 3000 ^{14}C years BP indicate the beginning of lead pollution from mining and smelting, and anthropogenic sources have dominated lead emissions ever since. The greatest lead flux of 15.7 mg/m^2/yr in c. 1979 was 1570 times the natural background value of 0.01 mg/m^2/yr from 8030 to 5320 ^{14}C years BP (Shotyk et al. 1998). Figure 5 shows calculated lead enrichment factors (PbEF) relative to the local background and the changes in lead isotopic composition to distinguish natural from anthropogenic sources of atmospheric lead. At 3000 ^{14}C years BP the ^{206}Pb/^{207}Pb ratio decreased, and the lead enrichment factor exceeded 2 for the first time; all peats samples above this depth have ^{206}Pb/^{207}Pb ratios less than 1.19 and PbEF values of 2 or higher. Therefore lead is enriched out of proportion with scandium (Sc), and this lead is not sufficiently radiogenic to have derived exclusively from soil dust: an additional, less radiogenic component is most likely to have been supplied by Palaeozoic and older lead ores (Shotyk et al. 1998; Weiss 1998).

Concise reviews for assessing past and recent atmospheric lead deposition using peat bogs have been presented by Glooschenko (1986), Livett (1988), Shotyk (1988, 1996).

Soils

The use of soils for detailed chronologies of atmospheric lead deposition is restricted by the insufficient stratigraphic layering of soils and by possible lead mobility. Estimates of the residence time of lead in soils are strongly debated, ranging between

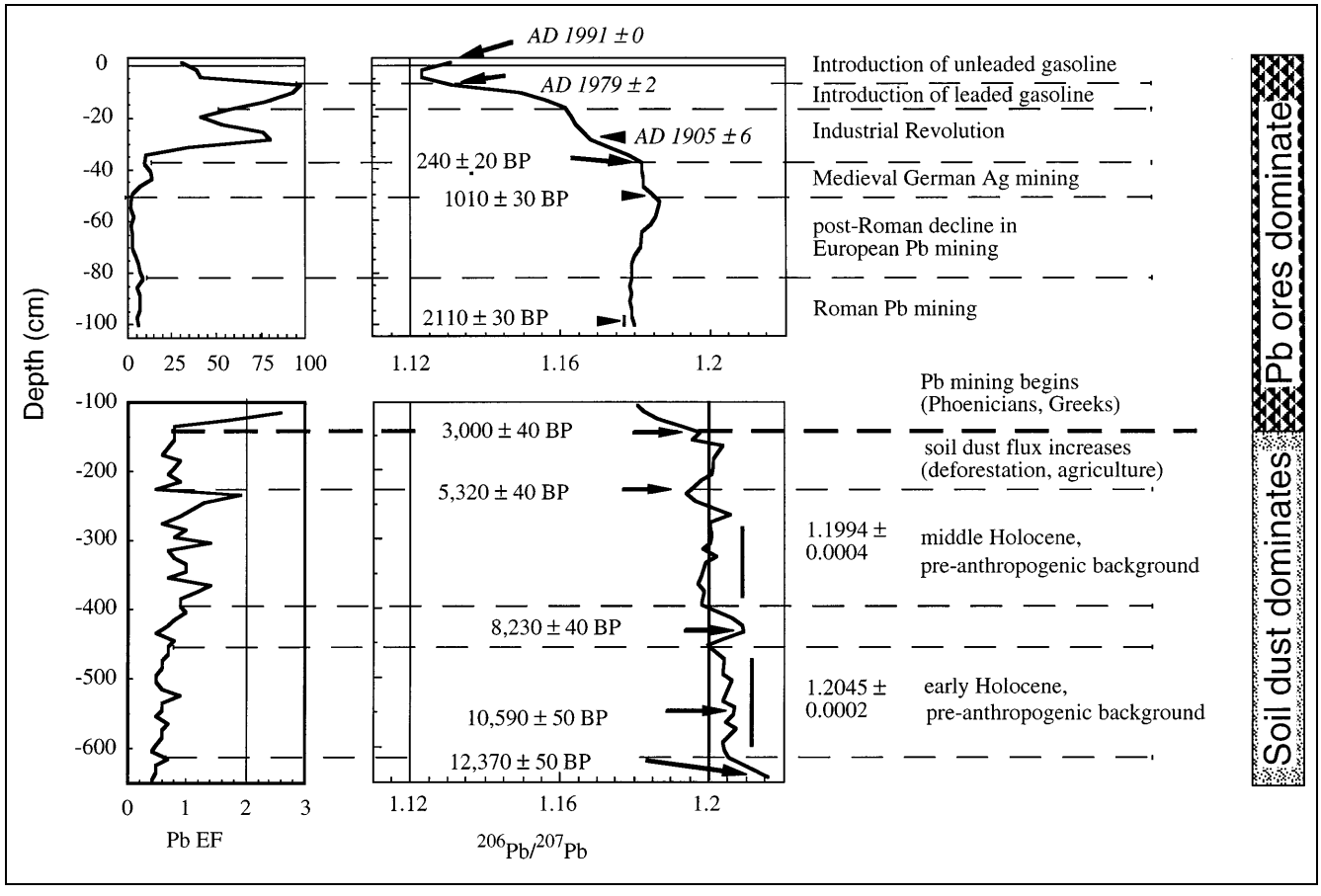

Fig. 5. Lead enrichment factor (*EFPb*), calculated as the ratio of Pb/Sc in the peats, normalized to the background value. The isotopic composition of lead is summarized as $^{206}Pb/^{207}Pb$, and the chronology of atmospheric deposition in a Swiss peat bog since 12,370 ^{14}C years BP is given. *Heavy, horizontal, dashed line* at 3000 ^{14}C years BP separates the lower sections of the peat profile where the dominant lead source is soil dust and the upper section where ore Pb predominate. Note different scale of upper and lower section for PbEF. (Redrawn from Shotyk et al. 1998)

17 (Miller and Friedland 1994) and 500 years (Siccama et al. 1980; Tyler 1981). Nevertheless, the study of soils has been successful for tracing the sources of recent, atmospherically derived lead contamination. In Switzerland (Steinmann and Stille 1997; Hansmann et al. 1999), Germany (Puchelt et al. 1993), Poland (Bacon and Steegstra 1994), the United Kingdom (Bacon et al. 1996), the Netherlands (Walraven et al. 1997), and Israel (Erel et al. 1997), lead concentrations in the topsoil are higher than in deeper horizons and the lead isotopes show a trend from radiogenic, natural ratios deeper in the profiles to less radiogenic, atmospheric lead in the topsoil, implying automobile and industrial emissions as the main sources (Fig. 6).

A detailed geochemical study of lead pollution in Israel has distinguished various geographic source regions (Turkey and Greece) for the lead recently transported by the atmosphere from across the Mediterranean Sea (Erel et al. 1997). Using concentrations and isotopic compositions, net rates of atmospheric lead input for various contaminants were calculated for a number of locations in Switzerland (Hansmann et al. 1999). This study also demonstrated that high lead concentrations in the topsoil can be derived from natural sources and do not necessarily reflect anthropogenic influence. Combining isotopic ratios and statistical analyses of geochemical data sets has provided a tool to trace the sources of contaminants in soils of a former village of whalers in the Netherlands (Walraven et al. 1997). There the major lead contaminant sources were shown to be: (a) local sources such as remnants of the old town (building materials), (b) coal ashes, and (c) alkyl-leaded petrol. The $^{206}Pb/^{207}Pb$ ratio of bulk soil samples collected at an agricultural station in the United Kingdom (Bacon et al. 1996) decreased from 1.187 in 1876 to 1.180 in 1984 (Fig. 6). The ratios, however, never reached values found in herbage samples collected at the same site (see below,

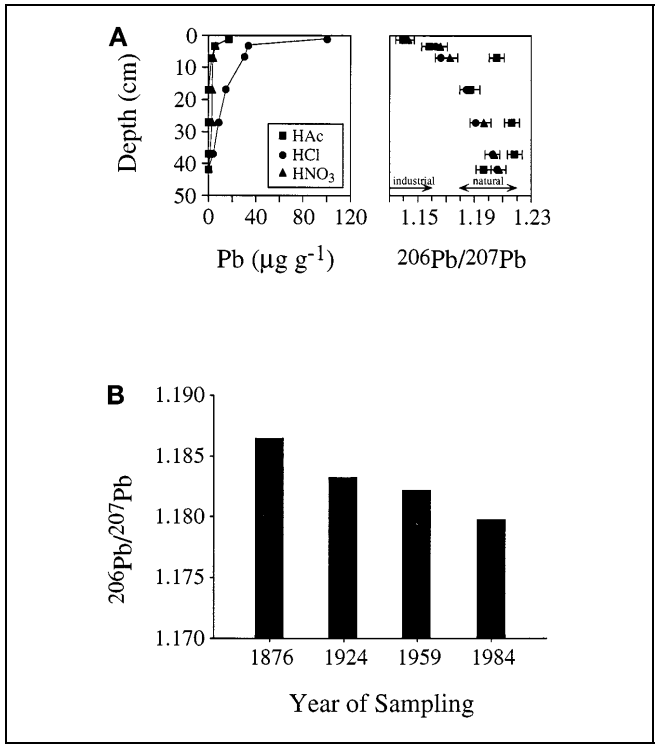

Fig. 6. a) $^{206}Pb/^{207}Pb$ isotope ratios demonstrate the retention of anthropogenic lead in the uppermost 30 cm of the soil. The samples were extracted sequentially in three steps with 1 N HNO_3 (*filled triangles*), 1 N HCl (*filled circles*), and 1 N HAc (*filled squares*). The limits of industrial and natural isotopic ratios are discussed in the text. (Redrawn from Steinmann and Stille 1997) b) $^{206}Pb/^{207}Pb$ ratios in bulk soil samples from the United Kingdom taken in 1876, 1924, 1959, and 1984. (Redrawn from Bacon et al. 1996)

Fig. 7). These findings were explained in terms of (a) natural lead present in the soil dominating total lead and (b) anthropogenic lead having had only a small impact.

Biomonitors: Corals, Trees, Herbarium Collections, and Human Tissue Material

Using annually banded corals, accurate chronologies of atmospherically derived lead pollution have been reconstructed for the Galapagos Islands in the seventeenth century (Linn et al. 1990) and for the western North Atlantic, Pacific, and Indian Oceans in the twentieth (Shen and Boyle 1987, 1988a,b). These studies reveal a 15-fold increase in lead until 1971 in the Atlantic near Bermuda. Since then a threefold decline has been observed, interpreted as the result of the curtailed alkyl lead use in the United States (Shen and Boyle 1988b; Wu and Boyle 1997). Coral samples from remote areas of the South Pacific and

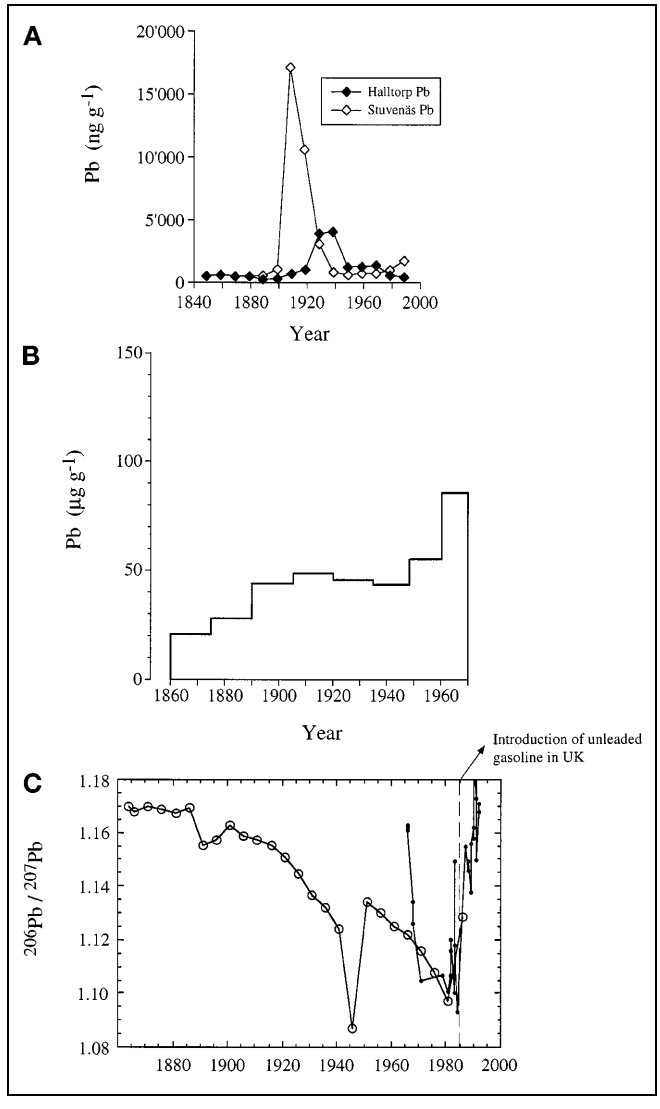

Fig. 7. a) Lead chronology for the twentieth century derived from oaks at two different locations (Halltrop, Stuvenäs) in Sweden. (Redrawn from Jonsson et al. 1997) b) Averaged lead concentrations of three different moss samples from a herbarium collection. (Redrawn from Rühling and Tyler 1970a). c) Changes in $^{206}Pb/^{207}Pb$ in 5-year composite samples of herbage from a grassland site in the United Kingdom since 1860 (*open circles*; redrawn from Bacon et al. 1996) and of aerosols from western Europe (*filled circles*; redrawn from Grousset et al. 1994)

Indian Oceans indicate, as expected, a much less pronounced industrial signal (Shen and Boyle 1988b). Seasonal and annual variations assessed with corals show that upwelling and the El Niño do not affect the lead record as much as, for example, the copper or cadmium record (Dodge and Gilbert 1984; Linn et al. 1990).

Tree ring analyses have proved useful for monitoring recent and reconstructing past emissions of lead and other heavy metals from point and diffuse

sources (Ault et al. 1970; Baes and McLaughlin 1984; Selin et al. 1993; Jonsson et al. 1997; Marcantonio et al. 1998). A chronology of lead pollution has been constructed in Sweden for the entire twentieth century using 23 oak trees (*Quercus robur L.*). The results agree reasonably well with estimated lead emission and accumulation rates in soils (Jonsson et al. 1997). Recent restrictions on industrial emissions and fuel additives, however, do no seem to have affected the lead uptake of the trees, and lead concentrations in the tree rings since 1980 have not decreased as expected (Fig. 7). Radial distributions of lead in a beech stem (*Fagus sylvatica*) in Germany show two periods of enrichment between 1900–1940 and since 1950 (Hagemeyer et al. 1992). However, this record was also found to have been subjected to temporal variability and thus to critical limitations (Hagemeyer et al. 1992). The use of trees as archives of atmospheric lead pollution is reviewed in detail by Cutter and Guyette (1993) and Hagemeyer (1993).

Biomaterial such as mosses (Rühling and Tyler 1970a, b; Lee and Tallis 1973; Ross 1990; Herpin et al. 1997; Rosman et al. 1998) and herbage plants (Williams 1974; Bacon et al. 1996) from plant collections have been used to identify the increase in atmospheric lead in various parts of Europe and to date lead pollution histories. Measurements of lead concentrations in and on plants and subsequent calculations of enrichment factors to quantify the anthropogenic influence, however, are limited (Markert 1993; Herpin et al. 1997). The amount of lead that is potentially available for plants in any given locality depends on various atmospheric as well as microenvironmental factors and can result in great spatial variability (Peterson 1978). Nevertheless, using concentration measurements of herbarium samples, research groups in Sweden (Rühling and Tyler 1970a), Germany (Herpin et al. 1997), and the United Kingdom (Lee and Tallis 1973) have shown increases in lead during two distinct periods in the past: towards the end of the nineteenth century and since 1950 (Fig. 7). The first increase was thought to originate from the burning of coal and wood (e.g., simultaneous increase in As concentrations in the German herbarium samples; Herpin et al. 1997) whereas the second peak was interpreted to result from increased gasoline consumption.

Lead isotopic analyses of herbage samples collected during the past 150 years at the Rothamsted Experimental Station in United Kingdom show a continuous reduction in the $^{206}Pb/^{207}Pb$ ratios from about 1.170 in 1880 to 1.098 in 1985 (Fig. 7). This was attributed to the use of coal, to industrial processes such as metal refining, and to leaded gasoline. An increase to more radiogenic values in 1986–1988 followed the introduction of unleaded gasoline in the United Kingdom (Bacon et al. 1996). Figure 7 also shows direct measurements of aerosols in western Europe (Grousset et al. 1994) for the same time period. The qualitative temporal patterns of change (e.g., the response to phasing-out of leaded gasoline) agree well. However, the absolute values differ quite strongly, which can be explained by isotopic variations in industrial or gasoline lead in the different countries and of the sampling sites (Hopper et al. 1991).

The preservation of lead within human tissues (Faure 1998) makes it possible to monitor long-term exposure of lead pollution to the element and to model changing sources during the lifetime of an individual (Budd et al. 1998) or throughout human history (Nriagu 1983). Important evidence of changing concentrations and sources of lead in the atmospheric environment have been derived from various materials, including teeth (Farmer et al. 1994; Budd et al. 1998; Yoshinga et al. 1998), bones (Keinonen 1992; Yoshinga et al. 1998), liver and lung (Keinonen 1992), and blood (Gulson et al. 1994; Stanek et al. 1998). A study of lead in prehistoric, historic, and contemporary Japanese, for example, shows that concentrations and isotopic composition in excavated (prehistoric and historic) bones, contemporary bones, and deciduous teeth differ from one other, for example, with elevated lead concentrations in historic persons (Yoshinga et al. 1998). Comparison with data from the literature on isotopic composition of environmental samples suggests that the lead of the prehistoric and historic bones were within the range of Japanese ores, rocks, and soils, indicating the absence of foreign lead sources. Contemporary bones, however, have isotopic compositions closer to gasoline lead and airborne particulate matter (Yoshinga et al. 1998). The use of archaeological material is currently problematic because of the site-specific nature of diagenesis and incomplete understanding of its chemistry, particularly in respect of lead uptake into the human tissue from the burial environment (Budd et al. 1998).

Pre-anthropogenic Aerosols

Records of atmospheric lead deposition covering the whole Holocene and thus dating back to pre-anthropogenic times are sparse for Europe. Such records, however, provide the natural background concentrations and isotopic ratios of aerosols and are thus very important for quantifying the effects of

human activities on the ecosystem. The ice cores in Greenland fail to give a complete lead record for the Holocene and Northern Hemisphere due to poor ice quality between approximately 3000 and 7600 years BP (Hong et al. 1994, 1996b). Lead concentration data are available for the last glacial and interglacial cycle between 8250–149,100 years BP, but isotopic data have not yet been published (Hong et al. 1996b). The Dome C ice core in Antarctica shows the presence of rather radiogenic lead ($^{206}Pb/^{207}Pb$ ratio of 1.252 ± 0.006) around 7500 years BP (Rosman et al. 1994) derived from terrestrial dust originating from South America. This ratio, however, may be restricted to the Southern Hemisphere. The complete and continuous vertical profile from the Swiss peat bog discussed above (Fig. 5) reveals the natural background concentration of aerosols in Europe (0.28 ± 0.04 μg/g). Similar concentrations (< 0.2 μg/g) have been found in layers of ancient peat in ombrotrophic peat bogs in Sweden (Bränvall et al. 1997). The background $^{206}Pb/^{207}Pb$ ratios of pre-anthropogenic aerosols were determined in the same Swiss peat core and ranged between 1.19 and 1.20, depending on the climatic conditions present during the time of peat formation (Fig. 5). This ratio agrees well with measurements from the peat bogs in Sweden with $^{206}Pb/^{207}Pb$ ratios of c .1.2 (Bränvall et al. 1997) and is consistent with possible sources such as soil dust of the Saharan region with a $^{206}Pb/^{207}Pb$ ratio of c. 1.19 (Grousset et al. 1994, 1995).

Conclusion

Hemispheric atmospheric lead pollution has been documented in many different geochemical archives in Europe and North America. It started 6000 years ago due to agricultural activities and soil tillage and showed the most prominent peaks around the turn of the century and between 1960 and 1980, reflecting industrial emissions during the Industrial Revolution and leaded gasoline combustion of traffic, respectively. Significant concentrations of anthropogenic lead obviously still exist in many archives such as soil and aquatic sediments, and it is thought that it will take many years to reduce these concentrations to prepollution values, even if no new sources of lead pollution emerge (Callender and van Meter 1997; Shotyk et al. 1998).

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