

Archives of Atmospheric Lead Pollution

Dominik Weiss¹, William Shotyk, Oliver Kempf
Geologisches Institut, Universität Bern,
Baltzerstrasse 1, CH-3012 Bern, Switzerland

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.

¹Present address: Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

Correspondence to: W. Shotyk
e-mail: shotyk@geo.unibe.ch

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:

$$\text{IF} = \frac{\text{global anthropogenic emission rates}}{\text{global natural emission rates}}$$

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

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

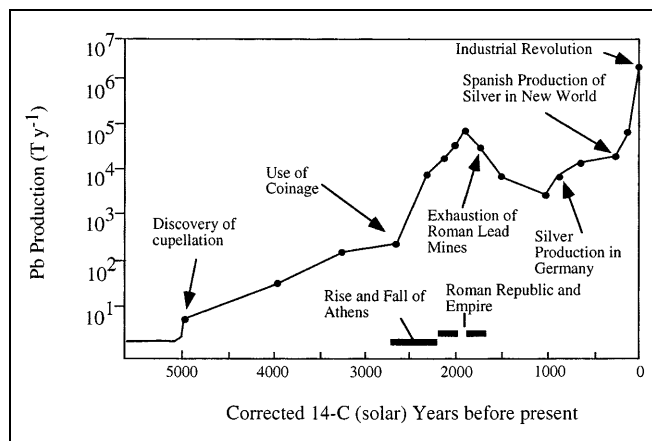
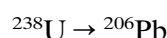


Fig. 1. Diagram showing worldwide lead production over the past 5000 years (Redrawn from Settle and Patterson 1980)

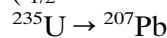
high as 10–20 mm/year (Shen and Boyle 1987, 1988a; Linn et al. 1990; Tudhope et al. 1998). Aquatic sediments and peat bogs are deposited at much slower rates: c. 10 mm/10⁶ years in Fe-Mn crusts (von Blanckenburg et al. 1996), c. 10–100 m/10⁶ years in shelf regions (Einsele 1992), c. 50–1000 m/10⁶ years 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.

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).

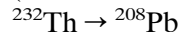
The isotopic composition is often determined to identify the sources of lead. Of the four stable lead isotopes, only ²⁰⁴Pb is nonradiogenic (Doe 1970; Dickin 1995). The other three are the final decay products of complex decay chains from uranium (U) and thorium (Th):



$$(t_{1/2} = 4.5 \times 10^9 \text{ years}; \lambda = 1.55 \times 10^{-10}/\text{year})$$



$$(t_{1/2} = 7.1 \times 10^8 \text{ years}; \lambda = 9.85 \times 10^{-10}/\text{year})$$



$$(t_{1/2} = 1.4 \times 10^{10} \text{ years}; \lambda = 0.49 \times 10^{-10}/\text{year})$$

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 ²⁰⁶Pb/²⁰⁷Pb 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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

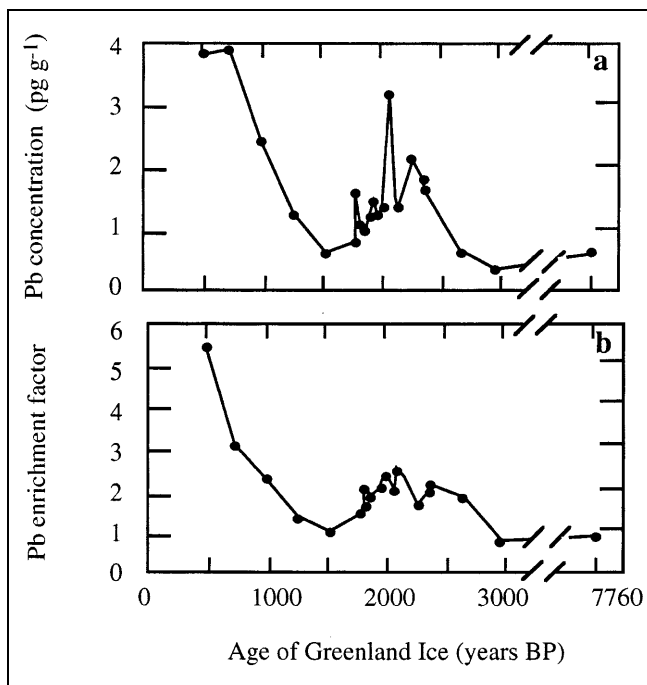


Fig. 2. Changes in lead concentration (a) and (b) lead enrichment (b) in central Greenland ice from 2960 to 470 years BP. Crustal enrichment ($EFPb$) was calculated as: $EFPb = (\text{Pb}/\text{Al})_{\text{sample}} / (\text{Pb}/\text{Al})_{\text{crust}}$ (Redrawn from Hong et al. 1994)

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

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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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; Chiariadia 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 $110 \mu\text{g/g}$ at a depth of 8 cm, corresponding to c. 1970, the time of the greatest lead emissions in

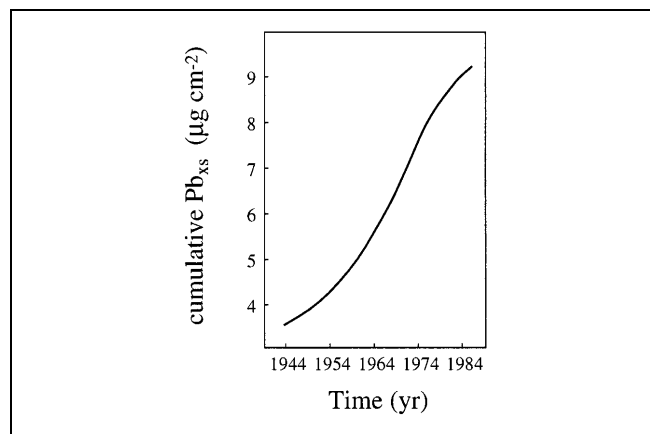


Fig. 3. Average inventory of the input of anthropogenic pollutant lead (Pb_{xs}) over the North Atlantic, derived from sediment concentrations. (Redrawn from Véron et al. 1987)

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.

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

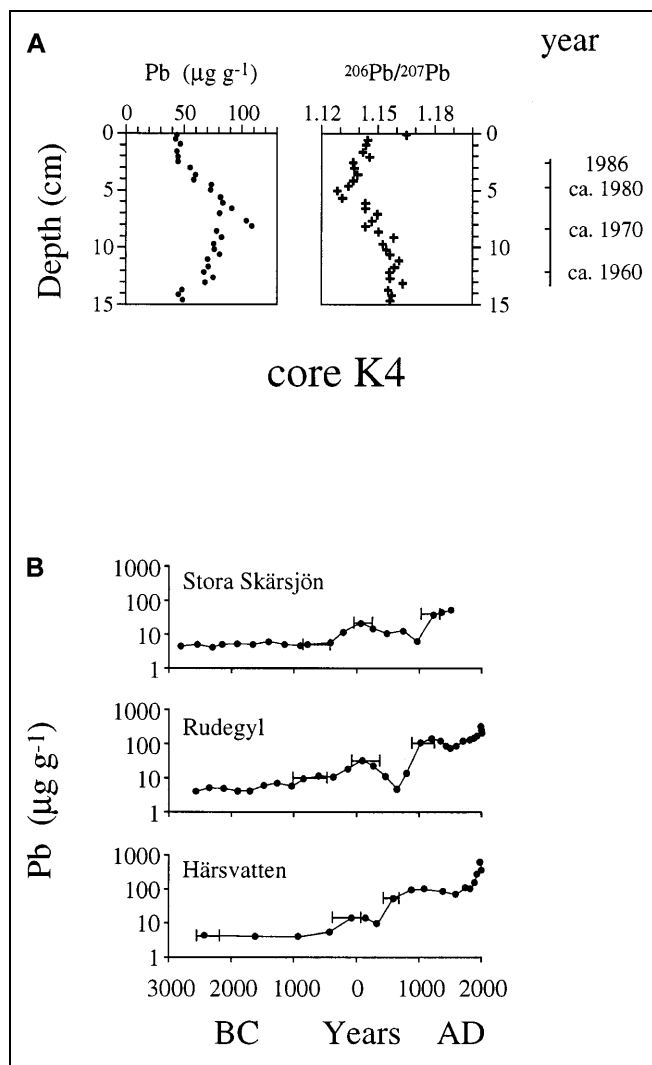


Fig. 4. a) Lead concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in a sediment core from Lake Zug, Switzerland. (Redrawn from Moor et al. 1996) b) Lead concentrations in three sediment cores from lakes in Sweden plotted against time (calibrated radiocarbon age dates). Lead deposition increased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

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 (Espí 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $\text{mg}/\text{m}^2/\text{yr}$ in c. 1979 was 1570 times the natural background value of 0.01 $\text{mg}/\text{m}^2/\text{yr}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreased, and the lead enrichment factor exceeded 2 for the first time; all peat samples above this depth have $^{206}\text{Pb}/^{207}\text{Pb}$ 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

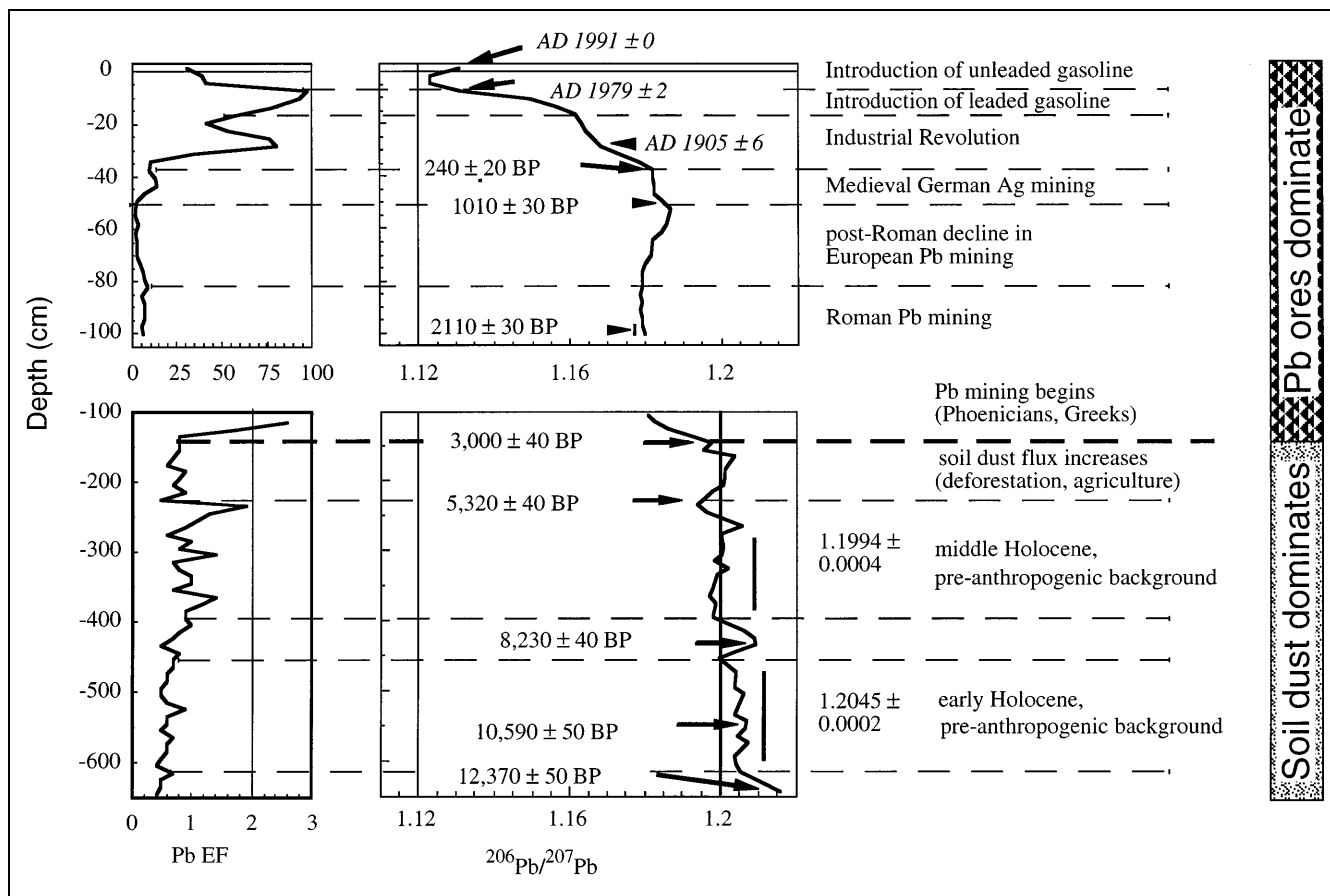


Fig. 5. Lead enrichment factor (EF_{Pb}), calculated as the ratio of Pb/Sc in the peats, normalized to the background value. The isotopic composition of lead is summarized as $^{206}\text{Pb}/^{207}\text{Pb}$, and the chronology of atmospheric deposition in a Swiss peat bog since 12,370 ^{14}C years 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 Shoty et al. 1998)

17 (Miller and Friedland 1994) and 500 years (Siccamma 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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,

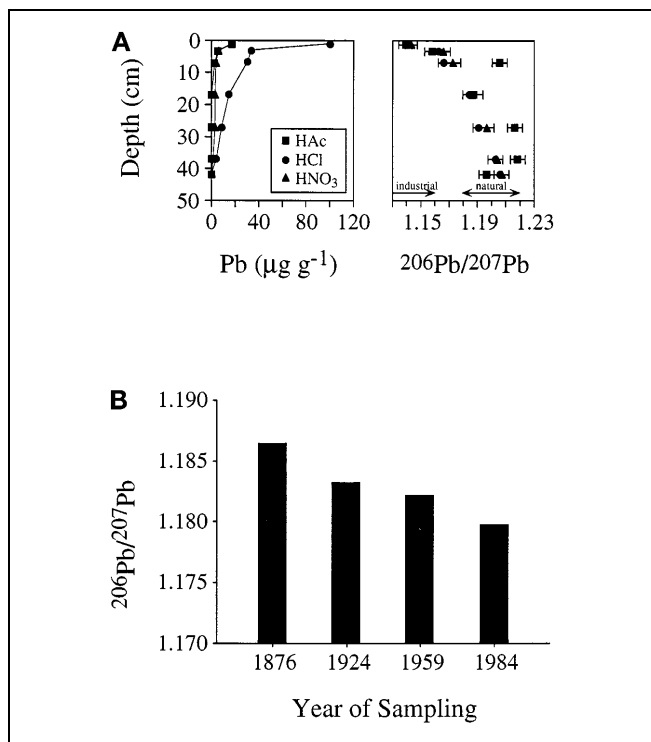


Fig. 6. a) $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios demonstrate the retention of anthropogenic lead in the uppermost 30 cm of the soil. The samples were extracted sequentially in three steps with 1 N HNO₃ (filled triangles), 1 N HCl (filled circles), and 1 N HAc (filled squares). The limits of industrial and natural isotopic ratios are discussed in the text. (Redrawn from Steinmann and Stille 1997) b) $^{206}\text{Pb}/^{207}\text{Pb}$ 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

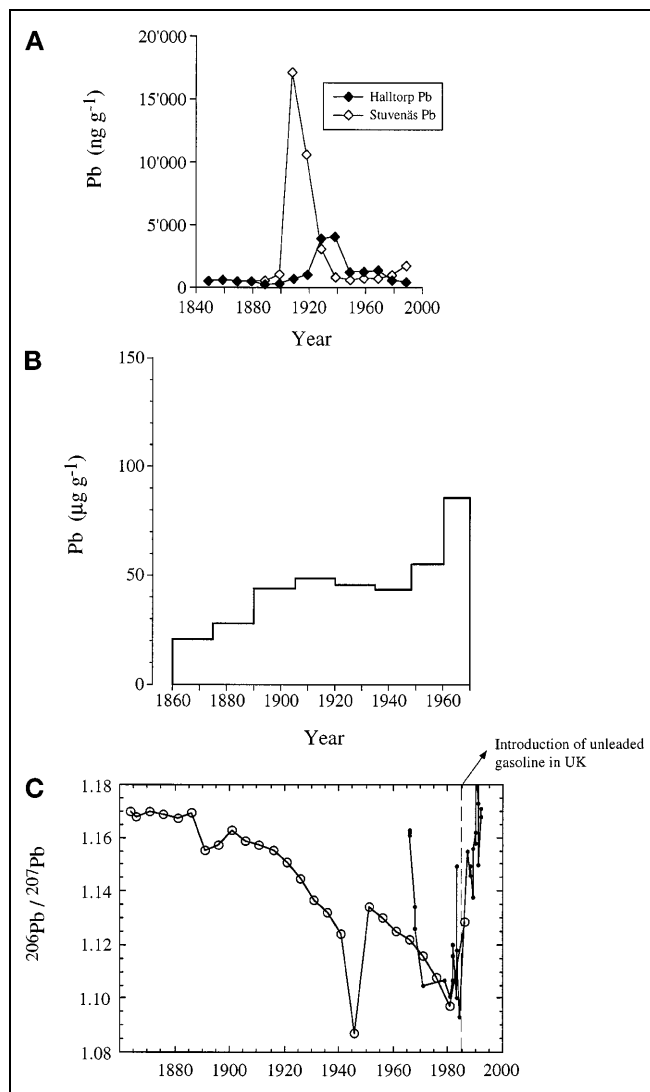


Fig. 7. a) Lead chronology for the twentieth century derived from oaks at two different locations (Halltrop, Stuvénäs) in Sweden. (Redrawn from Jonsson et al. 1997) b) Averaged lead concentrations of three different moss samples from a herbarium collection. (Redrawn from Rühling and Tyler 1970a). c) Changes in $^{206}\text{Pb}/^{207}\text{Pb}$ 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; Marcan-tonio 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 not 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 in-

crease 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 ($^{206}\text{Pb}/^{207}\text{Pb}$ 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 ($0.28 \pm 0.04 \mu\text{g/g}$). Similar concentrations ($< 0.2 \mu\text{g/g}$) have been found in layers of ancient peat in ombrotrophic peat bogs in Sweden (Bränvall et al. 1997). The background $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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).

Discussions with C. Weyhenmeyer, B. van Geel, J. D. Kramers, P. Blaser, V. Koepfel, E.A. Boyle, J.O. Nriagu, J.M. Pacyna, and many others are gratefully acknowledged. We thank Prof. C. Schlüchter and

Prof. A. Matter for their continuous support of our research on atmospheric deposition of heavy metals in peat bogs. This work was financially supported by the Swiss Science Foundation (SNF grant no. 20-42273.94). Reviews by C. Weyhenmeyer on an earlier version is greatly acknowledged. Comments from three anonymous reviewers are greatly appreciated. D.W. thanks I. Kunz for support.

- Atteia O (1994) Major and trace elements in precipitation in western Switzerland. *Atmos Environ* 22:3617–3624
- Ault WA, Senechal RG, Erlebach WE (1970) Isotopic composition as a natural tracer of lead in the environment. *Environ Sci Technol* 4:305–314
- Bacon JR, Steegstra M (1994). Proceedings: 6th International Conference on Environmental Contamination, Delphi, Greece, pp 174–176
- Bacon JR, Jones KC, McGrath SP, Johnston AE (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
- Baes CF III, McLaughlin SB (1984) Trace elements in tree rings: evidence of recent and historical air pollution. *Science* 224:494–497
- Baltensberg U, Gäggeler HW, Jost DT, Kugauer M, Schwikowski M, Weingartner E, Seibert P (1997) Aerosol climatology at the high-Alpine site Jungfraujoch, Switzerland. *J Geophys Res* 102:19707–19715
- Barbante C, Bellomi T, Mezzadri G, Cescon P, Scarponi G, Morel C, Jay S, van der Velde K, Ferrari C, Boutron CF (1997) Direct determination of heavy metals at picogram per gram levels in Greenland and Antarctic snow by double focusing inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 12:925–931
- Benoit G, Hemond HF (1991) Evidence for diffusive redistribution of ^{210}Pb in lake sediments. *Geochim Cosmochim Acta* 55:1963–1975
- Birch L, Hanselmann KW, Bachofen R (1996) Heavy metal conservation in Lake Cadagno sediments: Historical records of anthropogenic emissions in a meromictic alpine lake. *Water Res* 30:679–687
- Blais JM (1996) Using isotopic tracers in lake sediments to assess atmospheric transport of lead in eastern Canada. *Water Air Soil Pollut* 92:329–342
- Boutron CF (1990) A clean laboratory for ultra low concentration heavy metal analysis. *Fresenius J Anal Chem* 337:482–491
- Boutron CF (1995) Historical reconstruction of the Earth's past atmospheric environment from Greenland and Antarctic snow and ice cores. *Environ Rev* 3:1–28
- Boutron CF, Candelone JP, Hong S (1994) Past and recent changes in the large-scale tropospheric cycles of lead and other heavy metals as documented in Antarctic and Greenland snow and ice: a review. *Geochim Cosmochim Acta* 58:3217–3225
- Boyle EA, Sherrell RM, Bacon MP (1994) Lead variability in the western North Atlantic Ocean and central Greenland: implications for the search for decadal trends in anthropogenic emissions. *Geochim Cosmochim Acta* 58:3227–3238
- Bränvall ML, Bindler R, Emteryd O, Nilsson M, Renberg I (1997) Stable isotope and concentration records of atmospheric lead pollution and lake sediments in Sweden. *Water Air Soil Pollut* 100:243–252
- Buat-Ménard P (1993) Global change in atmospheric metal cycles. In: Sturges WT, Hewitt AE (eds) *Global atmospheric chemical change*. Elsevier, Amsterdam
- Budd P, Montgomery J, Cox A, Krause P, Barreiro B, Thomas R (1998) The distribution of lead within ancient and modern human teeth: implications for long-term and historical exposure monitoring. *Sci Total Environ* 220:121–136

- Callender E, van Metre P (1997) Reservoir sediment cores show U.S. lead declines. *Environ Sci Technol* 31:424–428
- Candelone JP, Hong S, Pellone C, Boutron CF (1995) Post-industrial revolution changes in large-scale atmospheric pollution of the northern hemisphere by heavy metals as documented in central Greenland snow. *J Geophys Res* 100:16605–16616
- Chester R, Nimmo M, Corcoran PA (1997) Rain water aerosol trace metal relationships at Cap Ferrat: a coastal site in the western Mediterranean. *Mar Chem* 58:293–312
- Chiaradia M, Chenhall BE, Depers AM, Gulson BL, Jones BG (1997) Identification of historical lead sources in roof dusts and recent lake sediments from an industrialised area: indications from lead isotopes. *Sci Total Environ* 205:107–128
- Chow TJ (1970) Lead accumulation in road side soil and grass. *Nature* 225:295–296
- Chow TJ, Patterson CC (1962) The occurrence and significance of lead isotopes in pelagic sediments. *Geochim Cosmochim Acta* 26:263–308
- Chow TJ, Snyder CB, Earl JL (1975). Proceedings: UN, FAO, and IAEA Symposium, IAEA-SM-191/4, Vienna, pp 95–105
- Christensen JN, Halliday AN, Godfrey LV, Hein JR, Rea DK (1997) Climate and ocean dynamics and the lead isotopic records in Pacific ferro-manganese crusts. *Science* 277:913–917
- Cutter BE, Guyette RP (1993) Anatomical, chemical, and ecological factors affecting tree species choice in dendrochemistry studies. *J Environ Qual* 22:611–619
- Damman AWH (1978) Distribution and movement of elements in ombrotrophic peat bogs. *Oikos* 30:480–495
- Damman AWH, Tolonen K, Sallantausta T (1992) Element retention and removal in ombrotrophic peat of Hådetkeidas, a boreal Finnish peat bog. *Suo* 43:137–145
- Dickin AP (1995) Radiogenic isotope geology, Cambridge University Press, Cambridge
- Dodge RE, Gilbert TR (1984) Chronology of lead pollution contained by banded coral skeletons. *Mar Biol* 82:9–13
- Doe RB (1970) Lead isotopes. Springer, Berlin Heidelberg New York
- Döring T, Schwikowski M, Gäggeler HW (1997) Determination of lead concentrations and isotope ratios in recent snow samples from high alpine sites with a double focusing ICP-MS. *Fresenius J Anal Chem* 359:382–384
- Dunlap CE, Steinnes E, Flegal AR (1999) A Synthesis of lead isotopes in two millennia of European air. *Earth Planet Sci Lett* 167:81–88
- Einsele G (1992) Sedimentary basins: evolution, facies, and sediment budget, Springer, Berlin Heidelberg New York
- Elbaz-Poulichet F, Hollinger P, Huang WW, Martin JM (1984) Lead cycling in estuaries, illustrated by the Gironde estuary, France. *Nature* 308:409–414
- Erel Y, Veron A, Halicz L (1997) Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. *Geochim Cosmochim Acta* 61:4495–4505
- Espi E, Boutron CF, Hong S, Pourchet M, Ferrari W, Shotyk W, Charlet L (1997) Changing concentrations of Cu, Zn, Cd, and Pb in a high altitude peat bog from Bolivia during the past three centuries. *Water Air Soil Pollut* 100:289–296
- Farmer JG, Sugden CL, Mackenzie AB, Moody GH, Fulton M (1994) Isotopic ratios of lead in human teeth and sources of exposure in Edinburgh. *Environ Technol* 15:593–599
- Farmer JG, Eades LJ, MacKenzie AB, Kirika A, Bailey-Watts TE (1996) Stable isotope record of lead pollution in Loch Lomond sediments since 1630 AD. *Environ Sci Technol* 30:3080–3083
- Farmer JG, MacKenzie AB, Sugden CL, Edgar PJ, Eades LJ (1997) A comparison of the historical lead pollution records in peat and freshwater lake sediments from central Scotland. *Water Air Soil Pollut* 100:253–270
- Faure G (1998) Principles and applications of geochemistry. MacMillan, New York
- Fyfe WS (1981) The environmental crisis: quantifying geosphere interactions. *Science* 213:105–110
- Gilbertson DD, Grattan JP, Cressey M, Pyatt FB (1997) An air-pollution history of metallurgical innovation in iron- and steel making: a geochemical archive of Sheffield. *Water Air Soil Pollut* 100:327–341
- Glooschenko WA (1986) Monitoring the atmospheric deposition of metals by use of bog vegetation and peat profiles. In: Nriagu JO, Davidson DI (eds) Toxic metals in the atmosphere. Wiley, New York
- Glooschenko WA, Capobianco JA, Mayer T, Gregory M (1979). Proceedings: 6th Intern Peat Congress, Minnesota, pp 551–553
- Gobeil C, Silverberg N (1989) Early diagenesis of lead in Laurentian Trough sediments. *Geochim Cosmochim Acta* 53:1889–1895
- Gobeil C, Johnson WK, MacDonald RW, Wong CS (1995) Sources and burden of lead in St. Lawrence estuary sediments: isotopic evidence. *Environ Sci Technol* 28:193–201
- Görres M, Frenzel B (1993) The Pb, Br, and Ti content in peat bogs as indicator for recent and past depositions. *Naturwissenschaften* 80:333–335
- Görres M, Frenzel B (1997) Ash and metal concentrations in peat bogs as indicators of anthropogenic activity. *Water Air Soil Pollut* 100:355–365
- Graney JP, Halliday AN, Keeler GJ, Nriagu JO, Robbins JA, Norton SA (1995) Isotopic record of lead pollution in lake sediments from northeastern United States. *Geochim Cosmochim Acta* 59:1715–1728
- Grousset FE, Quétel CR, Thomas B, Buat-Ménard P, Donard OFX, Bucher A (1994) Transient Pb isotopic signatures in the western European atmosphere. *Environ Sci Technol* 28:1605–1608
- Grousset FE, Quétel CR, Thomas B, Donard OFX, Lambert CE, Guillard F, Monaco A (1995) Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. *Mar Chem* 48:291–310
- Gulson B, Mizon K, Law A, Korsch M, Howarth D (1994) Sources and pathways of lead in humans from the Broken Hill mining community – an alternative use of exploration methods. *Econ Geol* 89:889–908
- Haerberli W, Wallén CC (1992) Glaciers and the environment. UNEP, Nairobi
- Hagemeyer J (1993) Monitoring trace metal pollution with tree rings: a critical reassessment. In: Markert B (ed) Plants as biomonitors. VCH, Weinheim
- Hagemeyer J, Lüllsmann A, Perk M, Breckle SW (1992) Are there seasonal variations of trace element concentrations (Cd, Pb, Zn) in wood of *Fagus* trees in Germany? *Vegetatio* 101:55–63
- Hamelin B, Grousset FE, Sholkovitz ER (1990) Pb isotopes in surficial pelagic sediments from North Atlantic. *Geochim Cosmochim Acta* 54:37–47
- Hamelin B, Ferrand JL, Alleman L, Nicolas E (1997) Isotopic evidence of pollutant lead transport from North America to the subtropical North Atlantic gyre. *Geochim Cosmochim Acta* 61:4423–4428
- Hamilton E, Clifton R (1979) Isotopic abundances of lead in estuarine sediments, Swansea Bay, Bristol Channel. *Estuar Coast Mar Sci* 8:271–278
- Hansmann W, Koeppel V, Saager R, Steiger R (1999) Lead-isotopes as tracers of pollutants in soils. *Chem Geol* (in preparation)
- Herpin U, Markert B, Weckert V, Berlekamp J, Siewers U, Lieth H (1997) Retrospective analysis of heavy metal concentrations at selected locations in the Federal Republic of Germany using moss material from a herbarium. *Sci Total Environ* 205:1–12
- Hong S, Candelone JP, Patterson CC, Boutron CF (1994) Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilization. *Science* 265:1841–1843

- Hong S, Candelone JP, Patterson CC, Boutron CF (1996a) History of ancient copper smelting pollution during Roman and Medieval times recorded in Greenland ice. *Science* 272:246–249
- Hong S, Candelone JP, Turetta C, Boutron CF (1996b) Changes in natural lead, copper, zinc, and cadmium concentrations in central Greenland ice from 8,250 to 149,100 years ago: their association with climatic changes and resultant variations of dominant source contributions. *Earth Planet Sci Lett* 143:233–244
- Hopper JF, Ross HB, Sturges WT, Barrie LA (1991) Regional sources discrimination of atmospheric aerosols in Europe using the isotopic composition of lead. *Tellus* 43B:45–60
- Horn P, Hoelzl S, Schaaf P (1993) Pb- und Sr-isotope signatures as tracers for anthropogenic and geogeneous influences. *Isotopenpraxis* 28:263–272
- Johansson K (1989) Metals in sediments of lakes in northwestern Sweden. *Water Air Soil Pollut* 49:441–455
- Jonsson A, Eklund M, Hakansson K (1997) Heavy metals of the 20th century recorded in oak tree rings. *J Environ Qual* 26:1638–1643
- Keinonen M (1992) The isotopic composition of lead in man and the environment in Finland 1966–1987: isotope ratios of lead as indicators of pollutant source. *Sci Total Environ* 113:251–268
- Kempton H, Görres M, Frenzel B (1997) Ti and Pb concentrations in rainwater-fed bogs in Europe as indicator of anthropogenic activity. *Water Air Soil Pollut* 100:367–377
- Kersten M, Garbe-Schönberg C, Thomsen S, Anagnostou C, Sioulas A (1997) Source appointment of Pb pollution in the coastal waters of Elefsis Bay, Greece. *Environ Sci Technol* 31:1295–1301
- Klimanov VA, Sirin AA (1997) The dynamics of peat accumulation by mires of north eurasia during the last 3000 years. In: Northern forested wetlands: ecology and management. CRC, Baton Rouge
- Lee J, Tallis J (1973) Regional and historical aspects of lead pollution in Britain. *Nature* 245:216–220
- Linn LJ, Delayney ML, Druffel ERM (1990) Trace metals in contemporary and seventeenth-century Galapagos corals: records of seasonal and annual variations. *Geochim Cosmochim Acta* 54:387–394
- Livett EA (1988) Geochemical monitoring of atmospheric heavy metal pollution: theory and applications. *Adv Ecol Res* 18:65–174
- MacKenzie AB, Farmer JG, Sugden CL (1997) Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. *Sci Total Environ* 203:115–127
- MacKenzie AB, Logan EM, Cook GT, Pulford ID (1998a) Distributions, inventories and isotopic composition of lead in ²¹⁰Pb-dated peat cores from contrasting biogeochemical environments: implication for lead mobility. *Sci Total Environ* 223:25–35
- MacKenzie AB, Logan EM, Cook GT, Pulford ID (1998b) A historical record of atmospheric depositional fluxes of contaminants in west-central Scotland derived from an ombrotrophic peat core. *Sci Total Environ* 222:157–166
- Marcantonio F, Flowers G, Thien L, Ellgaard E (1998) Lead isotopes in tree rings: chronology of pollution in Bayou Trepagnier, Louisiana. *Environ Sci Technol* 32:2371–2376
- Markert B (1993) Plants as biomonitors – indicators for heavy metals in the terrestrial environment. VCH, Weinheim
- Martinez-Cortizas A, Pontevedra-Pombal X, Munos JCN, Garcia-Rodeja E (1997) Four thousand years of atmospheric Pb, Cd, and Zn deposition recorded by the ombrotrophic peat bog of Penido Vello (northwestern Spain). *Water Air Soil Pollut* 100:387–403
- Miller EK, Friedland AJ (1994) Lead migration in forest soils: response to changing atmospheric inputs. *Environ Sci Technol* 28:662–669
- Mogollon J, Bifano C, Davies BE (1996) Geochemistry and anthropogenic inputs of metals in a tropical lake in Venezuela. *Appl Geochem* 11:605–615
- Monna F, Othman DB, Luck JM (1995) Pb isotopes and Pb, Zn, and Cd concentrations in the rivers feeding a coastal pond (Thau, southern France): constraints on the origin(s) and flux(es) of metals. *Sci Total Environ* 166:19–34
- Monna F, Lancelot J, Croudace IW, Clundy AB, Lewis JT (1997) Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: implications for Pb pollution sources in urban areas. *Environ Sci Technol* 31:2277–2286
- Moor H, Schaller T, Sturm M (1996) Recent changes in stable lead isotope ratios in sediments of Lake Zug, Switzerland. *Environ Sci Technol* 30:2928–2933
- Müller G (1997) Nur noch geringer Eintrag anthropogener Schwermetalle in den Bodensee – Daten zur Entwicklung der Belastung der Sedimente. *Naturwissenschaften* 84:37–38
- Müller K (1982) Die Bielerseesedimente. Thesis. University of Berne
- Müller N, Lambersdorf N (1995) Verteilung und Mobilität von Schwermetallen in einem pollenanalytisch datierten Torfkern aus dem Roten Moor (Hochharz). *Telma* 25:143–162
- Murozumi M, Chow TJ, Patterson CC (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. *Geochim Cosmochim Acta* 33:1247–1294
- Nicolas E, Ruiz Pino D, Buat-Ménard P, Béthoux JP (1994) Abrupt decrease of lead concentrations in the Mediterranean: a response to antipollution policy. *Geophys Res Lett* 21:2119–2122
- Norton SA, Kahl JS (1987) A comparison of lake sediments and ombrotrophic peat deposits as long-term monitors of atmospheric pollution. In: Boyle TP (ed) New approaches to monitoring aquatic ecosystems. STP 940. ASTM, Philadelphia
- Norton SA, Dillon PJ, Evans RD, Mierle G, Kahl JS (1990) The history of atmospheric deposition of Cd, Hg, and Pb in North America: Evidences from lake and peat sediments. In: Lindberg SE, Page AL, Norton SA (eds) Sources, deposition, and canopy interactions, vol 3. Springer, Berlin Heidelberg New York
- Norton SA, Evans GC, Kahl JS (1997) Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sergeant Mt. Pond, Maine, USA. *Water Air Soil Pollut* 100:271–286
- Nriagu JO (1978) Properties and the biogeochemical cycle of lead. In: Nriagu JO (ed) The biogeochemistry of lead in the environment, vol A. Elsevier/North Holland Biomedical, Amsterdam
- Nriagu JO (1983) Lead and lead poisoning in antiquity. Wiley, New York
- Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. *Nature* 338:47–49
- Nriagu JO, Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature* 333:134–139
- Oehlander B, Ingri J, Ponter C (1993) Lead isotopes as tracers of lead pollution from various sources: an example from northern Sweden. *Appl Geochem* 67–71
- Oeschger H, Langway CC (1989) The environmental record in glaciers and ice sheets. Proceedings: Dahlem Konferenzen, Berlin
- Olendrzynski K, Anderberg S, Bartnicki J, Pacyna JM, Stigliani W (1996) Atmospheric emissions and depositions of cadmium, lead, and zinc in Europe during the period 1955–1987. *Environ Rev* 4:300–320
- Pacyna JM, Scholtz TM, Li Y-F (1995) Global budget of trace metal sources. *Environ Rev* 3:145–159
- Parkinson GS, Catchpole WM (1973) The use of isotopic ratio as a means of detecting sources of lead emissions. *J Inst Petr* 59:59–65
- Patterson CC (1987) Global pollution measured by lead in mid-ocean sediments. *Nature* 326:244–245
- Patterson CC, Settle DM (1976) The reduction of orders of magnitude errors in lead analysis of biological materials and natural waters by controlling the extend and sources of industrial lead contamination introduced during sample collecting, handling and analysis. In: Lafleur P (ed) Accuracy in trace analysis: sampling, sample

- handling, analysis. Natl Bur Standards Spec, Publ no.422, Gaithersburg
- Peterson PJ (1978) Lead and vegetation. In: Nriagu JO (ed) The biogeochemistry of lead in the environment, vol B. Elsevier/North Holland Biomedical, Amsterdam
- Petit D, Mennessier JP, Lamberts L (1984) Stable lead isotopes in pond systems as tracer of past and present atmospheric lead pollution in Belgium. *Atmos Environ* 18:1189–1193
- Puchelt H, Kramar U, Cumming GL, Krstic D, Nöltner T, Schöttle M, Schweikle V (1993) Anthropogenic Pb contamination of soils, southwest Germany. *Appl Geochem [Suppl]* 2:71–73
- Rabinowitz MB, Wetherill G (1972) Identifying sources of lead contamination by stable isotope techniques. *Environ Sci Technol* 6:705–709
- Renberg I, Persson M, Emteryd O (1994) Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* 368:323–326
- Rosman KJR, Chisholm W, Boutron CF, Candelone JP, Görlach U (1993) Isotopic evidence for the source of lead in Greenland snows since the late 1960s. *Nature* 362:333–334
- Rosman KJR, Chisholm W, Boutron CF, Candelone JP, Patterson CC (1994) Anthropogenic lead isotopes in Antarctica. *Geophys Res Lett* 21:2669–2672
- Rosman KJR, Chisholm W, Hong S, Candelone JP, Boutron CF (1997) Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D. *Environ Sci Technol* 31:3413–3416
- Rosman KJR, Ly C, Steinnes E (1998) Spatial and temporal variation in isotopic composition of atmospheric lead in Norwegian moss. *Environ Sci Technol* 32:2542–2546
- Ross HR (1990) On the use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) for estimating atmospheric trace metal deposition. *Water Air Soil Pollut* 50:63–76
- Rühling A, Tyler G (1970b)
- Rühling A, Tyler G (1970a) An ecological approach to the lead problem. *Bot Notiser* 121:321–342
- Selin E, Standzenieks P, Boman J, Teeyasoontranont V (1993) Multi-element analysis of tree rings by EDXRF spectrometry. *X-ray Spectrom* 22:281–285
- Settle DM, Patterson CC (1980) Lead in Albacore: guide to lead pollution in Americans. *Science* 207:1167–1176
- Shen GT, Boyle EA (1987) Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. *Earth Planet Sci Lett* 82:289–304
- Shen GT, Boyle EA (1988a) Determination of lead, cadmium and other trace elements in annually-banded corals. *Chem Geol* 67:47–62
- Shen GT, Boyle EA (1988b) Thermocline ventilation of anthropogenic Pb in the western North Atlantic. *J Geophys Res* 87:8857–8869
- Shirahata H, Elias R, Patterson CC, Koide M (1980) Chronological variations in concentration and isotopic composition of anthropogenic atmospheric lead in sediments of a remote sub-alpine pond. *Geochim Cosmochim Acta* 44:149–162
- Shotyk W (1988) Review of the inorganic geochemistry of peats and peatland waters. *Earth Sci Rev* 25:95–176
- Shotyk W (1996) Peat bogs archives of atmospheric metal deposition: geochemical assessment of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environ Rev* 4:149–183
- Shotyk W, Cheburkin AK, Appleby PG, Fankhauser A, Kramers JD (1996a) Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountain, Switzerland. *Earth Planet Sci Lett* 145:E1–E7
- Shotyk W, Norton SA, Farmer JG (1996b) Summary of the workshop on peat bog archives of atmospheric metal deposition. *Water Air Soil Pollut* 100:213–219
- Shotyk W, Appleby PG, Cheburkin AK, Fankhauser A, Kramers JD (1997) Lead in three peat bog profiles, Jura Mountains, Switzerland: enrichment factors, isotopic composition, and chronology of atmospheric deposition. *Water Air Soil Pollut* 100:297–310
- Shotyk W, Weiss D, Appleby PG, Cheburkin AK, Frei R, Gloor M, Kramers JD, Reese S, van der Knaap WO (1998) History of atmospheric lead deposition since 12,370 ⁰¹⁴C yr BP from a peat bog, Jura Mountains, Switzerland. *Science* 281:1635–1640
- Siccama TG, Smith WH, Mader DL (1980) Changes in the lead, zinc, copper, dry weight, and organic matter content of the forest floor of white pine stands in central Massachusetts over 16 years. *Environ Sci Technol* 14:54–56
- Stanek K, Manton W, Angle M, Eskeridge K, Kueneman A, Hanson C (1998) Lead consumption of 18-to 36-month-old children as determined from duplicate diet collections: nutrient intakes, blood lead levels, and effects on growth. *J Am Diet Assoc* 155–158
- Steinmann M, Stille P (1997) Rare earth element behaviour and Pb, Sr, Nd isotope systematics in a heavy metal contaminated soil. *Appl Geochem* 12:607–623
- Tudhope S, Chilcott C, McCulloch M, Shimmield G, Ellam R, Lea D, Chappell J (1998). Proceedings: PAGES Open Science Meeting, Royal Holloway, University of London, pp 126
- Tyler G (1981) Leaching of metals from the A-horizon of a spruce forest soil. *Water Air Soil Pollut* 15:353–369
- Urban NE, Eisenreich SJ, Grigal DF, Schurr KT (1990) Mobility and diagenesis of ²¹⁰Pb in peat. *Geochim Cosmochim Acta* 54:3329–3346
- van Geel B, Bregman R, van der Molen PC, Dupont LM, van Driel-Murray C (1989) Holocene raised bog deposits in the Netherlands as geochemical archives of prehistoric aerosols. *Acta Bot Neerl* 38:467–476
- van Geen A, Adkins JF, Boyle EA, Nelson CH, Palanques A (1997) A 129 yr record of widespread contamination from mining of the Iberian pyrite belt. *Geology* 25:291–294
- Véron AJ, Lambert CE, Isley A, Linet P, Grousset FE (1987) Evidence of recent lead pollution in deep north-east Atlantic sediments. *Nature* 326:278–281
- Véron AJ, Church TM, Flegal AR, Patterson CC, Erel Y (1993) Response of lead cycling in the surface Saragossa Sea to changes in tropospheric input. *J Geophys Res* 98:18269–18276
- Véron AJ, Church TM, Patterson CC, Flegal AR (1994) Use of stable isotopes to characterise the sources of anthropogenic lead in North Atlantic surface waters. *Geochim Cosmochim Acta* 58:3199–3206
- von Blanckenburg F, O’Nions R, Hein J (1996) Distribution and sources of pre-anthropogenic lead isotopes in deep ocean water from Fe-Mn crusts. *Geochim Cosmochim Acta* 60:4957–2963
- von Gunten HR, Sturm M, Moser RN (1997) 200-year record of metals in lake sediments and natural background concentrations. *Environ Sci Technol* 31:2193–2197
- Wagenbach D (1989) In: Oeschger H, Langway CC (eds) The environmental record in glaciers and ice sheets. Proceedings: Dahlem Konferenzen, Berlin, pp 69–83
- Wagenbach D, Preunkert S, Schäfer J, Jung W, Tomadin L (1996) Northward transport of Saharan dust recorded in a deep alpine ice core. In: Guerzoni S, Chester R (eds) The impact of desert dust across the Mediterranean. Kluwer, Dordrecht
- Walraven N, van Os BJH, Klaver GT, Baker JH, Vriend SP (1997) Trace element concentrations and stable isotopes in soils as tracers of lead pollution in Graft-De Rijk, the Netherlands. *J Geochem Explor* 59:47–58
- Warner BG, Clymo RS, Tolonen K (1993) Implications of peat accumulation at Point Escuminac, New Brunswick. *Quat Res* 39:245–248
- Weiss D (1998) Geochemistry of atmospheric lead deposition: reconstruction of past perturbations using peat bogs in Switzerland. Thesis, University of Berne, Switzerland

- Weiss D, Shotyk W, Cheburkin AK, Gloor M, Reese S (1997) Atmospheric lead and dust deposition from 12,400 to ca. 2,000 yrs BP in a peat bog profile, Jura Mountains, Switzerland. *Water Air Soil Pollut* 100:311–324
- West S, Charman DJ, Grattan JP, Cheburkin AK (1997) Heavy metals in Holocene peats from south west England: detecting mining impacts and atmospheric pollution. *Water Air Soil Pollut* 100:343–353
- Williams C (1974) The accumulation of lead in soils and herbage samples at Rothamsted experimental station. *J Agric Sci Camb* 82:189–192
- Wu J, Boyle EA (1997) Lead in the western North Atlantic Ocean: completed response to leaded gasoline phaseout. *Geochim Cosmochim Acta* 61:3279–3283
- Yoshinga J, Yoneda M, Morita M, Suzuki T (1998) Lead in prehistoric, historic and contemporary Japanese: stable isotopic study by ICP mass spectrometry. *Appl Geochem* 13:403–413