

Recent atmospheric Pb deposition at a rural site in southern Germany assessed using a peat core and snowpack, and comparison with other archives

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Abstract

In a peat bog from Black Forest, Southern Germany, the rate of atmospheric Pb accumulation was quantified using a peat core dated by ^{210}Pb and ^{14}C . The most recent Pb accumulation rate ($2.5\text{ mg m}^{-2}\text{ y}^{-1}$) is similar to that obtained from a snowpack on the bog surface, which was sampled during the winter 2002 (1 to $4\text{ mg m}^{-2}\text{ y}^{-1}$). The Pb accumulation rates recorded by the peat during the last 25 yr are also in agreement with published values of direct atmospheric fluxes in Black Forest. These values are 50 to 200 times greater than the “natural” average background rate of atmospheric Pb accumulation ($20\text{ }\mu\text{g m}^{-2}\text{ y}^{-1}$) obtained using peat samples from the same bog dating from 3300 to 1300 cal. yr B.C. The isotopic composition of Pb was measured in both the modern and ancient peat samples as well as in the snow samples, and clearly shows that recent inputs are dominated by anthropogenic Pb. The chronology and isotopic composition of atmospheric Pb accumulation recorded by the peat from the Black Forest is similar to the chronologies reported earlier using peat cores from various peat bogs as well as herbarium samples of *Sphagnum* and point to a common Pb source to the region for the past 150 years. In contrast, Pb contamination occurring before 1850 in southwestern Germany, differs from the record published for Switzerland mainly due to the mining activity in Black Forest. Taken together, the results show that peat cores from ombrotrophic bogs can yield accurate records of atmospheric Pb deposition, provided that the cores are carefully collected, handled, prepared, and analysed using appropriate methods.

Keywords: Pb flux; Peat bogs; Lead isotopes; Pollution; Snow cover

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1. Introduction

Lead (Pb) is one of the most extensively investigated heavy metals. Indeed Pb, which has no physiological function and is potentially toxic, has been widely dispersed in the environment since the beginning of metallurgy (Nriagu, 1996). One major dispersion

pathway for Pb is atmospheric transport because Pb-bearing aerosols are emitted from industrial activities, combustion of coal and leaded gasoline (Nriagu, 1979; Shotyk and Le Roux, 2005).

Various techniques can be used to monitor atmospheric Pb contamination: for example direct isotopic and concentration measurements of aerosols and wet/dry deposition or biomonitoring. Past atmospheric Pb deposition can be assessed using environmental archives such as ice, firn and snow cores (e.g. Hong et al., 1994; Krachler et al., 2004b; Schwikowski et al., 2004), lake sediments (e.g. Brännvall et al., 1999; Kober et al., 1999) and peat bogs (e.g. Le Roux et al., 2004; Shotyk et al., 1998) as well as herbarium samples of bryophytes and other plants (e.g. Bacon et al., 1996; Weiss et al., 1999b). Peat bogs are useful archives of past Pb deposition because (1) they are widely distributed, (2) they receive only atmospheric inputs (i.e. they are rain-fed) and (3) they can be precisely dated using ^{14}C (bomb-pulse and “traditional”) or ^{210}Pb methods.

However, despite numerous studies and reasonable agreement between modelled or measured deposition rates (Vile et al., 2000; Von Storch et al., 2002), the comparison between atmospheric Pb deposition rates and the Pb accumulation rates by peat bogs has been called into question. For example, a recent study by Bindler et al. (2004) in Sweden suggested that individual peat cores yielded different cumulative Pb inventories during the last 110 years. Possible explanations include the difference in snow cover due to the microtopography of the bog surface and differences in canopy interception. Novak et al. (2003a) in a study of sulfur deposition in peat bogs also point out that “a single depth profile per peat bog may seriously under-represent the typical history of peat accretion” and therefore the record of atmospheric deposition. In contrast, Givelet et al. (2004) suggested that the principal limitation using peat cores as archives is not caused by the heterogeneity of the bogs themselves but rather the inadequate care in collecting, handling and preparing the peat core.

In this study, we compared the accumulation rate of Pb in a peat profile with that of the snow cover directly overlying the bog in the Black Forest, Southern Germany using state of the art techniques. The main aim of this study is to compare the accumulation rate and isotopic composition of atmospheric Pb in the snowpack, a single season record, with that of the peat core, a longer term record. Additionally, we compare the single peat record from the Black Forest with previously published data for direct deposition rates in Black Forest, for three peat cores from Étang de la Gruère, a peat bog 100 km away in Western Switzerland and for *Sphagnum* herbarium samples collected in the same area. To compare the accumulation rates quantitatively, Pb fluxes were calculated using the Pb concentrations and peat accumulation rates derived using ^{210}Pb .

Finally we examine the recent anthropogenic impact on the atmospheric Pb deposition record in this rural site and compare it with the rate of Pb deposition during the past 8,000 years at the same site and in Switzerland.

2. Experimental

2.1. Material

The “Kohlhütte Moor” (KM) is one of many *Sphagnum*-dominated peat bogs located in the Southern Black Forest, S.W. Germany (Fig. 1). It is a visibly domed bog, which has accumulated more than 5 m peat on a basement consisting of glacial clays. A complete peat profile was sampled following the procedure described by Givelet et al. (2004). The top meter was collected at the transition between a hummock and a hollow with a Ti Wardnaar corer and the following five meters with a stainless steel Belarussian corer. A detailed description of the site and the field work are given in the Field Report (Le Roux et al., 2002). The cores were cut precisely every cm. The edges of each slice were trimmed away to avoid possible contamination. Sub-samples were dried at 105 °C and pulverized in a Ti mill. Density

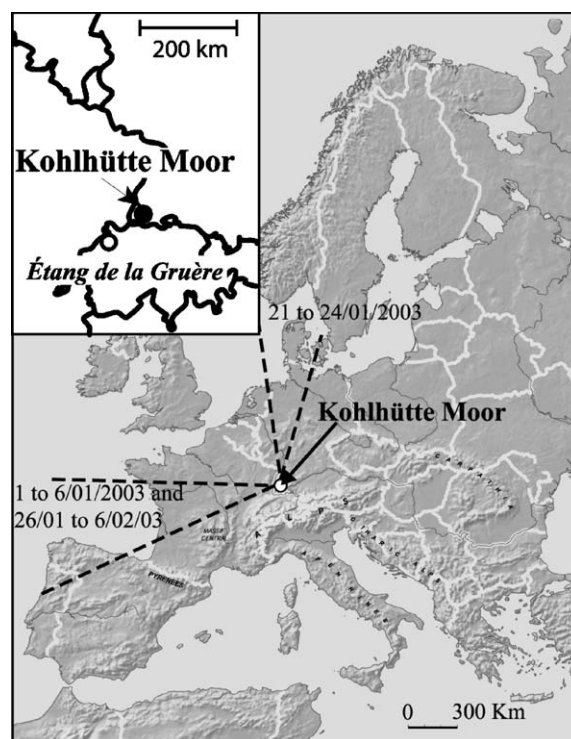


Fig. 1. Location of Kohlhütte Moor (KM) and air mass sectors for the three main periods of snow deposition in 2003 based on HISPLYT back trajectory calculations. Also shown is the location of Étang de la Gruère (EGR).

and pore water content were calculated as described elsewhere (Givelet et al., 2004).

The peat bog is typically covered each winter by one to two meters of snow. On the 19th of February 2003, we sampled a 70 cm snow pack at a distance of ca. four meters from the peat-coring site. A detailed description of the site and the field work are given in a second Field Report (Le Roux and Aubert, 2003). The snow was collected in increments of 10 cm, including the mixed layer between moss and snow. The surface snow of a larger area was also sampled. In addition, a snow sample was also collected near the road outside the pine forest surrounding the bog. The sampling of snow was done using strict clean lab procedures to avoid possible contamination (e.g. Nriagu et al., 1993). The hole was hand-dug while wearing polyethylene gloves and snow samples were collected in acid-washed bags, which were first rinsed twice with snow from the same layer. Snow samples were transported frozen until they could be processed at the Centre de Géochimie de la Surface (CNRS, Strasbourg). After melting at room temperature in clean room conditions (class 100) the samples were filtered with HAWP filters (0.45 µm) previously rinsed with high purity water (Millipore, Milford[®], MA, USA). Aliquots were acidified with HNO₃ (1 ml of suprapur HNO₃ for 250 ml of liquid) to avoid possible precipitation and adsorption of metals to the container walls. Snow particles collected on the filters were also removed using an ultrasonic bath to estimate dry (particulate) deposition.

2.2. Age dating of the peat profile

Radionuclides (²¹⁰Pb, ²⁴¹Am, ²¹⁴Pb, ¹³⁷Cs) were measured using low background gamma spectrometry (GCW4028, HPGE, Canberra) in Heidelberg.

For deeper samples, twenty-three ¹⁴C AMS dates were performed at the ETH Zürich using bulk peat samples.

2.3. Back trajectories

The snowpack was divided into seven samples of 10 cm each. Unfortunately, the snow did not accumulate continuously and phases of compression and even melting occurred during that winter especially for the icy bottom samples (Le Roux and Aubert, 2003). Therefore it is difficult to precisely attribute individual samples to specific snow events. However three phases of snow deposition could be distinguished from the snow accumulation inventory at the Feldberg weather station 15 km away: 1-6/01/2003; 26/01-6/02/2003 and 21-24/02/2003.

Three-days back trajectories were calculated using the HYSPLIT model (Draxler and Rolph, 2003) (Fig. 1) and they are in good agreement with wind directions measured at the Feldberg weather station (15 km North

of the site). Two dominant directions could be distinguished: for the first and last episodes of snow deposition, a Western influence (i.e. France and the Atlantic) and for the intermediate snow episode a Northern influence (North-West Germany, Holland, the North Sea).

2.4. Analytical measurements

Strontium, Ti and Pb were measured directly in peat powders using home-made X-ray fluorescence analysers in Heidelberg (Cheburkin and Shotykh, 2005; Cheburkin and Shotykh, 1996). Detection limits were 0.8, 1.5 and 0.6 µg g⁻¹ for Sr, Ti, Pb, respectively. The XRF method did not provide sufficiently low detection limits for Pb in the deeper and older samples. Precision of the XRF analysers is discussed elsewhere (Cheburkin and Shotykh, 1996; Givelet et al., 2003), but for Pb was approximately 30% at 1 µg g⁻¹, 10% at 10 µg g⁻¹ and 6% at 60 µg g⁻¹.

Strontium, Ca, Na, Mg, K were measured in snow samples in Heidelberg using ICP-OES (Vista MPX, Varian). The validity of the measurements was verified by repeated measurements of certified river water standard reference materials SRM 1640 (NIST, USA) and SLRS 2 (NRC, Canada) as well as internal standards. The procedural blanks were under the limit of detection of the instrument. Sodium was also measured by ET-AAS (Hitachi Z-8200) in Strasbourg yielding good agreement between both techniques. In addition, Sr measured using ICP-SF-MS was in good agreement ($r^2 = 0.992$, $n = 10$) with measurements by ICP-OES.

Concentrations of Pb, Ba in snow were determined using ICP-SF-MS (Element 2, Thermo Electron) in Heidelberg and by ICP-QMS (PQ 2+, VG) in Strasbourg. Measurements between the two instruments were in good agreement (for Pb, $r^2 = 0.997$, $n = 10$; for Ba, $r^2 = 0.94$, $n = 10$) Procedural blanks always accounted for less than 10% of the concentrations of both elements and these values only for the smallest measured concentrations. Analytical blanks were negligible and suggest that our washing procedures for the filters were the causes of contamination.

Some peat samples, especially deeper pre-anthropogenic peat samples, which have Pb concentrations under the lower limit of detection of the XRF, were measured using ICP-QMS. Two hundred mg of each sample was first digested in an HNO₃-HBF₄ mixture in a microwave autoclave (ultraCLAVE II, MLS, Leutkirch, Germany) at elevated pressure (Krachler et al., 2002). Digested samples were brought to Strasbourg and measured using ICP-OES and ICP-QMS for major and trace elements. Lead concentrations measured by ICP-QMS were in excellent agreement with measurements using XRF ($r^2 = 0.991$, $n = 25$). Pb concentrations in Plant Reference Standards (Peach Leaves NIST 1547, Rye Grass

BCR-CRM 281, Bush Branches and Leaves GBW 07602, Lichen IAEA 336) were also in agreement with certified values (less than 10% difference).

In addition, the elemental concentrations in the particles, obtained from the two snow samples (surface and road), were also measured by ICP-QMS after HNO₃ digestion. The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios in peat and snow were also measured using ICP-SF-MS as described elsewhere (Krachler et al., 2004a).

3. Results

3.1. Status of the bog

The KM bog is ombrotrophic as demonstrated (1) by the low pH values of the porewaters (~4 for the first meter, ~4.5 for the following meters), (2) the major element chemistry of bulk peat and (3) the chemical composition of the porewaters relative to rainwater. For example from the Sr concentration profile (Fig. 2), two distinct depositional environments can be distinguished: the deeper part (330 cm to 600 cm) with high concentrations reflecting inputs of Sr from mineral weathering, aquatic and atmospheric deposition and the upper part (330 cm, surface) with low Sr concentrations supplied only by atmospheric inputs.

3.2. Age dating

The maximum depth at which unsupported ²¹⁰Pb could be detected is 18 cm. The age-depth relationship was calculated using the CRS model (Appleby, 2001) (Fig. 3a). This model is in good agreement with the peak of ²⁴¹Am corresponding to the period of atmospheric nuclear weapons tests from 1945–1980, peaking at 1963. Uncertainties in the ²¹⁰Pb CRS Model and in the peat accumulation rate were calculated following Appleby (2001).

The ¹⁴C age dating allow the calculation of a robust age-depth model (Fig. 3b). Age-depth models based on ¹⁴C and ²¹⁰Pb are in good agreement when they overlap (Fig. 3a). Here, we used the ²¹⁰Pb age-depth model to study recent Pb pollution and use the deeper samples dated by ¹⁴C to assess natural Pb accumulation rates.

3.3. Pb in the peat profile

Pb concentrations in the peat profile are comparable to other peat profiles investigated in Europe (e.g. Klaminder et al., 2003; Shotyk et al., 1998) with a large increase in the topmost samples (Fig. 4). The two peaks resulting from intensive local mining during the Roman Period and the Middle Ages (Fig. 4) correspond to well-known periods of Pb dispersion (Renberg et al., 2001).

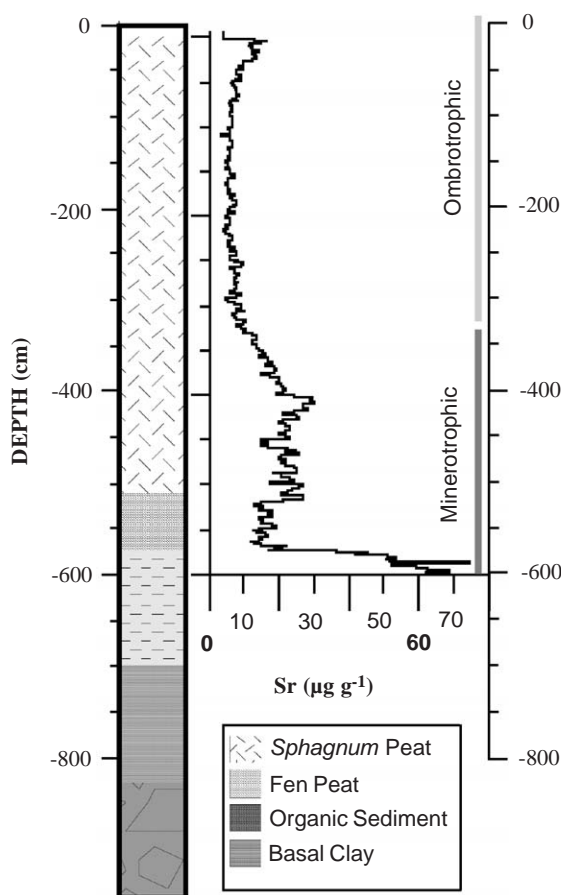


Fig. 2. Peat stratigraphy, Sr concentration profile and the identification of ombrotrophic and minerotrophic zones.

Background Pb concentrations are low in the ombrotrophic part ($0.40 \pm 0.07 \mu\text{g g}^{-1}$, $n = 20$ corresponding to the period 3300 B.C.- 1300 B.C.), and lower than at Étang de la Gruère, for the same period of time ($0.66 \pm 0.19 \mu\text{g g}^{-1}$, $n = 8$). These smaller concentrations are mainly due to the faster peat growth rates in the German bog (ca. 6 m of peat accumulation in 9000 years) compared to the Swiss bog (ca. 6 m of peat accumulation in 13000 years).

The Pb isotope ratios also follow trends similar to other bogs in Central Europe (Novak et al., 2003b; Weiss et al., 1999a) with less radiogenic values at the surface. The background Pb isotopic signature for the ²⁰⁶Pb/²⁰⁷Pb ratio is ~1.18–1.19; $n = 10$, 5500 B.C.–1300 B.C.). The bottom three samples, which are sediments (>50% ash) show a different isotopic ratio (²⁰⁶Pb/²⁰⁷Pb = 1.21). The large difference in Pb isotope ratio for the peats and the sediments, therefore, indicate that all of the Sphagnum peat samples above 500 cm have received Pb exclusively from the air.

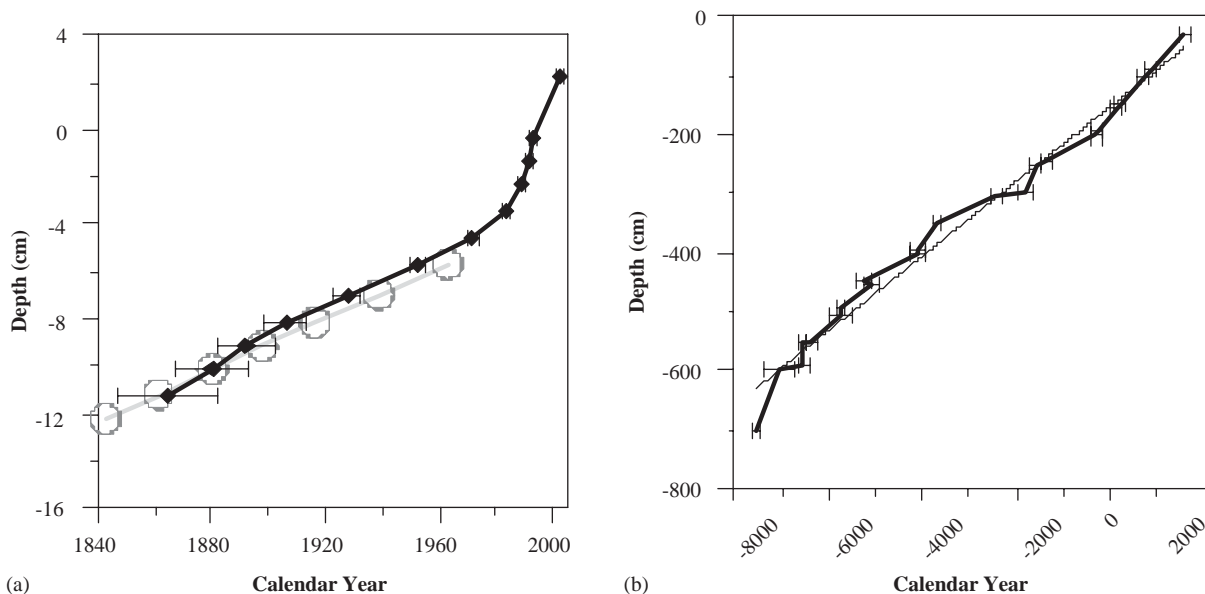


Fig. 3. Age depth models (a) ^{210}Pb CRS model and comparison with the upper end of the model based on ^{14}C dates (grey circles); (b) ^{14}C age depth model.

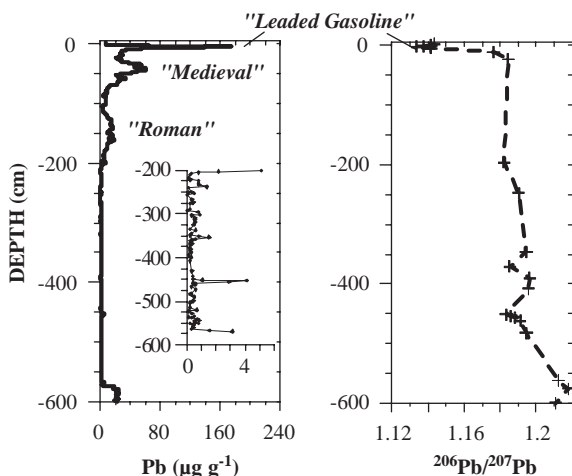


Fig. 4. Pb and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles in the Kohlhütte Moor peat core (for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, the symbols are larger than the error (2σ)).

3.4. Wet deposition

As represented by Na, the concentrations of major elements generally follow the electrical conductivity (Fig. 5a), in other words, the ionic strength. However some elements such as Na and Sr show high concentrations at the base of the snow pack (50–60 cm, 60–70 cm) where icy layers are located (Fig. 5a). Thus, there is clearly a compositional difference between the bottom

20 cm of compacted snow and the rest of the snow pack, which consisted of fresh uncompacted snow.

The Ca concentration profile (Fig. 5b) shows elevated concentration at both the bottom and the top of the snow pack. The elevated concentration at the top reflects a continuous deposition of atmospheric particles in absence of fresh snow for the two weeks prior to collection. These particles could have also dissolved during snow melt in the laboratory and partially explain the higher concentrations in the surface snow sample. The elevated Ca concentration at the bottom of the snow pack probably reflects “contamination” of the snow by living plants. The Ca/Sr ratio of the snow pack is elevated at the base indicating that Ca is more affected than Sr, but it corresponds with the Ca/Sr ratio of the water at the surface of the bog (ca. 400:1). Leaching of elements from particles due to rising acidity can also be invoked to explain increasing acidity in some snow layers (Barbaris and Betterton, 1996).

Lead concentrations (Fig. 6a) generally follow the concentrations of other elements. Whereas the top layer reveals elevated concentrations of both Ca and Pb, in contrast to Ca, there is no influence of the surface peat layer on the Pb concentration at the bottom (Fig. 6a). Whereas the snowpack appears to have liberated some Ca from the plant surface, this is neither true for Sr (Fig. 5) or Pb (Fig. 6). The Pb enrichment factor was calculated using Ba (Fig. 6c):

$$\text{Pb EF}_{\text{Ba}} = (\text{Pb}/\text{Ba})_{\text{sample}} / (\text{Pb}/\text{Ba})_{\text{cc}}$$

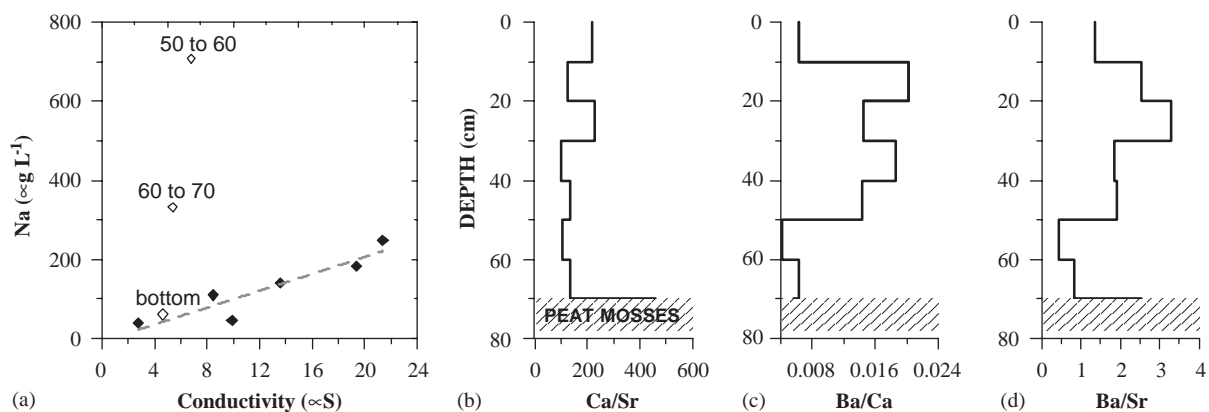


Fig. 5. Chemistry of the snow pack (a) Na ($\mu\text{g L}^{-1}$) vs. conductivity (μS); empty diamonds are samples from the base of the snow pack; (b) Ca/Sr; (c) Ba/Ca; (d) Ba/Sr.

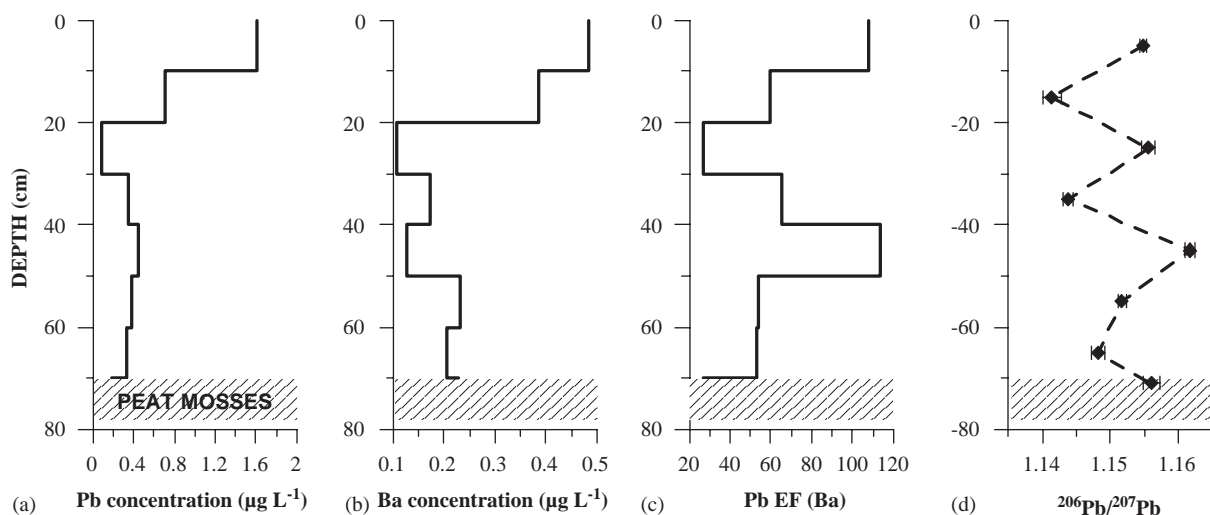


Fig. 6. Pb and Ba chemistry in the snow: (a) Pb and (b) Ba concentrations, (c) Pb Enrichment Factor in the snow and (d) $^{206}\text{Pb}/^{207}\text{Pb}$.

where $(\text{Pb}/\text{Ba})_{\text{cc}}$ is the ratio ($17/550 = 0.03$) of these two elements in the Upper Continental Crust (McLennan, 2001). Uncontaminated sediments under the peat have a Pb EF_{Ba} (substrate) of 1.14 ± 0.15 ($n = 7$). Therefore, calculation of the EF using the Pb/Ba ratio of crustal rocks and local sediments will provide similar results. Barium has been used as a reference element in many studies of Pb contamination in snow and ice (Vallelonga et al., 2002) as a proxy of soil dust deposition for the reasons given by Patterson and Settle (1987). The calculated values are of the same order of the enrichment factors found in fresh snow samples collected in the Alps in 1998–99 (Veysseyre et al., 2001) (Fig. 6c).

The Pb isotopic composition is neither correlated with the Pb concentration nor other elements. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio varies between 1.14 and 1.16 (Fig. 6d).

3.5. Particulate deposition

Particulate deposition was estimated using the solid particles collected on the filters. Scanning Electron Microscope analyse showed that the majority part of these particles are quartz and aluminosilicates. Biogenic particles (pollen and vegetation) are also present. Anthropogenic compounds such as framboidal particles were also found but in small quantities, even in the sample collected near the road.

Using the filtered water volume, the contribution of Pb contained in the particles to the volume of snow originally collected can be calculated. Particles account for approximately 2% of Pb deposited at the bog surface compared to up 33% in the snow sample collected near the road (Table 1). Particulate deposition was estimated

Table 1
Comparison between particulate and wet deposition in snow

Snow sample	Element	Particulate deposition ($\mu\text{g g}^{-1}$)	Particulate deposition (ng l^{-1})	Wet deposition (ng l^{-1})	Part./TOT(%)	Part.; EF(Ba)	Part.; EF(Ti)	WET, EF(Ba)
Road	Ti	2550	5440	n.d.	—	1.0	1.0	—
	Ba	340	720	870	45	1.0	1.0	1
	Pb	300	640	1260	34	28.8	28.4	47
Surface	Ti	446	700			0.8	1.0	
	Ba	74	116	480	19	1.0	1.2	1
	Pb	27	42	1600	3	11.7	14.5	108

Table 2
pre-anthropogenic AR of Pb in the present study compared to previous studies

Study	Country	pre-anthropogenic AR ($\mu\text{g m}^{-2}\text{y}^{-1}$)	Period	Note
This study	Southern Germany	20 ± 1 (range : 1–40, $n = 20$)	3300–1300 cal. BC	Geochemically ombrotrophic
This study	Southern Germany	30 ± 14 (1–90, $n = 51$)	5800–1300 cal. BC	Botanically ombrotrophic ^a
Shotyk et al. (1998)	Northern Switzerland	14 ± 3 (9–18, $n = 6$)	3500–1400 cal. BC	Geochemically ombrotrophic
Shotyk et al. (1998)	Northern Switzerland	10 ± 2 (5–14, $n = 18$)	7000–4100 cal. BC	Botanically ombrotrophic
Klaminder et al.(2003)	Southern Sweden	1–10	4000–1500 cal. BC	Botanically ombrotrophic

“botanically ombrotrophic”: Sphagnum peat; “geochemically ombrotrophic”: strict non-influence of substrate on the samples as demonstrate by mobile elements like Ca or Sr.

^afor the calculation of the AR in the botanically ombrotrophic layer, 2 cm highly enriched in mineral matter was omitted.

only for the surface snow and the road samples. Because the snow samples were collected on the 19th of February 2003 and the last snowfall was the 6th February 2003, these surface samples were exposed to the air for 13 days, which may explain why they yielded a higher particle load. In addition to particles emitted by vehicles near the road, differences in particulate deposition between the bog and the roadside might also be explained by particle capture by the tall pine trees growing around the perimeter of the bog (i.e. canopy interception).

4. Discussion

4.1. Background Pb accumulation rate in the Black Forest and comparison to other sites in Europe

Based on the age-depth model and the density measurements, the accumulation rate (AR) of pre-anthropogenic Pb averages $20 \pm 1 \mu\text{g m}^{-2}\text{y}^{-1}$ in the ombrotrophic part of the pre-anthropogenic peat (until 3300 B.C). In the minerotrophic peat, the Pb AR is similar. These Pb AR are comparable with other observations obtained using peat cores in Central and Northern Europe (Table 2). The Pb AR for the Black

Forest, which is more variable than in Sweden and Switzerland could be explained by the greater temporal resolution. Indeed in this study, each sample represents 20 years of peat accumulation whereas, for example, in the study in Switzerland, one sample represents ~150 years.

4.2. Recent Pb deposition in the Black Forest and comparison with Swiss peat cores

Cumulative Pb and ^{210}Pb were calculated for the period ~1850–2000 (Table 3). This period corresponds mainly to the industrial period and can be dated using ^{210}Pb . We use this approach to compare the Black Forest peat bog with data from three previously studied peat cores collected in Étang de la Gruère in 1991 and 1993: EGR 2F and 2K (Appleby et al., 1997; Shotyk et al., 1998; Weiss et al., 1999a) and EGR 2G (Shotyk et al., 2002). In contrast to EGR 2F and 2K (cut three cm slices by hand), EGR 2G was frozen and precisely cut into 1 cm slices (Givelet et al., 2004). It is also the first time that a complete and comparative interpretation of atmospheric Pb and ^{210}Pb deposition is presented for these three cores.

The cumulative Pb inventories recorded by the four cores are similar ($1.2\text{--}1.3 \text{g m}^{-2}$) even though the Black

Table 3
Cumulative inventories of Pb and ^{210}Pb in the Black Forest peat core and the Étang de la Gruère cores

CORE and year of collection	Pb cumulative inventory until no unsupported ^{210}Pb (g m^{-2})	^{210}Pb cumulative inventory (Bq m^{-2})
Black Forest (cut every cm) (2002)	1.2	7800
EGR 2G (cut every cm) (1993)	1.28	3300
EGR 2K (cut every 3 cm) (1993)	1.34	3100
EGR 2F (cut every 3 cm) (1991) (Appleby et al., 1997)	1.3	4400

Forest core was collected 10 years after the Swiss cores (which represent peat accumulation pre-dating 1992). In comparison, the cumulative ^{210}Pb inventory is higher in the Black Forest (7800 Bq m^{-2}) than at EGR ($2800\text{--}4400 \text{ Bq m}^{-2}$). This is probably due to the geology of the Black Forest (crystalline rocks) compared to the calcareous Jura Mountains where EGR is situated. Between the three cores of EGR, there are variations cumulative inventory of the ^{210}Pb , but not in that of total Pb. One possible explanation is that the atmospheric pathways for ^{210}Pb and Pb are different (e.g. a larger ratio dry/wet deposition for ^{210}Pb). Difference in particle deposition could be due to differences in interception, which reflect variations in micro-topography capture effects (Bindler et al., 2004). However these processes appear to affect only ^{210}Pb : this is in good agreement with the fact that wet deposition is the predominant source of Pb to the bog (Table 1). Indeed, the snow analyses presented here show that recent Pb supplied to the bog is mainly in the form of wet deposition. The Pb inventories for the three EGR cores are very similar suggesting that wet deposition is relatively uniform across the bog surface. In contrast ^{210}Pb , which is mainly absorbed onto soil-derived dust particles (Robbins, 1978), shows much more variation within the surface of EGR. Another explanation for the differences might be the way the cores were collected and prepared (Givelet et al., 2004). For example, the measurement of the density depends on careful sample preparation. Density is a key parameter to model the ^{210}Pb ages and for calculating the peat AR. Peat density might be affected by the heterogeneity of the samples, which, in turn, might reflect botanical differences.

The recent Pb AR of the different peat profiles are in good agreement (Fig. 7). They show peaks between 1970 and 1980 with a maximum Pb AR between 15 and 20 mg m^{-2} . During the past 10 years, however, the Pb AR appears to have stabilized at approximately $2.5 \text{ mg m}^{-2} \text{ y}^{-1}$. Explanations for the small differences in the chronology of Pb accumulation are diverse: local variations within the bog (Bindler et al., 2004), regional variations in Pb deposition (Le Roux et al., 2004; Weiss et al., 1999a), differences in sampling techniques and core quality (Givelet et al., 2004) and errors in the age-depth modelling.

4.3. Recent Pb AR in KM bog and comparison with direct deposition rates

It is possible to estimate the Pb flux based on the snow Pb concentration, and the yearly average precipitation ($\sim 1800 \text{ mm/y}$). This approach has some limitations because the Pb concentration in precipitation could vary seasonally. However the calculation yields a Pb flux of 1 to $4 \text{ mg m}^{-2} \text{ y}^{-1}$, which is comparable with the Pb AR in the most recent peat samples of Black Forest peat profile ($2.5 \text{ mg m}^{-2} \text{ y}^{-1}$).

More generally, comparison between the Pb AR chronology and direct measurements of Pb fluxes in Black Forest (Fig. 7) for the last 25 years show also a good agreement with decreasing deposition from $7\text{--}20 \text{ mg m}^{-2} \text{ y}^{-1}$ before 1985 (Bergkvist et al., 1989; Nürnberg et al., 1984; Schulte et al., 1996) to $1.5\text{--}5 \text{ mg m}^{-2} \text{ y}^{-1}$ after 1990 (Schulte et al., 1996; UBA, 2000) following the decline of Pb emissions by gasoline combustion and industries (Office Fédéral de l'environnement, 1995; Von Storch et al., 2003). The similarities between the Pb AR in peat and the direct measurements of precipitations confirm that the peat profile is recording the Pb atmospheric flux.

These fluxes of Pb obtained both using recent snow and peat are at least 100 times greater than the natural flux. While the decision to ban Pb from gasoline certainly has been helpful (as revealed by the declining Pb fluxes since 1970–1980), other sources of anthropogenic Pb must be dominating the atmospheric emissions.

4.4. Pre-industrial Pb deposition in the Black Forest and comparison with Switzerland

Whereas the Pb chronology for the last 150 years is similar for the Jura and the Black Forest, there are differences in Pb AR and cumulative Pb inventories recorded by the peat cores before the industrial period (Fig. 8). Atmospheric Pb deposition in Black Forest was always greater than in Switzerland. In Black Forest, $\frac{3}{4}$ of Pb deposition occurred before 1850. In Switzerland, in contrary, $\frac{1}{2}$ of Pb deposition occurred before 1850 (Shotyk et al., 2000). The main reason for these differences is the local mining activities in Black Forest. Despite the differences in accumulation rates in

Switzerland and Germany, similar trends are seen in the Pb chronologies beginning in both locations with a significant contamination during the Roman Period and

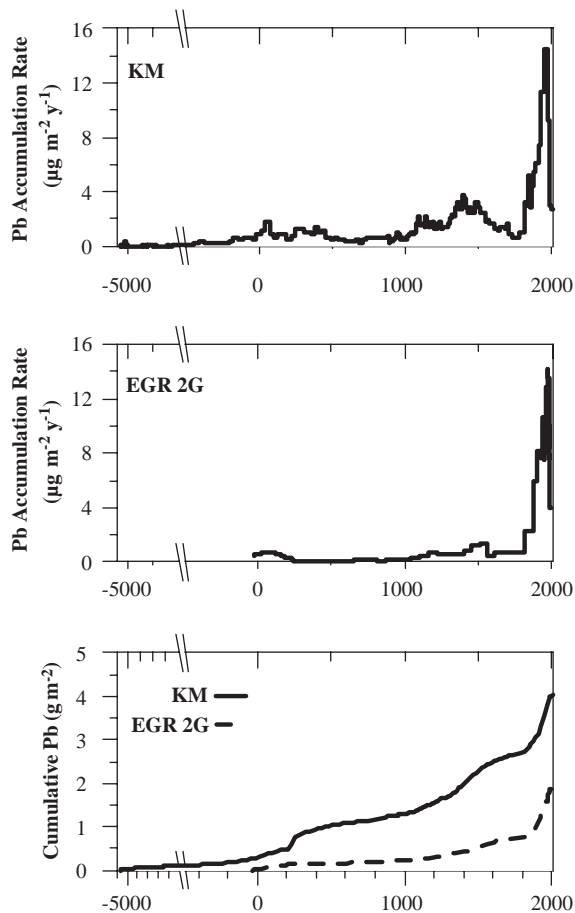
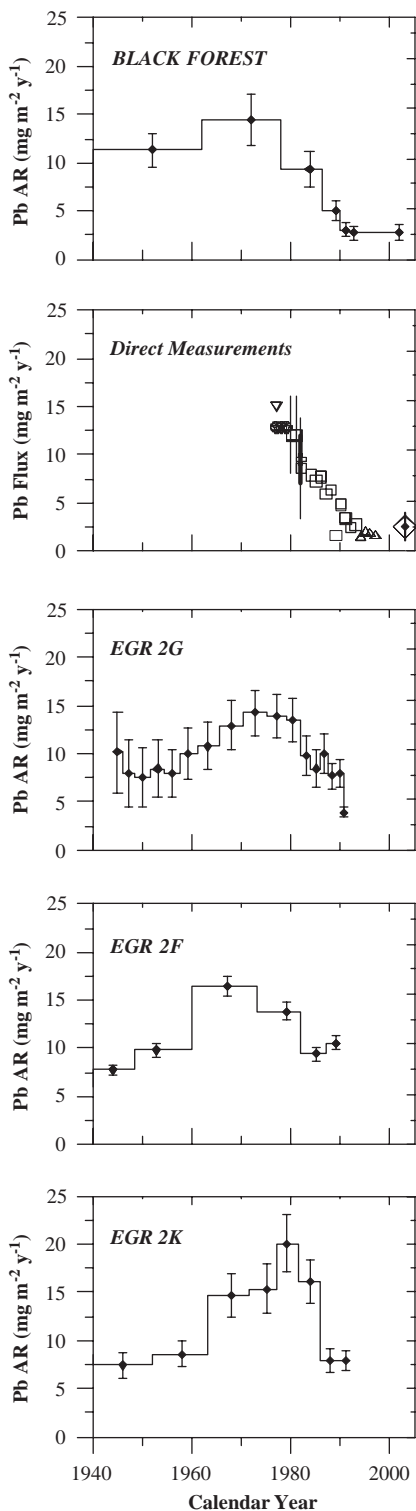


Fig. 8. Pb AR and Pb cumulative inventories for Kohlhütte Moor and comparison with EGR.

an increase during the second part of the Middle Ages (Fig. 8).

4.5. Recent Pb isotopic chronology and comparison with other archives

The approach of Weiss et al. (1999b) is used to compare our isotope measurements in the bog with measurements in herbarium *Sphagnum* samples collected during the last 200 y in the Black Forest and in Switzerland (Fig. 9). As already demonstrated by Weiss

←
 Fig. 7. Pb Accumulation rate in the Kohlhütte Moor compared with peat cores from EGR and direct measurements of Pb fluxes in Black Forest (references in text) including our estimation based on the snow pack (diamond); Pb AR in peat was calculated using the sedimentation rate given by the CRS model, errors on Pb AR were then calculated by error propagation using the errors on the sedimentation rate (Appleby, 2001) and the analytical error of the concentration measurement.

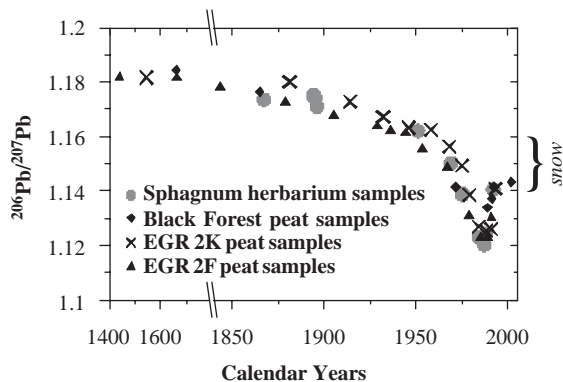


Fig. 9. $^{206}\text{Pb}/^{207}\text{Pb}$ vs. calendar years for herbarium samples (Weiss et al., 1999b) and peat cores.

et al, the isotope measurements in the Swiss peat cores are in very good agreement with the herbarium samples. Here we find that the peat core from the Black Forest provides a chronology of the isotopic composition of atmospheric Pb, which is also similar to that of the herbarium record. The similarities in the Pb isotopic composition of Pb in peat from EGR, the Black Forest and in the herbarium moss samples suggest that the age-depth models are valid and that Pb is immobile in the peat profiles. Moreover these data are evidence for common regional pollutant sources of Pb during the last 200 years in NW Switzerland and SW Germany.

Despite some variations in isotopic composition, the snow deposited in 2003 has an isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.141 to 1.161; weighted average: 1.151) similar to the bog ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.141 to 1.143; 1992 to 2002). This average isotopic signature represents a mixture of different atmospheric pollutants such as smelters or municipal incinerators (e.g. Carignan et al., 2005; Chiaradia and Cupelin, 2000). The most radiogenic snow sample ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.161) has a different origin since its presumed period of deposition coincides with an air mass coming not from the West but rather from the North (Fig. 1).

5. Conclusions

A peat bog in Southern Germany provides a record of the atmospheric flux and Pb isotopic signature since at least 5800 cal. B.C. The temporal trends and isotopic signatures are similar to those preserved in Swiss peat cores and point to a common Pb source to the region for the past 150–200 years. Moreover the data show that peat bogs constitute powerful tools to study atmospheric deposition over the ages. Direct comparison between a short-term archive (snow pack), direct deposition measurements and the peat profile also show good agreement both for the Pb flux and isotopic composi-

tion. Most of the Pb deposited during the winter on the bog surface is in the form of wet deposition.

Regardless of the Pb concentration and AR, Pb isotopes compared to the natural background show that anthropogenic Pb is still dominating the Pb input. Despite a decrease in Pb flux due to ban on leaded gasoline in Europe, the Pb flux recorded in recent peat and snow is at least 100 times greater than natural pre-anthropogenic flux in these rural sites. Lead deposition near a road is another factor of ten greater, which suggests modern Pb fluxes in urban areas deserve further investigation.

Acknowledgements

We would like to thank C. Scholz for the measurements of snow samples with the ICP-OES in Heidelberg, S. Person from the Regierungspräsidium Freiburg for coring permission, T. Noernberg, A. Martinez-Cortizas, H.J. Küster, N. Rausch and N. Givélet for help during the different field trips and L. Pourcelot for the internal peat radionuclides standard. The constructive comments of one anonymous reviewer are acknowledged. This work was funded by the Deutsche Forschung Gemeinschaft through the GRK 273 (www.geofluids.de).

References

- Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M., Smol, J.P. (Eds.), *Tracking Environmental Change Using Lake Sediments: Basin Analysis, Coring, and Chronological Techniques*, vol. 1. Kluwer Academics, Dordrecht, pp. 171–203.
- Appleby, P.G., Shotyk, W., Fankauer, A., 1997. Lead-210 Age Dating of Three Peat Cores in the Jura Mountains, Switzerland. *Water Air Soil Pollution* 100 (3/4), 223–231.
- Bacon, J.R., Jones, K.C., McGrath, S.P., Johnston, A.E., 1996. Isotopic character of lead deposited from the atmosphere at a grassland site in the United Kingdom since 1860. *Environmental Science and Technology* 30, 2511–2518.
- Barbaris, B., Betterton, E.A., 1996. Initial snow chemistry survey of the Mogollon Rim in Arizona. *Atmospheric Environment* 30 (17), 3103–3903.
- Bergkvist, B., Folkesson, L., Berggren, D., 1989. Fluxes of Cu, Zn, Pb, Cr, and Ni in temperate forest ecosystems, a literature review. *Water Air Soil Pollution* (47), 217–286.
- Bindler, R., Klarqvist, M., Klaminder, J., Förster, J., 2004. Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Moss, Sweden. *Global Biogeochemical Cycles* 18 (GB3020).
- Brännvall, M.-L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J., Billström, K., 1999. The Medieval Metal Industry was the cradle of modern large-scale atmospheric lead pollution in northern Europe. *Environmental Science and Technology* 33 (24), 4391–4395.

- Carignan, J., Libourel, G., Cloquet, C., Le Forestier, L., 2005. Lead isotopic composition of fly ash and flue gas residues from municipal combustors in France: implication for atmospheric lead source tracing. *Environmental Science and Technology* (39), 2018–2024.
- Cheburkin, A.K., Shotyk, W., 1996. An Energy-dispersive Miniprobe Multielement Analyser (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius Journal of Analytical Chemistry* 354, 688–691.
- Cheburkin, A., Shotyk, W., 2005. An energy-dispersive XRF spectrometer for Ti analysis (TITAN). *X-ray Spectrometry* (34), 69–72.
- Chiaradia, M., Cupelin, F., 2000. Behaviour of airborne lead and temporal variations of its source effects in Geneva (Switzerland): comparison of anthropogenic versus natural processes. *Atmospheric Environment* (34), 959–971.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory.
- Givelet, N., Roos-Barraclough, F., Shotyk, W., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural “background” values (past 8,000 years). *Journal of Environmental Monitoring* 5 (6), 935–949.
- Givelet, N., Le Roux, G., Cheburkin, A.K., Chen, B., Frank, J., Goodsite, M.E., Kempter, H., Krachler, M., Noernberg, T., Rausch, N., Rheinberger, S., Roos-Barraclough, F., Sapkota, A., Scholz, C., Shotyk, W., 2004. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. *Journal of Environmental Monitoring* 6, 481–492.
- Hong, S., Candelone, J.-P., Patterson, C.C., Boutron, C.F., 1994. Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia ago by Greek and Roman Civilizations. *Science* 265, 1841–1843.
- Klaminder, J., Renberg, I., Bindler, R., 2003. Isotopic trend and background fluxes of atmospheric lead in northern Europe: analyses of three ombrotrophic bogs from south Sweden. *Global Biogeochemical Cycles* 17 (1).
- Kober, B., Wessels, M., Bollhöfer, A., Mangini, A., 1999. Pb isotopes in sediments of Lake Constance, Central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere. *Geochimica et Cosmochimica Acta* 63 (9), 1293–1303.
- Krachler, M., Mohl, C., Emons, H., Shotyk, W., 2002. Analytical procedures for the determination of selected trace elements in peat and plant samples by inductively coupled plasma spectrometry. *Spectrochimica Acta Part B* 57.
- Krachler, M., Le Roux, G., Kober, B., Shotyk, W., 2004a. Optimising accuracy and precision of lead isotope measurement (^{206}Pb , ^{207}Pb , ^{208}Pb) in acid digests of peat with ICP-SMS using individual mass discrimination correction. *Journal of Analytical Atomic Spectrometry* 19 (3), 354–361.
- Krachler, M., Zheng, J., Fisher, D., Shotyk, W., 2004b. Direct determination of lead isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) in arctic ice samples at Picogram per Gram Levels Using Inductively Coupled Plasma-Sector Field MS coupled with a High-Efficiency Sample Introduction System. *Analytical Chemistry* 76, 5510–5517.
- Le Roux, G., Aubert, D., 2003. Post expedition field and Status report (<http://cf.geocities.com/gwanach/Fieldreportwinter.pdf>), pp. 11. Institute of Environmental Geochemistry.
- Le Roux, G., Shotyk, W., Kober, B., 2002. Post expedition field and Status report (<http://cf.geocities.com/gwanach/fieldreport.pdf>), p. 15. Institute of Environmental Geochemistry.
- Le Roux, G., Weiss, D., Grattan, J.P., Givelet, N., Krachler, M., Cheburkin, A.K., Rausch, N., Kober, B., Shotyk, W., 2004. Identifying the sources and timing of ancient and medieval atmospheric lead pollution in England using a peat profile from Lindow bog, Manchester. *Journal of Environmental Monitoring* 6, 502–510.
- McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry, Geophysics, Geosystems* 2 (4).
- Novak, M., Adamova, M., Milicic, J., 2003a. Sulfur metabolism in polluted Sphagnum peat bogs: a combined ^{34}S - ^{35}S - ^{210}Pb study. *Water, Air and Soil Pollution* 3, 181–200.
- Novak, M., Emmanuel, S., Vile, M.A., Erel, Y., Véron, A., Paces, T., Wieder, R.K., Vanecek, M., Stepanova, M., Brizova, E., Hovorka, J., 2003b. Origin of Lead in eight central European Peat bogs determined from Isotope Ratios, Strengths, and operation times of regional pollution sources. *Environmental Science and Technology* 37 (3), 437–445.
- Nriagu, J.O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279, 409–411.
- Nriagu, J.O., 1996. A history of global metal pollution. *Science* 272, 223–224.
- Nriagu, J.O., Lawson, G., Wong, H.K.T., Azcue, J.M., 1993. A Protocol for Minimizing Contamination in the Analysis of Trace Metals in Great Lakes Waters. *Journal of Great Lakes Research* 19 (1), 175–182.
- Nürnberg, H.W., Valenta, P., Nguyen, V.D., Götze, M., Urano de Carvahlo, E., 1984. Studies on the deposition of acid and of ecotoxic heavy metals with precipitations from the atmosphere. *Fresenius Journal of Analytical Chemistry* (317), 314–323.
- Office Fédéral de l’environnement, 1995. Emissions polluantes dues à l’activité humaine en Suisse de 1900 à 2010.
- Patterson, C.C., Settle, D.M., 1987. Review of data on eolian fluxes of industrial and natural lead to lands and seas in remote regions on a global scale. *Marine Chemistry* 22, 137–162.
- Renberg, I., Bindler, R., Brännvall, M.-L., 2001. Using the historical atmospheric lead-deposition record as a chronological marker in sediments deposits in Europe. *The Holocene* 11 (07), 511–516.
- Robbins, J.A., 1978. Geochemical and Geophysical Applications of Radioactive Lead. In: Nriagu, J.O. (Ed.), *The Biogeochemistry of Lead in the Environment*. Elsevier/North Holland Biomedical Press, pp. 285–393.
- Schulte, A., Balazs, A., Block, J., Gehrman, J., 1996. Entwicklung der Niederschlags-Deposition von Schwermetallen in West-Deutschland 1. Blei und Cadmium. *Z. Pflanzenernähr. Bodenk.* (159), 377–383.

- Schwikowski, M., Barbante, C., Doering, T., Gaggeler, H.W., Boutron, C.F., Schotterer, U., Tobler, L., Van de Velde, K., Ferrari, C.P., Cozzi, G., Rosman, K., Cescon, P., 2004. Post 17th Century changes of European Lead emissions recorded in high-alpine snow and ice. *Environmental Science and Technology*.
- Shotyk, W., Le Roux, G., 2005. Biogeochemistry and Cycling of Lead. In: Sigel, A., Sigel, H., Sigel, R.K.O. (Eds.), *Biogeochemical Cycles of the elements*, Vol. 43. M. Dekker.
- Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O., 1998. History of atmospheric Lead Deposition since 12,730 ¹⁴C yr BP from a Peat Bog, Jura Mountains, Switzerland. *Science* 281, 1635–1640.
- Shotyk, W., Blaser, P., Grünig, A., Cheburkin, A.K., 2000. A new approach for quantifying cumulative, anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat bog profiles. *The Science of the Total Environment* 249, 281–295.
- Shotyk, W., Weiss, D., Heisterkamp, M., Cheburkin, A.K., Adams, F.C., 2002. A new peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition, and organolead species. *Environmental Science and Technology* 36 (18), 3893–3900.
- UBA., 2000. Schwermetalldepositionen. In: *Umweltbundesamt (Eds.), Daten zur Umwelt 2000 Umweltbundesamt*, pp. 183–185.
- Vallelonga, P., Van de Velde, K., Candelone, J.P., Ly, C., Rosman, K.J.R., Boutron, C.F., Morgan, V.I., Mackey, D.J., 2002. Recent advances in measurements of Pb isotopes in polar ice and snow at sub-picogram per gram concentrations using thermal ionisation mass spectrometry. *Analytica Chimica Acta* 453, 1–12.
- Veysseyre, A.M., Bollhöfer, A., Rosman, K.J.R., Ferrari, C.P., Boutron, C.F., 2001. Tracing the Origin of Pollution in French Alpine Snow and Aerosols using Lead isotopic ratios. *Environmental Science and Technology* 35, 4463–4469.
- Vile, M.A., Wieder, R.K., Novak, M., 2000. 200 years of Pb deposition throughout the Czech Republic patterns and sources. *Environmental Science and Technology* 34 (1), 12–21.
- Von Storch, H., Hagner, C., Costa-Cabral, M., Feser, F., Pacyna, J.M., Pacyna, E.G., Kolb, S., 2002. Re-assessing Past European Gasoline Policies. *EOS, Transactions, American Geophysical Union* 83 (36), 393–399.
- Von Storch, H., Costa-Cabral, M., Hagner, C., Feser, F., Pacyna, J.M., Pacyna, E.G., Kolb, S., 2003. Four decades of gasoline lead emissions and control policies in Europe: a retrospective assessment. *The Science of the Total Environment* 311, 151–176.
- Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D., Cheburkin, A.K., 1999a. Atmospheric Pb deposition since The industrial Revolution Recorded by Five Swiss Peat Profiles: Enrichment Factors, Fluxes, Isotopic Composition, And Sources. *Environmental Science and Technology* (33), 1340–1352.
- Weiss, D., Shotyk, W., Kramers, J.D., Gloor, M., 1999b. Sphagnum mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmospheric Environment* 33, 3751–3763.