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Anthropogenic impacts in North Poland over the last 1300 years – A record of Pb, Zn, Cu, Ni and S in an ombrotrophic peat bog

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A B S T R A C T

Lead pollution history over Northern Poland was reconstructed for the last ca. 1300 years using the elemental and Pb isotope geochemistry of a dated Polish peat bog. The data show that Polish Pb–Zn ores and coal were the main sources of Pb, other heavy metals and S over Northern Poland up until the industrial revolution. After review of the potential mobility of each element, most of the historical interpretation was based on Pb and Pb isotopes, the other chemical elements (Zn, Cu, Ni, S) being considered secondary indicators of pollution. During the last century, leaded gasoline also contributed to anthropogenic Pb pollution over Poland. Coal and Pb–Zn ores, however, remained important sources of pollution in Eastern European countries during the last 50 years, as demonstrated by a high ²⁰⁶Pb/²⁰⁷Pb ratio (1.153) relative to that of Western Europe (ca. 1.10). The Pb data for the last century were also in good agreement with modelled Pb inventories over Poland and the Baltic region.

Keywords:

Peat
Lead
Lead isotopes
Pollution
Metal mobility
Last millennium
Poland
Baltic Sea

1. Introduction

Numerous studies have demonstrated the potential of ombrotrophic bogs to record past anthropogenic activities (e.g., Le Roux et al., 2004; Shotyk et al., 2003; Weiss et al., 2002; Mighall et al., 2002; Brännvall et al., 1999). However, studies dealing with peat inorganic geochemistry in Eastern European countries are scarce (e.g., Fialkiewicz et al. 2008; Syrovetnik et al., 2007; Mihaljevič et al., 2006; Novak et al., 2003; Vile et al., 2000). Poland is one of the top polluting countries in Europe, especially in terms of lead pollution (Van den Hout et al., 1999). Millennial records of anthropogenic impacts are lacking, despite successful mid-resolution attempts by Ciszewski and Malik (2004), and Strzyszc and Magiera (2001 and references therein). Within Poland, lake and peat bog deposits contain archive records, which are suitable for the reconstruction of historical pollution. Northern Poland is of particular interest because it

possesses several peat deposits, some of which are ombrotrophic, i.e., exclusively fed by atmospheric deposition. This region is also interesting as it is located at a relatively far distance (several hundreds of km) from the main Polish pollution centres (Fig. 1), which could possibly mask any middle- to long-range signal by a high level of local pollution. Finally, the selection of an appropriate near-shore site may offer the opportunity to investigate pollution over the Baltic region, which has been of high interest during the last decade (e.g., Schneider et al., 2000 and reference therein). During the last couple of decades, the dominant contributors of lead emission (from coal, lead mines and gasoline) over the Baltic Sea are Poland (23%), Germany (20%) and Finland (16%) (von Storch et al., 2003). By coupling elemental geochemistry and lead isotopes together with ¹⁴C and ²¹⁰Pb age-dating of a 1-m ombrotrophic peat core, we aim to: (1) reconstruct the history of lead pollution during the last millennium over North Poland, (2) link the Pb record to historical events, (3) trace the source of this lead, (4) replace our record into a more regional history of lead pollution over Eastern Europe.

2. Site description

Słowińskie Błoto bog (54°21'52.53"N, 16°29'24.72"E, 30 m a.s.l.) is located in northern Poland, 8 km to the South-East of Darłowo City,

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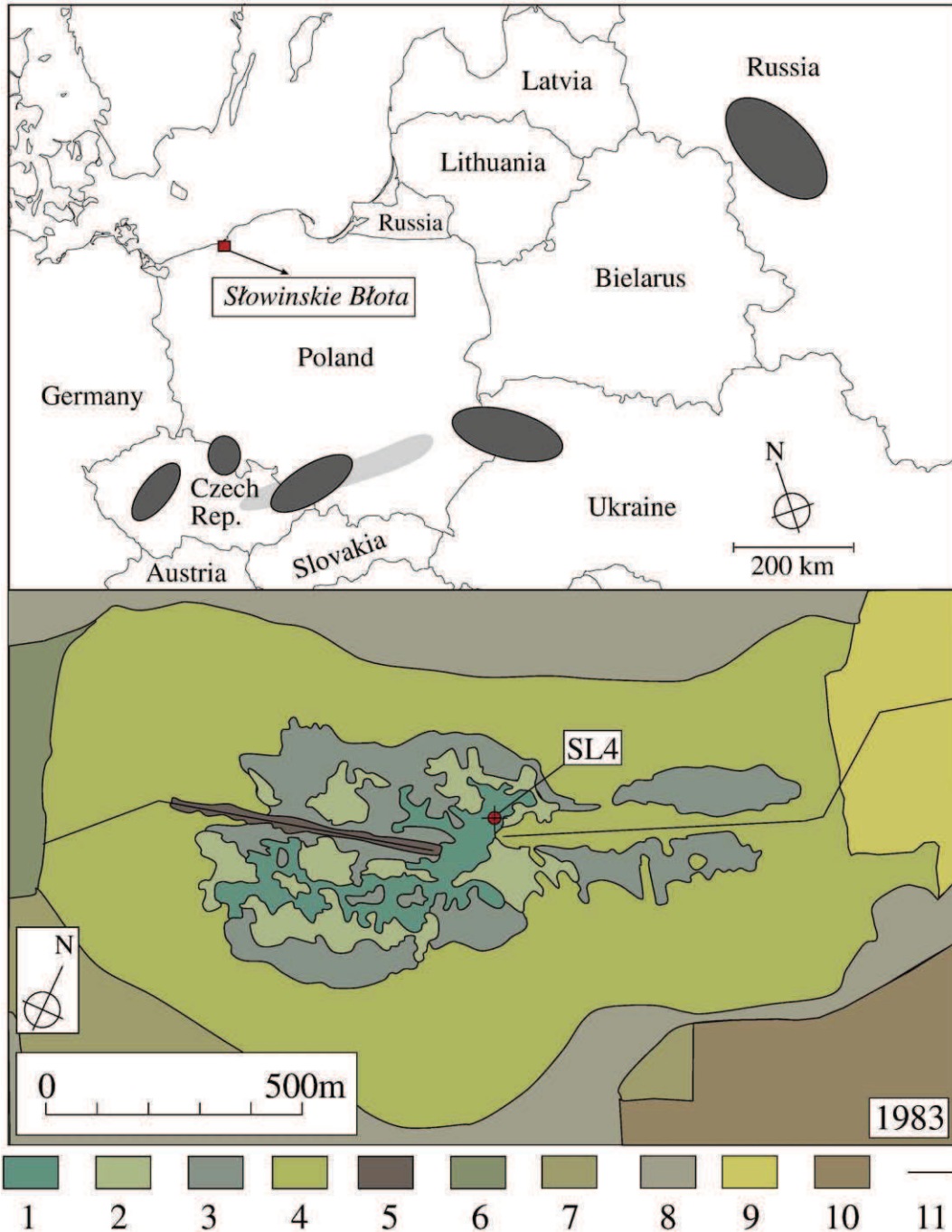


Fig. 1. Above. Site location and surrounding Pb-Zn ore (light grey) and coal (dark grey) basins in Poland (after Bibler et al., 1998; Mukai et al., 2001). Below – State of preservation in 1983 on the basis of stereoscopic aerial photographs (after Herbichowa, 1998). 1 – open peatland complex of *Sphagno-tenelli-Rhynchosporium alba*, *Sphagnetum magellanici typicum* i S. m. and <5% single dwarf pines of ca. 2 m high. 2 – open *Sphagnetum magellanici pinetosum* peatland with more densely (max. 10%) distributed pines of 2 to 5 m height. 3 – small patches of open *Sphagnetum magellanici pinetosum* peatland with initial state of *Vaccinio uliginosi-Pinetum*, small patches of *Sphagnetum magellanici typicum* and sparse pine of 4 to 8 m high. 4 (4 + 5) – Eight-meter to 20-m high Pine and birch-pine cover (50% to 80%) tree (*Vaccinio uliginosi-Pinetum* and *Betuletum pubescentis*). 5 – community with *Calluna vulgaris* on a dried peat, 6 – degenerated form of alder and young pine forest, 7 – meadow and pasture communities (class *Molinio-Arrhenatheretea*) on humified peat, 8 (9 + 10) – deciduous forest meadow communities from *Molinio-Arrhenatheretea* class on mineral soils. 9 – initial stage of development of peatland vegetation and young forest planted in remnants of peat exploitation, 10 – anthropogenic vegetation (i.e., recent), 11 – active ditches.

and 10 km away from the Baltic Sea (Fig. 1). It is described as a Baltic bog (e.g., Kulczyński, 1949). The area covered by the bog is ca. 120 ha. A study by Herbichowa (1998) on 59 cores revealed an average peat thickness of 2.8 m and a consistent peat stratigraphy over most of the bog. The base of the mire was dated at 3693–3965 BC (Herbichowa, 1998). Raised-bog vegetation began to develop around AD 50–356 (now at 2 m peat depth) with mainly *Sphagnum* and *E. vaginatum*. *Sphagnum fuscum*-peat started to develop between ca. AD 470 and

AD 1400 (Herbichowa, 1998). The actual vegetation of the central part of the bog is composed of several species of *Sphagnum* (*S. fallax* and *S. magellanicum*) with *Eriophorum vaginatum*, *Trichophorum cespitosum* and rare dwarf *P. sylvestris* (Herbichowa, 1998). In the outer parts, *Vaccinium uliginosum*, *Calluna vulgaris* and *Betula pubescens* are also present (Fig. 1). Until the end of 18th century, Słowińskie Błoto bog has been an open bog (i.e., not covered by the forest). It has been drained twice: (1) in 1880 when surrounding ditches were dug and

(2) in 1970 when two ditches were dug through the central part of the bog. These latter were renewed in 1985.

3. Methods

3.1. Coring and subsampling

In August 2005, a one-meter core was retrieved at a distance of 20 m from the central part of the bog (Fig. 1), but away from the drainage ditches, using a stainless steel 10 × 10 cm Wardenaar corer (Wardenaar, 1986). The core was then wrapped in a plastic bag, stored in a fridge and sub-sampled soon after. The edges of the core were removed to avoid any metal contamination by the corer. The remaining core was then sliced in ca. 1 cm-thick samples using a titanium knife. All the sub-samples were stored in plastic bags.

3.2. Chronological control of the peat core

The chronological control of the core consists of 10 radiocarbon measurements performed by accelerator mass spectrometry on selected plant macrofossils (mainly *Sphagnum* spp. stems and opercula, *Calluna vulgaris* stems, *Erica tetralix* stems and inflorescences, and *Andromeda polifolia* leaves), following the protocols developed by Kilian et al. (1995) and Mauquoy et al. (2004). The samples were prepared at the GADAM Centre (Gliwice, Poland) using an acid-alkali-acid washing, drying and graphitisation following Goslar and Czernik (2000). The measurements took place at the Poznan radiocarbon Laboratory (Poznan, Poland) following the protocol from Goslar et al. (2004). Calibration of radiocarbon dates was undertaken using the IntCal04 calibration curve (Reimer et al., 2004) and OxCal 4.0 software (Bronk Ramsey, 1995, 2001).

Lead 210 was also measured in recent layers (down to 35 cm depth) after ^{210}Po extraction from 2 g of dry peat powder spiked with ^{208}Po using a sequential H_2O_2 - HNO_3 -HCl digestion. Measurements were performed using an α -spectrometer (Canberra model 7401) for two days for each sample in order to obtain sufficient accuracy. The results of the calculation were corrected for the radioactive decay of ^{208}Po since the moment of its calibration, and the decay of ^{210}Pb since the moment of polonium extraction from the sediment. More details about the ^{210}Pb measurements at the GADAM Centre (Gliwice, Poland) can be found in Sikorski (2008 and reference therein). The Constant Rate of Supply (CRS) model (Appleby, 2001) was then applied in order to build the ^{210}Pb age-model.

3.3. X-ray fluorescence

Selected samples ($n=44$) were freeze-dried and then powdered in an automatic agate mortar (400 rpm, 1 h). One gram of the resulting powder was analysed for selected elements at the Institute of Environmental Geochemistry (Heidelberg, Germany) using two different XRF instruments. Energy-dispersive Miniprobe Multielement analyzer EMMA (Cheburkin and Shotyk, 1996) was used to analyse trace elements (Ni, Cu, Zn, Pb) while Energy dispersive XRF spectrometer TITAN (Cheburkin and Shotyk, 2005) was used to analyse minor elements (S and Ti). The two analysers are calibrated with various organic international standards: coals (NIST1632b, NIST1635, SARM19 and SARM 20) and plant material (NIST1515, NIST1547, NIST1575, BCR 60 and BCR62). Accuracies are below or equal to 10% except for Ni, which displays an accuracy of 15%. Results are given in Table 1 along with accuracy and detection limits.

3.4. Isotopic analyses

Regarding the Pb concentration in peat, 10 to 500 mg of dry peat powder was taken, in order to obtain 2000 ng of Pb in the final solution. Galenas and one bulk coal from various locations were also digested and

analysed in order to provide isotopic signature of the local mining background. About 1 mg of galena and 150 mg of coal were taken, respectively. For peat and coal samples, the powder was firstly calcined (550 °C, 4 h) and then digested in 6 ml HF 24 N *suprapur* (Merck) + 1 ml HNO_3 14 N *cc. sub.* in Teflon beakers (120 °C, 48 h) in class 1000 laminar flow clean air cabinets (University of Brussels, Belgium). For galena samples, the powder was directly digested in 2 ml of HCl 6.8 N. After complete evaporation, HCl 6.8 N was added and the solutions were slowly evaporated. Dried residues were dissolved in HBr 0.8 N prior to chromatographic separation. Lead was separated using pre-conditioned anionic resin (AG1X8) exchange micro-columns by successive HBr and HCl additions (Weis et al., 2005). The eluted pure Pb solution was evaporated and stored. Before isotopic analysis, the Pb elution was re-dissolved in 100 μl of HNO_3 14 N *cc. sub.*, evaporated and finally dissolved in 1.5 ml of HNO_3 0.05 N.

Lead isotopic ratios were measured on a Nu Instruments Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the *Département des Sciences de la Terre et de l'Environnement* (DSTE, University of Brussels) during a one-day analytical session. Details about MC-ICP-MS tuning and calibration for this type of sample are reported in De Vleeschouwer et al. (2007). As an internal isotopic standard, a Tl solution was added to each sample and standard to monitor and correct for mass dependent isotopic fractionation. The sample solutions were prepared to obtain a beam-intensity in the axial collector (^{204}Pb) of a minimum of 100 mV and a Pb/Tl ratio of 5, matching the Pb and Tl concentrations of the NIST-SRM 981 Pb standard (200 ppb in Pb, with 50 ppb in Tl). Repeated measurements of NIST-SRM 981 Pb standard were carried out before starting the analysis of samples, and between each sample. The reproducibility on each measured ratio is equal to 100% ($n=25$). Average values of the NIST-SRM 981 Pb standard are $^{208}\text{Pb}/^{204}\text{Pb} = 36.715 \pm 0.005$ (2SD), $^{207}\text{Pb}/^{204}\text{Pb} = 15.497 \pm 0.002$, $^{206}\text{Pb}/^{204}\text{Pb} = 16.941 \pm 0.002$, which are in agreement with the long-term internal laboratory reproducibility ($n = \pm 1000$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.713 \pm 0.012$ (2SD), $^{207}\text{Pb}/^{204}\text{Pb} = 15.495 \pm 0.004$, $^{206}\text{Pb}/^{204}\text{Pb} = 16.939 \pm 0.004$) and literature values (Galer and Abouchami, 1998; Weis et al., 2005, 2006). Although the NIST-SRM 981 Pb standard results were within the error of the triple-spike values after online correction for instrumental mass bias by Tl addition, the sample results were further corrected by the sample-standard bracketing method described by White et al. (2000) and Weis et al. (2006) to circumvent any instrumental drift during the analytical session. Accuracies derived from standard deviations average from 14 to $49 \cdot 10^{-4}$ for $^{208}\text{Pb}/^{204}\text{Pb}$, 5.8 to $10 \cdot 10^{-4}$ for $^{207}\text{Pb}/^{204}\text{Pb}$, 6.1 to $14 \cdot 10^{-4}$ for $^{206}\text{Pb}/^{204}\text{Pb}$, 2.9 to $8 \cdot 10^{-5}$ for $^{208}\text{Pb}/^{206}\text{Pb}$ and from 0.9 to $2 \cdot 10^{-5}$ for $^{207}\text{Pb}/^{206}\text{Pb}$ (Table 2). One replicate (*i.e.*, a re-run of the same sample solution) of the peat sample 9 and one duplicate (*i.e.*, sample which is processed twice from weighting, acid digestion to analysis) of galena 2 have been analysed. Results fall within the measurement accuracies of their counterparts. Results are summarized in Table 2.

4. Results and discussion

4.1. Ombrotrophy

The vegetation characteristics (*i.e.*, *Sphagnum* dominance, see Section 2) described in Herbichowa (1998), and more recently in Lamentowicz et al. (2008) and De Vleeschouwer et al. (2009) indicate the presence of acidic, nutrient-poor conditions and strongly support the ombrotrophic character of the bog. Moreover, Herbichowa (1998) reported that the dome of the bog is elevated at ca. 1.2 m above its surroundings, which makes it a raised bog.

4.2. Chronology

Both ^{210}Pb and ^{14}C models were linked by the sample at 34.5 cm depth (dated by both techniques) and combined in a non-linear age-

Table 1
Elemental geochemistry on bulk dry samples.

Sample label	Mean depth (cm)	Mean density g cm ⁻³	Mean acc. rate cm yr ⁻¹	Age cal yr. AD	Unc. cal yr. AD	Ti mg kg ⁻¹	S mg kg ⁻¹	Ni mg kg ⁻¹	Cu mg kg ⁻¹	Zn mg kg ⁻¹	Pb mg kg ⁻¹
04-05	4.5	0.023	0.830	2002	3	36	1442	5.64	11.77	89.2	5.38
05-06	5.5	0.024	0.826	2001	2	32.36	1229	2.65	7.56	55.9	3.39
06-07	6.5	0.024	0.973	2000	2	27.3	1176	5.54	6.92	51.4	4.25
07-08	7.5	0.024	1.120	1999	2	34.9	1157	D.L.	6.07	54.4	3.65
08-09	8.5	0.027	1.024	1998	2	35.1	1258	D.L.	8.98	61.2	4.7
09-10	9.5	0.03	0.883	1997	2	38.7	1235	2.81	8.04	64	3.41
10-11	10.5	0.032	0.590	1996	2	69	1400	D.L.	8.47	90.3	5.23
13-14	13.5	0.057	0.369	1991	2	31.6	1284	3.95	9.72	123	9.48
16-17	16.5	0.056	0.429	1983	3	62.8	1584	4.63	5.31	170	19.6
18-19	18.5	0.05	0.358	1978	3	57.7	1494	5.47	5.49	160	33.3
21-22	21.5	0.044	0.275	1970	3	81	2157	4.62	7.05	155	64.8
23-24	23.5	0.047	0.176	1962	3	95.3	2716	7.63	8.79	152	99.1
26-27	26.5	0.065	0.117	1945	3	244	3992	6.77	17.73	126	204
29-30	29.5	0.066	0.095	1920	3	272	3654	7.1	18.58	80.3	156
32-33	32.5	0.065	0.029	1888	5	138	3566	4.46	13.14	59.8	125
34-35	34.5	0.058	0.020	1820	41	155	2372	2.74	9.16	52.7	101
36-37	36.5	0.071	0.022	1719	31	376	3873	3.64	7.24	55.2	155
38-39	38.5	0.116	0.026	1627	29	353	2863	3.66	5.64	44.5	109
41-42	41.5	0.101	0.031	1512	31	206	2007	D.L.	D.L.	34.7	52.5
43-44	43.5	0.141	0.033	1447	32	180	1688	3.2	2.6	28.5	37
45-46	45.5	0.149	0.036	1387	35	148	1462	3.93	3.22	26	31.4
47-48	47.5	0.126	0.036	1331	39	138	1516	3.2	3.11	23.7	29.2
50-52	51.0	0.05	0.073	1234	46	56	1364	D.L.	D.L.	22.1	18.7
52-53	52.5	0.048	0.054	1214	47	34.3	1348	D.L.	D.L.	21.5	14.4
54-55	54.5	0.045	0.063	1177	47	42.5	1320	D.L.	3.37	18.4	13.3
57-58	57.5	0.03	0.071	1129	45	23.6	994	D.L.	D.L.	15.4	12
59-60	59.5	0.033	0.077	1101	42	60.1	1505	2.68	D.L.	15.7	18.1
61-62	61.5	0.031	0.089	1075	39	38.5	1483	D.L.	D.L.	17.6	15.2
66-67	66.5	0.035	0.103	1019	30	23.3	974	D.L.	D.L.	11.9	7.87
68-69	68.5	0.031	0.114	1000	27	18.9	924	D.L.	D.L.	8	5.72
71-72	71.5	0.032	0.122	974	32	20.2	1121	D.L.	D.L.	8	4.42
73-74	73.5	0.035	0.126	957	36	32.5	1116	D.L.	D.L.	7.8	4.83
77-78	77.5	0.028	0.122	925	43	22.4	999	D.L.	D.L.	3.97	4.83
79-80	79.5	0.028	0.116	909	46	25.5	1225	D.L.	D.L.	4.68	1.48
82-83	82.5	0.037	0.110	883	49	28.3	1142	D.L.	D.L.	12.9	2.84
84-85	84.5	0.04	0.106	865	51	32.5	1249	D.L.	D.L.	6.59	2.72
86-87	86.5	0.04	0.104	846	52	37.1	1361	D.L.	D.L.	6	1.2
88-89	88.5	0.028	0.101	827	54	30.4	1302	3.07	D.L.	5.96	1.1
91-92	91.5	0.024	0.099	797	56	34.5	1171	D.L.	D.L.	3.53	D.L.
95-96	95.5	0.031	0.098	757	59	34.9	1245	D.L.	D.L.	5.44	0.91
97-98	97.5	0.025	0.098	736	60	22.5	1246	D.L.	D.L.	4.17	D.L.
LLD						0.9	70	2.5	2.5	2	0.6
Error (%)						7	10	15	5	8	10

D.L. refers to measurements below detection limit. Model-derived ages reported from De Vleeschouwer et al. (2009).

depth model approach (generalized additive model, GAM) described by Heegaard et al. (2005). Complete details of these measurements and the resulting age model are reported in De Vleeschouwer et al. (2009). The agreement between the oldest ²¹⁰Pb derived ages and the youngest radiocarbon ages are also discussed in Piotrowska et al. (in press).

De Vleeschouwer et al. (2009) provided a modelled-age for each sample (here reported in Table 1). Using multiple linear regressions, De Vleeschouwer et al. (2009) also demonstrated three main periods of different accumulation rates. From the base of the core up to 52.5 cm depth (5 dates), the peat accumulation rate averages ca. 1 mm yr⁻¹. Between 52.5 cm and 34.5 cm depth (4 dates), the mean peat accumulation rate decreases towards 0.3 mm yr⁻¹. Then it increases dramatically towards the surface (²¹⁰Pb-dated interval) with a mean accumulation rate of 5.7 mm yr⁻¹.

4.3. Mobility of heavy metals in peat – a short review

Heavy metals have been abundantly monitored in peat. Studies are dedicated to two main topics: (1) the history of past heavy metals pollution (e.g., Shoty et al., 1998) and (2) their mobility (mainly because of their potential toxicity) linked to various phenomena such as adsorption on organic matter (e.g., Grybos et al., 2007) and scavenging by oxo-hydroxides (e.g., Tessier et al., 1996). However, despite the

numerous studies undertaken, their behaviour is not always well understood.

Numerous studies have concluded that ombrotrophic bogs are probably the best continental Pb archive since these ecosystems only receive Pb from the atmosphere (e.g., Shoty et al., 1998; Weiss et al., 2002; Mighall et al., 2002). Lead is by far the most intensively studied heavy metal in peat mainly because it is considered by most authors to be immobile in ombrotrophic peat. These peat deposits efficiently retain Pb despite a low pH, the abundance of organic acids and seasonal variation in redox conditions (e.g., Shoty and Le Roux 2005; Mighall et al., 2002; Shoty et al., 1998). Also, the isotopic composition of lead keeps a fingerprint of its source, making a powerful tool for distinguishing natural from anthropogenic sources (e.g., Shoty et al., 1998; Mighall et al., 2002; Shoty and Le Roux, 2005). Moreover, using such isotopic fingerprints, Weiss et al. (1999) demonstrated Pb immobility by comparing Pb isotopic composition in dated herbarium *Sphagnum* samples from Swiss and Southern Germany and in ²¹⁰Pb-dated peat samples from the same age and same location. The similarity of age dating made using the ²¹⁰Pb CRS model and ¹⁴C Bomb Pulse Curve also supports the immobility of Pb (Goodsite et al., 2001). Over the last few years however, as some authors have continued to investigate the behaviour of lead in peat, the debate over Pb mobility reopened. For example, Sonke et al. (2002) demonstrated that in organic sediment (including peat), Pb

Table 2

Isotopic measurements on selected peat samples from Słowińskie Błoto bog (above), galenas and coal from Poland (below).

Sample no.	Mean depth (cm)	$^{208}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$2\text{se} \times 10^{-5}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$2\text{se} \times 10^{-5}$
1	6.5	38.0758	49	15.6151	10	18.1974	14	2.09251	4.3	0.85803	1.1
2	13.5	37.9713	20	15.6048	6.8	18.0843	7.4	2.09974	4.3	0.86284	1.0
3	21.5	37.8992	25	15.5911	9.8	17.9892	10	2.10677	3.8	0.86665	0.9
4	26.5	37.9656	21	15.5963	7.3	18.0324	7.9	2.10541	3.6	0.86485	1.0
5	29.5	38.0678	19	15.6012	6.1	18.1164	7.0	2.10133	3.9	0.86112	1.1
6	32.5	38.1612	18	15.6102	7.3	18.1871	9.2	2.09830	3.8	0.85828	1.0
7	36.5	38.2696	17	15.6176	6.7	18.2759	7.0	2.09402	4.6	0.85447	1.2
8	41.5	38.3550	22	15.6218	7.8	18.3564	7.7	2.08948	3.8	0.85099	1.0
9	59.5	38.3176	20	15.6269	7.3	18.3346	8.2	2.08992	3.9	0.85228	1.1
9*	59.5	38.3164	17	15.6265	6.3	18.3343	6.2	2.08986	4.0	0.85226	1.0
10	68.5	38.3025	19	15.6238	7.6	18.3315	9.1	2.08946	2.9	0.85225	0.9
11	77.5	38.3270	16	15.6262	5.8	18.3555	6.1	2.08809	4.4	0.85127	1.3
Samples	Location	$^{208}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$2\text{se} \times 10^{-4}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$2\text{se} \times 10^{-5}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$2\text{se} \times 10^{-5}$
Galena 1	Chrzanow	38.4018	31	15.6144	10	18.4103	11	2.08589	8	0.84809	2
Galena 1 ^a	Chrzanow	38.4089	24	15.6165	8	18.4148	8	2.08578	6	0.84801	2
Galena 2	Chrzanow	38.4091	20	15.6160	7	18.4158	8	2.08567	5	0.84794	1
Galena 2 ^b	Chrzanow	38.4052	24	15.6146	10	18.4136	9	2.08566	6	0.84793	2
Galena 3	Olkusz	38.3760	28	15.6226	9	18.3942	9	2.08632	6	0.84928	1
Galena 4	Olkusz	38.3795	23	15.6222	8	18.3992	8	2.08588	5	0.84904	1
Galena 5	Pomorzany	38.3837	26	15.6245	9	18.3992	9	2.08615	7	0.84914	2
Galena 6	Pomorzany	38.3737	30	15.6218	10	18.3931	10	2.08632	7	0.84928	1
Galena 7	Pomorzany	38.3772	31	15.6210	10	18.3966	10	2.08609	8	0.84908	2
Galena 8	Pomorzany	38.3812	25	15.6217	9	18.4016	10	2.08573	7	0.84889	1
Galena 9	Chrzanow	38.4106	22	15.6162	8	18.4133	9	2.08594	7	0.84805	1
Coal	Katowice	38.1621	20	15.6173	8	18.2320	8	2.09311	3	0.85654	1

2se refers to accuracy calculated from 2 standard deviation.

^a Replicate, i.e., a re-run of the same sample solution.^b Duplicate, i.e., sample which is processed twice from weighing, acid digestion to analysis.

could be slightly leached. Recently, Novak and Pacherova (2008) also showed that Pb can be mobile to some extent, but it is still considered as immobile by most authors.

The behaviour of Zn is somewhat different to that of lead and is still under debate. Zinc usually accompanies lead in geochemical studies of peat, mainly because these two metals are associated in ores, which are an important source of pollution. In ombrotrophic peat, Mighall et al. (2002 and reference therein) showed relatively similar concentration profiles for Pb and Zn, suggesting the immobility of Zn in raised peat bogs. However, in his synthesis of inorganic components found in peat, Shotyk (1988) explained that Zn distribution is linked, among others, to bioaccumulation, water table fluctuations and pH conditions. Nieminen et al. (2002) showed that Zn was highly mobile in ombrotrophic peat as the Zn concentration profile showed low Zn concentrations compared to high Zn emission from nearby smelters, but showed no relation with other elemental profiles. Novak and Pacherova (2008) showed that Zn was highly mobile by comparing its particulate and pore water content. It seems therefore that in an attempt to use Zn as a tracer, one should carefully interpret its elemental profile and compare it to the Pb profile.

Compared to lead and zinc, less studies exist for copper behaviour in peat. Cu has been demonstrated to be either immobile or mobile. Nieminen et al. (2002) showed possible preservation of Cu after atmospheric deposition, regarding the rapid evolution of the vertical Cu enrichment factor gradient. Using herbarium samples, Shotbolt et al. (2007) showed the immobility of Cu. However, Shotyk et al. (2002) and Ukonmaanaho et al. (2004) argued that, in ombrotrophic peat, Cu could be affected by plant uptake like Zn. Novak and Pacherova (2008) also recently concluded that Cu was highly mobile. In a detailed study of three ombrotrophic bogs in Finland, Rausch et al. (2005) demonstrated that Cu mobility was affected by pH and mineralogy. At one site with relatively high pH and where CuFeS₂ (chalcopyrite) was the dominant Cu bearing phase, Rausch et al. (2005) found that Cu was immobile. In a second site presenting lower pH and dominance of Cu oxide, Rausch et al. (2005) found Cu to be mobile.

Very few studies have been carried out to investigate the behaviour of Ni in ombrotrophic peat, and the conclusions of this

research are contradictory. Krachler et al. (2003) concluded that Ni is mainly immobile in ombrotrophic peat, although it may be affected by weathering in minerotrophic peat. In contrast, Nieminen et al. (2002) showed that Ni is mobile in ombrotrophic peat. Ukonmaanaho et al. (2004) demonstrated that Ni was very mobile and affected by leaching. Rausch et al. (2005) also demonstrated the high mobility of Ni in three ombrotrophic peat cores from Finland, one of which is nearby a Cu–Ni mine and another one close to a Cu–Ni smelter. All the Ni records did not follow the exploitation history of the nearby mines and smelters. The mobility of Ni was recently confirmed using herbarium samples, by comparing Ni concentrations and Pb (assumed immobile) concentrations in specific peat vegetation samples of various ages (Shotbolt et al., 2007).

4.4. Natural vs. anthropogenic sources

Enrichment factors (E.F., Table 3) relative to the upper continental crust (U.C.C.) were calculated using Ti as a conservative element (e.g., Shotyk et al., 2002; Kempter, 1996). It was not possible to calculate a regional natural background from deep samples as only a 1-m core was retrieved. However, the mean Pb concentration in natural (i.e., non-polluted) soils from Poland is ca. 16 mg kg⁻¹ (Jarosinska et al., 2003), which is in good agreement with the mean U.C.C. value (17 mg kg⁻¹). The main particle sources to Słowińskie Błoto bog are rainwater, sea salt sprays, atmospheric dust and particles due to human activities (coal burning, metal smelting and gasoline use). The latter is the main source for Ni, Cu, Zn, Pb and S. However, EF is limited in deciphering between the various anthropogenic sources. Therefore, lead isotopes will be used in order to specify which anthropogenic source is dominant over a period of time.

Selected trace element depth profiles record similar trends, especially for Pb and S (Fig. 2). Low values are observed below 40 cm depth. Copper and nickel are below detection limits until ca. 40 cm depth, where they increase towards maximum values at ca. 25 cm depth (AD 1955). Two peaks in Pb concentration are recorded at 36.5 (AD 1719) and 26.5 cm depth (AD 1945), respectively, in addition to sulphur. Towards the surface, all the concentrations

Table 3

Enrichment factors calculated in the five depth intervals of the core using values from the upper continental crust (Mc Lennan, 2001) and Ti as a conservative element.

	Concentrations in UCC (mg kg ⁻¹)	Values/Ti UCC	100 cm–50 cm E.F. (Ti)	50 cm–35 cm E.F. (Ti)	35 cm–25 cm E.F. (Ti)	20 cm–10 cm E.F. (Ti)	10 cm–0 cm E.F. (Ti)
S	953	0.24	168	52	63	117	156
Ni	18.6	0.0046	16	4	6	19	28
Cu	14.3	0.0036	22	10	20	37	68
Zn	52	0.013	25	17	31	182	142
Pb	17	0.004	53	93	166	122	29

decrease progressively. The zinc profile is different from the other heavy metal profiles. It records only one peak between 23 cm and 15 cm depth. The discrepancies between the Zn and the other heavy metals have been linked to zinc mobility and zinc plant uptake (e.g., Nieminen et al., 2002; Shoty, 1988). Zinc is therefore not the best reference element to detect historic metal pollution. Lead is generally preferred as it is considered to be immobile in ombrotrophic bogs (Shotbolt et al., 2007; Weiss et al., 1999; Shoty et al., 1998). Cu and Ni are considered by most authors to be mobile (e.g., Rausch et al., 2005) because they can be affected by changing redox conditions and therefore be leached. Their profile must therefore be interpreted with care. We may only assume that they are evidence for pollution by these metals, even in this remote area of Poland.

Lead isotopic ratios (Table 2) show relatively stable values from the base of the core up to 40 cm depth: $38.303 < ^{208}\text{Pb}/^{204}\text{Pb} < 38.355$, $15.624 < ^{207}\text{Pb}/^{204}\text{Pb} < 15.627$, $18.332 < ^{206}\text{Pb}/^{204}\text{Pb} < 18.356$. This interval corresponds to the Middle Ages. Above 40 cm depth, Pb isotopic ratios decrease towards a minimum at 21.5 cm depth ($^{208}\text{Pb}/^{204}\text{Pb} = 37.900$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.591$; $^{206}\text{Pb}/^{204}\text{Pb} = 17.990$), which corresponds to AD 1970. Isotopic ratios finally increase towards the surface ($^{208}\text{Pb}/^{204}\text{Pb} = 38.076$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.615$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.197$). Such stable trends mainly during the Middle Ages, less radiogenic values during 1970–1980 and a recent increase were also observed in *Sphagnum* bogs from the Czech Republic (Novak et al., 2003).

The isotopic composition of selected peat samples from Słowińskie Błoto are compared to the isotopic signatures of (a) the U.C.C. (i.e., Upper Continental Crust as a natural source of dust particles),

(b) galena and coal samples from south Poland, and (c) modern aerosols (1994–1999) from Eastern European countries (Fig. 3) measured by Bollhöfer and Rosman (2001). Isotopic ratios for Słowińskie Błoto samples confirm the hypothesis given by Pb E.F. that the main source of lead supplied to the bog is anthropogenic. In the $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ biplot, all the peat samples are spread between the isotopic field of (1) Polish galena and coals, and (2) modern aerosols (Fig. 3). No sample is found close to the isotopic field of continental crust. Samples from ca. AD 800 to ca. AD 1700 fall close to the galena isotopic field. It is difficult to distinguish between Polish galena and coal using the lead isotopic signatures, as both fields overlap. However, historical studies on metal trade in Medieval Poland show that galena was mined and smelted throughout Medieval times in Poland, and the peak of mining and smelting occurred between ca. AD 1500 and AD 1650 (Carter, 1994; Molenda et al., 1965). It is therefore assumed that the main anthropogenic Pb source over Poland during the medieval period was Pb–Zn (and Pb–Ag) mining and smelting. During the 20th century, samples fall into the field of modern aerosols, recording a more mixed signature, due to various lead emissions from coal burning, lead smelting and gasoline combustion. Samples spanning the last two centuries display isotopic ratios similar to aerosols from Ukraine, Russia and Lithuania. However, Bykowszczenko et al. (2006) noticed that, owing to wind directions, the main atmospheric pollutants reaching the Słowińskie Błoto area originated from Western and South Western Poland and East Germany. It is assumed that although the lead isotopic signature found in Słowińskie Błoto during the last two centuries is in good

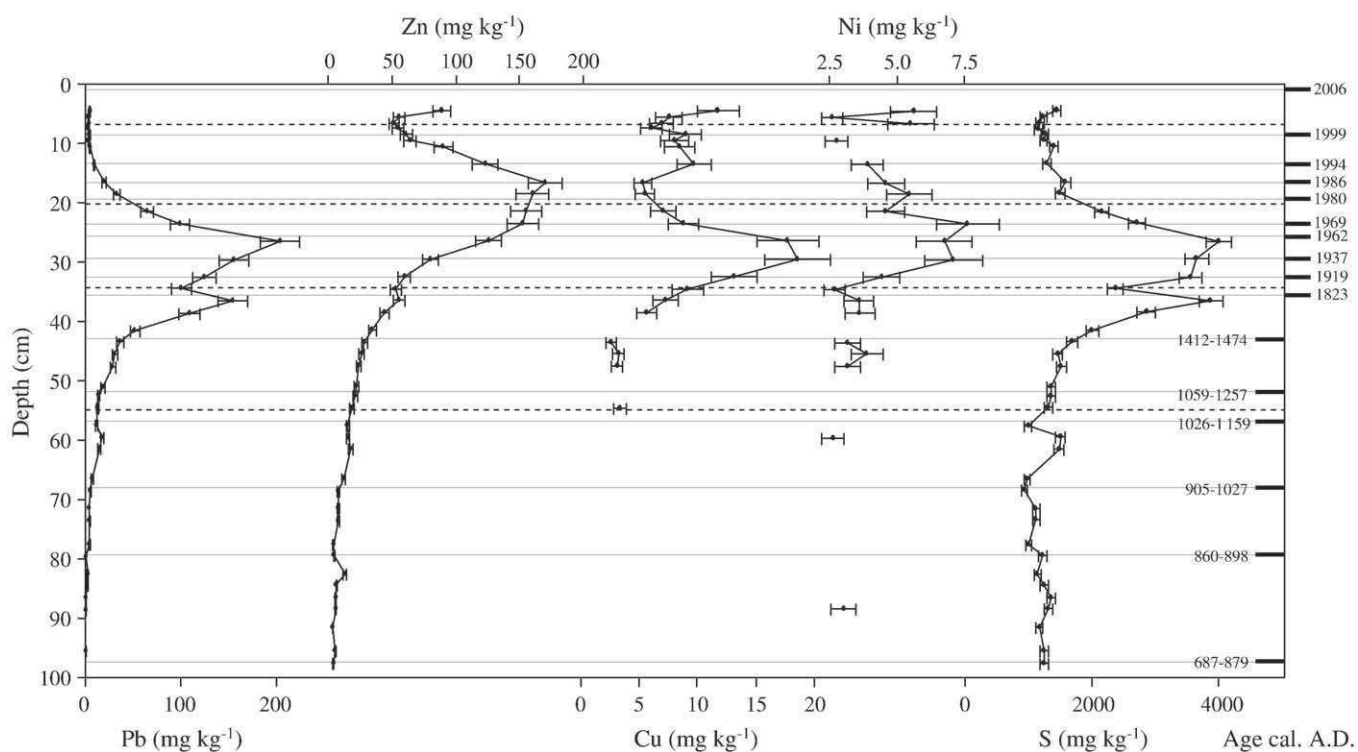


Fig. 2. [Pb], [Zn], [Cu], [Ni] and [S] vs depth. ¹⁴C age intervals and some ²¹⁰Pb reference points are also reported.

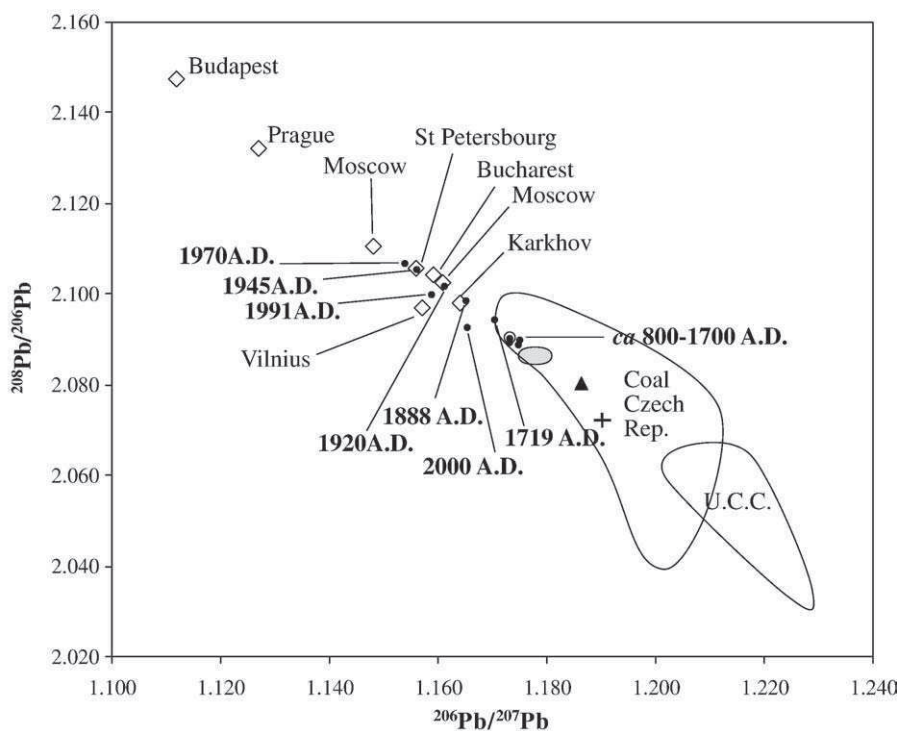


Fig. 3. $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ three-isotope plot and comparison with pollution sources. Plain black circles: samples from Słowińskie Błoto peat bog. Open circle: replicate of sample 9. Black triangle: coal from Poland this study), cross: coal from Poland (Farmer et al., 1999), grey shaded area: galena from Poland ($n=11$). White area: coal from Czech Republic taken from Mihaljevič et al. (2009). U.C.C.: Upper continental crust field from Millot et al. (2004), Hemming and McLennan (2001), Grousset et al. (1994) and Asmeron and Jacobsen (1993). Modern industrial aerosols from Eastern Europe taken from Bollhöfer and Rosman (2001).

agreement with lead originating from Russia and Ukraine, its signature is roughly similar to all the east European countries, and significantly different from the western part of Europe. The trend of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in northern Poland during the last two centuries follow the one recorded in the other locations (Fig. 5). It decreases from the early 19th century to the 1960s. From the 1960s, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Słowińskie Błoto starts to increase drastically. Although the other records also display such an increase, their values generally stay below 1.15. This can be explained by the predominance of leaded gasoline (with low $^{206}\text{Pb}/^{207}\text{Pb}$ values) among the pollution sources in western European countries. In Eastern European countries, coal burning (with higher $^{206}\text{Pb}/^{207}\text{Pb}$ values) remained more important. This fact was previously mentioned by Novak et al. (2003), who noticed that the main difference between eastern and western Europe in terms of lead isotopic signature was that atmospheric $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Eastern Europe averaged 1.15 during the 1970s, and not 1.10, because Pb-ore treatment and coal burning remained important sources of Pb. In Słowińskie Błoto, $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in 1970 is equal to 1.153, which is in good agreement with the importance of extractive industries relative to lead gasoline in Eastern European countries. In Poland, leaded gasoline was progressively withdrawn in favour of unleaded gasoline during the first years of the 21st century. This introduction is also clearly recorded by the lead isotopes in Słowińskie Błoto, displaying higher $^{206}\text{Pb}/^{207}\text{Pb}$ and lower $^{208}\text{Pb}/^{206}\text{Pb}$ values (sample at 2000 AD on Fig. 3).

4.5. History of pollution recorded in Słowińskie Błoto and a comparison with European pollution history

The calculated lead accumulation rate (Fig. 4) displays two peaks around AD 1600 and AD 1940, separated by a low-value period around AD 1800. This trend can be explained by the history of Poland and its extractive industry. By its commonwealth pact with the Duchy of Lithuania, Poland entered the apogee of its cultural and economic development between ca. AD 1500 and 1650 (Lukowski and Zawadzki,

2001). This prosperity gradually decreased between ca. AD 1650 and 1800 when Poland entered a period of semi-permanent war, ending with its partition by the countries bordering it: the Russian Empire, Austria and Prussia (Lukowski and Zawadzki, 2001). The production of lead is strongly affected by this cultural trend. Lead production in Silesia, detailed in Molenda (1969) and in Keckowa and Molenda (1978), increased from 500 t yr^{-1} in ca. AD 1500 to 3000 t yr^{-1} in ca. AD 1650, to dramatically decrease afterwards. This apogee and phasing out of the Medieval and Renaissance Polish culture and economy is clearly recorded in the lead accumulation rate at Słowińskie Błoto (Fig. 4), suggesting that metal extraction and processing was relatively important during the Polish apogee and subsequently decreased during the 17th century. This peak of lead pollution during the Polish Renaissance was also recorded in a peatland from southern Poland, 30 km north of the Silesian region (Chrost, 1990). During the industrial revolution, the increasing mining activities and, more recently, the introduction of leaded gasoline explain why the lead accumulation rate increased so dramatically to reach a maximum between 1920 and 1940 and remains elevated until the eighties (Fig. 5). The calculated cumulative lead (assuming a negligible amount of lead deposited prior to AD 750) shows an almost perfect exponential increase from AD 750 towards the present, with a slowing down during the last 25 years (Fig. 4). It also shows that approximately one half of the lead was deposited prior to AD 1820, while the other half was deposited during the last two centuries. This trend emphasises the significant pollution during the industrial revolution. The decline of the communist regime in Poland caused a strong decrease in industrial activities in addition to new EU regulations introduced to reduce particle emissions from smelters. As a consequence, the Pb accumulation rate starts to decrease during the 1970s (Fig. 5). The amount of lead accumulated during the past 25 years is therefore less important, explaining the attenuation in the slope of the cumulative lead curve for this period.

The lead enrichment factor profile (Fig. 4) shows two periods of enrichment (AD 1000–AD 1200 and AD 1700–present) separated by lower values between AD 1200 and AD 1700. This last period in

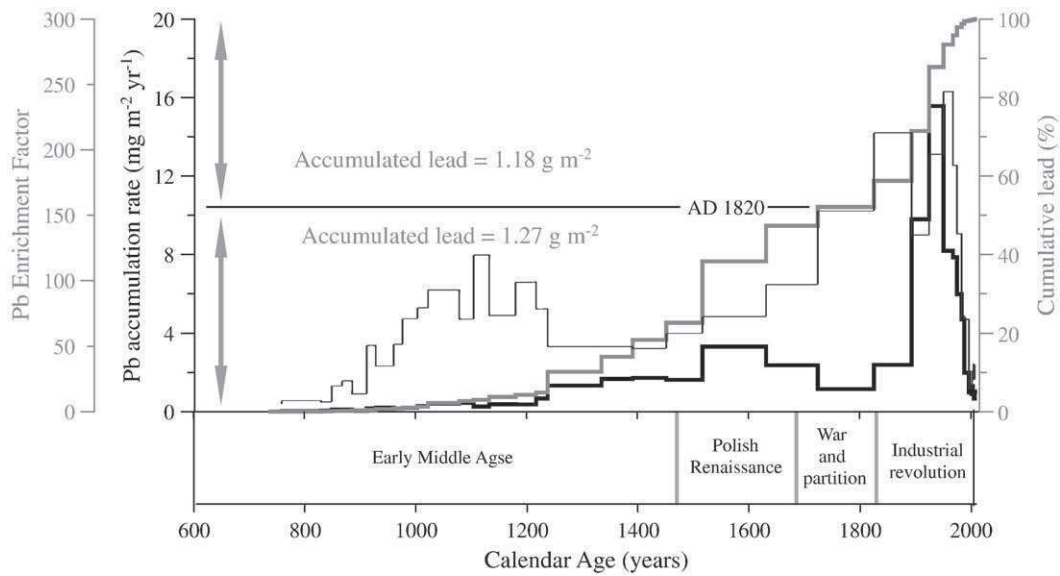


Fig. 4. Lead accumulation rate (black line), accumulated lead (grey line) and lead enrichment factor (thin grey line) in Słowińskie Błoto peat bog. Horizontal segments represent the time interval of each sample. Note that ca. 50 % (1.18 g m^{-2}) of the total lead has been deposited during the last two centuries.

characterized by high Ti content from high atmospheric soil dust input (De Vleeschouwer et al., 2009), therefore decreasing the lead EF. The last Pb EF maximum (Pb E.F. = 250) is around between ca. AD

1965 and AD 1985 (Fig. 5). However, the maximum calculated Pb accumulation rate is found in the deeper adjacent layer ^{210}Pb dated between 1920 and 1940. This discrepancy between these two

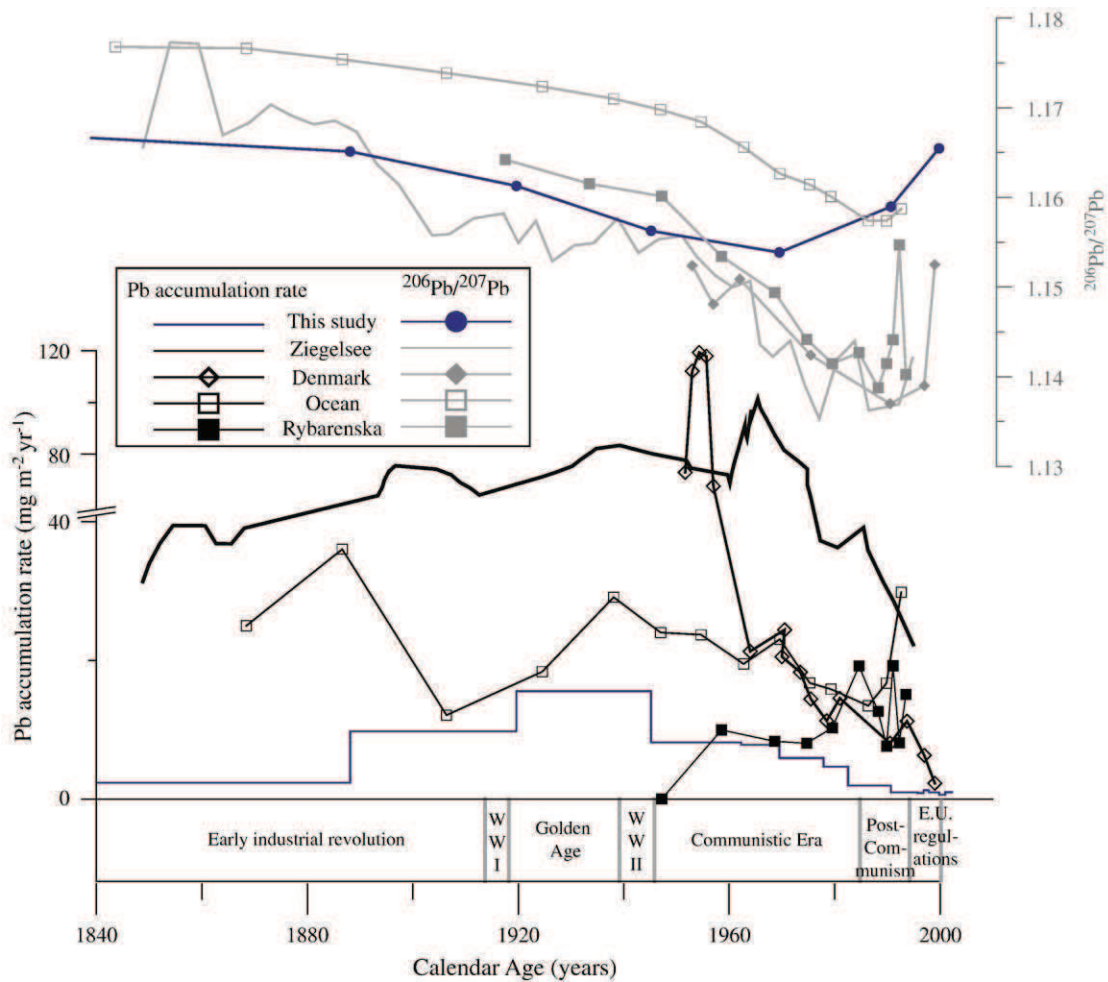


Fig. 5. Comparison of $^{206}\text{Pb}/^{207}\text{Pb}$ and Pb accumulation profiles in Słowińskie Błoto since AD 1840 with peat records from Denmark (Shotyk et al., 2003), Ocean and Rybarenska peat bogs, Czech Republic (Novak et al., 2008), and a lake record from Ziegelsee, North Germany (Gäbler and Suckow, 2003).

indicators of Pb atmospheric pollution can be explained by the largest Pb E.F. induced by leaded gasoline combustion which would not produce any particles containing Ti. Coal combustion on the other hand would produce particles enriched in Pb but also in Ti (Eskenasy and Stefanova, 2007; Xu et al., 2003), which does not make Pb E.F. the best indicator to follow Pb pollution. The Pb E.F. maximum around ca. AD 1000 can be associated with medieval Pb smelting production in Germany and Poland (e.g., Brännvall et al., 1999), and the Pb accumulation rate peak around AD 1800 with coal combustion.

The lead accumulation for the last two centuries in Słowińskie Błoto is compared with peat records from Denmark (Shotyk et al., 2003), the Czech Republic (Novak et al., 2008) and with a lake record from North Germany (Gäbler and Suckow, 2003) in Fig. 5. The Pb accumulation rate found in Northern Poland (this study) is generally lower than the ones found in nearby Denmark and Northern Germany. Discrepancies also occur in the timing of the highest lead accumulation rate periods. This maximum occurs between 1920 and 1940 in Słowińskie Błoto, then later in Denmark (late 1950s) and later still in northern Germany (1970s). Historical data show that maximum lead emission over Europe generally took place between 1970 and 1985 (von Storch et al., 2003 and references therein). Moreover, Pacyna and Pacyna (2000) showed that the maximum lead emission over Poland occurred in AD 1975, when the mean annual Pb emission was 7000 metric t yr⁻¹. The former U.S.S.R. recorded maximum lead emission during the 1970s (annual mean = 54,100 metric t yr⁻¹), in addition to Germany (annual mean = 16,500 metric t yr⁻¹). Schneider et al. (2000) also demonstrated that the maximum lead emission to the nearby Baltic Sea occurred during the early 1970s. Using peat bog records from the Czech Republic, Vile et al. (2000) also demonstrated that a maximum of Pb emission took place between 1965 and 1990 and was due to coal burning and lead smelting. These authors also noted a decrease in Pb emission between AD 1975 and AD 1980. The strong decrease of pollution levels recorded in Słowińskie Błoto during the last 30 years is also in good agreement with results found by Bykowszczenko et al. (2006 and reference therein) who estimated a 38% decrease in anthropogenic particle emissions over Poland during the 1990s, due to better control of dust emission and better filter technologies introduced in Polish industries. Similarly, Grodzinska and Szrek-Lukaszewska (2001) noticed a decrease in Pb and other heavy metal concentrations in mosses between 1975 and 1998. However, the peak in Pb accumulation rate found in Słowińskie Błoto between AD 1920 and AD 1940 seems to be in good agreement with Ocean bog (Czech Republic), which also displays a peak in accumulation rate during the 1930s. The late 19th century-peak in this bog is due to local Ag–Pb ore mining and smelting and is therefore not to be taken into consideration for our site. The fact that like Ocean bog, Słowińskie Błoto displays a maximum Pb accumulation rate between 1920 and 1940 is contradictory with the general trend over Europe, where maximum lead pollution generally occurs during the seventies. Like Ocean bog and conversely to Rybarenska bog (Fig. 5), Słowińskie Błoto may record distal pollution, and therefore lack some recent historical pollution peaks. The Pb flux cannot be correlated with Pb emission in the environment if the sources and the factors of emissions are changing.

The calculated lead accumulation rate (Fig. 5) in the top-most sample (1 mg m⁻² yr⁻¹) is also in very good agreement with the lead deposition scenario (between 1.1 and 1.2 mg m⁻² yr⁻¹) provided by the Meteorological Synthesizing Centre-East (www.msceast.org) and with lead wet deposition (1.16 mg m⁻² yr⁻¹) in this region of Poland measured by EMEP (www.emep.int) in 2005 (the year when the core was collected).

4.6. Sulphur record

In Słowińskie Błoto, lead and sulphur variations with depth are generally similar. Novak et al. (2005) show that S was mobile in the peat cores they studied. However, Jeker and Krähenbühl (2001)

published a reconstruction of S deposition over Switzerland using peat cores. In our case (Table 1), Pb and S are very well correlated with r^2 equal to 0.96. Different temporal phases can be distinguished: (1) from the bottom of the core to AD 1000 moderate values of S, (2) from AD 1300 to AD 1700 decrease in S values, (3) from AD 1700 to AD 1945 increase in S values and (4) from AD 1945 until present, decrease of values. These periods are in good agreement with the periods deduced from the Pb isotopes. Sulphur inventories over the ²¹⁰Pb-age-dated period (34.5 cm depth to top) show an average 6.2 mg cm⁻². This value is above the value calculated from the Finnish polluted bogs near smelters investigated by Rausch et al. (2005), which is 2.4 mg cm⁻². It also above the values found in the Black forest (4.8 mg cm⁻², Le Roux and Shotyk, pers. com.). However, it is well below the value calculated from Novak et al. (2008), which averages 15 mg cm⁻². This comparison clearly shows the fact that, even if Słowińskie Błoto is located in a rural area, not as polluted as Polish Silesia (SW-Poland) or northern Czech Republic, remote areas in Poland are still more polluted compared to similar areas (e.g., Black Forest, Germany) elsewhere or even compared to some smelting localities (e.g., Finland). However more investigations on parameters such as pH, water-table fluctuation, S species, S content in pore-water should be undertaken before using it as a tracer of anthropogenic activities in Słowińskie Błoto.

5. Conclusions

This investigation of a 1-m peat core recovered from Słowińskie Błoto bog (Pomerania) records 1300 years of anthropogenic pollution over northern Poland. Lead is mainly supplied by anthropogenic sources, which are Pb–Zn ore mining and smelting (from the Middle Ages), coal industries and gasoline. Other metals (Zn, Ni and Cu) may also originate from anthropogenic sources, but their history is difficult to interpret because of their possible mobility. Lead accumulation rates are in good agreement with the history of Poland and its cultural changes. The Polish Renaissance (ca. AD 1450–AD 1600) is clearly recorded by the lead accumulation rate, which peaks around AD 1600. The lead accumulation rate then decreases as a consequence of a period of political instability in the territory of Poland. The isotopic trend in Słowińskie Błoto is in good agreement with other records from Denmark and Germany during the last 200 years, although the maximum lead accumulation rate (between AD 1920 and AD 1940) in Słowińskie Błoto is not in agreement with the general trend over Europe (maximum emission between AD 1960 and AD 1980). This kind of discrepancy was recorded in another site from the Czech Republic (Ocean bog, Novak et al. 2008) but is still not understood. Interestingly, half of the lead in northern Poland was emitted during the last 200 years. Finally the reconstructed lead accumulation rate in the most recent peat layer in Słowińskie Błoto are in good agreement with the modelled lead level for the Baltic Region.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.scitotenv.2009.07.020](https://doi.org/10.1016/j.scitotenv.2009.07.020).

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