

# Mid- to Late Holocene elemental record and isotopic composition of lead in a peat core from Wolbrom (S Poland)

F. Pawełczyk<sup>1</sup>, A. Michczyński<sup>1</sup>, J. Tomkowiak<sup>2</sup>, K. Tudyka<sup>1</sup> and N. Fagel<sup>3</sup>

<sup>1</sup>Silesian University of Technology, Institute of Physics - Centre for Science and Education, Gliwice, Poland

<sup>2</sup>University of Szczecin, Faculty of Geosciences, Geology and Palaeogeography Unit, Szczecin, Poland

<sup>3</sup>University of Liège, Department of Geology, Liège, Belgium

---

## SUMMARY

Peat Core W3 was taken from the fen in Wolbrom (Silesian-Cracovian Upland, Southern Poland) in September 2015. Previous analyses of Core W3 showed a significant increase in lead concentration during the time of the Roman Empire as well as some changes in peat accumulation conditions. The work reported here investigates its geochemical composition in terms of major and trace elements (Pb, Zn, Na, K, Ca, Fe, Mg, Mn, Cu, Ni, Cr by AAS) as well as Pb isotopic composition, to identify the sources of metal pollution in the Wolbrom peat deposit. The geochemical record spans the period from 4900 BC to modern times, with a likely hiatus corresponding to the period from the Middle Ages to the beginning of the contemporary metallurgical industry. The Pb isotopic composition combined with a cluster analysis allows identification of the primary sources of Pb. In addition, Principal Component Analysis (PCA) helps to decipher the most important factors that affected the chemical composition of sediments at Wolbrom. These factors were linked to chemical denudation and human activity.

**KEY WORDS:** AAS, fen peatland, geochemistry, MC-ICP-MS, radiocarbon dating, stable lead isotopes

---

## INTRODUCTION

Numerous investigations (*e.g.* Martinez-Cortizas *et al.* 1997, Shotyk *et al.* 1998, Weiss *et al.* 1999, Baron *et al.* 2005, De Vleeschouwer *et al.* 2007, 2009a, 2009b, 2010) have demonstrated that peatlands can provide information on past natural environmental changes as well as on anthropic impacts such as heavy metal pollution. Investigation of both ombrotrophic and minerotrophic peat deposits may yield insights that are valuable in reconstructing natural palaeoecological changes (*e.g.* in botanical composition or climate) and heavy metal pollution. In such studies, peat layers are dated and their chemical composition is used to assess past geochemical conditions. Therefore, the mobility of metal elements is a crucial factor. It is determined by the element type, chemical form, sediment type, absorption by plants (MacKenzie *et al.* 1998), pH variations, and adsorption on oxy-hydroxides (Rausch *et al.* 2005) *etc.* Lead is rather immobile in peat (MacKenzie *et al.* 1997, 1998; Vile *et al.* 1999, Ali *et al.* 2008) although some studies have shown that this element can also migrate (Novak & Pacherova 2008).

In the natural environment, lead from different sources contains different ratios of lead isotopes

(Shirahata *et al.* 1980). Hence, lead isotope ratios in peat are commonly used to identify anthropic and natural sources of this element (*e.g.* Shotyk *et al.* 1998, Weiss *et al.* 1999, 2004; De Vleeschouwer *et al.* 2007, Renson *et al.* 2008, Allan *et al.* 2013, Tudyka *et al.* 2017). Previous studies of minerogenic peatlands in Poland have shown that primitive smelting could have started during the 9<sup>th</sup> century AD (Chróst 2013, Godzik & Woch 2015, Magiera *et al.* 2016, Pawełczyk *et al.* 2017).

In this study we investigate a fen near Wolbrom (Southern Poland) which provides an opportunity to reconstruct the history of human activity. Peat deposits from this fen were first studied by Trela (1928), who reported the results of pollen analysis. Subsequent palaeobotanical studies were undertaken by Latałowa (1976), Obidowicz (1976) and Latałowa & Nalepka (1987). These studies showed that Wolbrom is a minerogenic peatland and the peat contains numerous remains of *Carex*, *Phragmites* and *Bryales*. The palaeobotanical analysis was supplemented by some radiocarbon dates; however, the dating was performed with low resolution.

The aim of the study described here was to decipher the fen archive at Wolbrom using elements and lead isotopes as proxies, with emphasis on anthropic sources of lead.

## METHODS

### Study area and site

The peatland at Wolbrom (Figure 1A) is located at 50° 22.636' N, 19° 46.870' E in the eastern part of the Silesian-Cracovian Upland, in the Wolbrom Gate subregion (Kondracki 2013) about 40 km north of Cracow. Peatlands are very rare in this vicinity and, indeed, throughout southern Poland (IMUZ 2006). The present climate is temperate with mean annual temperature around 7 °C and average precipitation about 700 mm yr<sup>-1</sup> (Kruczała 2000). The most common winds are westerly and south-westerly. Atmospheric fallout in this area is enriched in potentially toxic elements because lead (Pb) and zinc (Zn) ores occur nearby. These ores were extracted 15–30 km south-west of Wolbrom at Olkusz, Klucze and Chrzanów (Figure 1B).

The Wolbrom fen is situated on a forest-covered watershed between the Szreniawa and Biała Przemsza rivers. Two hundred metres south of the fen there is a railway line which is near Wolbrom town centre (Figure 1B). The dimensions of the fen are about 1000 m × 500 m, and the peat thickness is >260 cm. Liquid scintillation counting (LSC) measurements (Tudyka & Pazdur 2012, Tudyka *et al.* 2015) have shown that the oldest peat dates back to *ca.* 9900 BC.

### Coring

Peat Core W3 was taken from the south-eastern part of the fen (Figure 1B) in September 2015, using a Wardenaar peat sampler. The core was 105 cm long with a cross section of 15 cm × 15 cm, and it was divided into 0.5–1 cm thick samples. This core was

previously <sup>14</sup>C and <sup>210</sup>Pb dated. An age-depth model (see Figure 1C) and some preliminary geochemical and botanical analyses were reported by Pawełczyk *et al.* (2017).

### Major and trace elements analysis

Geochemical analyses were carried out on 36 peat samples, whose thickness varied depending on the depth. In the upper part of the core, from the surface down to 15 cm depth, the samples were 0.5 cm thick, and from 15 cm depth to the bottom the resolution of sampling was 1 cm. The concentrations of the selected major and trace elements (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Pb, Ni and Cr) were measured in 1.5 g of well-dried and homogenised peat powder. The samples were ground manually in an agate mortar which was cleaned and dried after preparation of each sample. After grinding and drying at 105 °C, the samples were combusted by heating to 550 °C for five hours. This removed organic matter (OM) and allowed determination of OM content. Afterwards, each sample was put into a PTFE vial, then digested in 8 ml of 65 % HNO<sub>3</sub>, 2 ml of 10 % HCl and 2 ml of 30 % H<sub>2</sub>O<sub>2</sub>. Next, the samples were put into a mineraliser for one hour. Afterwards, the samples were transferred into polypropylene beakers and made up to 50 ml with de-ionised water. The concentrations of major and trace elements were measured after further proper dilution, using Atomic Absorption Spectrometry (AAS). The chemical preparation and the measurements were performed in the Geochemical Laboratory at the Faculty of Geosciences of the University of Szczecin, Poland. The routine methodology of the laboratory was used.

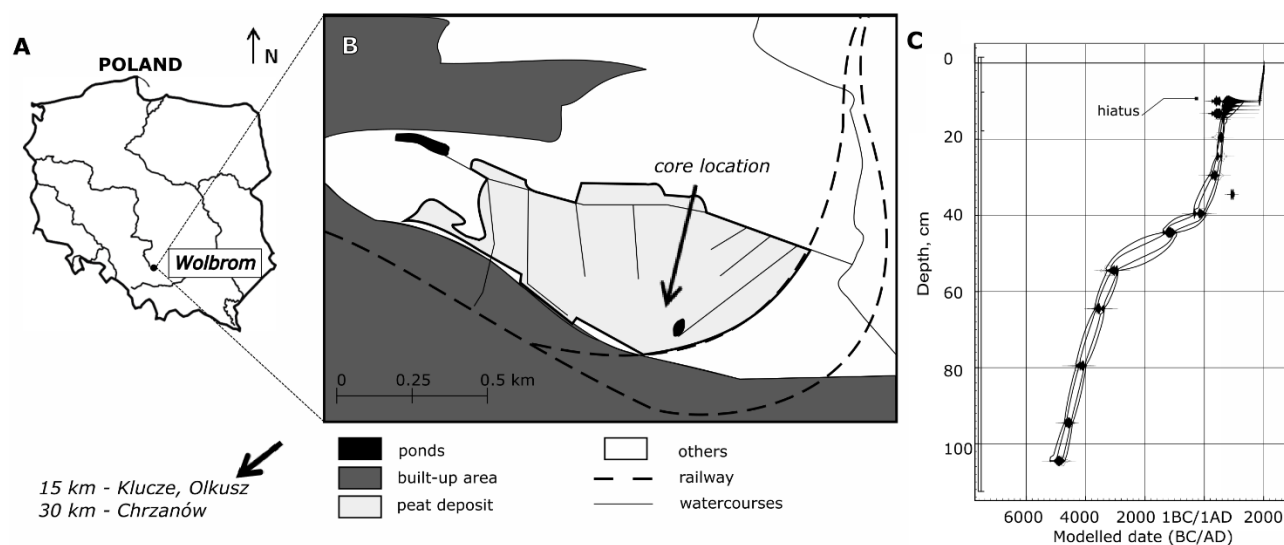


Figure 1. Maps showing the locations of the site (A) and Peat Core W3 (B). The direction and approximate distances to the Klucze, Olkusz and Chrzanów mineral ore mines are indicated. The age-depth model for Peat Core W3 (C) was previously reported by Pawełczyk *et al.* (2017).

### Pb isotopes analyses

To measure the Pb isotopic composition, 24 samples were dried and homogenised, then ground in an agate mortar. After grinding, 1.3 g of each sample was dried at 105 °C, placed in a PTFE vial and dissolved in a mixture of 1 ml of 14 N HNO<sub>3</sub> and 4 ml of 22 N HF, then heated at 125 °C for 48 hours in a laminar flow clean air cabinet. After drying, 2 ml of 6 N HCl and 2 ml of 14 N HNO<sub>3</sub> were added to ensure complete digestion, and the solution was evaporated at 125 °C. For separation of Pb isotopes and rare earth elements, the samples were dissolved in 500 µl of 0.8 N HBr and centrifuged (12200 rpm, 10 min). Next, to separate lead, the samples were passed through exchange micro-columns filled with pre-conditioned AG1-X8 anionic resin and rinsed with HCl and HBr. The eluted pure Pb solution was evaporated and re-dissolved in HNO<sub>3</sub> before the isotopic analysis. The chemical preparation was performed according to the protocol described by Weis *et al.* (2005), in the Department of Geology at the University of Liège. Pb isotope ratios were measured using a Nu Plasma multi-collector - Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) (©Nu Instruments, Wrexham, UK) at the Department of Earth and Environmental Sciences, Free University of Brussels.

### Enrichment factor calculation

Determining an enrichment factor (EF) allows the separation of anthropic supplies of trace metals from natural mineral matter. For this purpose it was necessary to select a conservative element indicative of mineral matter as well as an indicator for the geochemical background. We determined EFs for Pb, Zn, Cu, Cr and Ni as follows:

$$EF = ([M]_s/[X]_s)/([M]/[X])_{local} \quad [1]$$

where  $[M]_s$  is the total concentration of the element measured in a specific sample,  $[X]_s$  is the total concentration of the conservative element measured in the same sample, and  $([M]/[X])_{local}$  represents the natural geochemical background of the site, derived by calculating the median  $[M]$  and  $[X]$  for ten samples taken from depths in the range 59–106 cm. The depth limit for background samples was determined arbitrarily with reference to the results of geochemical analysis, which showed constant low concentrations of the majority of tested elements below 50 cm. The samples representing natural geochemical background span the period 4900 ± 110 BC to 3270 ± 130 BC. The procedure applied accords with methods adopted elsewhere in environmental research (*e.g.* Galuszka 2006, Shotyk *et al.* 2000).

### Dating

Radiocarbon (LSC technique) and <sup>210</sup>Pb datings were performed, and an age-depth model (Figure 1C) of Core W3 was constructed using OxCal v4.2.4 software (Bronk Ramsey & Lee 2013). The model was based on 13 <sup>210</sup>Pb dates and 12 <sup>14</sup>C dates, and its average uncertainty was 118 years. The model revealed a hiatus which lasted from 930 ± 200 to 1860 ± 15 AD (calculated using OxCal, function “Interval”). The mean peat accumulation rate varied between 0.53 and 6.48 mm yr<sup>-1</sup>. The age-depth model and a more detailed description of the dating methodology have already been reported by Pawełczyk *et al.* (2017).

### Statistical analysis

To obtain meaningful insight into a broad set of geochemical data, we used multivariate statistical analysis with cluster analysis. The levels of similarity at which observations are merged were used to determine distinct geochemical zones (GZ1–GZ5). Principal components analysis (PCA) was used to identify the sources from which the components were supplied to the fen deposits. The input variables were standardised values of the concentrations of organic matter and all tested major and trace elements. Statistical analyses were performed using PAST software (Hammer *et al.* 2001).

## RESULTS

### Element geochemistry

The geochemical analysis of Core W3 showed the variability of selected major and trace elements (Figure 2). It confirmed and extended the analysis previously conducted by Pawełczyk *et al.* (2017). In this next step, five geochemical zones were distinguished within the core by using cluster analysis in the PAST software (Hammer *et al.* 2001). The zones (coded as GZ1–GZ5) differ in terms of both their major and trace element concentrations and their geochemical indices (Figure 3).

- **GZ1 (106.5–47.5 cm)** - from 4900 ± 110 BC to 1730 ± 360 BC. This zone is characterised by high content of organic matter (88–91 %) and low content of the majority of the measured elements. Only Ca, Na and Mg reach significant concentrations in this zone. The Fe/Mn quotient is relatively low and increases only in the upper part of the core, reaching a value of 165 at the GZ1/GZ2 boundary. Na/K and Ca/Mg reach the highest values found in Core W3 (5.9 and 49, respectively).

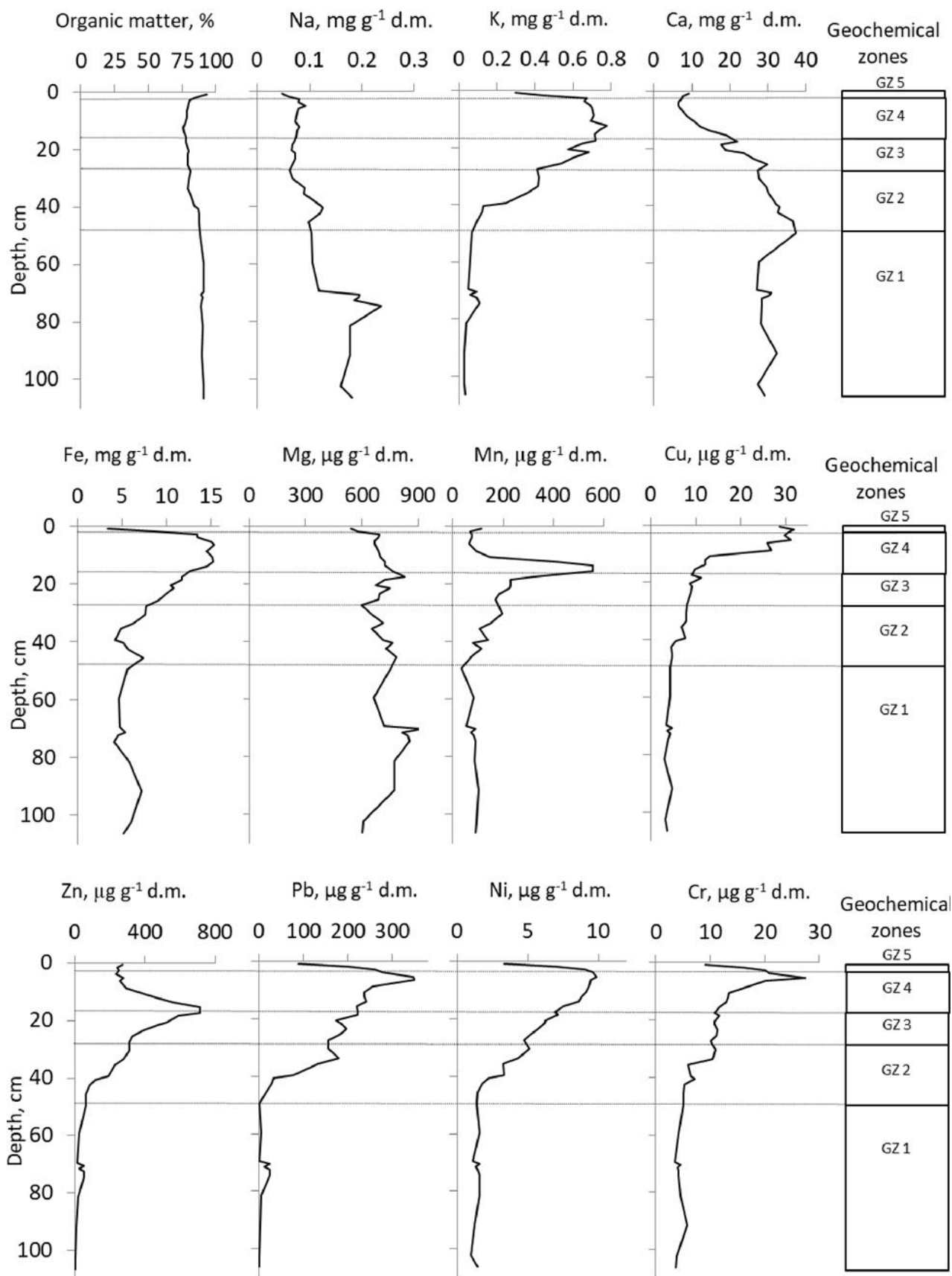


Figure 2. Concentrations of selected major and trace elements in Core W3, obtained by AAS analysis; d.m. = dry mass.



- **GZ2 (47.5–26.5 cm)** - from  $1730 \pm 360$  BC to  $425 \pm 65$  AD. Rapid increase in the concentrations of Pb, Zn, K, Fe, Mn, Cu, Ni and Cr occurs in this zone. The content of OM varies between 79 % and 87 %. The concentrations of Na, Ca, and Mg decrease.
- **GZ3 (26.5–14.63 cm)** - from  $425 \pm 65$  AD to  $655 \pm 55$  AD. The concentrations of Pb, Zn, K, Fe, Mn, Cu, Ni and Cr increase while the content of Ca decreases and Mg slightly increases up to  $828 \mu\text{g g}^{-1}$  at 17.5 cm. The content of Zn increases and reaches its highest value ( $715 \mu\text{g g}^{-1}$ ) at the boundary between GZ3 and GZ4. Ca/Mg decreases in this zone.
- **GZ4 (14.63–2.25 cm)** - from  $655 \pm 55$  AD to  $1990 \pm 5$  AD. The deposits of this zone are characterised by high contents of most of the elements. K, Fe, Mn, Pb, Ni, and Cr reach the highest concentrations found in the core ( $0.78 \text{ mg g}^{-1}$ ,  $15.33 \text{ mg g}^{-1}$ ,  $557.8 \mu\text{g g}^{-1}$ ,  $347.4 \mu\text{g g}^{-1}$ ,  $9.9 \mu\text{g g}^{-1}$  and  $27.4 \mu\text{g g}^{-1}$ , respectively), while the content of OM reaches its minimum value ( $<76$  %). The concentration of Ca decreases while Cu content increases rapidly. This observation is probably related to the facility of carbonates to precipitate Cu (Kabata-Pendias 2011). The Fe/Mn, Na+Mg+K/Ca, and Fe/Ca quotients reach their maximum values (222, 0.22 and 2.19, respectively) while Na/K reaches its lowest value (0.1) and Ca/Mg continues to decrease. In this zone, a hiatus occurs. It is supposed that this results from the decomposition of OM, which

would increase the concentration of mineral matter, as indicated by the increased concentrations of elements.

- **GZ5 (2.25–0 cm)** - from  $1990 \pm 5$  AD to 2015 AD. The uppermost zone is characterised by the smallest thickness. Its OM content is the highest in the whole profile ( $>92$  %). The concentrations of Na, K, Fe, Mg, Pb, Ni and Cr decrease. The Ca, Mn and Zn contents are also low relative to those found elsewhere in the core. The Fe/Mn, Fe/Ca and Na+Mg+K/Ca quotients decrease while Ca/Mg increases slightly.

### Lead isotope quotients

The isotopic composition of lead is shown in Table 1. The isotope quotients  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  show a decreasing trend along the core, from  $38.5169 \pm 0.0011$  to  $38.3150 \pm 0.0010$ , from  $15.6467 \pm 0.0005$  to  $15.6282 \pm 0.0005$ , and from  $18.5047 \pm 0.0005$  to  $18.3481 \pm 0.0004$ , respectively. The change observed at 40 cm depth coincides with variations in Pb concentration. The binary diagram of  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  (Figures 4A and 4B), constructed using data for 23 Wolbrom samples and 12 ombrotrophic 700–2000 AD peat samples from Słowińskie Błoto obtained from published literature (De Vleeschouwer *et al.* 2009a), is used to determine the origin of lead in the Wolbrom peatland. Figure 4A also shows the lead isotope quotients for modern industrial aerosols (Bollhöfer & Rosman 2001) and the Upper Continental Crust (UCC; data from Millot *et al.* 2004). Figure 4B focuses on Wolbrom samples

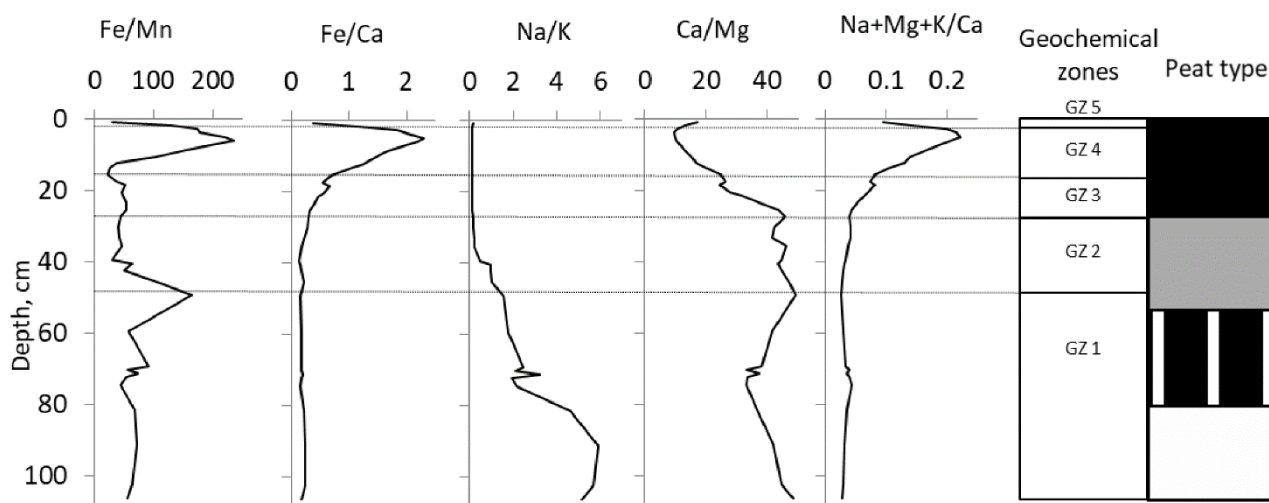


Figure 3. Depth profiles of some geochemical attributes of Core W3. GZ: geochemical zones. Peat type according to Pawełczyk *et al.* (2017): black = *Sapristis*; grey = *Magnocaricioni*, *Cariceto-phragmiteti*; striped = *Bryalo-Parvocaricioni*, *Cariceto-Bryaleti*; white = *Magnocaricioni-Cariceti*.

Table 1. Lead isotope quotients of samples from Core W3 with  $2\sigma$  uncertainty. Replicates are indicated by asterisks (\*). For depths indicated by #, values were not calculated in the age-depth model.

Depth (cm)	Modelled age range (68.2 % probability)	$^{208}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{206}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{208}\text{Pb}/^{206}\text{Pb}$	$2\sigma$	$^{206}\text{Pb}/^{207}\text{Pb}$	$2\sigma$
0.25	#	38.31499	0.000972	15.62816	0.000500	18.34813	0.000420	2.088231	0.000017	1.174037	0.000023
1.75	1998–2009 AD	38.36027	0.000880	15.62748	0.000394	18.37643	0.000392	2.087463	0.000019	1.175881	0.000024
2.75	1985–1998 AD	38.36395	0.000884	15.62661	0.000466	18.37474	0.000372	2.087865	0.000025	1.175831	0.000016
3.75	1964–1978 AD	38.35076	0.000902	15.62199	0.000396	18.37166	0.000418	2.087503	0.000022	1.176012	0.000021
5.25	1938–1957 AD	38.36285	0.001012	15.62357	0.000524	18.37559	0.000452	2.087722	0.000025	1.176129	0.000021
6.25	1913–1933 AD	38.36228	0.000950	15.62212	0.000438	18.37683	0.000352	2.087513	0.000025	1.176347	0.000022
7.25	1897–1916 AD	38.37438	0.001240	15.62234	0.000578	18.38259	0.000440	2.087544	0.000035	1.176684	0.000032
8.75	1874–1893 AD	38.38536	0.001180	15.62683	0.000450	18.38586	0.000494	2.087781	0.000022	1.176577	0.000025
10.75	#	38.39738	0.000968	15.62665	0.000520	18.39312	0.000434	2.087592	0.000028	1.177052	0.000029
12.75	#	38.39216	0.000994	15.62338	0.000458	18.39370	0.000466	2.087242	0.000025	1.177327	0.000017
13.75	#	38.39779	0.001286	15.62430	0.000542	18.39645	0.000532	2.087237	0.000023	1.177449	0.000022
15.5*	600–660 AD	38.43146	0.000892	15.63350	0.000412	18.40728	0.000390	2.087847	0.000018	1.177441	0.000021
15.5*	600–660 AD	38.41084	0.001074	15.62649	0.000542	18.40182	0.000486	2.087301	0.000023	1.177608	0.000027
20.5	500–595 AD	38.40316	0.000820	15.62378	0.000408	18.40116	0.000340	2.086974	0.000018	1.177776	0.000019
25.5	395–495 AD	38.40091	0.001276	15.62427	0.000602	18.39612	0.000500	2.087425	0.000034	1.177407	0.000024
30.5	215–395 AD	38.43335	0.000832	15.63554	0.000364	18.40100	0.000314	2.088669	0.000021	1.176865	0.000019
35.5	90 BC–175 AD	38.40710	0.000914	15.62388	0.000420	18.40413	0.000334	2.086903	0.000025	1.177940	0.000019
40.5	490–75 BC	38.44476	0.001002	15.63867	0.000608	18.41780	0.000478	2.087407	0.000029	1.177667	0.000030
49.5	2530–1695 BC	38.49801	0.001040	15.64634	0.000470	18.46169	0.000408	2.085320	0.000022	1.179929	0.000021
59.5	3430–3170 BC	38.46130	0.000934	15.64024	0.000424	18.41979	0.000416	2.088092	0.000023	1.177717	0.000019
69.5	3855–3610 BC	38.50595	0.000804	15.64753	0.000412	18.45877	0.000338	2.086085	0.000017	1.179656	0.000024
81.5	4285–4090 BC	38.45490	0.000806	15.64238	0.000352	18.41505	0.000346	2.088226	0.000019	1.177250	0.000019
91.5	4585–4410 BC	38.51694	0.000954	15.64674	0.000520	18.50472	0.000468	2.081459	0.000021	1.182633	0.000025
106.5	4995–4790 BC	38.44524	0.001092	15.63576	0.000500	18.44128	0.000478	2.084745	0.000020	1.179431	0.000023

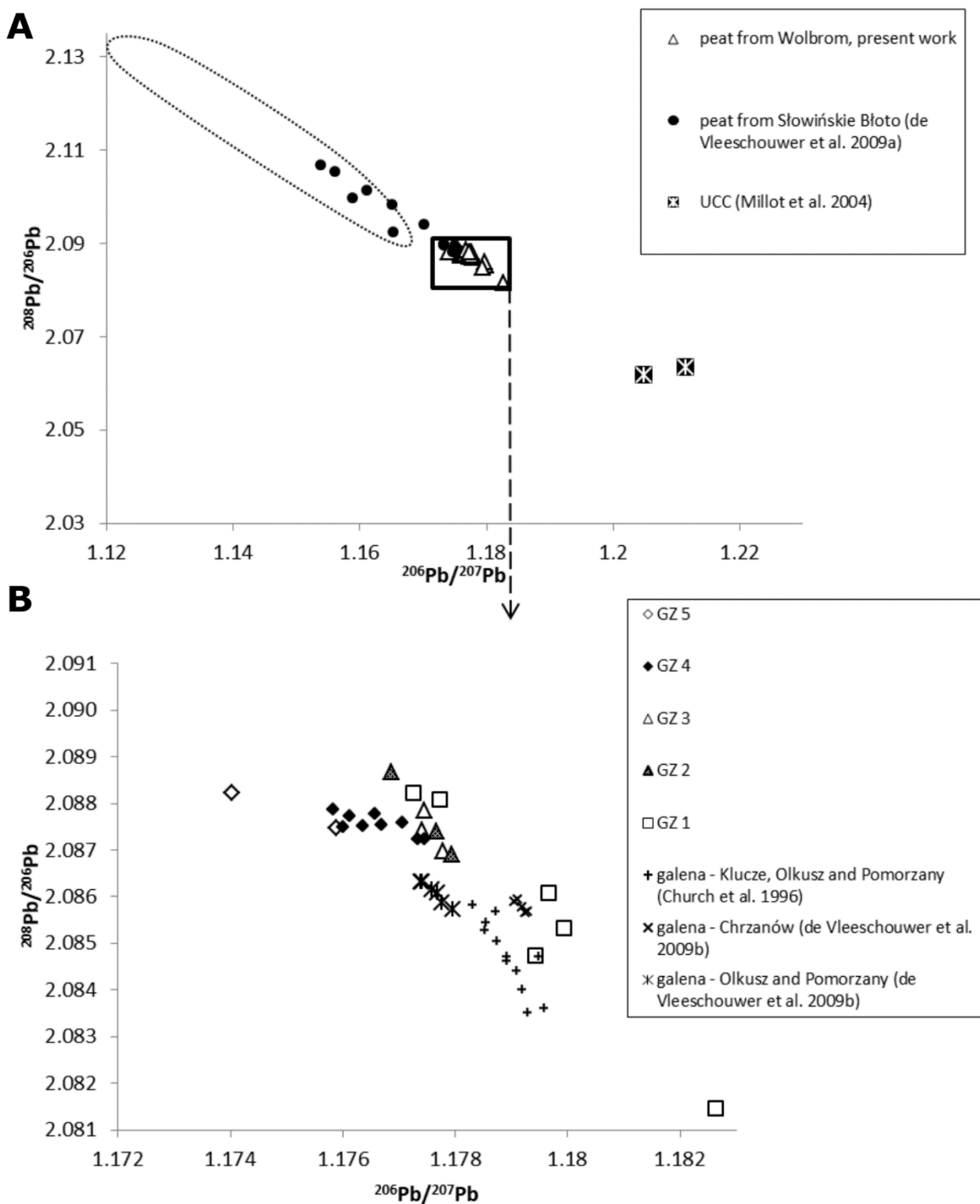


Figure 4.  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  diagrams. (A) shows 24 peat samples from Wolbrom (this work), 12 peat samples from Słowińskie Błoto (De Vleeschouwer *et al.* 2009a), modern urban airborne particles from Europe (Bollhöfer & Rosman 2001) - marked with a dotted line, and Upper Continental Crust (UCC) (Millot *et al.* 2004). (B) shows the peat samples from Wolbrom, distinguished on the basis of geochemical zones (GZ 1–5), set against the background of local galena ore samples: 9 from Klucze (the nearest location to Wolbrom), 2 from Olkusz and 1 from Pomorzany (Church *et al.* 1996); and 5 from Chrzanów, 4 from Pomorzany and 2 from Olkusz (De Vleeschouwer *et al.* 2009b). The error bars are negligible.

distinguished according to the geochemical zones GZ1–GZ5 and shows them alongside local Silesian galena samples from Klucze, Olkusz and Pomorzany (Church *et al.* 1996) and from Olkusz, Pomorzany and Chrzanów (De Vleeschouwer *et al.* 2009b).

The binary diagram in Figure 5 shows the relationship between lead content and isotopic composition. It was constructed by combining the isotopes data from Table 1 with lead concentration data (see Figure 2). It documents changes in the Pb isotope composition that are consistent with Pb contamination.

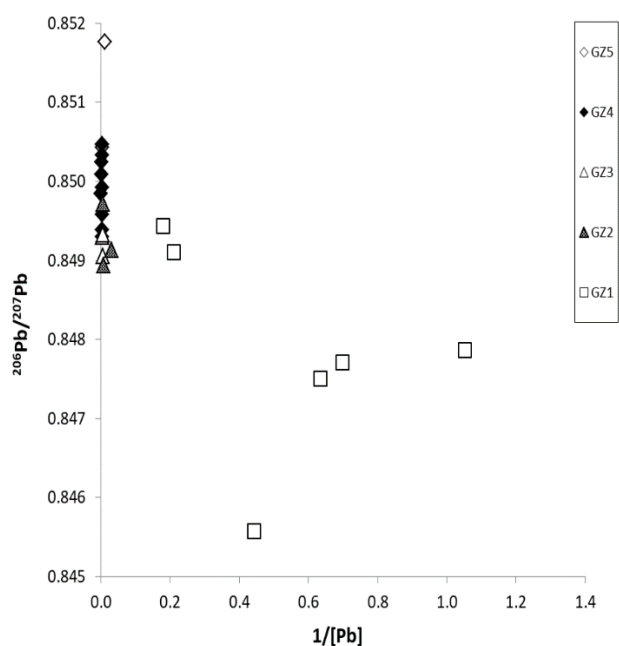


Figure 5.  $1/\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  binary diagram, distinguishing the five geochemical zones in Core W3. Constructed by combining  $^{206}\text{Pb}/^{207}\text{Pb}$  data from Table 2 with Pb content data (see Figure 2).

### Enrichment factor

The calculated enrichments of heavy metals which characterise the fen in Wolbrom are related both to the supply of natural mineral matter and anthropic influence (Figure 6). The EFs are most pronounced for Pb and Zn, reaching maximum values of 5.2 and 2.4 for these two elements, respectively. The maximum EF value for Cu (1.4) occurs close to the ground surface. Cr and Ni are characterised by EF values oscillating around 0.5 times the background values, which are statistically insignificant. For each measured metal, EF increases from 45 cm depth, reaching a peak at ~40 cm (except for Pb, whose first peak is at 33.5 cm) which corresponds to a date of 170 BC ( $\sigma = 115$  yrs). Then, the EFs for Cu, Cr and Ni decrease up to 33.5 cm, subsequently remain stable up to 10.75 cm, and finally increase slightly towards the surface. From 30 to 15 cm depth (335 to 640 AD), the EF for Pb fluctuates around 3. It reaches its maximum value (5.2) at ~5 cm depth (~1955 AD). The value of EF for Zn ranges between 0.9 and 2.4. It changes from 1.5 at 40–21 cm to 2.4 at 20–15 cm (560–640 AD), then decreases to 0.9 at 3 cm (1990 AD) before increasing again, reaching 2 near the surface.

### INTERPRETATION AND DISCUSSION

Principal component analysis (PCA) enabled the most important factors affecting the chemical composition of the sediment to be distinguished using Kaiser's criterion (Stanisz 1998), as the factors that had eigenvalues of correlation matrix greater than unity. Based on the concentrations of the 12 studied geochemical components of the deposit, three complementary components were identified that explained 91.6 % of the geochemical variability of the Wolbrom peat (Figure 7).

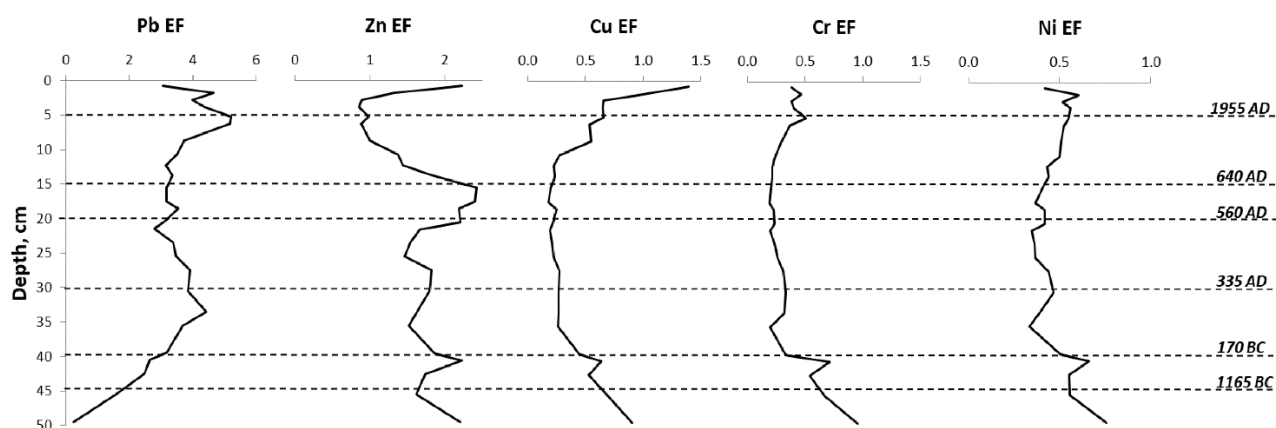


Figure 6. Pb, Zn, Cu, Cr and Ni enrichment factors (EFs) in Core W3. The EFs were calculated using K as the reference element.



The first component (PC1) explains 67.2 % of the total variation and is connected to human activity because it is positively correlated with the concentrations of K, Fe, Mn, and the heavy metals Cu, Zn, Pb, Ni and Cr (Figure 7A). Moreover, it is strongly negatively correlated ( $R = -0.88$ ) with OM,

Na and Ca content. The positive correlation with K, which is a part of aluminosilicate, indicates a relative concentration of clay minerals in biogenic deposits (Last 2001). It is noteworthy that the highest values of PC1, indicative of high content of trace elements (Cu, Zn, Pb, Ni, Cr), occur in the geochemical zones

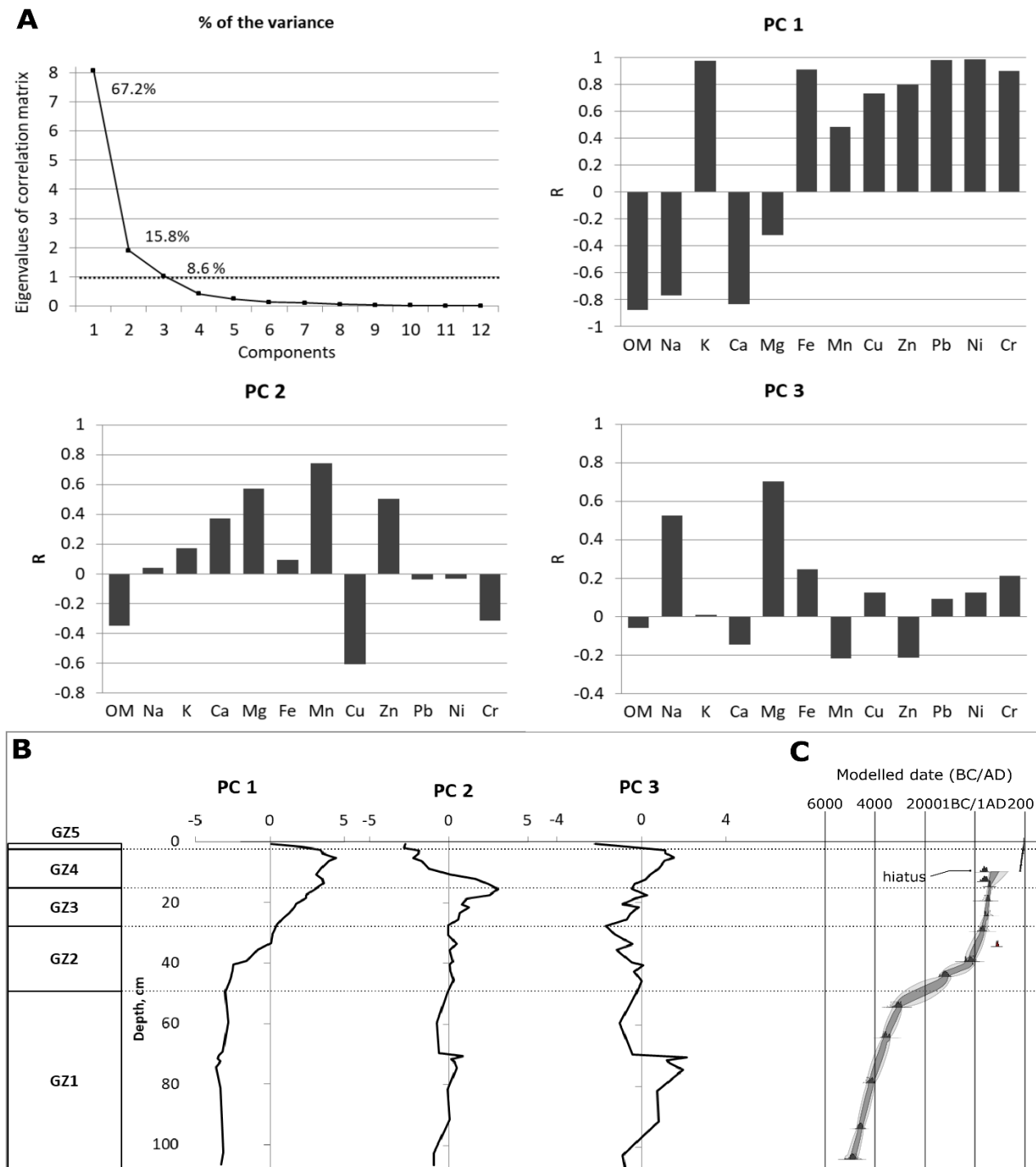


Figure 7. A: Eigenvalues of the correlation matrix (top left) and correlations of the geochemical variables determined by chemical analysis with the first three principal components ( $R$ =correlation coefficient); B: depth profiles of geochemical zones (GZ1–5) and the principal components PC1–PC3 in Core W3; and C: the age-depth model previously reported by Pawełczyk *et al.* (2017).

GZ3–GZ4 (Figure 7B). The enrichment of K, Fe and the heavy metals Zn, Pb, Ni, and Cr in the same zones suggests increased human activity (*e.g.* mining, smelting), which is also indicated by the lead isotope composition. The strong positive correlation with Fe and Mn ( $R=0.9$  and  $0.48$ , respectively) combined with negative correlation with Ca suggests some groundwater involvement. The increasing  $\text{Na}+\text{Mg}+\text{K}/\text{Ca}$  quotient in GZ4 ( $0.2 <$ ) and negative correlation with OM content means a positive contribution of mineral matter in PC1, suggesting increased mechanical denudation and allochthonous supply of mineral matter and selected elements (*e.g.* Cu, Cr and Ni migrate passively with mineral matter) to the deposit as a result of surface runoff or aeolian supply (Landner & Reuther 2004). PC1 is of low importance in the remainder of the profile.

The component PC2 explains 15.8 % of the total variance. It is positively correlated with Ca, Mg, Mn, and Zn content and negatively correlated with the content of OM, Cu and Cr (Figure 7A). This component reaches its maximum values within zones GZ3–GZ4, in parallel with the highest Zn concentration. This may indicate some exploitation of Zn-rich galena ores at that time (560–640 AD). However, the negative correlation with Pb, Ni, and Cr suggests that anthropic influence is less obvious during this period and, rather, a connection with the hiatus, which is an effect of the decomposition of OM. A small peak in PC2 at a 70–80 cm in GZ1 is connected with an increase of measured elements and may indicate some selective chemical denudation.

The third component (PC3) is positively correlated with the concentrations of Na, Mg, and Fe and negatively correlated with Mn and Zn content. While PC3 is less important and explains only 8.6 % of the total variance, possibilities for any further interpretation are limited. The geochemical variations are reflected by changes in the peat accumulation rate (see Figure 7C).

A review of the possible geochemical and archaeological sources of Pb pollution indicates that local Pb ores are the most likely sources of the contamination observed in Wolbrom peat. The results of the Pb isotope analysis allowed us to reconstruct the lead sources (Shirahata *et al.* 1980). In Figure 4, the samples from Wolbrom are scattered within a triangle, which suggests that there are at least three different contributing sources:

- The first end-point is characterised by high  $^{206}\text{Pb}/^{207}\text{Pb}$  (1.183) and low  $^{208}\text{Pb}/^{206}\text{Pb}$  (2.082), and corresponds to the oldest GZ1 samples (4900–1165 BC). The concentration of Pb at this point is  $7.78 \mu\text{g g}^{-1}$ . It coincides with the natural crustal source represented by UCC (Millot *et al.* 2004).

- The second end-point, with average values  $^{206}\text{Pb}/^{207}\text{Pb} = 1.174$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.088$  and  $[\text{Pb}] = 88.34 \mu\text{g g}^{-1}$ , comes from the uppermost part of the core (0.75 cm) and is consistent with the average signature of modern urban airborne particles ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.145$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.116$ ; Bollhöfer & Rosman 2001). Therefore, this end-point represents the modern anthropic Pb pollution derived from industrial activity and fossil fuel combustion. The most recent samples (GZ4–GZ5) are located close to the second (modern) end-point. They also plot close to peat samples from Słowińskie Błoto (De Vleeschouwer *et al.* 2009a).
- The third end-point is located in an area of the diagram represented by the local Pb-Zn ores. The linear trend of samples from GZ2 and GZ3 indicates local ores as a source of lead.

Most of the samples define a linear mixing trend between modern pollution and natural crust. However, there are points from the middle part of the core that suggest a contribution from local Zn-Pb ores as a third source. Moreover, the changes in Pb isotope quotients are related to the ages of the samples. The decrease in  $^{206}\text{Pb}/^{207}\text{Pb}$  throughout the core is associated with an increase in Pb. It is noteworthy that a small increase in  $^{206}\text{Pb}/^{207}\text{Pb}$  is visible between the fifth and sixth centuries AD (GZ3). During the same period, we notice a decrease in Zn and Pb enrichment factors which could have been caused by decreased human activity in the Great Migration Time, *i.e.*, a period of extremely cold climate in Europe (Büntgen *et al.* 2011).

## CONCLUSIONS

The investigated profile (W3) from the fen in Wolbrom spans the period from 4900 BC to the present day. The deeper layers of peat (from 4900 BC to *ca.* 1730 BC) are undisturbed, and no reflection of human activity is observed there. The Pb isotope composition in this part of the core resembles that for Upper Continental Crust, indicating a natural origin. The middle and upper parts of the core (~ 1730 BC to present day) show the effects of the most important factor for development of the fen which was, simply, human activity. There is an early connection to local ore mining and smelting. The first significant change in Pb isotope quotients (at the boundary between zones GZ1 and GZ2) indicates ore exploitation before the time of the Roman Empire. Next, we can observe a progressive increase in the value of PC1 from 40 cm depth (*ca.* 370 BC to 30 AD), although

this trend has changed over time - for example, when human activity decreased during the Great Migration Time between the fifth and sixth centuries AD. Recently, a regional human impact connected to fossil fuel combustion is visible, especially in the uppermost part of the core (corresponding to the last ~50 years) where the Pb isotope composition in conjunction with Pb concentration indicates heavy airborne pollution. The PCA confirms previous conclusions about human activity in the study area and shows that it took place even earlier than previously thought. Additional factors that influenced the fen at Wolbrom were chemical and mechanical denudation, surface runoff (which can result from human activities such as deforestation) and changes in the water table level, but their effects were smaller and harder to assess because the PCA provided only sparse relevant information. Moreover, the fluctuations of lead isotope quotients indicated that exploitation of local ores started between 370 BC and 30 AD (95.4 % probability), which is much earlier than shown by previous investigation. Our results demonstrate the usefulness of peatlands as archives of lead pollution, as well as the high level of past human impact on the environment.

## ACKNOWLEDGEMENTS

The measurement of lead isotopes was funded by Walloon Region within the framework of the MSWiA and WBI bilateral agreements between Poland and Belgium (WBI: 2014–2016; PIs: N. Fagel and A. Pazdur). FP would like to thank Mohammed Allan and Joel Ottén for constructive discussions and their assistance with chemical preparation. FP and KT acknowledge Grant LIDER/001/404/L-4/2013 from the National Centre for Research and Development in Poland, which funded radiocarbon dating. We also thank Nadine Mattielli and members of ULB G-Time Laboratory for ICP-MS analyses, Daniel Okupny (Pedagogical University of Cracow) for valuable tips and loaning his Instorf corer, and two anonymous reviewers for their valuable comments on an earlier version of this manuscript.

## REFERENCES

- Ali, A.A., Ghaleb, B., Garneau, M., Asnong, H. & Loisel, J. (2008) Recent peat accumulation rates in minerotrophic fens of the Bay James region, Eastern Canada, inferred by  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  radiometric techniques. *Applied Radiation and Isotopes*, 66(10), 1350–1358, doi: 10.1016/j.apradiso.2008.02.091.
- Allan, M., Le Roux, G., De Vleeschouwer, F., Bindler, R., Blaauw, M., Piotrowska, N., Sikorski, J. & Fagel, N. (2013) High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium. *Environmental Pollution*, 178, 381–394, doi: 10.1016/j.envpol.2013.03.018.
- Baron, S., Lavoie, M., Ploquin, A., Carignan, J., Pulido, M. & De Beaulieu, J.L. (2005) Record of metal workshops in peat deposits: history and environmental impact on the Mont Lozère Massif, France. *Environmental Science & Technology*, 39(14), 5131–5140, doi: 10.1021/es0481651.
- Bollhöfer, A. & Rosman, K.J.R. (2001) Isotopic source signatures for atmospheric lead: the Northern Hemisphere. *Geochimica et Cosmochimica Acta*, 65(11), 1727–1740, doi: 10.1016/S0016-7037(00)00630-X.
- Bronk Ramsey, C. & Lee, S. (2013) Recent and planned developments of the program OxCal. *Radiocarbon*, 55(2–3), 720–730, doi: 10.2458/azu\_js\_rc.55.16215.
- Büntgen, U., Tegel, W., Nicolussi, K., McCormick, M., Frank, D., Trouet, V., Kaplan, J.O., Herzig, F., Heussner, K.U., Wanner, H., Luterbacher, J. & Esper, J. (2011) 2500 years of European climate variability and human susceptibility. *Science*, 331(6017), 578–582.
- Chróst, L. (2013) Ołowiowy ślad Wiślan odczytany z torfowisk obszaru kruszczońskiego śląsko-malopolskiego (The lead trace of the Vistulan tribe read from peat bogs in the Silesian-Malopolska metalliferous zone). In: Boroń, P. (ed.) *Argenti Fossore at Alii (Gold Miners and Others (L.)). Znaczenie Gospo-darcze Wschodniej Części Górnego Śląska i Zachodnich Krańców Małopolski w Późnej Fazie Wczesnego Średniowiecza [X-XII wiek] (The Economic Importance of the Eastern Part of Upper Silesia and the Western Ends of Malopolska in the Late Phase of the Early Middle Ages [X-XII century])*, Chronicon, Wrocław (ISBN 978-83-935760-6-7), 175–186 (in Polish).
- Church, S.E., Vaughn, R.B., Gent, C.A. & Hopkins, R.T. (1996) Lead-isotopic, sulphur-isotopic, and trace-element studies of galena from the Silesian-Cracow Zn-Pb ores, polymetallic veins from the Gory Swietokrzyskie MTS, and the Myszkow porphyry copper deposit, Poland. *Prace-Panstwowego Instytutu Geologicznego*, 154, 138–156.
- De Vleeschouwer, F., Gérard, L., Goormaghtigh, C., Mattielli, N., Le Roux, G. & Fagel, N. (2007)

- Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning the last two millennia: human impact on a regional to global scale. *Science of the Total Environment*, 377(2–3), 282–295, doi: 10.1016/j.scitotenv.2007.02.017.
- De Vleeschouwer, F., Piotrowska, N., Sikorski, J., Pawlyta, J., Cheburkin, A., Le Roux, G., Lamentowicz, M., Fagel, N. & Mauquoy, D. (2009a) Multiproxy evidence of ‘Little Ice Age’ palaeoenvironmental changes in a peat bog from northern Poland. *The Holocene*, 19(4), 625–637, doi: 10.1177/0959683609104027.
- De Vleeschouwer, F., Fagel, N., Cheburkin, A., Pazdur, A., Sikorski, J., Mattielli, N., Renson, V., Fialkiewicz, B., Piotrowska, N. & Le Roux, G. (2009b) Anthropogenic impacts in North Poland over the last 1300 years - A record of Pb, Zn, Cu, Ni and S in an ombrotrophic peat bog. *Science of the Total Environment*, 407(21), 567–5684, doi: 10.1016/j.scitotenv.2009.07.020.
- De Vleeschouwer, F., Le Roux, G. & Shoty, W. (2010) Peat as an archive of atmospheric pollution and environmental change: A case study of lead in Europe. *PAGES Magazine*, 18(1), 20–22.
- Galuszka, A. (2006) Metody określania tła geochemicznego w badaniach środowiska przyrodniczego (Methods for determining the geochemical background in environmental research). *Problemy Ekologii Krajobrazu*, 16(1), 507–517 (in Polish).
- Godzik, B. & Woch, M.W. (2015) History of mining in the Olkusz region. In: Godzik, B. (ed.) *Natural and Historical Values of the Olkusz Ore-bearing Region*. Polish Academy of Sciences W. Szafer Institute of Botany, Kraków, 29–36.
- Hammer, O., Harper, D.A.T. & Ryan, P.D. (2001) PAST: Paleontological statistics software package for education and data analysis. *Palaeontologia Electronica*, 4, 1–9.
- IMUZ (2006) *System Informacji Przestrzennej o Mokradlach Polski (Polish Wetlands Spatial Information System)*. Instytut Melioracji i Użytków Zielonych (IMUZ), Falenty (in Polish). Online at: <http://www.gis-mokradla.info>, accessed 10 Aug 2018.
- Kabata-Pendias, A. (2011) *Trace Elements in Soils and Plants*, fourth edition. CRC Press, Boca Raton, 505 pp.
- Kondracki, J. (2013) *Geografia Regionalna Polski (Regional Geography of Poland)*. Wydawnictwo Naukowe PWN, Warsaw, 468 pp. ISBN 978-83-01-16022-7 (in Polish).
- Kruczała, A. (ed.) (2000) *Atlas Klimatu Województwa Śląskiego (Climate Atlas of Silesia Province)*. Instytut Meteorologii i Gospodarki Wodnej, Katowice (ISBN: 83-85862-64-1), 34, 57, 74 (in Polish).
- Landner, L. & Reuther, R. (2004) *Metals in Society and in the Environment: A Critical Review of Current Knowledge on Fluxes, Speciation, Bioavailability and Risk for Adverse Effects of Cooper, Chromium, Nickel and Zinc*. Kluwer Academic Publishers, Dordrecht, 407 pp.
- Last, W. (2001) Mineralogical analysis of lake sediments. In: Last, W.M. & Smol, J.P. (eds.) *Tracking Environmental Change Using Lake Sediments, Volume 2: Physical and Geochemical Methods*. Kluwer Academic Publishers, Dordrecht, 143–187.
- Latałowa, M. (1976) Diagram pyłkowy osadów późnoglacialnych i holocenijskich z torfowiska w Wolbromiu (Pollen diagram of Late-Glacial and Holocene peat deposits from Wolbrom (S Poland)). *Acta Palaeobotanica*, 17(1), 55–80 (in Polish with English summary).
- Latałowa, M. & Nalepka, D. (1987) A study of the Late-glacial and Holocene vegetational history of the Wolbrom area (Silesian-Cracovian Upland). *Acta Palaeobotanica*, 27(1), 75–115.
- MacKenzie, A.B., Farmer, J.G. & Sugden, C.L. (1997) Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. *Science of the Total Environment*, 203, 115–127, doi: 10.1016/S0048-9697(97)00139-3.
- MacKenzie, A.B., Logan, E.M., Cook, G.T. & Pulford, I.D. (1998) Distributions, inventories and isotopic composition of lead in <sup>210</sup>Pb-dated peat cores from contrasting biogeochemical environments: Implications for lead mobility. *Science of the Total Environment*, 223, 25–35, doi: 10.1016/S0048-9697(98)00302-7.
- Magiera, T., Mendakiewicz, M., Szuszkiewicz, M., Jabłońska, M. & Chróst, L. (2016) Technogenic magnetic particles in soils as evidence of historical mining and smelting activity: A case of the Brynica River Valley, Poland. *Science of the Total Environment*, 566–567, 536–551, doi: 10.1016/j.scitotenv.2016.05.126.
- Martinez-Cortizas, A., Pontevedra-Pombal, X., Novoa-Munoz, J.C. & Garcia-Rodeja, E. (1997) Four thousand years of atmospheric Pb, Cd and Zn deposition recorded by the ombrotrophic peat bog of Penido Vello (Northwestern Spain). *Water, Air, & Soil Pollution* 100, 387–403.
- Millot, R., Allègre, C.J., Gaillardet, J. & Roy, S. (2004) Lead isotopic systematics of major river sediments: a new estimate of the Pb isotopic composition of the Upper Continental Crust.



- Chemical Geology*, 203(1), 75–90, doi: 10.1016/j.chemgeo.2003.09.002.
- Novak, M. & Pacherova, P. (2008) Mobility of trace metals in pore waters of two Central European peat bogs. *Science of the Total Environment*, 394(2), 331–337, doi: 10.1016/j.scitotenv.2008.01.036.
- Obidowicz, A. (1976) Genesis and development of the peat-bog at Wolbrom (S Poland). *Acta Palaeobotanica*, 17(1), 45–54 (in Polish).
- Pawełczyk, F., Chróst, L., Magiera, T., Michczyński, A., Sikorski, J., Tudyka, K. & Zajac, E. (2017) Radiocarbon and lead-210 age-depth model and trace elements concentration in the Wolbrom fen (S Poland). *Geochronometria*, 44(1), 40–48, doi: 10.1515/geochr-2015-0046.
- Rausch, N., Ukonmaanaho, L., Nieminen, T., Krachler, M. & Shotyk, W. (2005) Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites. *Environmental Science & Technology*, 39, 8207–8213.
- Renson, V., Fagel, N., Mattielli, N., Nekrassoff, S., Streef, M. & De Vleeschouwer, F. (2008) Roman road pollution assessed by elemental and lead isotope geochemistry in East Belgium. *Applied Geochemistry*, 23(12), 3253–3266, doi: 10.1016/j.apgeochem.2008.06.010.
- Shirahata, H., Elias, R.W., Patterson, C.C. & Koide, M. (1980) Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. *Geochimica et Cosmochimica Acta*, 44(2), 149–162, doi: 10.1016/0016-7037(80)90127-1.
- 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 12,370 <sup>14</sup>C yr BP from a peat bog, Jura Mountains, Switzerland. *Science*, 281(5383), 1635–1640, doi: 10.1126/science.281.5383.1635.
- 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. *Science of the Total Environment*, 249(1–3), 281–295.
- Stanisz, A. (1998) *Przystępny Kurs Statystyki w Oparciu o Program "STATISTICA PL" na Przykładach z Medycyny (An Affordable Statistics Course Based on the "STATISTICA PL" Software With Medical Examples)*. StatSoft Polska, Kraków, 362 pp. ISBN: 83-904735-4-2 (in Polish).
- Trela, J. (1928) Torfowisko w Wolbromiu (wyniki analizy pyłkowej) (Peatland in Wolbrom /the results of pollen analysis/). *Acta Societatis Botanicorum Poloniae*, 5(3), 337–351.
- Tudyka, K. & Pazdur, A. (2012) <sup>14</sup>C dating with the ICELS liquid scintillation counting system using fixed-energy balance counting window method. *Radiocarbon*, 54: 267–273, doi: 10.2458/azu\_js\_rc.v54i2.15832.
- Tudyka, K., Bluszcz, A., Kozłowska, B., Pawlyta, J. & Michczyński, A. (2015) Low level <sup>14</sup>C measurements in freshly prepared benzene samples with simultaneous <sup>214</sup>Bi/<sup>214</sup>Po pairs counting for routine <sup>222</sup>Rn contamination correction. *Radiation Measurements*, 74, 6–11, doi: 10.1016/j.radmeas.2015.01.010.
- Tudyka, K., Pazdur, A., De Vleeschouwer, F., Lityńska-Zajac, M., Chróst, L. & Fagel, N. (2017) Holocene elemental, lead isotope and charcoal record from peat in southern Poland. *Mires and Peat*, 19(07), 1–18, doi: 10.19189/MaP.2016.OMB.257.
- Vile, M.A., Wieder, R.K. & Novák, M. (1999) Mobility of Pb in *Sphagnum*-derived peat. *Biogeochemistry*, 45, 35–52, doi: 10.1007/BF00992872.
- Weis, D., Kieffer, B., Maerschalk, C., Pretorius, W., & Barling, J. (2005) High-precision Pb-Sr-Nd-Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials. *Geochemistry, Geophysics, Geosystems*, 6(2), 1–10, doi: 10.1029/2004GC000852.
- Weiss, D., Shotyk, W., Kramers, J.D. & Gloor, M. (1999) *Sphagnum* mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmospheric Environment*, 33(23), 3751–3763, doi: 10.1016/S1352-2310(99)00093-X.
- Weiss, D.J., Kober, B., Dolgoplova, A., Gallagher, K., Spiro, B., Le Roux, G., Mason, T.F.D., Kylander, M. & Coles, B.J. (2004) Accurate and precise Pb isotope ratio measurements in environmental samples by MC-ICP-MS. *International Journal of Mass Spectrometry*, 232(3), 205–215, doi: 10.1016/j.ijms.2004.01.005.

Submitted 04 Apr 2018, revision 27 Jun 2018  
Editor: Frank Chambers

Author for correspondence: Fatima Pawełczyk, Department of Radioisotopes, Institute of Physics - Centre for Science and Education, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland.  
Email: fatima.pawelczyk@polsl.pl