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Reconstruction of atmospheric lead and heavy metal pollution in the Otrębowskie Brzegi peatland (S Poland)

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We reconstruct palaeoenvironmental changes since the Late Holocene in the Orava–Nowy Targ Basin, with an emphasis on anthropogenic influence (Walker et al., 2018). This reconstruction employs multiproxy analyses of the Otrębowskie Brzegi poor fen. We combined radiocarbon and ^{210}Pb dating with elemental geochemistry, stable lead isotopes, and palaeobotanical analyses. The core we investigated covers a period from 4200 ± 100 BC to the present, with a peat accumulation rate varying between 0.001 and 0.243 cm y^{-1}. Heavy metal concentrations, Pb isotopic ratios, and a palynological analysis revealed a significant impact of human activities in the past. The highest concentration and accumulation rate of Pb, were found around 1950 AD. The ^{206}Pb/^{207}Pb quotient ranged between 1.168 and 1.223, with average value around 1.198. Most of the interpretation was based on Pb and its stable isotopes; however, other elements were also important indicators of natural and anthropogenic environmental changes. Our results revealed similarities between the geochemical composition of the peatland studied and other peatlands from the Orava–Nowy Targ Basin.

Key words: Pb isotopes, pollution, elemental record, human activity, ^{14}C and ^{210}Pb dating, palynological analysis.

INTRODUCTION

Peat sediments, having accumulated for thousands of years, can provide important information about natural and anthropogenic environmental changes, e.g., dry and wet periods, changes in plant species, and human activities in the past (e.g., Mauquoy et al., 2002; Barber et al., 2003; Fiałkiewicz et al., 2008; Fiałkiewicz-Kozieł et al., 2014a). These sediments are also collectors of atmospheric particles of crustal and anthropogenic origin, among them pollutants. Records of trace elements in peatlands show periods of increased atmospheric pollution caused by human activities, such as coal mining and combustion, smelting, agriculture, and even urban traffic (e.g., Martínez-Cortizas et al., 2002; Coggins et al., 2006; Komárek et al., 2008; De Vleeschouwer et al., 2009; Fiałkiewicz-Kozieł et al., 2008, 2011, 2014b, 2015). In particular, Pb, which is highly toxic to people and the environment (Kabata-Pendias, 2011), is one of the most intensively investigated elements in recent years (e.g., Poller et al., 2001; Renson et al., 2008; De Vleeschouwer et al., 2010; Hansson et al., 2017). The isotopic ratios of stable lead isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, can be used to decipher sources of Pb and their changes in the past (Shotyk et al., 1998). The lead isotope approach is a very helpful tool for environmental research, however, the partial mobility of lead isotopes in peatlands has been discussed by some authors. Also, other chemical elements are widely discussed in terms of their mobility (Novak and Pacherova, 2008; Śmieja-Król et al., 2010, 2015; Kabata-Pendias, 2011). This study is part of a larger work, including comparative analysis of two peatlands in Southern Poland – Otrębowskie Brzegi and Wolbrom. These peatlands differ in terms of location, lithology and anthropogenic impact (see Pawełczyk et al., 2017, 2018a, 2018b). In this study we investigated a core from the Otrębowskie Brzegi poor fen, located in the

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Orava–Nowy Targ Basin. It is an extensive, mid-mountainous basin in the Outer Western Carpathians, in southern Poland. In this area numerous peatlands were formed during the Holocene (Łajczak, 2009). This location makes them very interesting material for palaeoecological research, including for reconstructions of environmental changes and human activities. Early studies of the Orava–Nowy Targ Basin peatlands concerned changes in vegetation (Dyakowska, 1928; Koperowa 1962; Wójcikiewicz, 1979). Later geochemical analysis (Hołyńska et al., 1998) showed an anthropogenic impact. Subsequently peat sediments in this region have been studied in terms of human influence and degradation (e.g., Fiałkiewicz-Kozieł et al., 2011, 2014a, 2015, 2018; Michczyńska and Margielewski, 2016; Pawełczyk et al., 2018b). Other Carpathian peatlands (in Slovakia and Romania) have been studied as well. Attempts to reconstruct the history of the Carpathian region have been made by e.g. Rybniček and Rybničkova (1985, 2002), Rösch and Fischer (2000), Hájková et al. (2012) and Jamrichová et al. (2014).

The first phase of land utilization in Orava–Nowy Targ Basin took place in the Bronze and Iron ages and was connected with foraging, hunting and the first settlements in the river valleys (Ładygin, 1984; Rydlewski and Valde-Nowak, 1984). At the beginning of the 13th century more regular colonization began, mostly connected with grazing. The 14th century was a period of intensified settlement and agriculture in this region. At that time, the Czarny Dunajec, Odrowąż and Bańska settlements were established. Around the end of the 14th century, when Wallachian shepherds arrived in that region, the development of pastoralism began. The beginning of metallurgy in the area studied took place in the 15th century and was connected with first foundries in the Hucisko village, not far from Babia Góra mountain (Jost, 2004). From that time, mining and metallurgy was the main factor of settlement development in the Carpathian foreland (Solecki, 1977). In the Tatra Mountains iron, silver and copper ores were extracted. In 19th century, many steelworks processed the Tatra flysch rocks, in the Orava–Nowy Targ Basin and its vicinity, i.e. in Stryszawa, Maków, Podczerwone, Huciska. Kośne Hamry, Kuźnice, Jaworzyna Spiska and so on (Fig. 1C; Jost, 1962, 2004).

The Carpathian region is an area with a long history of human presence as regards mining and metallurgy (Borcoş and Udubaşa, 2012; Longman and Veres, 2016; Longman et al., 2016, 2018). While the characteristics of past emission sources and effects of heavy metal pollution are well known in Western Europe, there is a deficit of such studies in Eastern Europe. This study aims to partially fill this gap, by reconstruction of the anthropogenic impact on the Otrębowskie Brzegi peatland, along with the course of its natural changes in the past. We performed geochemical analysis, with special emphasis on heavy metal concentrations and lead isotopic composition. These data, as well as botanical and palynological analyses, were compiled with ^{14}C and ^{210}Pb chronology. As a result, we reconstructed the history of the peatland from ~4200 BC to the present.

MATERIAL AND METHODS

STUDY SITE, CORING AND SAMPLING

Otrębowskie Brzegi is a poor fen, which means that the sources of water and nutrients are mainly precipitation, with secondary contributions from groundwater and flowing waters. The peatland is located in the western part of the Orava–Nowy Targ Basin, near the village of Jabłonka (Fig. 1A), at ~1 km from the Polish-Slovak border (Fig. 1B, C). The peatland is situated close to the mountains. The massif of Babia Góra is about 10 km NW from the peatland and the Tatra Mountains are about 30 km to the south, thus the area is partially protected from pollution coming from the main Polish mining areas (Olkusz, Silesia) and central urban areas (Katowice, Kraków). However, the Otrębowskie Brzegi peatland may receive some pollution from the west, from the Orava region.

The peatland is about 600 m long and 500 m wide – 42 ha (Lipka and Zając, 2014), situated 620 m above sea level and gently sloping toward the south (Fig. 1B, C). The climate of the Orava–Nowy Targ Basin is slightly more severe than the average conditions in Poland, with mean annual temperature about 5.5°C and mean annual precipitation varying around 800 mm (Olszewski, 1988). Westerly and southwesterly winds prevail. The Otrębowskie Brzegi peatland has been described by several authors: the development conditions by Łajczak (2009, 2013), a stratigraphic transect by Lipka and Zając (2014) and there have been some analyses of mercury content (Sławińska et al., 2018). However, the chronology of Otrębowskie Brzegi, its palaeobotanical history, major and trace element concentrations and isotope geochemistry have not been investigated.

In September 2016 the Otrębowskie Brzegi peatland was probed using a peat corer to measure the peat thickness. An interpolated model was developed by using the kriging interpolation method on 71 drillings (Fig. 2). The average thickness of peat is about 1.63 m; the thickest layer of peat occurs north of the center of the study area. In the southern part of the peatland, the thickness of the peat layer gradually decreases toward the meandering channel of the Czarna Orawa River. A 3.21 m long peat core (JB-1) was taken using an Instorf corer at N49°27.771’ E19°39.278’. The core was transported to the laboratory, divided into samples and stored prior to dating and other analyses.

CHRONOLOGY

The chronology for Otrębowskie Brzegi was constructed by merging radiocarbon and ^{210}Pb dates. For radiocarbon dating, 13 samples were selected: ten were prepared following the procedure of Skripkin and Kovaliukh, (1998) and dated using the liquid scintillation technique (LSC) on a *Quantulus 1220*™ spectrometer in the Gliwice Radiocarbon Laboratory (Pawlyta et al., 1998). The other three samples were dated using acceleration mass spectrometry (AMS) because of the smaller amount of peat in the upper part of the core. The samples were prepared in accordance with the protocol by Piotrowska (2013). The upper 20 cm of the cores were also dated by measuring ^{210}Pb activity using alpha spectrometry (Sikorski and Bluszcz, 2008). Details of preparation and measurement methods for both radiocarbon and ^{210}Pb dating are described in Pawełczyk et al. (2017). In order to build the final age-depth model, ^{14}C and ^{210}Pb data were calibrated and analysed using *OxCal* software (Bronk Ramsey and Lee, 2013) with the calibration data set of the *IntCal13* (Reimer et al., 2013) and *Bomb13 NH1* calibration curves (Hua et al., 2013). The resulting age-depth model was used to calculate the Pb accumulation rate (*AR* in mg m^{-2} y^{-1}) according to the formula:

$$AR \quad c \quad b \quad ar \quad 10$$

where: c – the concentration of the element measured in mg kg^{-1}, b – the bulk density of peat in g cm^{-3}; ar – accumulation rate of peat in cm y^{-1}.

A peat core was divided into samples, intended for different analyses, and dried directly after coring. This procedure caused

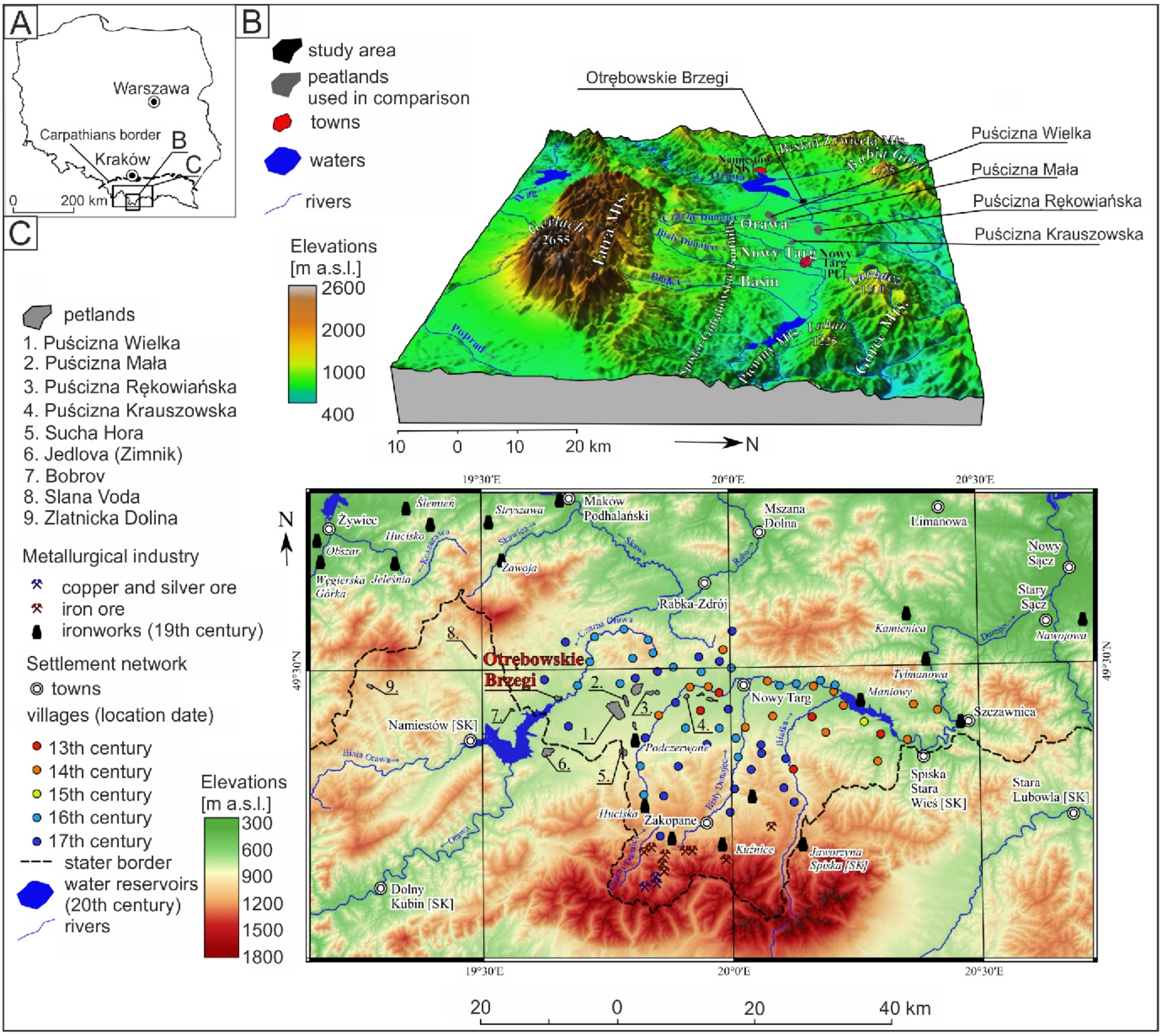

Fig. 1A–C – site location (villages location dates after Jost and Paulo, 1985; Jost, 2004)

a lack of fresh peat material, so bulk density was estimated using the data from Ilnicki (1967). The values of density were in the range of 0.08 to 0.185 g cm^{-3}.

PALAEOBOTANICAL ANALYSES

BOTANICAL COMPOSITION

The degree of decomposition and the types of peat were recorded in 12 samples from different depths, using standard methodology (Maciak and Liwski, 1996; Maksimow, 1965; Myślińska, 2001; Tobolski, 2000). Microscopic analysis (PN-G-04595, 1997) was used to determine botanical composition, using comparative samples and literature (Kac et al., 1977; Tobolski, 2000; Mauquoy and Van Geel, 2007). The samples were washed on a 0.2 mm sieve and each sample was divided into 3 slides, which were analysed under a microscope at magnification 100–400 . Typological units of peat were defined using the genetic classification of Tołpa et al. (1967). The types of gyttja were defined using the classification of Ilnicki (2002). The analyses were performed at the Department of Land Reclamation and Environmental Development, at the University of Agriculture in Kraków.

POLLEN ANALYSIS

Twenty-nine 1 cm^3 samples from JB-1 were taken at resolutions of 2 cm (from the top to 35 cm depth) and 10 cm (from 35 to 315 cm depth). The material was macerated in HF for 10 days, then washed in 10% HCl and distilled water. Next, the samples were boiled in 10% KOH solution in a water bath and then treated with acetolysis, using standard methodology (Fægri and Iversen, 1989). Two *Lycopodium* tablets produced by the Department of Quaternary Geology, the University in Lund (Batch No. 483216) were added to the sediment in order to enable the pollen concentration to be calculated (Stockmarr, 1971). The samples were not subjected to a dyeing process.

Microscopes (*Nikon Eclipse E200* and *Zeiss Axio Image A2* with Nomarski's contrast) were used at 400 to count at least 1000 arboreal pollen grains. Non-arboreal pollen and non-pol-

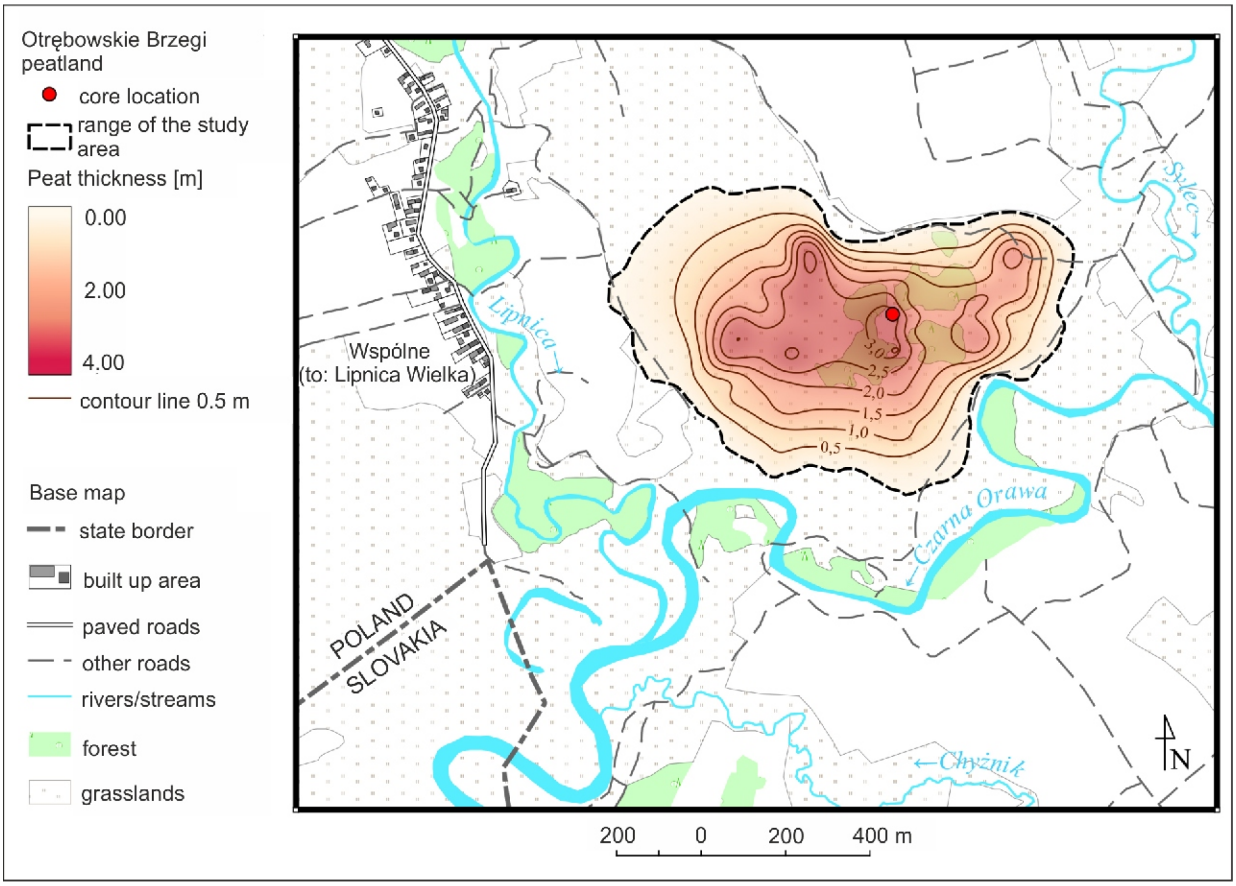

Fig. 2. The thickness of the Otrębowskie Brzegi peatland

len palynomorphs – mostly fungal spores and microscopic charcoal particles – were also counted. Sporomorphs were counted on the whole surface of the slide. The collection of reference slides at the Department of Geology and Palaeogeography of Szczecin University were used to identify the sporomorphs. Reference books and illustrated handbooks were also used (e.g., Fægri and Iversen, 1989; Moore et al. 1991; Beug, 2004). The nomenclature of palynological taxa was adopted according to the Polish Palynological Database.

The pollen analysis results are presented in the form of percentage diagrams developed in *POLPAL 2004* software, ver. 2011.11 (Walanus and Nalepka, 2004). The basis of the percentage calculation is the sum of AP + NAP; AP comprises pollen grains of all trees and shrubs, while NAP includes sporomorphs of terrestrial herbs, i.e. graminides. In general, pollen of limnophytes and telmatophytes are not included in the calculated sum. Palynological analysis was performed at the Geology and Palaeogeography Unit in the Faculty of Geosciences at the University of Szczecin.

GEOCHEMICAL ANALYSIS

ELEMENTAL CONCENTRATIONS

The concentrations of selected major and trace elements (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Pb, Ni, and Cr) were measured in 48 peat samples. Every sample consisted of about 1 g of manually ground peat. The samples were homogenized and thoroughly dried at 105°C. Next, the samples were combusted at 550°C for 5 hours to remove organic matter, and then digested in 8 ml of 65% HNO_3, 2 ml of 10% HCl, and 2 ml of 30% H_2O_2 in individual PTFE vials. Afterwards they were put into a mineralizer for 1 hour. After mineralizing, the samples were transferred into polypropylene beakers and diluted to 50 ml with de-ionized water. The concentrations of major and trace elements were measured using atomic absorption spectrometry (AAS). Whole chemical preparation and 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. The geochemical zones from the JB-1 core were distinguished using multivariate statistical analysis with cluster analysis from the *PAST* software (Hammer et al., 2001).

Pb ISOTOPES

Thirty samples from JB-1 were selected to measure their ratios of stable lead isotopes. The samples were dried, homogenized, and ground in an automatic agate mortar. After drying (105°C, 12 h) the samples were combusted (550°C, 5h), dissolved in a mixture of 1ml of 14 N HNO_3 and 4 ml of 22 N HF at 125°C for 48 h in a laminar flow clean air cabinet. After drying, the samples were dissolved again in 2 ml of 6 N HCl and 2 ml of 14 N HNO_3 at 125°C to evaporation. The separation of Pb, using exchange micro-columns filled with pre-conditioned AG1-X8 anionic resin, was performed according to the protocol of Weis et al. (2005). The chemical preparation was carried out at the Department of Geology of the University of Liège in Belgium. Pb isotopic measurements were performed using multi-collector inductively coupled plasma mass spectrometry, Nu plasma (MC-ICP-MS) at the Department of Earth and Environmental Sciences at the Free University of Brussels, Belgium.

Table 1

Results of ^{14}C analysis, ^{14}C data were used to construction of an age-depth model, using *OxCal* software (Bronk Ramsey and Lee, 2013) with the calibration data set of *IntCal13* (Reimer et al., 2013) and *Bomb13* NH1 calibration curves (Hua et al., 2013)

Lab code	Depth [cm]	Conventional ^{14}C age/radioactivity [BP/ pMC]	Modelled age range 68.2% [cal BC/AD]	Modelled age range 95.4% [cal BC/AD]
GdA-5222	9	136.81 ± 0.36	1958–1964 AD	1958–1958 AD (91.4%) 1974–1977 AD (4.0%)
GdA-5223	19	1370 ± 30	635–670 AD	605–680 AD
GdA-5224	27	1615 ± 30	505–540 AD	485–550 AD
GdS-3479	37	1510 ± 55	425–475 AD	410–500 AD
GdS-3562	53	1650 ± 50	255–300 AD (37.0%) 325–365 AD (31.2%)	245–395 AD
GdS-3563	73	1895 ± 50	20–115 AD	40 BC–145 AD
GdS-3530	98	2510 ± 55	460–405 BC	520–395 BC
GdS-3569	125	2490 ± 55	760–640 BC	790–590 BC
GdS-3480	164	2935 ± 60	1120–1015 BC	1180–970 BC
GdS-3570	189	3045 ± 50	1320–1230 BC	1380–1195 BC
GdS-3526	213	3150 ± 50	1505–1430 BC	1605–1580 BC (1.8%) 1545–1385 BC (93.6%)
GdS-3531	254	3570 ± 55	2015–1995 BC (4.2%) 1985–1870 BC (59.6%) 1845–1825 BC (4.4%)	2035–1770 BC
GdS-3396	288	5385 ± 90	4335–4220 BC (36.3%) 4210–4160 BC (13.7%) 4135–4065 BC (18.2%)	4370–3985 BC

lab codes GdA – AMS method, lab codes GdS – LSC method

RESULTS

AGE-DEPTH MODEL

The results of radiocarbon dating are shown in Table 1. The age-depth model derived is shown in Figure 3. The chronology of the upper 16.5 cm of the core is very well-defined by nine ^{210}Pb dates and one ^{14}C date. It covers a time span from ~1890 AD to the present. The ^{14}C date from a depth of 9 cm is in agreement with ^{210}Pb dates. The first ^{14}C date below that part of the chronology (from 19 cm depth) is much older (605–680 AD; 95.4% confidence interval) than the last ^{210}Pb date (from 16.5 cm). It shows that a hiatus occurs at a depth of 17–18 cm. The remaining dates, down to the bottom of the peat profile, located at 285 cm depth and dated at 2250 BC ± 120 yrs, present an undisturbed stratigraphic order. The last sample at 288 cm (dated at 4370–3985 BC) is a gyttja sample older than the bottom of the peat profile. This difference may be caused by an ageing effect. A reservoir effect is highly probable because the bottom sample is a lake sediment-organic gyttja (see Table 2); interpretation of the bottom part should with caution. The total agreement index of the model is almost 60%, sufficient to consider the model reliable.

PALAEOBOTANICAL DATA

The analysis of botanical macrofossils demonstrates the occurrence of numerous *Carex* and *Sphagnum* remains (Table 2). This botanical composition is characteristic of poor fens. The lower parts of the JB-1 profile (220–280 cm) contain *Alnus* remains, characteristic of fen peat. The lowest parts of the profile (286–293 cm) consist of organic and clay gyttja, which indicates a lacustrine origin of the Otrębowskie Brzegi peatland. A part of the peatland, from which the JB-1 core was taken, was classified as a Rheic Hemic Histosol (Dystric), according to international soil classification (WRB).The palynological diagram (Fig. 4) reveals the main taxa in the Otrębowskie Brzegi peatland. It shows changing trends in the composition of AP and NAP. Four local pollen assemblage zones (LPAZ) are characterized in Table 3.

GEOCHEMICAL ANALYSIS

The geochemical analysis showed variability of both the elements measured and geochemical indices (Fig. 5). The highest concentration of Pb is also reflected in the calculated accumulation rate for this element (Fig. 6).

Using the *PAST* software (Hammer et al., 2001) three zones with additional sub-zones were distinguished in the peat profile:

– GZ1 (321–212 cm); from 4370–3985 BC to 1510–1325 BC. This zone was divided into two sub-zones:

a. 321–279 cm; from 4370–3985 BC to 2430–1970 BC; this zone covers gyttja deposits and the lowest part of the peat profile. At the bottom of this zone the content of organic matter (OM) reaches its lowest value (about

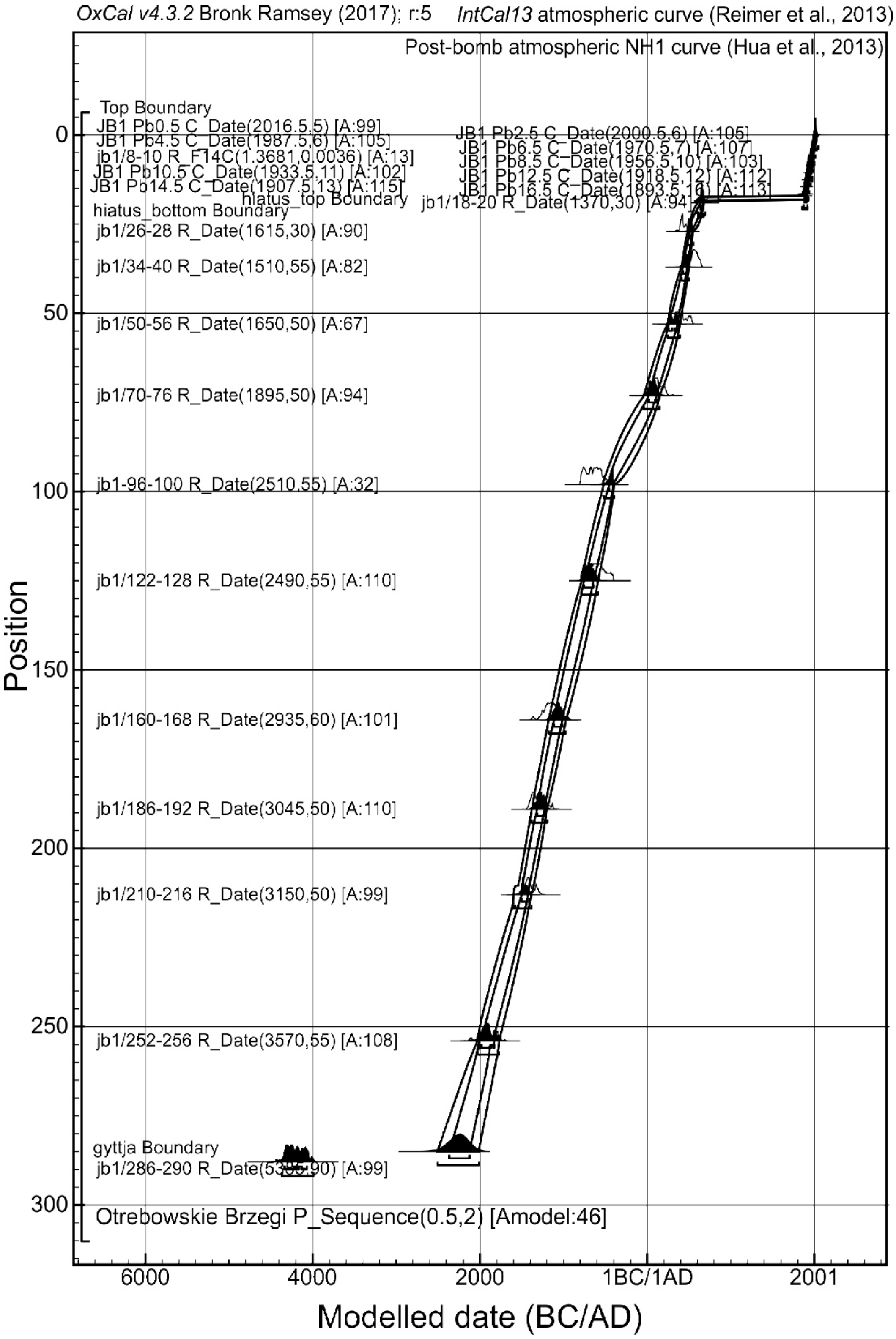

Fig. 3. Age-depth model of the JB-1 core

Table 2

Otrębowskie Brzegi – results of botanical analysis

Depth [cm]	Botanical composition – Species	[%]	Peat species Type of gyttja	D [%]
36–46	*Sphagnum* sp.	20	*Sphagno-Cariceti*	35
	Carex lasiocarpa	45		
	Carex rostrata			
	Carex sp.div.			
	Eriophorum angustifolium	5		
	Rhynchospora alba	+		
	Pterodiophyta sp.	5		
	Pinus sylvestris	5		
	Unidentified	5		
70–80	*Sphagnum fallax*	35	*Sphagno-Cariceti*	25
	Sphagnum sp. s. Cuspidata			
	Carex lasiocarpa	25		
	Carex rostrata			
	Carex sp. div.			
	Eriophorum vaginatum	15		
	Rhynchospora alba	5		
	Scheuchzeria palustris	+		
	Menyanthes trifoliata	10		
	Pinus sylvestris	5		
	Unidentified	5		
106–116	*Sphagnum* sp.	20	*Sphagno-Cariceti*	35
	Carex lasiocarpa	35		
	Carex rostrata			
	Carex sp.			
	Eriophorum vaginatum	15		
	Menyanthes trifoliata	10		
	Andromeda polifoila	15		
	Oxyccocus palustris			
	Unidentified	5		
130–140	*Sphagnum* sp. div.	30	*Sphagno-Cariceti*	30
	Carex lasiocarpa	35		
	Carex rostrata			
	Rhynchospora alba	5		
	Menyanthes trifoliata	15		
	Ericaceae sp. (bark)	5		
	Pinus sylvestris	5		
	Unidentified	5		
150–160	*Sphagnum* sp. div.	40	*Sphagno-Cariceti*	20
	Carex rostrata	20		
	Eriophorum vaginatum	5		
	Rhynchospora alba	5		
	Menyanthes trifoliata	10		
	Comarum palustre	5		
	Andromeda polifoila?	10		
	Ericaceae sp.			
	Unidentified	5		
174–184	*Sphagnum* sp. div.	35	*Sphagno-Cariceti*	30
	Carex rostrata	30		
	Carex sp.			
	Eriophorum vaginatum	10		
	Rhynchospora alba	+		
	Menyanthes trifoliata	10		
	Oxyccocus palustris	10		
	Ericaceae sp.			
	Pinus sylvestris	+		
	Unidentified	5		
190–200	*Sphagnum* sp. div.	35	*Sphagno-Cariceti*	25
	Aulacomium palustre	+		
	Carex sp.	35		
	Eriophorum vaginatum	10		
	Scheuchzeria palustris	+		
	Menyanthes trifoliata	10		
	Oxyccocus palustris	5		
	Ericaceae sp. div.			
	Pinus sylvestris	+		
	Unidentified	5		
220–230	*Sphagnum fallax*	15	*Alneti*	40
	Bryales sp. div.	20		
	Carex rostrata	15		
	Carex fusca			
	Carex riparia			
	Carex sp.			
	Eriophorum sp.	+		
	Scheuchzeria palustris	+		
	Menyanthes trifoliata	5		
	Phragmites australis	+		
	Equisetum fluviatile?	+		
	Alnus glutinosa	40		
	Salix sp. (bark)			
	Picea sp. (bark)			
	deciduous wood			
	Unidentified	5		
270–280	*Sphagnum fallax?*	+	*Alneti*	50
	Bryales sp.	5		
	Equisetum fluviatile?	+		
	Alnus glutinosa	+		
	Salix sp. (bark)	35		
	Frangula alnus	10		
	Pinus?	15		
	Picea sp. (bark)	20		
	deciduous and coniferous wood	5		
	Unidentified	10		
286–290			Organic gyttja	
290292			Clay gyttja	
296–322			Mineral substrate	

Peat species were classified according to Tołpa et al. (1967) and gyttja as per Ilnicki (2002); degree of decomposition (D) was determined according to Polish Standard (PN-G-04595, 1997)

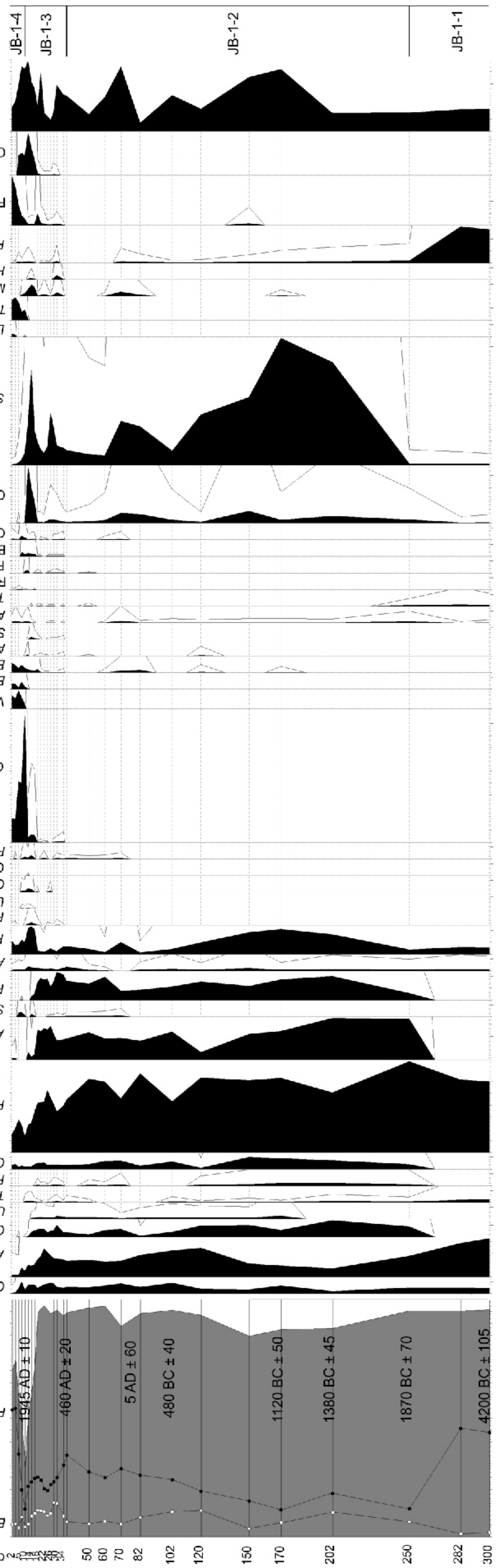

Fig. 4. Palynological diagram of the JB-1 core

Table 3

Characteristics of local pollen assemblage zones (LPAZ)

Local PAZ	Name of PAZ	Depth [cm]	Approx ages BC/AD	Description of pollen spectra
JB-1-1	*Pinus–Alnus*	300	4200 BC	Curves of *Pinus* relatively stable with high value 45%; *Betula* increase; *Corylus* and *Tilia* stable represented by low values; *Alnus* decrease (mean. 14%, max. 16%); *Poaceae* max 3%, *Artemisia* less than 1%; High value of *Polypodiaceae* curve (14%); **JB-1-1/JB-1-2 limit *Pinus* and decrease, *Picea* increase**
JB-1-2	*Picea–Carpinus*–Poaceae	250	1870 BC	*Quercus, Fraxinus, Carpinus, Abies, Fagus* curves appears; High percentage of *Pinus* (mean. 11%, max. 28%); *Betula* increase (max. 11%); *Corylus* stable with value between 1 and 4%; *Picea* curve remains high (38%) similar to *Poaceae* (10%); *Carpinus* is represented by high values (5%); *Sphagnum* curve rising and later dominates in diagram similar to *Cyperaceae*; *Plantago lanceolata* curve appears; **JB-1-2/JB-1-3 limit *Betula* and *Fagus* increase, *Pinus* decrease**
JB-1-3	*Betula–Fagus–Abies*	36	460 AD	*Pinus* decrease, *Betula* curve rises to 15%; Increasing values of *Corylus* and *Alnus*; *Ulmus* and *Tilia* are represented in low percentage; relatively significant proportion of *Abies*; *Picea* values between 11 and 26%; high percentages of *Poaceae* (11%); Curves of crops, cultivated plants and field weeds appear; Amount of charcoal particles rise max. 26%; Curves of *Telmatophytes* and *Limnophytes* appear, with maximum of *Menyantes trifoliata* (5%); **JB-1-3/JB-1-4 limit increase of *Pinus* and *Picea***
JB-1-4	*Pinus–Picea–Calluna*	10	1945 AD	Dramatic increase of *Pinus* (max. 54%); curve fluctuations of *Betula*, *Corylus* and *Alnus*; *Picea* rise to 13%; continuous curve of *Atremisia;* Sharp increase of *Calluna* with max. 55%; *Typha* is represented at high percentage 9%; *Poaceae* pollen values between 3 and 6%.

2%), then increases up to about 70%. K, Mg, Fe and Cr reach their highest values (5131.6, 7458.4, 18,182.6 and 38.2 µg g^{-1}, respectively). The content of Ca is low at the bottom of the zone (133.2 µg g^{-1}), then increases rapidly up to over 11,000 µg g^{-1} at the sub-zone boundary. In this sub-zone the Na/K ratio increases rapidly and reaches its highest value at 285 cm (1.6).

b. 279–212 cm; from 2430–1970 BC to 1510–1325 BC; in this sub-zone the content of OM increases from ~70% to 93%. The concentrations of all measured elements decrease.

– GZ2 (212–6 cm); from 1510–1325 BC to 1960–1990 AD, was divided into three sub-zones:

a. 212–105 cm; from 1510–1325 BC to 465–540 AD; this sub-zone is characterized by a high concentration of OM (>93%). Concentrations of Ca, Fe, and Mn decrease, while concentrations of heavy metals (Cu, Zn, Pb and Cr) slightly increase. There is a distinct peak of Cu at 129 cm (52 µg g^{-1}). The Cu/Zn ratio reaches its highest value in this zone (6.3).

b. 105–49 cm; from 465–540 AD to 275–425 AD; in this sub-zone the concentration of OM is high and rather stable – only small variations, between 95 and 97%, occur. The concentrations of Cu, Zn, and Pb still increase, while the contents of Ca, Fe, and Mn decrease slightly.

c. 49–6 cm; from 275–425 AD to 1965–1985 AD – the deposits of this sub-zone are characterized by decreasing concentrations of OM (down to 90%). The concentrations of Na, K, Ca, Mg, Fe, Zn, and Pb increase and Pb content reaches its highest value (102.6 µg g^{-1}). The Fe/Mn ratio increases, and it is very high at the boundary between GZ2 and GZ3 (~9000, while the average value for the whole core is about 200). In this sub-zone a hiatus occurs. The increased concentrations of metal elements, together with increased content of mineral matter, may be an effect of decomposition of organic matter.

– GZ3 (6–0 cm); from 1960–1990 AD to 2016 AD; this zone reflects modern times, ca. the past 40 years. It is characterized by increasing content of OM (up to over 95%), Ca, Mg, Mn, Cu, Zn, and Ni and decreasing concentrations of Pb. The concentrations of Na, Mn, Cu, Zn, and Ni are the highest of those in the entire core, reaching 617.1, 881, 139.2, 403.6 and 186.8 µg g^{-1}, respectively).

Pb ISOTOPIC COMPOSITION

The lead isotopic composition is reported in Table 4. The values of $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios in the deepest part of the peat core (283 cm) are 38.9863 ± 0.0028 (maximum value), 15.6997 ± 0.0010 and 19.1401 ± 0.0012, respectively. The values of $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios slightly increase with decreasing depth in the lower part of the core (between ~4200 BC and 1530 BC) and reach their maxima at a depth of 219 cm: 15.7115 ± 0.0007 and 19.2225 ± 0.0008, respectively. The value of the $^{208}Pb/^{204}Pb$ ratio generally decreases upwards along the core. From about 23 cm depth (~580 AD) the values of all measured Pb ratios ($^{208}Pb/^{204}Pb$,

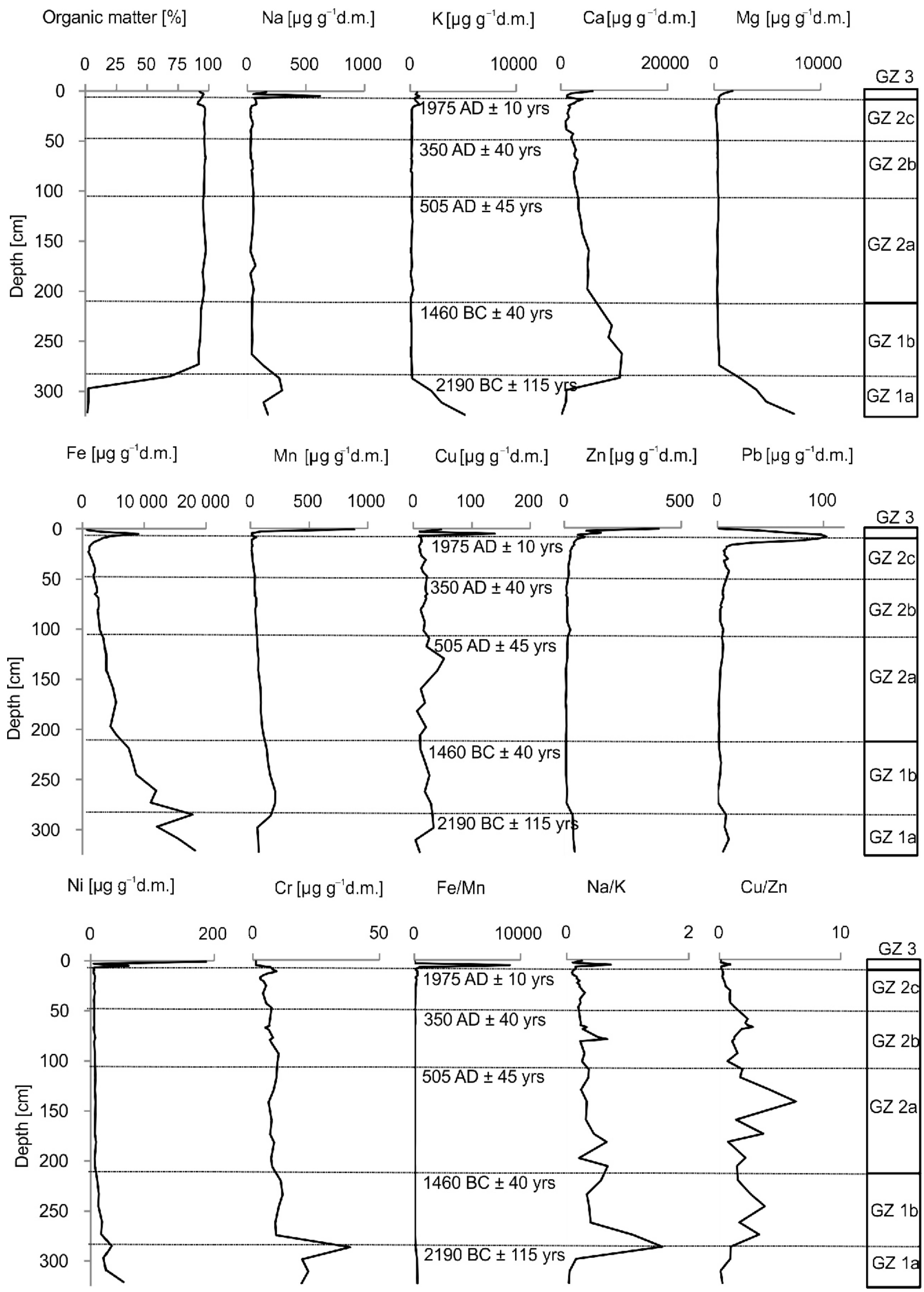

Fig. 5. Concentrations of selected elements, obtained by AAS analysis, contents of organic matter and geochemical indices

d.m. – dry mass, GZ – geochemical zone

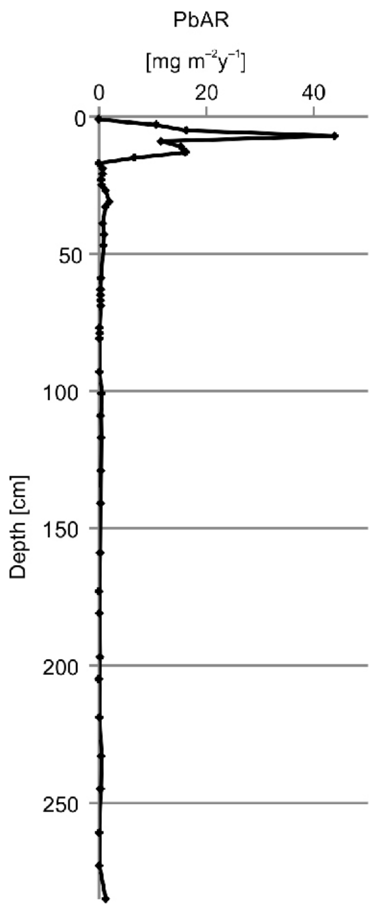

Fig. 6. Pb accumulation rate in the JB-1 core

^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb) start to decrease more rapidly and at about 6 cm depth (1975 AD) they reach their minima: 38.1947 ± 0.0021, 15.6128 ± 0.0007 and 18.2467 ± 0.0008, respectively. This stratum is also the boundary between GZ2 and GZ3. Then, towards the surface (1 cm depth, present), the values of ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{206}Pb/^{204}Pb ratios increase, reaching 38.2642 ± 0.0015, 15.6260 ± 0.0006 and 18.3315 ± 0.0007, respectively.

These variations clearly coincide with changes in the Pb concentration. The binary diagram ^{208}Pb/^{206}Pb vs. ^{206}Pb/^{207}Pb, shown in Figure 7A, is helpful in determining the origin of lead in the Otrębowskie Brzegi peatland. It includes the isotopic ratios of 29 peat samples, as well as the data from Puścizna Mała and Puścizna Krauszowska peatlands (Fiałkiewicz-Kozieł et al., 2018) and from Słowińskie Błoto peatland (De Vleeschouwer, et al., 2009). The diagram in Figure 7B shows the samples from Otrębowskie Brzegi, grouped by age, with respect to the Pb isotopic ratios of upper continental crust (UCC, data from Millot et al., 2004) and modern industrial aerosols (Bollhöfer and Rosman, 2001).

Figure 8 shows the relation between Pb concentration (see Fig. 5) and isotopic composition (Table 4), in order to document any changes in ^{206}Pb/^{207}Pb corresponding to Pb contamination. The increase in Pb contamination is strongly associated with an increase in the isotopic ratio (R^2 = 0.9367).

DISCUSSION

Palynological data and botanical macrofossils analyzes showed that the development of the peatland is strongly marked through the well-defined presence of *Sphagnum* and *Carex*. There are noticeable changes in the species composition of tree stands from the deepest layers toward the surface with proximity to the more open areas. The beginning of the peatland development (fen-type) is visible ~2150 BC (Fig. 9). Then, the content of *Sphagnum* increased up to its maximum ~1120 BC, when the peatland evolved into a raised bog. Next, the content of *Sphagnum* decreased down to a minimum at 100 cm depth (460 BC), which occurred simultaneously with a maximum of AP. At that time, the PAR and PbAR slowed down. From ~840 BC the first slight increases in Zn, Pb, and other heavy metal concentrations were observed. In that period, a decrease in AP and increase of *Cyperaceae* is observeable, which suggests some natural processes leading to deforestation and exposure of the area to increased contamination from the atmosphere. At that level, slight changes in Pb isotopic composition are visible. The next local minimum of AP, with co-occurrence of an increase in *Sphagnum*, is visible at about 70 cm depth (~100 AD). From that point, an increase in Pb concentration is pronounced. That peat layer corresponds to the beginning of the Roman Period, so changes in chemical composition may be suspected to have an anthropogenic origin. This supposition is supported by changes in Pb isotopic composition. Additionally, the appearance of *Plantago lanceolata* at the BC/AD boundary suggests grazing, thus the changes may be connected with deforestation. Between 70 and 45 cm depth (100–380 AD) a visible change in lead isotopic composition occurs, with co-occurrence of an increase of lead concentration. These changes are obviously associated with human activity. The nearest Zn-Pb ore deposit that could be a source of Pb in JB-1 is in the Olkusz region. It is located ~100 km to the north of the Orava-Nowy Targ Basin. The values of the ^{206}Pb/^{207}Pb ratio in JB-1 in the Roman Period range between 1.194–1.206; corresponding values for galena (Pb ore) from the Olkusz region range between 1.177–1.179 (De Vleeschouwer, 2009), and for peat from the Wolbrom mire between 1.174–1.183 (Pawełczyk et al., 2018a). These findings suggest that ores from the Olkusz region could not be the only source of Pb in JB-1. Another possible source could be mining activity in the Carpathian region, which started in the Roman Period (Borcoş and Udubaşa, 2012). Between 405 and 585 AD a visible increase in ^{206}Pb/^{207}Pb ratio was noticed. This is connected with the Great Migration Time – a period in Europe with extremely cold climate conditions. During that time, human activity decreased. From about 500 AD *Calluna vulgaris* and *Cerealia* in co-occurrence of charcoal remains are present, which correlates with deforestation, visible in the AP/NAP ratio. The presence of *Ledum palustre*, *Empetrum, Vaccinium* and increasing value of *Typha latifolia* indicates an increase in humidity. Interestingly, while the general direction of historical settlement in Orava-Nowy Targ Basin was from the east (see Fig. 1C), the appearance of cereal pollen in Otrębowskie Brzegi took place a few hundred years earlier than in Puścizna Wielka (see Krąpiec et al., 2016). About 630 AD (20 cm depth) a sharp increase of Pb and other heavy metal concentrations in the JB-1 profile is observed. That period also showed a beginning of rapid changes in lead isotopic composition: the ^{206}Pb/^{207}Pb ratio started to decrease. This change

Table 4

Lead isotope quotients of samples from the JB-1 core with 2 uncertainty

Depth [cm]	$^{208}Pb/^{204}Pb$	2	$^{207}Pb/^{204}Pb$	2	$^{206}Pb/^{204}Pb$	2	$^{208}Pb/^{206}Pb$	2	$^{206}Pb/^{207}Pb$	2
1	38.264153	0.001528	15.626005	0.000610	18.331530	0.000690	2.087357	0.000033	1.173142	0.000015
5	38.194683	0.002120	15.615223	0.000826	18.246696	0.000846	2.093230	0.000048	1.168520	0.000022
7	38.197218	0.00197	15.612814	0.000718	18.252252	0.000844	2.092743	0.000036	1.169056	0.000016
9	38.222210	0.002120	15.614909	0.000838	18.268449	0.001022	2.092295	0.000044	1.169936	0.000017
11	38.256788	0.002220	15.617840	0.000820	18.290690	0.000926	2.091644	0.000039	1.171141	0.000015
13	38.290174	0.001842	15.619256	0.000650	18.314920	0.000752	2.090665	0.000043	1.172586	0.000015
15*	38.364760	0.002080	15.626628	0.000806	18.384243	0.000882	2.086824	0.000032	1.176469	0.000015
15*	38.366522	0.002520	15.628103	0.000918	18.385938	0.001022	2.086763	0.000046	1.176466	0.000015
17	38.500809	0.001478	15.641062	0.000612	18.540347	0.000718	2.076609	0.000036	1.185364	0.000017
19	38.650229	0.001814	15.661787	0.000714	18.709403	0.000842	2.065828	0.000036	1.194589	0.000016
21	38.676215	0.001604	15.665228	0.000658	18.751735	0.000732	2.062504	0.000039	1.197029	0.000017
23	38.791384	0.002200	15.679210	0.000792	18.881939	0.001018	2.054439	0.000039	1.204266	0.000017
25	38.802875	0.001748	15.679784	0.000648	18.897347	0.000866	2.053380	0.000035	1.205205	0.000016
27	38.808430	0.001850	15.681871	0.000718	18.899300	0.000866	2.053450	0.000032	1.205169	0.000014
29	38.798024	0.001398	15.680515	0.000518	18.888424	0.000632	2.054081	0.000035	1.204579	0.000015
31	38.827412	0.001450	15.685340	0.000588	18.920423	0.000708	2.052163	0.000027	1.206249	0.000013
33	38.809449	0.001598	15.681594	0.000638	18.908195	0.000800	2.052556	0.000032	1.205757	0.000014
41	38.812546	0.001980	15.682493	0.000820	18.905009	0.001032	2.053016	0.000030	1.205485	0.000015
45	38.627465	0.001466	15.659862	0.000580	18.693583	0.000684	2.066367	0.000035	1.193726	0.000015
53	38.800763	0.002920	15.679664	0.001010	18.907427	0.001010	2.052136	0.000043	1.205857	0.000016
61	38.797903	0.002240	15.682689	0.000870	18.902045	0.001026	2.052607	0.000033	1.205281	0.000014
69	38.658893	0.002020	15.663161	0.000752	18.748074	0.000862	2.062027	0.000044	1.196953	0.000014
77	38.862397	0.002620	15.690569	0.000950	18.998450	0.001112	2.045606	0.000040	1.210820	0.000017
85	38.866721	0.002220	15.693928	0.000758	19.008371	0.000852	2.044774	0.000041	1.211193	0.000017
113	38.859943	0.002300	15.690284	0.000872	19.023683	0.001002	2.042718	0.000035	1.212450	0.000016
145	38.916753	0.002540	15.700797	0.000886	19.136266	0.001154	2.033678	0.000033	1.218809	0.000014
185	38.944079	0.001486	15.706575	0.000566	19.182106	0.000746	2.030176	0.000033	1.221279	0.000015
219	38.955528	0.001904	15.711526	0.000728	19.222495	0.000832	2.026572	0.000040	1.223465	0.000018
249	38.938959	0.002140	15.705576	0.000874	19.179028	0.001068	2.030290	0.000030	1.221160	0.000014
283	38.986251	0.002840	15.699702	0.000982	19.140067	0.001174	2.036933	0.000038	1.219136	0.000016

* – replicates

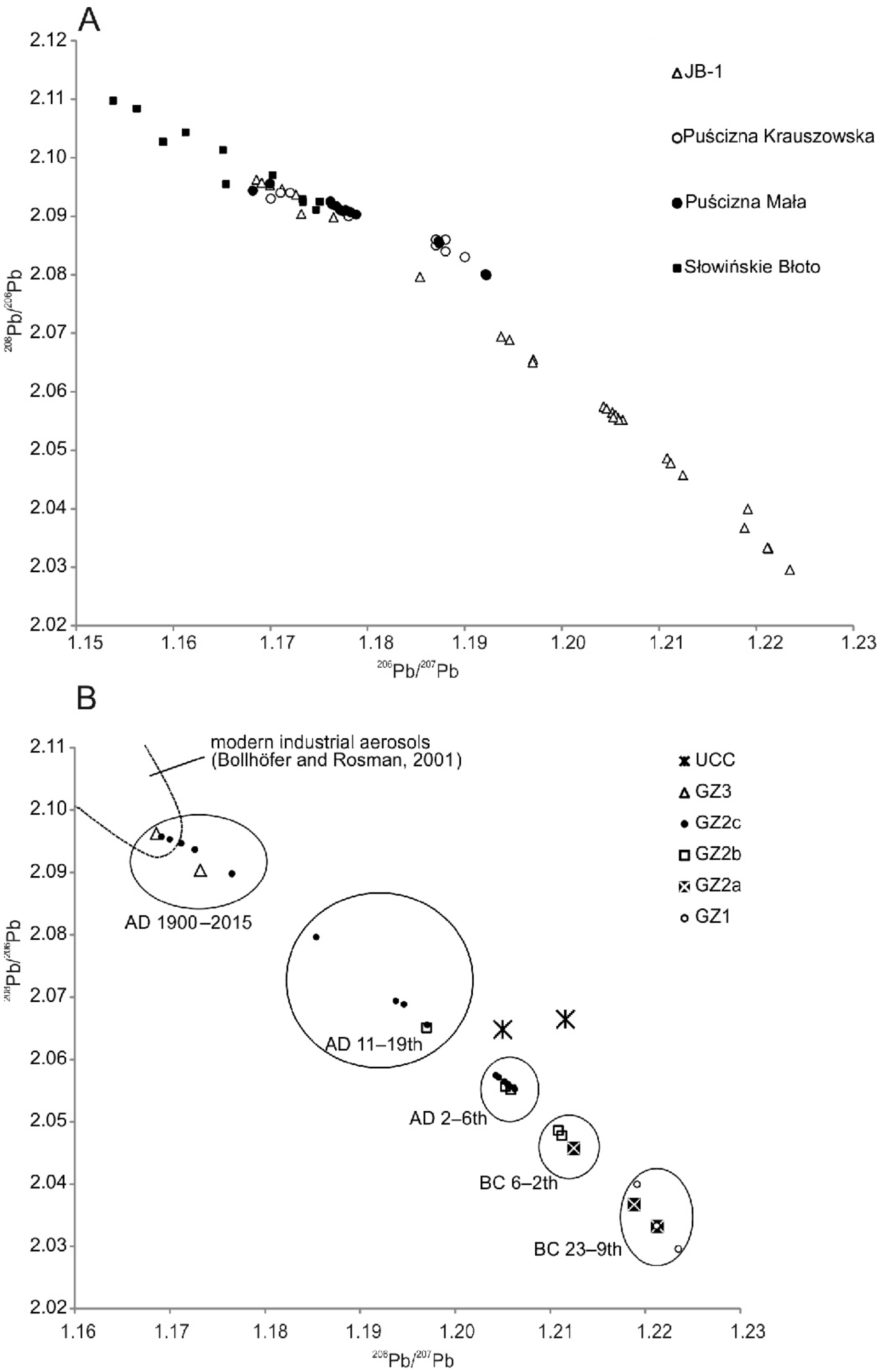

Fig. 7. $^{208}Pb/^{206}Pb$ *versus* $^{206}Pb/^{207}Pb$ diagrams

A – peat samples from Otrębowskie Brzegi (this work), 14 samples from Puścizna Mała, 10 samples from Puścizna Krauszowska (Fiałkiewicz-Kozieł et al., 2018) and 12 samples from Słowińskie Błoto (De Vleeschouwer et al., 2009); **B** – peat samples from Otrębowskie Brzegi distinguished on the basis of geochemical zones (GZ 1–3), modern urban airborne particles from Europe (Bollhöfer and Rosman, 2001) and Upper Continental Crust (UCC) (Millot et al., 2004); the error bars are negligible

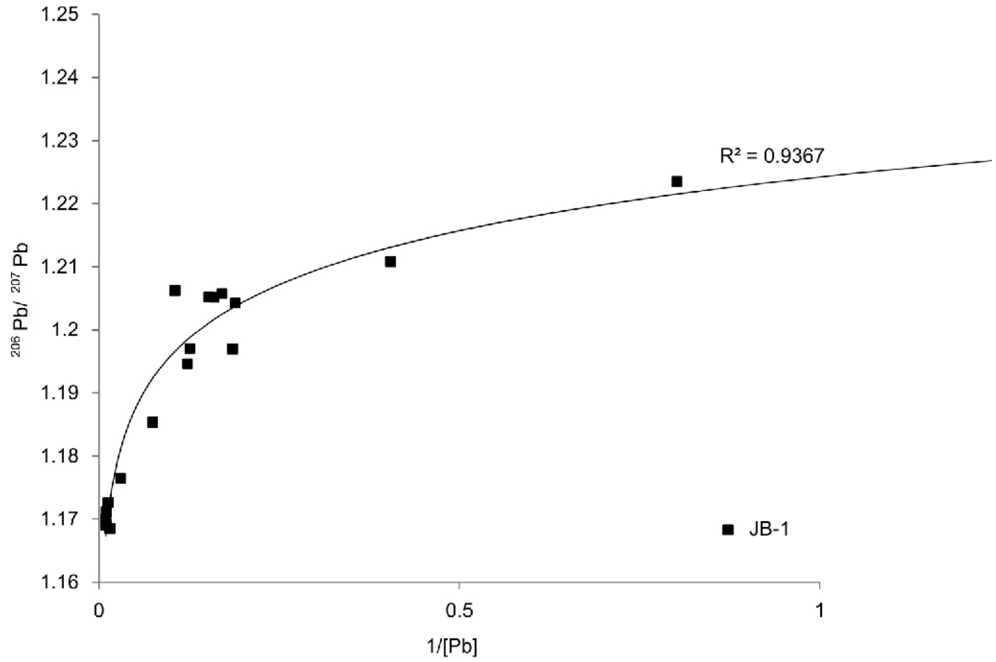

Fig. 8. $^{206}Pb/^{207}Pb$ vs. 1/Pb binary diagram, distinguishing the geochemical zones in JB-1, constructed by combining $^{206}Pb/^{207}Pb$ data from Table 4 with Pb concentration data (see Fig. 5)

is connected with a strong anthropogenic impact, i.e. mining, smelting, coal combustion, etc. Similar changes have been noticed in other peatlands in the Orava–Nowy Targ Basin, including Puścizna Mała and Puścizna Krauszowska at a similar time (606 AD in Puścizna Mała and 625 AD in Puścizna Krauszowska; Fiałkiewicz-Kozieł et al., 2018). A local minimum of *Sphagnum* is also visible. From that time the level of AP decreased rapidly, a likely effect of deforestation and agricultural cultivation in the neighborhood of the peatland. The presence of charcoal suggests that forests were burned to clear areas for cultivation. Between 640 and 1905 AD there was a period of hiatus. At about 10 cm depth (~1945 AD), a maximum concentration of Pb and minimum of AP were observed. At that time the presence of *Erica tetralix* is visible. It is a very rare species, occurring mostly in the northern part of Poland, so its presence in Orava–Nowy Targ Basin needs additional research. It may be an effect of animal or human migrations. This was a time of total disappearance of *Sphagnum*, representing the end of peatland development, with clear symptoms of anthropogenic desiccation (changes of LOI, palynological composition). It was the time of maximum anthropogenic impact, including deforestation, agriculture, mining, industry, and coal combustion. This impact is also consistent with changes in geochemical composition, such as increases in K and heavy metal concentrations, and in Pb isotopic ratios. The $^{206}Pb/^{207}Pb$ ratio reaches its minimum value (1.169) during this period. The decrease may have been influenced by waste incinerators that were built in the Czech Republic and Slovakia at the beginning of the 20th century AD, as well as an introduction of leaded gasoline. Average values of the $^{206}Pb/^{207}Pb$ ratio for ashes from waste incinerators are 1.14–1.16 (Komárek et al., 2008) and for Polish gasoline, 1.174 (Yao et al., 2015). From that time up to the present, the AP content increases and Pb content decreases.

The Pb isotopic analysis supported reconstruction of the lead sources in the peatland. In the binary diagram (Fig. 7B), the samples from Otrębowskie Brzegi are scattered linearly between natural crust and modern urban airborne sources, which suggests a generally undisturbed lead supply and shows the contribution of two main sources of lead:

- the first end-point is characterized by high $^{206}Pb/^{207}Pb$ (1.224) and low $^{208}Pb/^{206}Pb$ (2.027) ratios; its total concentration of Pb (1.25 μg g^{-1}) corresponds to the oldest GZ1 samples (4200–1460 BC). The first end-point is compatible with a natural crustal source represented by UCC (Millot et al., 2004);
- the second end-point is located on the opposite site of the diagram and is characterized by low $^{206}Pb/^{207}Pb$ (1.169) and high $^{208}Pb/^{206}Pb$ (2.093) ratios. At this point the total concentration of Pb is 38.67 μg g^{-1}. This end-point is connected with the GZ3 and indicates modern airborne particles as a source of lead pollution in the peat samples.

CONCLUSIONS

The profile JB-1 from Otrębowskie Brzegi represents the time period from 4200 BC to the present (2016 AD), however, the interpretation of the oldest gyttja sample should be qualified because of a probable aging effect. In the deepest layer (321–205 cm), which corresponds to the period from 4370–3985 BC to 1500–1310 BC, the peat is undisturbed and no evidence of human activity is observed. Using that layer as a natural background allowed for the reconstruction of Pb pollution in this area in the past.

As the Pb isotopic analysis showed, the deepest and oldest samples are associated with upper continental crust, while the upper part of the core, which corresponds to the period from the Industrial Revolution to the present, is characterized by modern airborne pollution.

From about 140 cm depth (840 BC) a slight increase of heavy metal concentrations was noted. Taking into account the results of palynological analysis, we infer that this effect was caused by natural processes. However, at the same time,

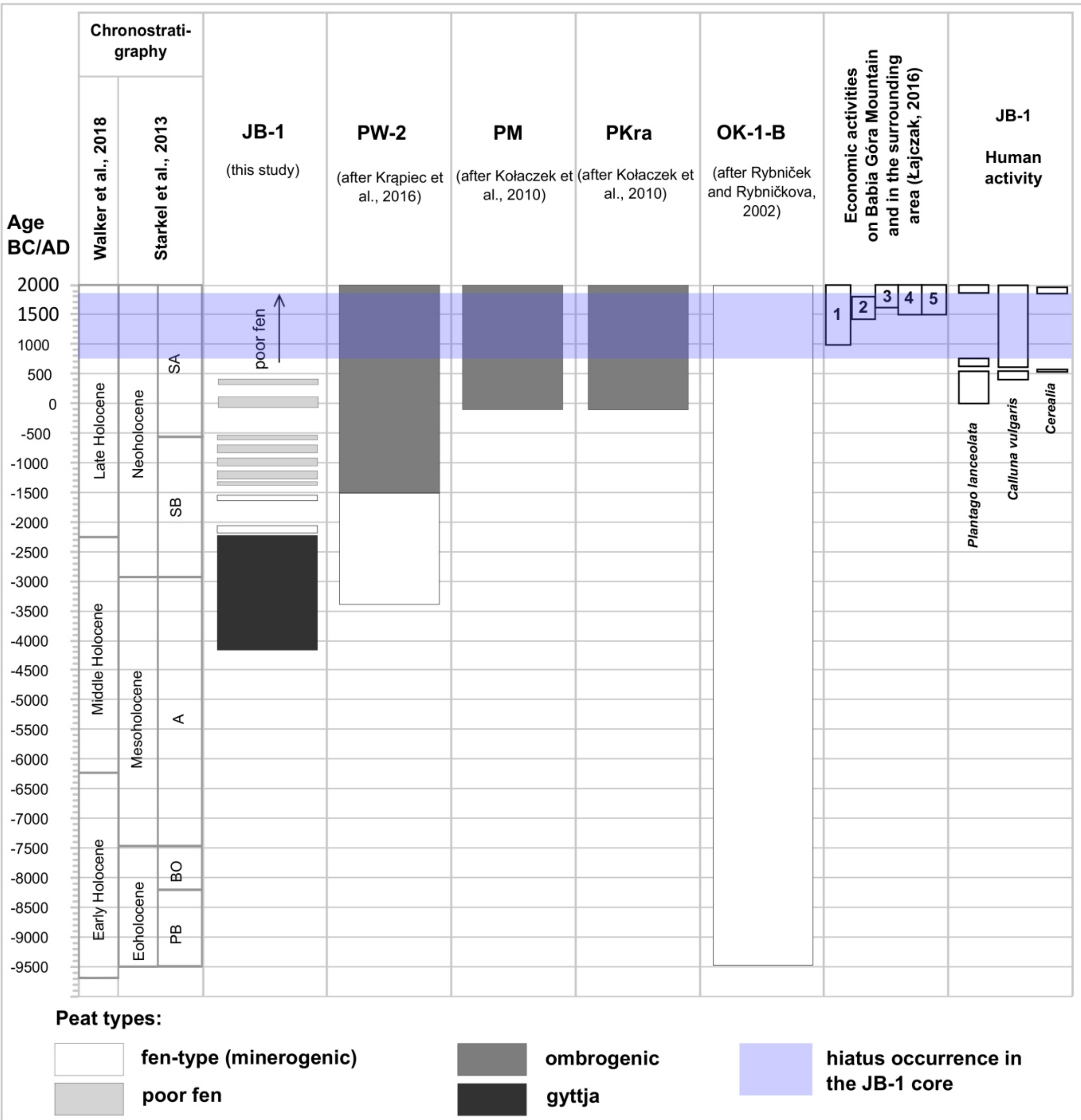

Fig. 9. Human impact recorded in the Otrębowskie Brzegi peatland (on the basis of pollen analysis), in comparison with other peatlands from the Orava–Nowy Targ Basin (Rybniček and Rybničkova, 2002; Kołaczek et al., 2010; Krąpiec et al., 2016)

PW-2 – Puścizna Wielka; PM – Puścizna Mała; PKra – Puścizna Krauszowska; OK-1-B – Bobrov; economic activities after Łajczak (2016): 1 – settlement and agriculture; 2 – flysch rocks extraction; 3 – cutting down forests for pastoralism; 4 – pastoralism; 5 – forestry and wood management; Holocene chronostratigraphy after Starkel et al. (2013), Walker et al. (2018)

a slight increase in $^{208}Pb/^{206}Pb$ ratio as well as a decrease in $^{206}Pb/^{207}Pb$ ratio was observed, which may reflect some human activities, such as smelting. The next well-marked changes in chemical composition, including changes in Pb isotopic ratios, are connected with deforestation and grazing in the Orava–Nowy Targ Basin. These observations may also reflect some mining and smelting occurring in the Carpathian or Olkusz regions during the Roman Period. The increase of Zn and Pb concentrations, correlated with significant changes in lead isotopic composition and the presence of *Plantago lanceolata*, indicates the activity of the Przeworsk Culture people (see Fig. 9). A period of decreased human activity, supported by Pb isotopic changes, was noticed during the Great Migration Time, between the 5th and 6th centuries AD.

The top 30 cm of the profile (corresponding to a period from ~500 AD to the present), given the presence of anthropogenic indicators such as *Calluna vulgaris* and cereal pollen grains, indicates fires/burning and human activity (see Behre, 1981). Changes in chemical composition indicate that as well. At the end of the hiatus that occurred about 1890 AD more rapid increases of Pb concentration and $^{208}Pb/^{206}Pb$ ratio were observed. That was also a period of an abrupt increase of PbAR, linked to intensive human activities such as coal combustion, waste incineration, and smelting during the industrial period, and also to the introduction of leaded gasoline. The maximum of lead concentration occurred about 1960 AD as a direct effect of fuel combustion (leaded gasoline) and intensified industry after the Second World War. After 1970, the level of Pb pollution decreased, consistent with the withdrawal of leaded gasoline. From the second half of the 20th century AD, the peatland deteriorated and became overgrown by trees.

The geochemical pattern of the Otrębowskie Brzegi peatland as well as its lead isotopic composition during the 19th and 20th centuries is similar to that of other peatlands from the Orava–Nowy Targ Basin, i.e. Puścizna Krauszowska and Puścizna Mała. The patterns, however, differ in earlier periods. While there was a hiatus in JB-1, disturbances were observed in the other two peatlands (see Fiałkiewicz-Kozieł et al., 2018). In comparison to the Słowińskie Błoto peatland, differences in lead isotopic composition are apparent, especially in the top layers of the profiles, where regional pollution is more pronounced.

Because of a hiatus in the profile, interpretation of the portion between 19 and 16 cm depth (640–1890 AD) should be made with caution. The maxima of heavy metal concentrations were found immediately after the hiatus, which is why we infer that the hiatus was caused by desiccation of the peatland and decomposition of peat.

This work shows the usefulness of peatlands, including poor fens, as natural archives of palaeoenvironmental information, especially in terms of anthropogenic influence. Our results complement research on old mining and metallurgy in Central Europe, indicating peaks in metal production over some time periods, during which production was thought to be low. However, the analyses should be viewed with caution for the portion of the profile corresponding to the hiatus. Lead concentrations and stable lead isotopes are very helpful tools in reconstruction of anthropogenic atmospheric contamination in the past, at both local and regional scales.

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