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# HEAVY METAL ACCUMULATION IN TWO PEAT BOGS FROM SOUTHERN POLAND

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**Abstract**

The dynamic changes in selected heavy metal concentrations were analyzed in two ombrotrophic peat bogs from southern Poland: Puścizna Mała (PK) and Puścizna Krauszowska (PM). The highest contents of Pb and Zn occur at the top of profiles examined: 115.36 mg/kg (PM1), 90.61 mg/kg (PM2), 182.40 mg/kg (PK1), 121.68 mg/kg (PK2) and 127.43 mg/kg (PM1), 89.73 mg/kg (PM2), 170 mg/kg (PK1), 130.4 mg/kg (PK2), respectively. Concentrations of copper are similar to those of local soils varying from 9.4 to 12.8 mg/kg. Cadmium strongly varies with depth, which indicates distinct mobility of this element. Two peaks of elevated Fe concentrations are observed at the top and bottom of the Puścizna Mała profile, while the maximum in Puścizna Krauszowska was at the top of the peat bog. The Ti content distinctly varies with depth and correlates with the ash content ($R^2$ = 0.91–0.99). The strongest and positive correlation is observed between Zn-Pb and Ti-Pb contents. The significant differences of metal concentrations are noted between the profiles, which is probably connected with a rate of peat accumulation and plant composition of the profiles investigated, as well as with their disturbance by human activity.

**Key words:** heavy metals, variability, ombrotrophic peat bog

## INTRODUCTION

Rain-fed bogs are considered to be good and reliable archives of heavy metal pollution (Coggins *et al.* 2006, Givelet *et al.* 2004, Monna *et al.* 2004, Martinez-Cortizas 2002, Mighall *et al.* 2002, Kempter, Frenzel 1999, Vile *et al.* 1999, Shotyk *et al.* 1997, Steinmann, Shotyk 1997). They are also a good collector and filter of air pollutants. However the behavior of metals after deposition in acidic, reducing environment of peat bogs still remains unclear. Some attempts to explain the phenomenon of mobility were conducted by Smieja-Król *et al.* (2010), Grybos *et al.* (2007), Arias *et al.* (2005), Tessier *et al.* (1996), Twardowska, Kyziol (1996), Schwertmann, Murad (1988), Shuman (1988), Schwertmann *et al.* (1986) and Cavallaro and McBride (1984). Smieja-Król and co-authors (2010) described the alteration of elements after deposition in a transitional mire, which is controlled by mineral dissolution-precipitation processes.

Many authors concluded the need of use more than one profile for analysis, but there is a general lack of information about trends of heavy metal concentrations within the same peat bog in Poland. The study of heavy metal pollution in Polish mires was conducted by Bojakowska and Lech (2008). Mean values of 17 elements were established in almost hundred mires throughout Poland using the ICP-MS technique. Minerotrophic mire from the Silesian Upland was analyzed by Fiałkiewicz and co-authors (2008) and Ekonomiuk and co-authors (2006). Some information about heavy metal concentration in a 1-m profile from the Słowińskie Błota ombrotrophic peat bog, (North of Poland) was provided by De Vleeschouwer *et al.* (2009).

The present paper shows the patterns of distributions of metals in four profiles collected from two peat bogs from the same region.

## THE SITE DESCRIPTION

The research was carried out on two ombrotrophic peat bogs (Puścizna Mała and Puścizna Krauszowska) located in southern Poland (the Orawsko-Nowotarska Basin). The distance between these two mires is about 30 km. The total area of Puścizna Mała and Puścizna Krauszowska is 125 and 79 ha, respectively (Łajczak 2006). The exploitation of the first one is closed, while the latter one is still being used for domestic purposes. Puścizna Krauszowska is more destroyed. The vicinity of both mires is drained by numerous ditches, but Puścizna Mała is almost overgrown (Łajczak 2006). The peat bogs are covered by plant communities, which are typical for ombrotrophic mires. More detailed description can be found elsewhere (Kołaczek *et al.* 2010).

**Table 1**

Values of bulk density (g/cm$^3$) in the profiles examined

| Depth (cm) | PM1 | PM2 | PK1 | PK2 |
|---|---|---|---|---|
| 1.5 | 0.07 | 0.06 | 0.05 | 0.09 |
| 3 | 0.06 | 0.08 | 0.04 | 0.15 |
| 4.5 | 0.08 | 0.08 | 0.05 | 0.13 |
| 6 | 0.08 | 0.08 | 0.05 | 0.16 |
| 7.5 | 0.13 | 0.09 | 0.06 | 0.13 |
| 9 | 0.12 | 0.11 | 0.07 | 0.13 |
| 10.5 | 0.07 | 0.18 | 0.07 | 0.14 |
| 12 | 0.16 | 0.16 | 0.07 | 0.12 |
| 13.5 | 0.18 | 0.15 | 0.08 | 0.12 |
| 15 | 0.16 | 0.15 | 0.07 | 0.11 |
| 18 | 0.12 | 0.13 | 0.1 | 0.12 |
| 21 | 0.12 | 0.11 | 0.11 | 0.11 |
| 24 | 0.11 | 0.11 | 0.14 | 0.11 |
| 27 | 0.11 | 0.11 | 0.15 | 0.1 |
| 30 | 0.12 | 0.12 | 0.12 | 0.1 |
| 33 | 0.1 | 0.12 | 0.12 | 0.09 |
| 36 | 0.11 | 0.09 | 0.14 | 0.08 |
| 39 | 0.11 | 0.09 | 0.14 | 0.09 |
| 42 | 0.12 | 0.1 | 0.13 | 0.08 |
| 45 | 0.11 | 0.09 | 0.13 | 0.08 |
| 48 | 0.12 | 0.09 | 0.14 | 0.07 |
| 51 | 0.1 | 0.09 | 0.12 | 0.08 |
| 54 | 0.1 | 0.09 | 0.11 | 0.1 |
| 57 | 0.1 | 0.1 | 0.09 | 0.07 |
| 60 | 0.1 | 0.1 | 0.09 | 0.09 |
| 63 | 0.1 | 0.1 | 0.08 | 0.08 |
| 66 | 0.1 | 0.1 | 0.09 | 0.06 |
| 69 | 0.09 | 0.08 | 0.05 | 0.07 |
| 72 | 0.09 | 0.08 | 0.09 | 0.06 |
| 75 | 0.09 | 0.08 | 0.1 | 0.07 |
| 78 | 0.1 | 0.08 | 0.11 | 0.05 |
| 81 | 0.1 | 0.1 | 0.12 | 0.06 |
| 84 | 0.11 | 0.12 | 0.11 | 0.05 |
| 87 | 0.11 | 0.11 | 0.11 | 0.05 |
| 90 | 0.11 | 0.11 | 0.1 | |
| 93 | 0.13 | 0.11 | 0.08 | |
| 96 | 0.13 | 0.11 | 0.08 | |
| 99 | 0.13 | 0.13 | 0.09 | |
| 102 | 0.11 | 0.13 | | |
| 105 | 0.09 | 0.12 | | |
| 108 | 0.09 | 0.11 | | |
| 111 | 0.09 | 0.09 | | |
| 114 | 0.09 | 0.09 | | |
| 117 | 0.09 | 0.09 | | |
| 120 | 0.12 | 0.08 | | |
| 123 | | 0.08 | | |

## MATERIAL AND METHODS

Three monoliths per mire (PM0, PM1, PM2, PK0, PK1, PK2) were collected and stored in a wooden box (Tobolski 1999) and Wardenaar corer (Wardenaar 1987). A detailed study and chronology of PM0 and PK0 will be published in a separate paper (Fiałkiewicz-Kozieł and co-authors, in prep.). The core samples for analysis were obtained after removal of the top portion of fresh peat. The cores were carefully sliced into 1.5 cm (first 15 cm) and 3 cm pieces using stainless steel knife. The air-dried samples were re-dried at a temperature of 105°C prior to ashing at 460°C and acid digestion in Teflon Savillex beakers. Metal extraction consisted of two steps. First, samples were treated with 65% $HNO_3$ and 45% HF for 48 h, in 130°C, then evaporated and treated with concentrated HCl in 90°C for 24 h. Total concentrations of lead, zinc, cadmium, copper, iron, calcium and titanium were assessed by the ICP-AOS technique. Bulk density was determined using fresh material collected with a 5 cm$^3$ cylinder. The ash content was expressed as a percentage of dry (105°C) weight of peat sample. All measurements were carried out twice. The results of the ICP-AOS measurements were calibrated with a standard material of low ash peat (Yafa 2004). Mean values with extended uncertainties (coverage factor of 2) were then calculated. Inorganic particles in the peat samples were examined using the Philips XL30 environmental scanning electron microscopy coupled with energy dispersive spectroscopy (ESEM/EDS). The backscattered electron detector (BSE) was used for particles imaging.

## RESULTS AND DISCUSSION

### Ash content, bulk density and mineralogy

Bulk density (Table 1) is an important property of peat, which is used for assessing rates of heavy metals accumulation (Givelet *et al.* 2004). Both investigated peat bogs are characterized by bulk density values in the range of 0.06–0.18 g/cm$^3$, which are typical for ombrotrophic peat bogs (De Vleeschouwer *et al.* 2009, Kempter, Frenzel 1999, Martinez-Cortizas *et al.* 1997, Shotyk 1996). The strongest variations are observed at the top of profiles, where density correlates with ash content.

The average values of ash content range from 0.8% to 2% and are considered as typical for *Sphagnum*-bogs. A distinct increase up to 10.2%, 9.1%, 6.5% and 9.1% is observed in the upper layers of the monoliths (Fig. 1). The maximum ash values correlate with higher density and heavy metal content. The mineralogical analysis proved the presence of spheroidal, often porous particles (Fig. 2) of anthropogenic origin in the upper peat layers. The fly-ash particles are composed of Si and Al with lesser amount of K, Mg, Na, Ca and Fe. The high content of spheroidal alumino- silicates together with often found aggregates of such particles (Fig. 3) indicates peat pollution from coal burning processes. Görres and Frenzel (1997) also described the corre- lation between ash value, titanium and lead content as a result of increased air pollution due to human activity. The investigations using SEM also revealed the presence of detrital minerals, like quartz, feldspars, clays as well as lesser amounts of Ti oxides, ilmenite,

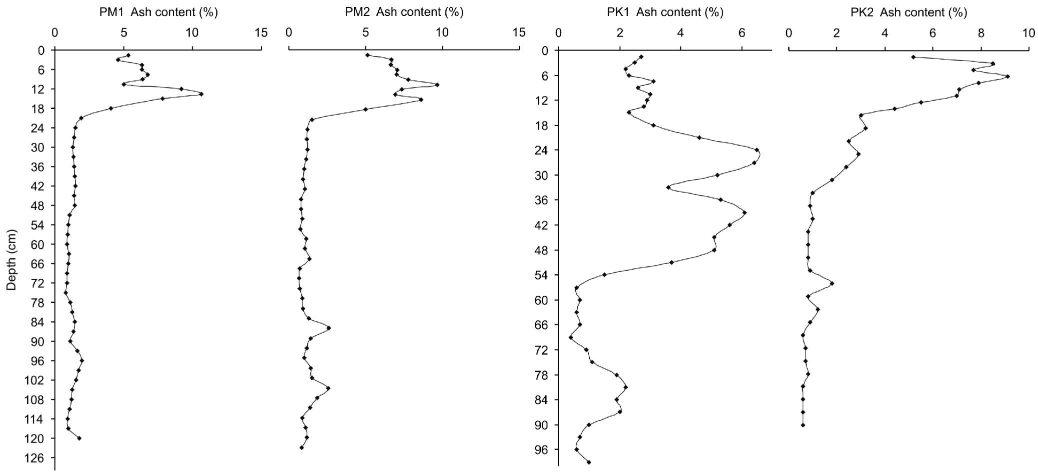


**Fig. 1.** Changes in ash content along depth in the profiles examined.

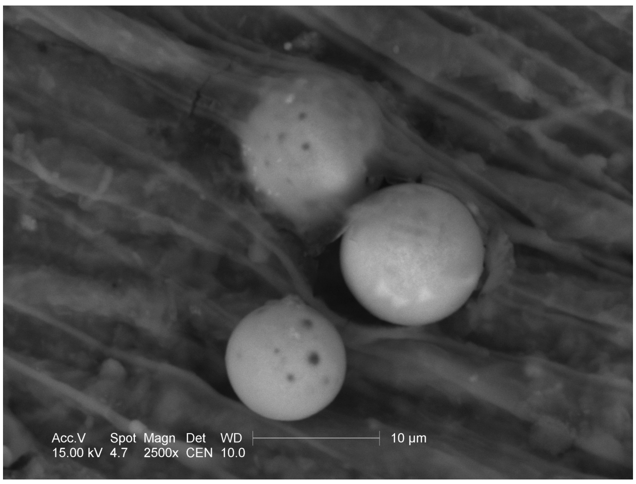


**Fig. 2.** Spheroidal aluminosilicates. SEM (BSE).

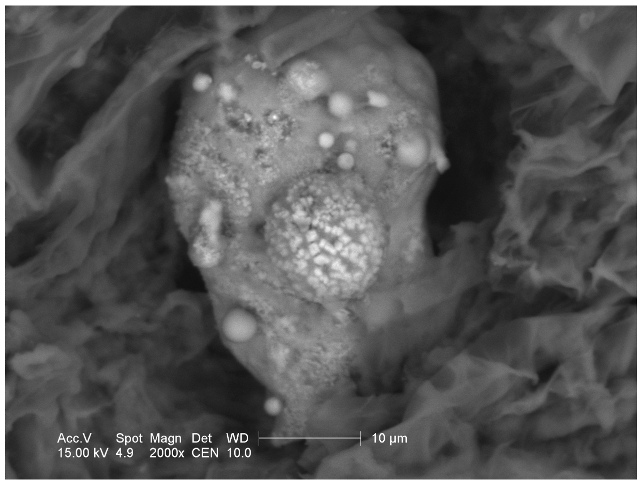


**Fig. 3.** Aluminosilicate aggregate of anthropogenic origin. SEM (BSE).

REE phosphates and zircon. Particles hosting heavy metals, of both geogenic and anthropogenic origin, were rare.

## Dynamics of heavy metal concentration

The results of total concentrations of Pb, Zn, Cu, Cd, Ti, Fe, Ca are presented in Figs 4–10. The general trend of decreasing values with depth is noticed, which is in good agreement with the results from other European countries (*i.e.* Bindler 2006, Martinez-Cortizas *et al.* 2002, Shotyk *et al.* 1996). Lead is known to be immobile in peat bogs. It is a reliable indicator of human impact (Bindler 2006, Shotyk, Le Roux 2005, Shotyk 1998, MacKenzie *et al.* 1998, Shotyk 1996). The highest content of lead, varying from 90.61 to 189.81 mg/kg, was observed at the top of profiles (Fig. 4). In the $Pb^{210}$-dated Puścizna Rękowiańska mire located 3 km of Puścizna Mała the highest Pb concentration was 112 mg/kg, almost four times higher than that in soils from the surrounding area (Holynska *et al.* 1998). De Vleeschouwer *et al.* (2009) recorded 204 mg/kg in the Słowińskie Błota peat bog from northern Poland. It is interesting to note that the maximum values strongly differ within the investigated peat bogs. The highest content is observed in PK1. It is the most distinct profile. The observed changes could be linked to possible disturbance of this profile and redistribution of elements.

Differences in copper concentrations between the profiles are insignificant (maximum content varies from 9.4 to 12.8 mg/kg). The surprisingly low Cu levels in PM and PK are similar to those in local soils in spite of the copper mining and smelting in this region during 16th century (Jost 2004). No distinct variations in Cu concentrations occur with depth (Fig. 5). In the other investigated Polish peat bogs, the geochemical background amounting to 9 and 18.58 mg/kg was established (De Vleeschouwer *et al.* 2009, Holynska *et al.* 1998). The behavior of copper in an acidic peat environment is not well understood, and additionally Cu distribution pattern can be influenced by plants, as this metal is an essential microelement for their growth.

Zinc is also a common element of the Earth's crust, which is actively used by plants, animals and people to support physiological processes. In the described profiles an increase of Zn concentration is observed in the upper peat layer

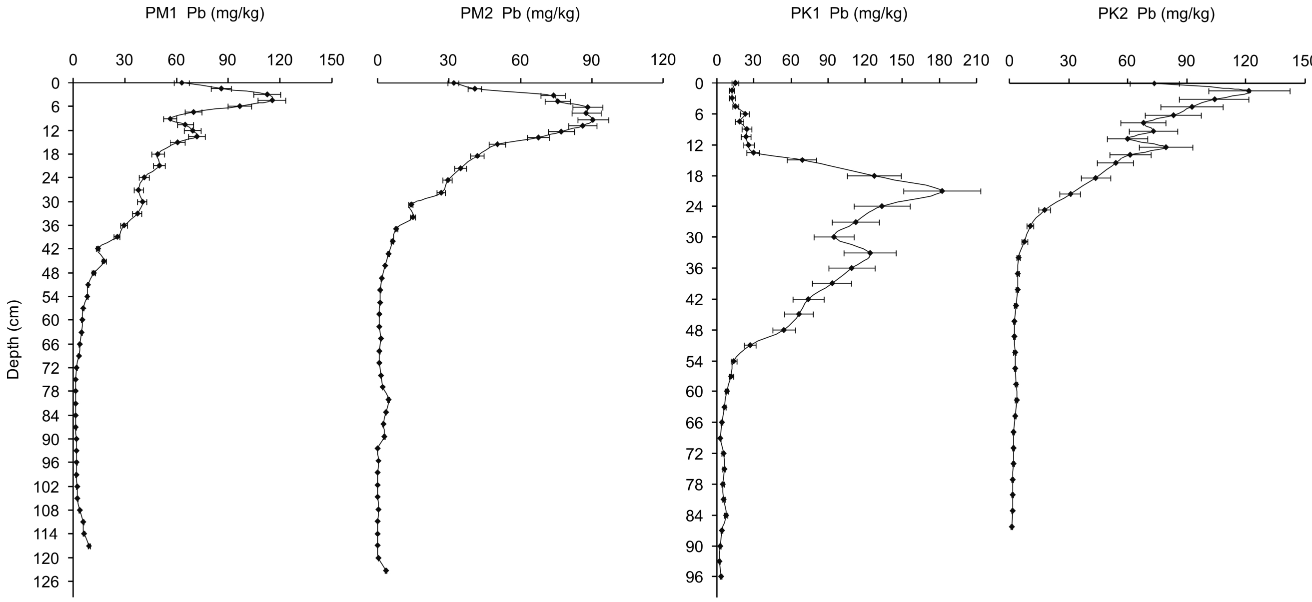


**Fig. 4.** Changes in concentration of lead along depth in the profiles examined.

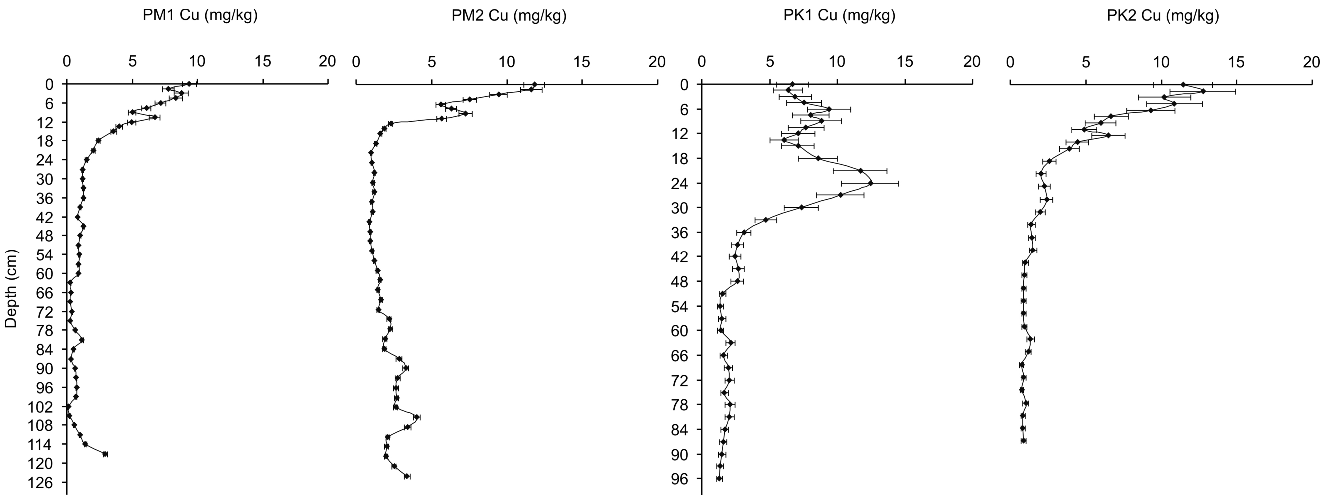


**Fig. 5.** Changes in concentration of copper along depth in the profiles examined.

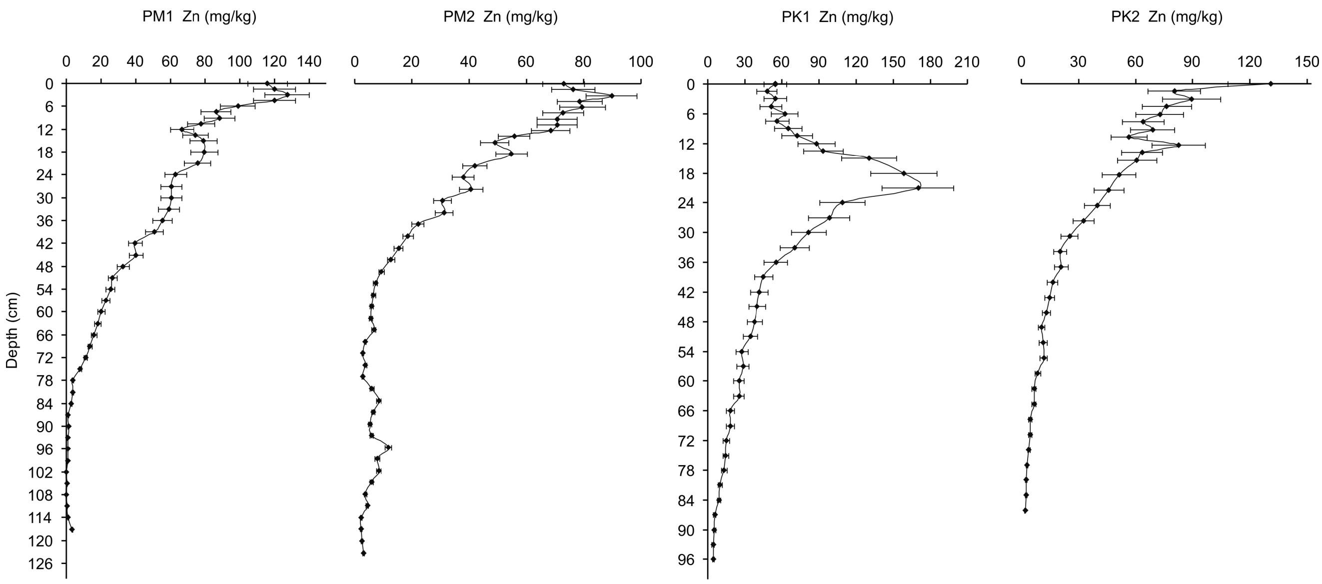


**Fig. 6.** Changes in concentration of zinc along depth in the profiles examined.

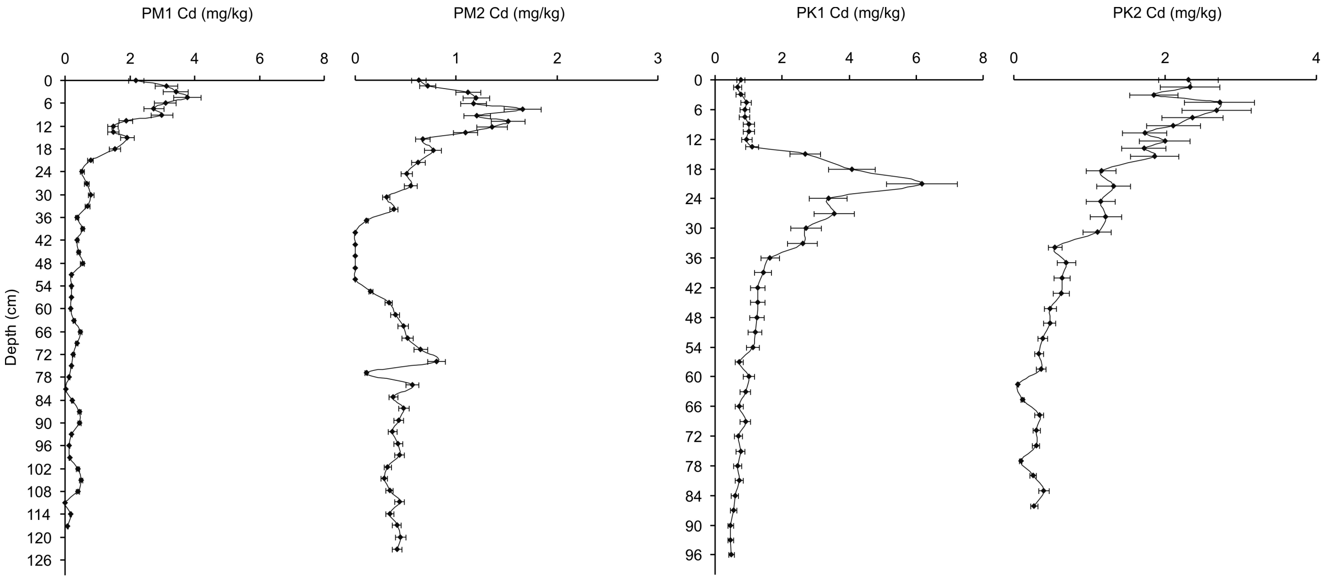


**Fig. 7.** Changes in concentration of cadmium along depth in the profiles examined.

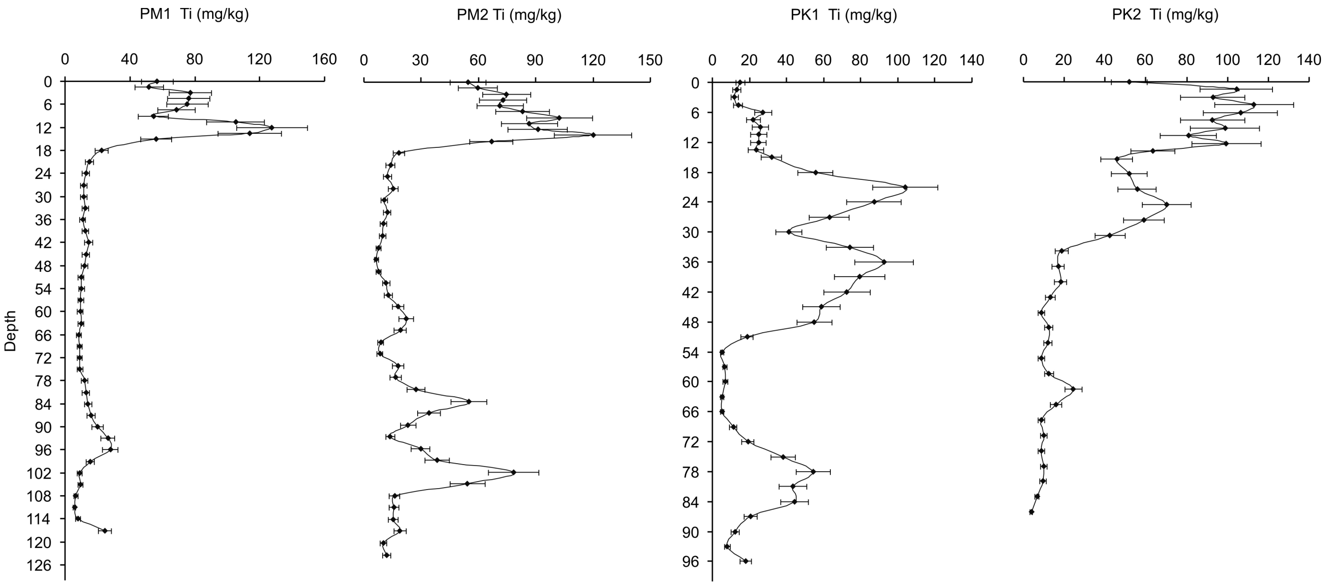


**Fig. 8.** Changes in concentration of titanium with depth in the profiles examined.

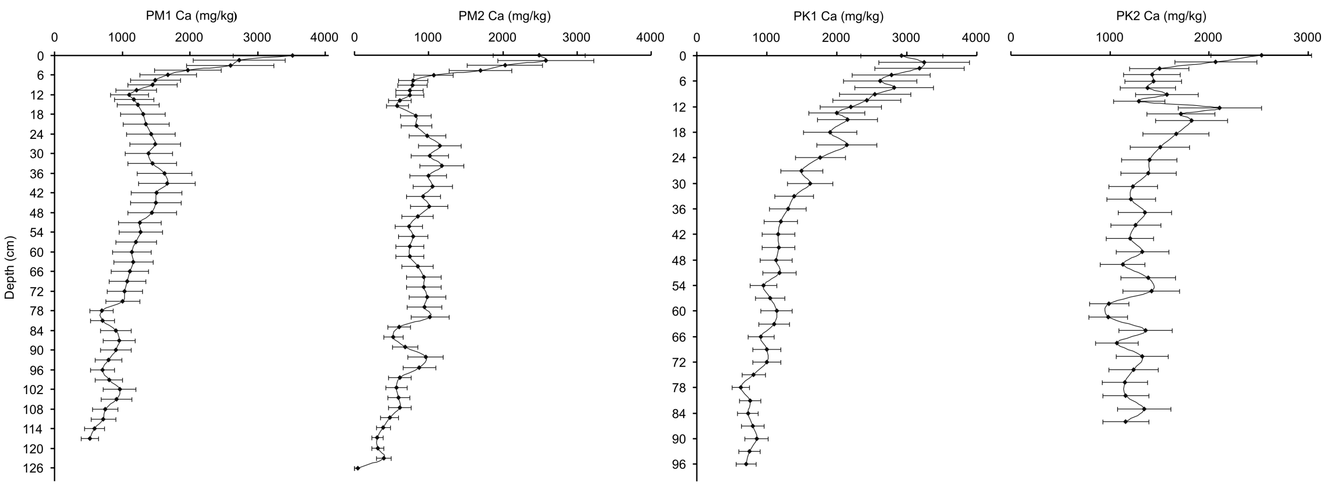


**Fig. 9.** Changes in concentration of calcium along depth in the profiles examined.

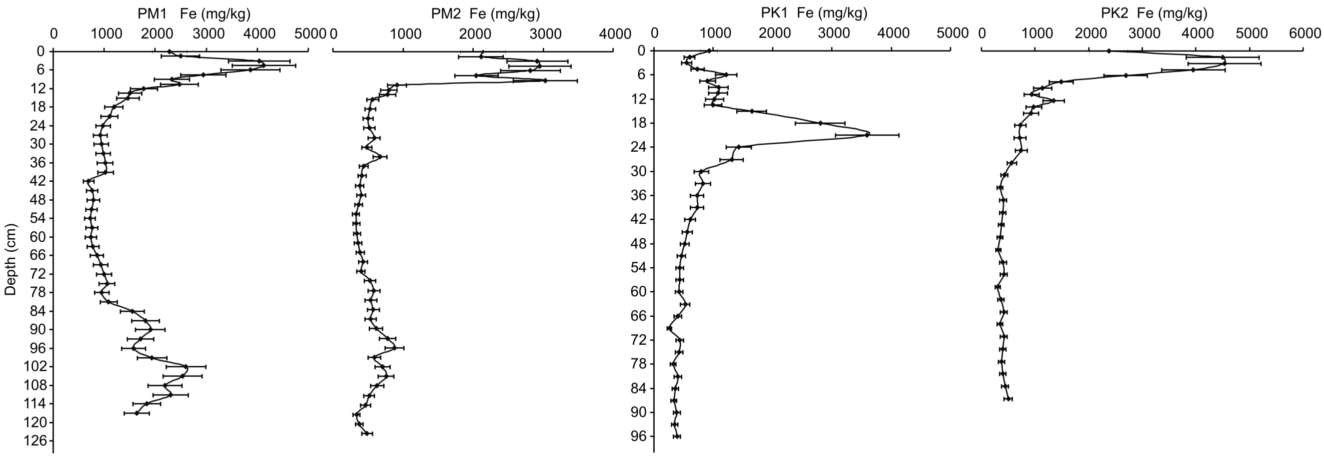


**Fig. 10.** Changes in concentration of iron along depth in the profiles examined.

(Fig. 6). The strong correlation between zinc and lead was noticed. The Zn concentrations obtained for PM and PK (89.73–127.43 mg/kg and 130.94–170 mg/kg, respectively) are higher then those in local soils (26–59 mg/kg; Holynska *et al.* 1998). Slightly higher maximum values (200 mg/kg and 170 mg/kg, respectively) were estimated for Puścizna Rękowiańska and Słowińskie Błota (De Vleeschouwer *et al.* 2009, Holynska *et al.* 1998). Differences in the maximum values could be explained by the fact that zinc is one of the most mobile and soluble element, weakly bound to organic matter and easily assimilated by plants. The degree of assimilation is linked to plant species (Kabata-Pendias, Pendias 1999).

Information about cadmium in peat bogs is scarce. An average content of cadmium in soils of Poland vary from 0.03 to 0.22 mg/kg (Kabata-Pendias, Pendias 1999). The highest Cd concentration (6.18 mg/kg) is observed at the interval of 21–24 cm in PK1, what may indicate some disturbances within this profile. In PM1, PM2, PK2 values varied from 1.66 to 3.78 mg/kg (Fig. 5). The similar value (1.9 mg/kg) was observed in an Irish peat bog (Coggins *et al.* 2006) and 1.5 mg/kg in a Spanish one (Martinez-Cortizas *et al.* 1997).

**Table 2**

Correlation between selected heavy metals and peat parameters. All values are significant at 0.05 probability level

| | PM1 | PM2 | PK1 | PK2 |
|---|---|---|---|---|
| Ash-Ti | 0.99 | 0.93 | 0.91 | 0.93 |
| Ash-Fe | 0.60 | 0.80 | 0.60 | 0.88 |
| Ash-Pb | 0.81 | 0.92 | 0.90 | 0.95 |
| Ash-Zn | 0.69 | 0.86 | 0.67 | 0.85 |
| Fe-Ti | 0.57 | 0.65 | 0.50 | 0.76 |
| Fe-Pb | 0.63 | 0.79 | 0.73 | 0.88 |
| Fe-Zn | 0.45 | 0.79 | 0.92 | 0.75 |
| Ti-Pb | 0.79 | 0.79 | 0.86 | 0.91 |
| Ti-Zn | 0.66 | 0.71 | 0.49 | 0.84 |
| Zn-Pb | 0.95 | 0.93 | 0.77 | 0.91 |
| Ash-D | 0.41 | 0.44 | 0.63 | 0.89 |

Cadmium is a very mobile element, weakly bound to organic matter (Vile *et al.* 1999, Krosshavn *et al.* 1993). Coggins *et al.* (2006) described the highest enrichment of cadmium at the surface of peat profiles. The similar phenomenon was noticed by Espi *et al.* (1997) and Steinnes (1997). The observed variation with depth in the monoliths sampled indicate mobility of this element in the peat bogs examined.

The titanium concentration strongly correlates with ash content (Table 2). The highest values (127.60 mg/kg) occur at a depth of 0–18 cm in PM1. In PM2 increases of concentrations are observed at a depth of 0–18 cm, 78–90 cm and 93–105 cm (Fig. 8) and are in the range of 6.56–119.97 mg/kg. The highest Ti concentrations are recorded in PK1 at 21–24 cm (103.92 mg/kg) and in PK2 at 4.5–6 cm (113.03 mg/kg) (Fig. 8). Titanium is an inferior, conservative element of the Earth's crust, and its concentration varies from 0.03 to 1.4% (Kabata-Pendias, Pendias 1999). Compared to other peat bogs, the mires examined exhibit lower Ti levels (103.03 to 127.60 mg/kg). In Puścizna Rękowiańska the highest concentration reaches 500 mg/kg, whereas the ash content exceeds 15% (Holynska *et al.* 1998); the higher ash value can be explained by occurrence of peat bog fires. For comparison, 374 mg/kg was found in Słowińskie Błota from northern Poland (De Vleeschouwer *et al.* 2009).

Calcium is a macroelement needed for all organisms. A calcium-to-magnesium ratio is used to assess trophic status of mires. The investigated profiles are characterized by concentrations in the range of 2526–3515 mg/kg. The content of calcium in Puścizna Rękowiańska is lower and equals to 1700 mg/kg (Holynska *et al.* 1998). All profiles examined exhibit similar trends of changes in calcium content along depth (Fig. 9). An increase of concentration at the surface is connected with active plant assimilation.

The concentrations of iron range from 694 to 4129 mg/kg. The highest values were observed at the top and bottom of profile PM1 (Fig. 10). In PM2 and PK2 the maximum levels (3030 mg/kg and 4538 mg/kg) decrease with depth. The highest content of iron in PK1 (3596 mg/kg) is noticed at the interval of 15–30 cm (Fig. 10). Iron is a main constituent of the Earth's crust with a mean concentration of 5%. It is known that iron can be used together with calcium to assess the trophic status of mires. Ombrotrophic peat bogs are characterized by an average content of 2000 mg/kg. In Puścizna Mała and Puścizna Krauszowska the maximum values are in the range of 2955–4539 mg/kg. The mineralogical study exhibits an occurrence of anthropogenic particles of iron oxide, both spheroidal (Fig. 11) and of irregular morphology in the peat layer showing higher iron concentration, what indicates possible pollution by industry. Oval particles of iron oxides are characterized by high magnetic susceptibility (Strzyszcz, Magiera 2001). In some parts of the investigated profiles with a higher ash content, concentration of iron as well as concentration of lead and zinc may show higher magnetic susceptibility.

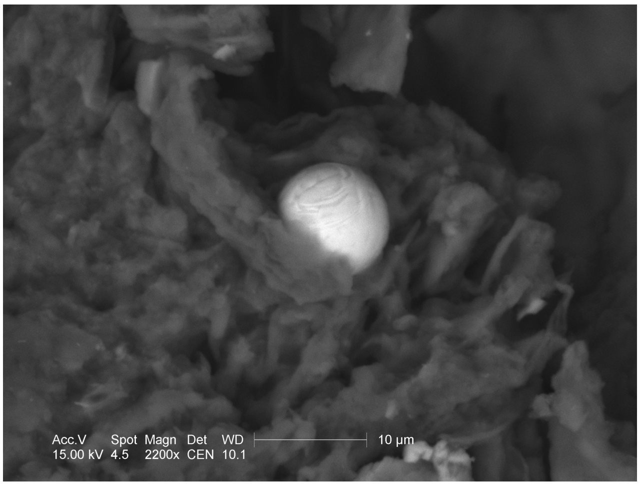


**Fig. 11.** Anthropogenic particle of iron oxide. SEM (BSE).

## Variability in concentration of heavy metals within peat bogs

Dynamics of heavy metal variation with depth in PM and PK is generally similar. However, concentrations of heavy metals described above strongly differ between the investigated mires and profiles. Many authors have studied variability between hummocks and hollows (*i.e.* Norton *et al.* 1997, Shotyk 1996, Jones, Hao 1993). All the profiles were placed within hummocks to obtain comparable conditions. The observed variability is probably linked to an irregular growth of peat bog and differences in plant composition. Olid and co-authors (2010) also investigated profiles from the same region (Galicia, NW Iberian Peninsula) and explain observed variability as spatial one. They also indicated the influence of degree of decomposition, compaction of mire and element uptake on diverse metal concentrations. Profile PK1 from Puścizna Krauszowska strongly differs from the others. The analysis of ash content and mineralogical study indicate possible perturbation of this profile.

## CONCLUSIONS

Strong pollution of peat bogs by lead, zinc and cadmium is observed comparing to local soils. The general trend of increased concentrations in the upper parts of the investigated monoliths is noticed. PK1 is the most distinct profile, which indicates a possible disturbance of this profile and remobilization of some elements. Significant differences in metal concentrations are observed between the profiles, linked to the rate of peat accumulation, composition of plants in peat bog and exploitation by humans.


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