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SELECTED GEOCHEMICAL CRITERIA IN MIRE PROFILES OF PORĘBY WOJSŁAWSKIE (SANDOMIERZ BASIN, POLAND SE)

Abstract. The geochemical analysis of biogenic sediments was used to reconstruct environmental conditions and the impact of human activity from a small mire geo-system in the Sandomierz Basin (Poland SE). Changes in the nature of selected geochemical indicators show a significant impact on the transformation of the mire during the early stages of human activity. It is reflected in the geochemical record by means of a high proportion of heavy metals – cadmium, lead and copper. Evident variability of main geochemical components concentration is also visible in a vertical record of analysed cores. This is a consequence of the sedimentary basin asymmetric configuration and the ensuing variable biogenic sedimentary succession.

The geochemical analysis is one of basic test methods for examination of biogenic sediments deposited in mire [6]. The chemical composition of biogenic sediments is contingent upon numerous factors, therefore mire ecosystems constitute an excellent source of both paleo-environmental and human activity data [1–3, 7, 9, 18]. Human activity, particularly industrial, leads to an increase in the concentration of heavy metals in the environment. Industrial human activity (atmospheric dust precipitation, wastewater run-off), transport, and agriculture are the sources of biogenic sediments contamination with heavy metals. Peatlands are characterised by the particularly high concentration of pollutants. The content of trace metals, especially lead, copper, zinc or cadmium in mire may be regarded as an indicator of intensity of anthropogenic impact on the local environment or, on the other hand, as an indicator of environmental purity.

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The analysis of the vertical variability of Fe:Mn and Cu:Zn indicators allows for identification of changes in oxidative-reductive conditions prevailing during sediment accumulation [5, 6, 19, 20]. Over the recent decades, geochemical indicators have become increasingly widespread in the geo-system study, being applied to reconstruct changes in hydrological and environmental conditions[10].

The aim of the work is to reconstruct changes in the conditions of the natural environment and anthropopression in the western part of the Sandomierz Basin (Polish SE), based on the geochemical analysis.

MATERIALS AND METHODS

The research was conducted in the Poręby Wojsławskie mire geo-system (PW) (γ 50o16’33.56”N; λ 21o30’18.76”E; area 7.9 ha, 185 m a.s.l.), filling interdunal, landlocked depression area, located in the western part of the Sandomierz Basin macro-region [13] (Fig. 1).

The mire is situated within the area of the Pleistocene fluvial terrace of the Wisłoka Valley, located 10–15 m above the level of the river. It is mainly composed of sandy and sand-gravely deposits. Main elements of the surface relief are dunes, aeolian sands field sand and deflationary and/or interdunal depressions. Landlocked depressions (interdunal depressions) that separate dunes are often filled with mire of 1–3 m in thickness. Thickness of organic deposits filling the examined peatland does not exceed 2.5 m. The mire consists of sphagnum peats, sphagnum-sedge and sedge peats.

According to the Polish Soil Classification [23] the analysed mire core PW-1 contains shallow sapric peat soil (Hyperdystric Drainic Sapric Histosol). PW-8 core, however, typically consists of sapric peat soil (Hyperdystric Murshic Sapric Histosol (Hyperorganic)) [24].

At present the mire is of ombrotrophic profile. Precipitation is crucial for water supply. The system of water supply and drainage is, however, modified by human activity. A detailed description may be found in the following paper [8].

The geochemical analysis was performed for samples from PW-1 and PW-8 cores (at 5 cm interval), previously dried at 105ºC. Chromium, zinc, cadmium, manganese, copper, and lead were determined by atomic absorption spectroscopy by means of Perkin Elmer AAS 3300 analyser, after mineralization with mixture of HCl and HNO_3 acids according to the volume ratio of 3:1 [12]. Element concentrations approximated to the total content and were converted into the amount in dry matter.

The geochemical analyses were verified by reference material SO-2 and SO-4 from the Canada Centre for Mineral and Energy Technology. Test precision for SO-2 amounted to the following percentage: Fe (2.1%), Mn (1.8%), Cu (2.2%), Zn (2.9%), while the SO-4: Fe (4 1%), Mn (3.8%), Cu (3.7%) and

Zn (4.4%) in relation to the recommended values. Data on the pH in water and organic matter content quoted in [8] was used in the article.

The pH was determined in water, potentiometrically [16], and organic matter content – on the basis of loss during calcination at 550 ° C [4].

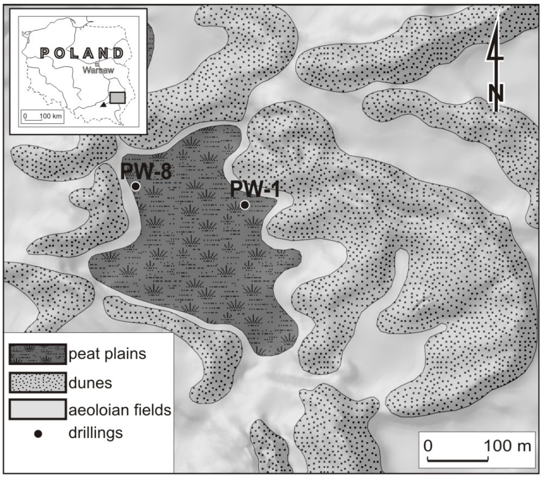

Fig. 1. Location of the Poręby Wojsławskie (PW) site: – in Poland; – geomorphological situation.

RESULTS AND DISCUSSION

Biogenic formations building mire deposit achieve maximum thickness of 250 cm (in the western part of the geo-system). Distinct variability in the concentration of the main geochemical components in the vertical record of both analysed cores is visible. This is a consequence of sedimentary basin asymmetric configuration and the ensuing variable biogenic sedimentary succession. On the basis of the figures resulting from the geochemical analyses, the following geochemical zones may be distinguished in both cores (except for bedrock) (Fig. 2):

PW-1 core

PW-1/I (65–72 cm) zone. This zone is the record of the initial stage of biogenic sedimentation in the eastern part of the basin. The content of organic matter rises significantly and reaches 90.20%. The pH value is low and ranges from 3.85 to 3.64. The iron content is low and reaches the value of 0.46 $g \cdot kg^{-1}$, which is the lowest in the whole core. In this part of the core the lowest values of manganese (2.90 $mg \cdot kg^{-1}$), and lead (1.85 $mg \cdot kg^{-1}$) are reached as well. In the lower part of the zone very low concentrations of copper (0.98 $mg \cdot kg^{-1}$), zinc (3.85 $mg \cdot kg^{-1}$), chromium (5.21 $mg \cdot kg^{-1}$) and cadmium content, below the limit of quantification, were reported.

PW-1/II (44–65 cm) zone. The increase in the organic matter content (up to 96.36%) is noted. The pH reaches the value of 4.04. A significant increase in iron, copper, zinc and cadmium content is noticed, together with the highest value of chromium content in the core observed in the lower part of the zone (20.83 $mg \cdot kg^{-1}$). A significant content of organic matter and high values of redox indicators Fe:Mn and Cu:Zn are the evidence of biogenic sediment accumulation in terms of reduction, at high water level [5, 10, 19, 20].

PW-1/III (33–44 cm) zone. A significant decrease in the content of organic matter (up to 86.31%) with concurrent increase in ash content (up to 13.69%) is observed; this suggests delivery of mineral origin material (water or Aeolian transport) to the basin. In this part of the core, pH value and the content of manganese and cadmium are stabilising. Lead content increases significantly in the zone. Copper and Cu:Zn indicators show a downward trend.

PW-1/IV (10–33 cm) zone. Repeated increase in organic matter content is recorded up to the highest values in the whole core (96.93%). Cadmium content clearly increases up to the value of 1.28 $mg \cdot kg^{-1}$. The ratio of Fe:Mn in this zone shows a downward tendency, which may be indicative of the change in the sedimentation conditions to become more aerobic [20].

PW-1/V (5–10 cm) zone. This zone is characterised by a visible decrease in organic matter content (down to 81.26%). Iron (1.32 $mg \cdot kg^{-1}$), copper (14.11 $mg \cdot kg^{-1}$), lead (77.98 $mg \cdot kg^{-1}$) ,and cadmium (1.47 $mg \cdot kg^{-1}$) have reached the highest concentration values in the whole core.

PW-1/VI (0–5 cm) zone. This zone is associated with the modern stage of development of the mire. Organic matter content is relatively high (92.01%); the highest concentration values in whole core are those of manganese (30.41 $mg \cdot kg^{-1}$) and zinc (31.54 $mg \cdot kg^{-1}$). Moreover, high content of lead is observed. In comparison to the lower PW-1/V zone, the content of iron, copper, and cadmium decreases. Fe:Mn and Cu:Zn indicators also show lower values.

PW-8 core

PW-8/I (215–250 cm) zone. The following zone designates the beginning of biogenic sedimentation throughout the basin, first in limnic terms, next in paludic terms. The content of organic matter in the zone visibly increases (up to 98.21%). The pH value decreases from 4.57 to 4.17. The content of iron and manganese, as well as copper and zinc, on the other hand, increases. Considerably high chromium content (16.25 $mg \cdot kg^{-1}$) is additionally noted in the zone.

PW-8/II (200–215 cm) zone. The organic matter content decreases with concurrent increase in ash content, which may be explained by an increased supply of allogenic mineral. Maximum content of copper (15.64 mg · kg-1) and zinc (18.71 mg · kg-1) is reported in the analysed core. There is a visible increase in the content of manganese, iron, lead, and chromium. The values of Fe:Mn and Cu:Zn ratios also grow.

PW-8/III (175–200 cm) zone. Progressive growth of paludification processes expressed in terms of a high content of organic matter (up to 99.31%) at low pH values is documented. The content of iron, manganese, and lead also shows a downward tendency. Chrome, on the other hand, reaches the highest value in the analysed core: 22.92 mg·kg^{-1}. Cu:Zn ratio values show an upward tendency, while Fe:Mn ratio values are variable.

PW-8/IV (155–175 cm) zone. Separated on the basis of a visible decline in the percentage share of organic matter (88.69%). The pH value significantly decreases. The content of iron, manganese, zinc, lead, and chromium visibly increases. Fe:Mn and Cu:Zn ratio values show a downward tendency.

PW-8/V (130–155 cm) zone. Organic matter content in this zone is high, that is generally above 98%. PH value rises significantly up to 3.84. Manganese reaches the highest content (18.02 mg·kg^{-1}) in the analysed core. A visible decline in iron content value is observed. There is a discernible increase in the content of cadmium and chromium.

PW-8/VI (115–130 cm) zone. Organic matter content decreases within this zone to the value of 82.74%. The pH value also decreases whereas the percentage share of manganese, chromium ,and iron grows.

PW-8/VII (106–115 cm) zone. There is a repeated growth in the organic matter content (up to 98.55%). The content of manganese, copper, zinc, lead, and chromium also increases whereas the iron content decreases.

PW-8/VIII (92–106 cm) zone. Organic matter content in the zone is relatively high, however, at the depth of 95 cm it rapidly decreases to 83.62%. At the same depth iron reaches its maximum content in the analysed core (2.22 g·kg^{-1}). What is more, the highest lead content in the core has been furthermore reported in this zone (45.45 mg · kg1). In contrast, the content of manganese, copper, zinc, and chromium significantly decreases. Fe:Mn and Cu:Zn indicators reach the highest values in this zone of the core.

PW-8/IX (48–92 cm) zone. The zone includes a layer of peat with a high content of organic matter (96.65–98.52%). The pH value in the layer significantly decreases. In the upper part of this layer, manganese, zinc, and lead content rapidly increases.

PW-8/X (42–48 cm) zone. A decline in organic matter content is visible in this zone. The content of iron and cadmium grows. The content of manganese, zinc, and lead rapidly decreases. The values of Fe:Mn and Cu:Zn, on the other hand, rise.

PW-8/X(25–42 cm) zone. High content of organic matter remains. PH reaches the value of 3.06, that is the lowest in the whole core. The iron content decreases to the lowest value in the analysed core, that is 0.19 g·kg^{1}. The values of Fe:Mn and Cu:Zn indicators show a downward tendency.

PW-8/XII (5–25 cm) zone. This zone is a geochemical record of a contemporary stage of mire development. The content of organic matter decreases from 98.18% to 92.14%. The decline in the organic matter content may be caused by rotting process accompanying groundwater level decrease. In the subsurface zone the increase in heavy metals content is observed, especially in the case of cadmium (1.37 $mg \cdot kg^{-1}$ – the highest value in the analysed core).

STRATIGRAPHIC DIVERSIFICATION OF SELECTED GEOCHEMICAL PARAMETERS

Organic matter. In the case of PW-1 core a high content of organic matter remains down to the depth of 65 cm (from 81.26% to 96.93%). Below this depth the content of the component visibly decreases. In the PW-8 core, however, a high content of organic matter extends to the depth of 242 cm (from 55.65% to 99.31%). A sharp decline and increase in ash content (up to 97.27% in mineral matrix) is observed below that point.

The higher organic matter content, with concurrent growth in the percentage share of iron in relation to manganese and copper to zinc, indicates phases of low water level (Wojciechowski, 2000). The increase in the mineral material (ash) content is the evidence of increased erosion due to climate change or anthropogenic deforestation [14, 17]. The loss in organic matter may also be the result of drainage and development of rotting process [15].

PW geo-system is characterised by high dynamics of changes in the organic matter content pH. It is an important geochemical mire parameter as it affects the intensity of biological material decay and the formation of humus compounds. In PW-1 core down to the depth of 72 cm, little variation of pH (pH from 3.42 to 4.04, Fig. 2) has been observed. Below this depth, i.e. in mineral matrix pH, it increases up to the value of 5.20. In PW-8 core pH values are kept within the range of 3.06 – 4.77 and increase with depth.

Iron and manganese. These elements are characterised by varying mobility depending on prevailing in aqueous environment redox conditions [5, 6, 20].

Heavy metals. High concentration of heavy metals particularly in uppermost sediment layers may be indicative of anthropogenic environmental pollution [6, 10, 20–22]. The average total content of heavy metals in PW-1 core is composed in the following series: Pb>Zn>Cr>Cu>Cd, taking the respective values: 21.21 $mg \cdot kg^{-1}$ 12.96 $mg \cdot kg^{-1}$, 9.32 $mg \cdot kg^{-1}$, 4.65 $mg \cdot kg^{-1}$ and 0.71 $mg \cdot kg^{-1}$. In PW-8 core the average total content of heavy metals is composed in the following series: Cr>Zn>Pb>Cu>Cd, reaching respective values: 9.41 $mg \cdot kg^{-1}$, 8.05 $mg \cdot kg^{-1}$, 5.64 $mg \cdot kg^{-1}$, 3.71 $mg \cdot kg^{-1}$ and 0.10 $mg \cdot kg^{-1}$.

The maximum concentration of heavy metals Cu, Zn, Pb, and Cd in PW-1 core has been observed in the uppermost part (Fig. 2). Such a distribution of heavy metal content may indicate the impact of contemporary anthropic pressure on the geochemistry of sediments filling the analysed mire. In addition, the rate of accumulation of the peat and the peat-forming plants composition may affect the heavy metal content [11]. Distribution of heavy metal content in PW-8 core shows no trends observed in the PW-1 profile, except for cadmium.

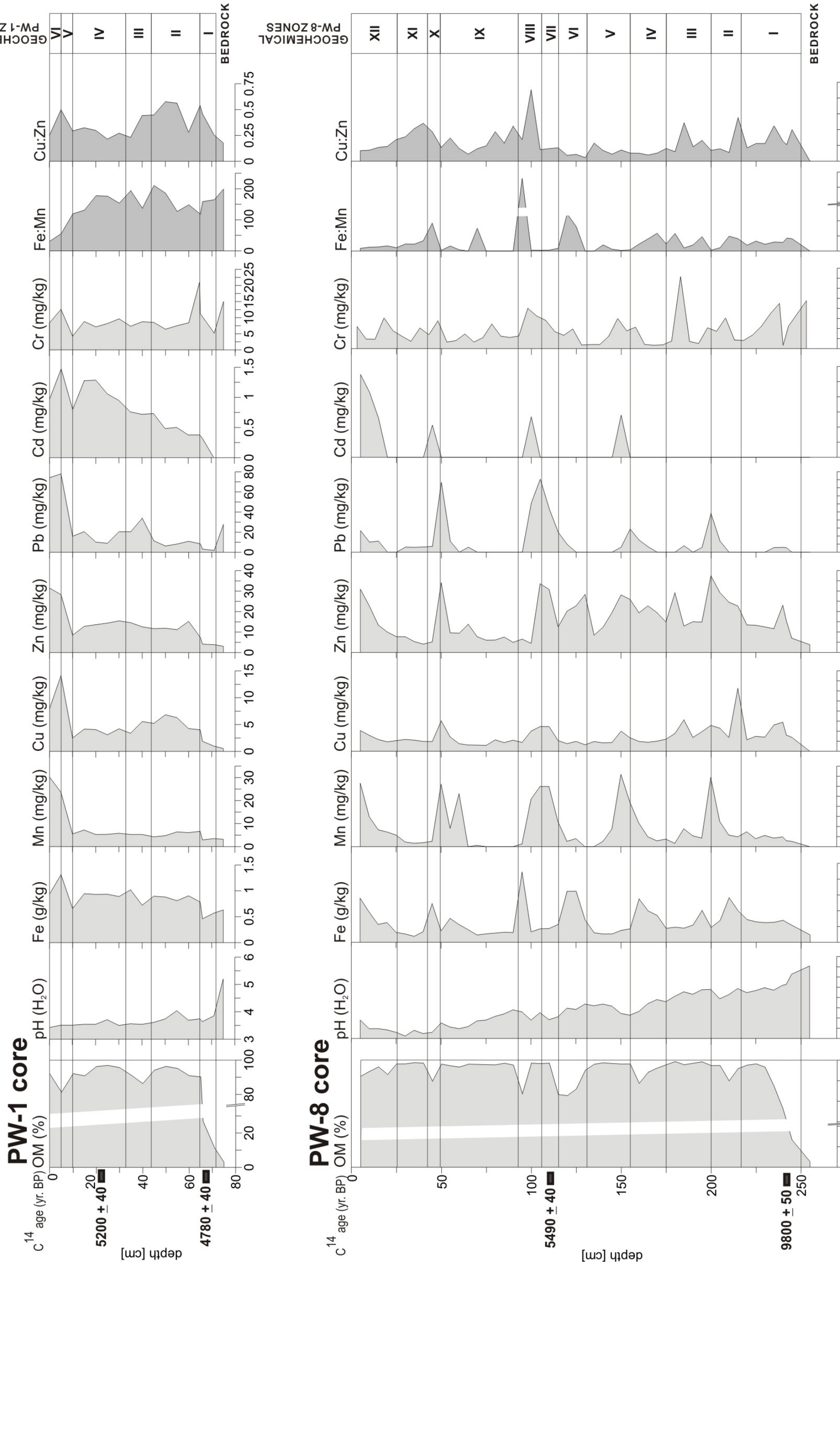

Fig. 2. Geochemistry and results of radiocarbon dating of infilling deposits of the Poręby Wojsławskie (PW) site.

Redox condition change indicators (Fe:Mn, Cu: Zn). Changes in oxidative-reductive conditions occurring during sediments accumulation are examined by means of the analysis of Fe:Me, Cu:Zn indicators vertical variation [5, 6, 19, 20]. Higher values of Fe:Mn, Cu:Zn ratios indicate that sediment accumulation took place in more reductive conditions, during the lowering of groundwater level [10, 12]. In geochemical zones: PW-8/II (200–215 cm), PW-8/III (175–200 cm), PW-8/VI (115–130 cm) relatively high Fe:Mn ratio values have been observed, while, inter alia, in the PW-8/IV (155–175 cm) zone, relatively low redox indicator values have been observed (indicating more aerobic condition and lower based water level).

High redox condition indicators Fe:Mn and Cu:Zn are peculiar to the geochemical PW-8/VIII (92–106 cm), PW-8/X (42–48 cm) and PW-1/II (44–65 cm) zone.

CONCLUSIONS

1. In the analysed geo-system distinct variability of the main geochemical compound concentration is observed in the vertical record of both cores

2. The geo-system in question demonstrates high dynamics of organic matter content, the decrease in organic matter content is an indicator of intensified erosion caused by climate change or anthropogenic deforestation, and moreover it is a result of draining and rotting processes.

3. Groundwater level fluctuation record, resulting from changes in supply-related characteristics, shows a great change in redox indicators values specific for different development stages of the analysed object.

4. Significant anthropopression impact on mire transformation is visible in surface layers of analysed cores throughout high concentration of heavy metals, particularly in uppermost sediments layers.

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WYBRANE PRAWIDŁOWOŚCI GEOCHEMICZNE W PROFILACH TORFOWISKA PORĘBY WOJSŁAWSKIE (KOTLINA SANDOMIERSKA, POLSKA SE)

Analizy geochemiczne stanową jedną z podstawowych metod badań osadów biogenicznych deponowanych w torfowiskach. W pracy wykorzystano analizę geochemiczną osadów biogenicznych z małego geosystemu torfowiskowego in the Sandomierz Basin (Poland SE) do odtworzenia warunków środowiskowych i wpływu działalności człowieka. Zmiany charakteru wybranych wskaźników geochemicznych zaznaczają znaczący wpływ na transformację torfowiska w najmłodszych fazach działalności człowieka. Rejestrowana jest ona w zapisie geochemicznym poprzez wysoki udział metali ciężkich – kadm, ołów i miedź. Zaznacza się także wyraźna zmienność koncentracji głównych składników geochemicznych w zapisie pionowym analizowanych rdzeni. Jest to konsekwencją asymetrycznej konfiguracji zbiornika sedymentacyjnego i wynikającej z niej zmiennej w czasie biogenicznej sukcesji osadowej.