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Research Article

Comparison of Metals Content in Peatlands with Different Anthropopressure in Welski Landscape Park (Poland)

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Abstract: There are over 49,000 peat bogs in Poland, the vast majority of which occur in the north of the country, near the Baltic coast, in Masuria and Kurpie, and in the valleys of the Noteć and Biebrza. Of these, 90% are low bogs, 6% are raised bogs, and the rest are temporary forms. Peat bogs are wetland habitats, occurring mainly in moderate and cool areas. They are covered with marsh and marsh-meadow plant communities. They are characterized by the high capacity to absorb and accumulate water, which makes them a regulator of water relations, which is of great importance in steppe Poland. The main objective of the study is to find out how the contents of metals such as Ni, Zn, Fe, Ca, Pb, Cr, Al, Mg change in a peat bog with strong anthropopressure (Wąpiersk bog) and weak anthropopressure (Las Nadwelski bog) after and before vegetation. The results of the study show that the concentration of metals, especially heavy metals in peat bogs in Welski Landscape Park, is generally low. The method of used analysis was Wavelength Dispersive X-Ray Fluorescence (WD-XRF) method. In both bogs, the concentration of heavy metals was lower in the center than on the border. This shows that heavy metals are absorbed by the peat at the border and limit further migration of the heavy metals. There are more elements such as Fe, Ca and Mg in the Las Nadwelski bog. The border of the forest received more light, which also plays an important role in decomposing plant debris, releasing metals. Heavy metals content was higher in Wąpiersk bog-a bog with higher anthropopressure. To sum up, the peat bog actively captures heavy metals, immobilizing them, and acts as a kind of "filter". Peat is a good agent for retrospective monitoring of metals migration and accumulation in the environment.

***Keywords*:** peat, peat bog, metals, WD-XRF, Welski Landscape Park

1. Introduction

Peat, defined as young Quaternary, mainly Holocene, organogenic sedimentary rock in the first stage of coalification, has received increasing attention due to its potential to act as a ubiquitous effective agent for the recovery of valuable metals, for the removal of metal ions from wastewater and dumping site leachate. Peat is a good agent for retrospective monitoring of metals migration and accumulation in the environment. Agricultural management and exploitation of peat are the most common, causing drastic and sometimes irreversible changes in their structure and functioning. As a result of these activities, peat bogs have lost the diversity of their natural habitats and have been

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deprived of many plant species associated with them. On the other hand, as a result of the mechanical exploitation of peat and its manual extraction, completely new habitats have appeared.[1]

Peat could be an adsorbent for metals in polluted waters because generally, it has a high adsorption capacity. The adsorption potential of peat can be expected to be strongly dependent on the chemical properties of the water and metal activity.[2,3] Ombrotrophic peat bogs are built up above the groundwater table. What follows is that the accumulation of magnetic particles is not influenced by groundwater and the deposited particles remain largely "in situ".[4,5]

Peat bogs are wetland habitats, occurring mainly in moderate and cool areas. They are covered with marsh and marsh-meadow plant communities. They are characterized by the high capacity to absorb and accumulate water, which makes them a regulator of water relations, which is of great importance in steppe Poland.[6,7]

Peatlands are still underestimated as communities preventing climate change. Proper functioning peatland areas constitute valuable carbon reservoirs with a constant possibility of their absorption. The deposition of carbon in the form of peat resembles phenomena from distant geological epochs when deposits of fossil fuels were created-hard coal, lignite, crude oil or natural gas. Peat bogs play a very important and diverse role in nature-they are refuges for biodiversity and also act as a geochemical barrier.[1] In this case, peat bogs take part in the processes of the environment of self-cleaning.[8,9] Peatlands are peat-forming ecosystems.[10,11]

If the peat bog is functioning properly, the elements and chemical compounds accumulated in the sediments are practically inaccessible to organisms.[12] In the event of disturbances, especially drying, the release of substances in the sediments may occur. It is of particular importance in ombrotrophic peat bogs, which are characterized by relatively low soil pH. In this case, increased release of heavy metals from the sorption complex into the environment and their greater availability to living organisms are observed.[13,14] Ombrotrophic peat bogs trap atmospherically deposited metals as they hold great potential for recording pollution through time.[15,16]

Peat bogs are particularly sensitive archives of atmospheric pollution and human activities in general.[2,17] Most importantly, peat is particularly effective at preserving atmospheric metal deposition in the form of lead,[18] copper,[19] nickel[20] and zinc.[19]

Rapid industrial development contributed to the accumulation of large amounts of toxic substances in the atmosphere and in the soil (and in the peat bog) especially in the form of heavy metals.[21] The specificity of metal pollution is that it is present in the form of elements, i.e. it is not biodegradable (unlike organic compounds). Heavy metal contamination is characterized by a very long half-life in the surface soil levels.[22]

Ombrotrophic bogs bring useful information about human activity on heavy metal contamination in the past. On Oostriku (Estonia) the content of metals (Fe, Zn, Mn, Cu, As) was researched.[23] Consistent with previous results,[9] the distribution of metals deep in the ground showed that the ochre layer (iron oxide accumulation) and the top peat layer were crucial natural geochemical barriers accumulating heavy metals in the Oostriku peat. The extraction process for leaching metals from the peat made it possible to differentiate between the metals strongly bound within the peat and the metals weakly associated with the peat. The conclusion indicates that Fe mostly appears as amorphous iron oxide in the peat. Dominating binding agents for the metals Pb, Zn, and Mn are dominated by the iron oxide. Cu is the only element that is strongly connected to organic matter at an appreciable amount, although a considerable fraction of Cu is also bound to the iron oxide. Surface complexity at the iron oxide and/or organic matter surfaces is relatively weakly bound in the peat by a fraction of Pb, Ca, Zn, and Mn. Ca may also be found as carbonate in the peat. Therefore, a fraction of the metals (e.g. Pb or Zn) leached with the acid could also be bound by carbonates.

The major goal of Borgulat et al.[2] research was to assess of heavy metal accumulation potential in peat bogs and in leaves of species growing on these peat bogs, namely Scots pine (*Pinus sylvestris* L.), birch (*Betula pendula* Roth), and wild rosemary (*Ledum palustre* L.). The accumulation of Cd and Pb in the peat of Bagno Bruch (the Upper Silesia Industrial Region) exceeded the permissible levels for soils of protected natural areas. No toxic levels of heavy metal concentrations in growing plants have been found in all. In the examined species, birch presented the highest ability to accumulate Zn and Cd The biggest concentration of heavy metals was found in Bagno Bruch peat, which has been affected by intensive anthropopression for many years. It is particularly pronounced for Cd, Pb and Zn-all of which are characteristic elements emitted during zinc processing. In spite of the technological improvement of parameters of this process, the level of these metals in peat still exceeds the permissible level of heavy metals for natural protected areas.

The main objective of the study is to find out how the contents of metals such as Ni, Zn, Fe, Ca, Pb, Cr, Al, Mg change in a peat bog with strong anthropopressure (Wąpiersk bog) and weak anthropopressure (Las Nadwelski bog) after and before vegetation. All the results presented in the study were obtained using the WD-XRF (Wavelength Dispersive X-Ray Fluorescence) method, which allows to determine both the qualitative and quantitative composition of the metals tested.

2. Research area

The research was carried out in the Wąpiersk bog and Las Nadwelski bog in the Welski Landscape Park (Poland) (Figure 1). It is located in the borderland between the two voivodships-the Warmińsko-Mazurskie and Kujawsko-Pomorskie Voivodship. In terms of the physical-geographical division, the investigated area belongs to the macroregion of the Chełmińsko-Dobrzyńskie Lakeland.[24]

Northern Poland is of particular interest because it possesses several peat deposits, some of which are ombrotrophic, i.e., exclusively fed by atmospheric deposition. This region is also interesting as it is located at a relatively far distance (several hundreds of km) from the main Polish pollution centers-Śląskie Voivodeship (south of Poland).[25]

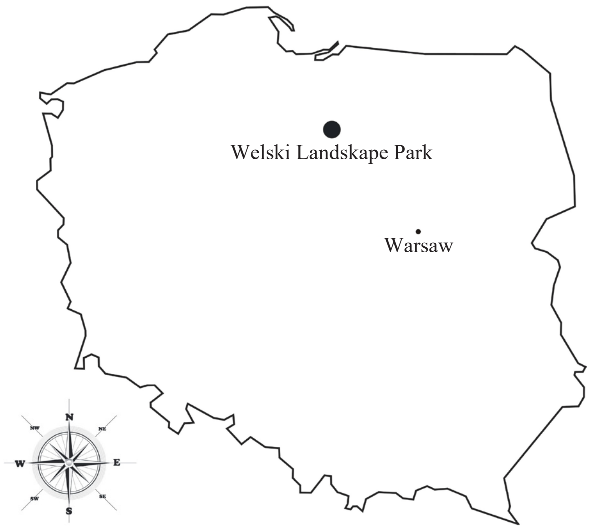

Figure 1. Localization of Welski Landskape Park

Welski Landscape Park was established in December 1995. It is situated in the southern part of the Warmińsko-Mazurskie Voivodeship. It covers part of the Wel River valley, numerous lakes, and adjacent forests and marshes. It covers an area of over 20,000 ha. This area is distinguished mainly by a high degree of naturalness of aquatic and peat ecosystems, a high share of protected and relict flora species and a rich and interesting fauna of vertebrates, especially fish and birds.[24]

The Wąpiersk bog is directly surrounded by pastures lying partly on mineral and partly organic grounds, created as a result of the lowering of the groundwater level in the peat deposit. Farmed fields are located at a distance of a few to about 50 meters from the border of the "living" bog (Figure 2).[6]

The border of the Wąpiersk bog was strongly dehydrated, while the entire peat deposit settled as a result of the groundwater level lowering. Among the plant species characteristic for this type of bogs, there are bog cranberries, bog rosemary, bog bilberries, pod grass and round-leaved sundews.[6]

In turn, the Las Nadwelski bog is surrounded by forests, away from farmland (Figure 3). The occurrence of scattered mid-forest swamps with high and transitional morphological moss is characteristic of this area.[6]

Figure 2. Wąpiersk bog, November 2018 (photo: B. Igliński)

Figure 3. Las Nadwelski bog, November 2018 (photo: B. Igliński)

The research was carried out after vegetation time (November, Figure 2 and Figure 3) and just before vegetation (March).

Peat was collected from depth of 0.5 meters with an auger INSTORF. Figure 4 shows the cross-section of the peat core Las Nadwelski bog (before vegetation time, March).

Figure 4. The cross-section of the peat core Las Nadwelski bog, March 2019 (photo: A. Iglińska)

3. Methods

The WD-XRF method is based on the measurement of the secondary radiation of the elements obtained as a result of their excitation by X-rays. This radiation knocks electrons out of the inner electron shells (K and L) closest to the atomic nucleus. The resulting electron vacancy is filled by an electron from higher electron shells. During the passage, a radiation quantum, called secondary radiation is released, which is subject to the process of detection and further analysis (Figure 5). The basis of the quantitative analysis was the measurement of the line intensity on the basis of standard curves.[25,26]

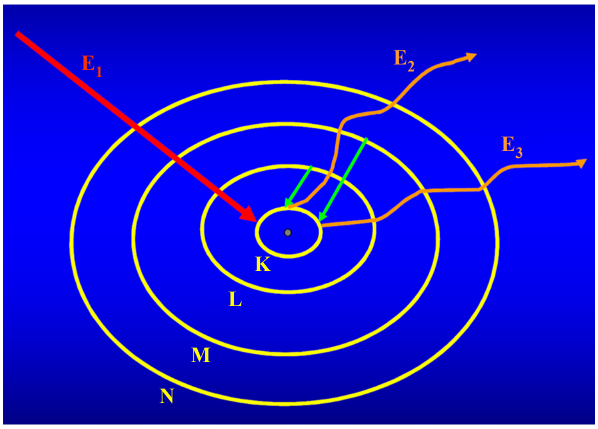

Figure 5. Mechanism of WD-XRF method

WD-XRF analysis allows us to quickly and very accurately examine all elements, starting with boron and ending with transuranium elements. The sensitivity of the method depends on factors related to:

the amount of energy needed to excite electrons;

the amount of X-ray emission;

the atomic number of the element under study.[27]

The analysis was performed on the Spectron-Optel RMA WD-XRF spectrometer with 46Pd anode (Figure 6). The quantitative analysis of metals in the peat ash was carried out using certified standards.[27,28]

Figure 6. Spectron-Optel RMA WD-XRF spectrometer (photo: B. Igliński)

The next stage of sample preparation was weighing a certain amount of dry peat and eliminating organic parts. This was done by burning dry peat in crucibles, initially on an electric stove, in order to get rid of the so-called "white fumes" and then in a furnace at 530°C. The incineration process, which led to the incineration, took about 12 hours. The temperature in the furnace could not be higher than 530°C, in order to avoid volatility losses of some minerals. After carrying out the described activities, the organic compounds evaporated and the resulting ash was prepared for the WD-XRF analysis, which determined the type and amount of metals in the sample.

The first stage of the WD-XRF analysis was the preparation of spectra (an example-Figure 7) of the examined ash, which formed the basis for the qualitative and quantitative analysis.

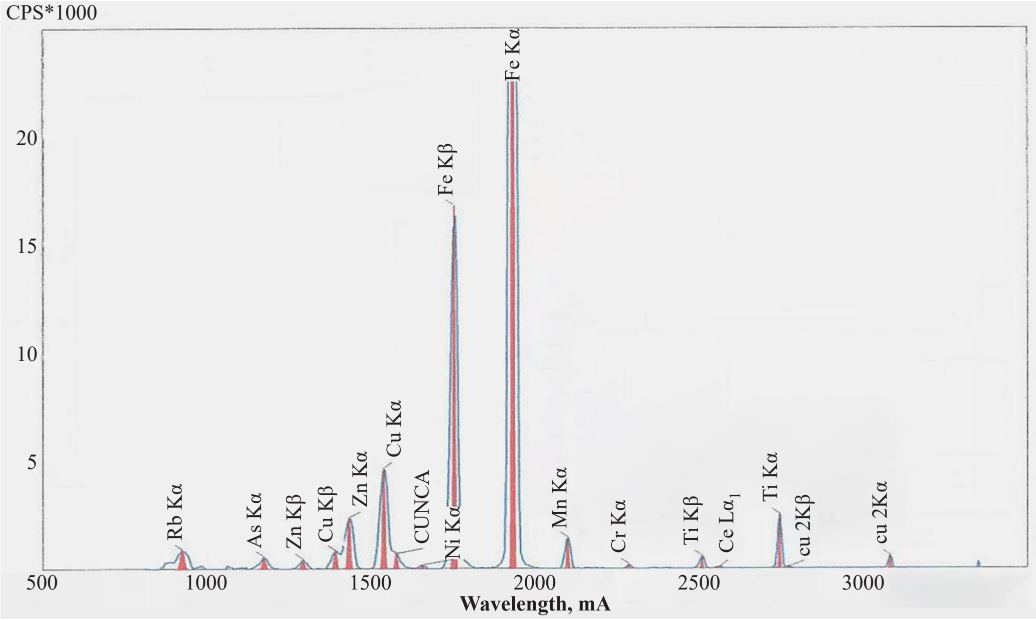

Figure 7. Spectrum showing peaks characteristic for metals in peat ash Wąpiersk bog, the border

For the quantitative determination of metals, the analytical lines were selected on the basis of the manufacturer's indications, after checking whether the tested sample does not contain any elements that strongly interfere with the measured ones. Performing the quantitative analysis was related to the determination of calibration curves. It was important to use certified reference materials with a known composition of the elements to be determined when creating the calibration curve for the analysis of ashes.

4. Results

Burning dry peat showed that more volatile parts were present in peat collected before the growing season. This fact is due to the increasing number of plant debris decomposing due to the limited supply of oxygen caused by high water content in the peat. The temperature, which in March is favorable for the changes in question, also affects the plant decomposition process.

The obtained results of the analysis are presented in Table 1 (retrieved after the growing season) and in Table 2 (retrieved before the growing season).

When analyzing Table 1, it should be stated that in the case of the Wąpiersk bog, the concentration of metals in the peat is always higher on the border-where the impact of anthropopressure is the greatest. Peat absorbs metals actively, including heavy metals. Apart from Zn, no heavy metals in the peat from the center of the Las Nadwelski bog were found. As for metals actively used by nature (Ca, Mg), the Las Nadwelski bog has a similar content both at the border and in the center of the peat bog.

Table 1. Summary of the results on the content of metals in peat collected after the growing season

Peat collection point	Metal content [%]							
	Ni	Zn	Fe	Ca	Pb	Cr	Al	Mg
Wąpiersk-the border	0.0004	0.0016	0.2367	0.4367	0.0001	0.0002	1.4599	0.1497
Wąpiersk-the center	0.0001	0.0005	0.0389	0.2643	LOQ	LOQ	0.2469	0.0472
Las Nadwelski-the border	0.0001	0.0013	0.1934	0.6701	LOQ	LOQ	1.1068	0.1446
Las Nadwelski-the center	LOQ	0.0007	0.2199	0.5566	LOQ	LOQ	1.5324	0.1738

LOQ-limit of quantification

Table 2. Summary of the results concerning the content of metals in peat collected before the growing season

Peat collection point	Metal content [%]							
	Ni	Zn	Fe	Ca	Pb	Cr	Al	Mg
Wąpiersk-the border	0.0005	0.0012	0.0927	0.0240	0.0010	0.0002	0.8019	0.1095
Wąpiersk-the center	0.0001	0.0011	0.0919	0.3462	0.0001	LOQ	0.9549	0.1441
Las Nadwelski-the border	0.0005	0.0026	0.4578	0.7493	0.0005	0.0005	4.8006	0.7324
Las Nadwelski-the center	0.0002	0.0005	0.0889	0.4630	0.0001	0.0001	0.5825	0.1044

When analyzing Table 2, it should be stated that this time in the case of the Las Nadwelski bog there are fewer metals in the center of the peat bog than on its border. In the case of Wąpiersk bog, more Ca, Al and Mg were found in the center of the peat bog-these are elements used by the nature of the peat.

Comparing the tables, it should be stated that the content of heavy metals is generally increasing in both bogs in the period after and before vegetation. This may be due to the fact that at the time of the first frosts, the decomposition process of plant debris begins, during which heavy metals are moved into the peat. It is worth mentioning that the overall content of heavy metals is lower in the peat from the Las Nadwelski bog.

In general, Fe, Ca and Mg are more abundant in the Las Nadwelski bog, mainly on its border-this is where the greatest biodiversity of flora is found, and these elements are actively used by it.

5. Conclusions

It should be noted that the WD-XRF method has proven successful in determining metals in peat, both qualitatively and quantitatively. The results of our study show that the concentration of metals, especially heavy metals in peat bogs in Welski Landscape Park (Poland) is low in general.

Rapid industrial development is a particular threat to humans due to the widespread of heavy metals. Heavy metals contained in the atmosphere or in water dust are absorbed by plant roots or animals and thus incorporated into the food chain. These elements are not biodegradable. Many of the metals are micronutrients and trace elements necessary for the proper functioning of the body, e.g. Cu, Zn, and only after exceeding a certain level can they cause a toxic effect and disrupt the absorption of other elements.

In both bogs, the concentration of heavy metals was lower in the center than on the border. The center of the investigated object is mostly lack of rain-water supply, whilst the border part is supplied by water flowing from the catchment area. This shows that heavy metals are absorbed by the peat at the border and limit further migration of the heavy metals.

There are more elements such as iron, calcium and magnesium in the Las Nadwelski bog. The border of the forest received more light, which also plays an important role in decomposing plant debris, releasing metals.

In the period just after the end of vegetation, more metals are found on the border of the Wąpiersk bog, which is associated with their runoff from the fields. During the vegetation break, plant mass was decomposed in this peat bog, so there are more biometals such as Ca and Mg in the peat before vegetation.

It should be noticed that the content of heavy metals is generally increasing in both bogs in the period after and before vegetation. This may be due to the fact that at the time of the first frosts, the decomposition process of plant debris begins, during which heavy metals are removed into the peat. It is worth mentioning that the overall content of heavy metals is lower in the peat from the Las Nadwelski bog.

Probably a fraction of Mn, Ca, Zn, and Pb is rather weakly bound in the peat, possibly via surface complexation at the iron oxide and/or organic matter surfaces.

To sum up, the peat bog actively captures heavy metals, immobilizing them, and acts as a kind of "filter". That is why it is so important to preserve the already existing peat bogs, which not only purify water but above all accumulate it, which is of great importance in steppe Poland.

Conflict of interest

The authors declare no competing financial interest.

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