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Original Research

Heavy Metals Accumulation in Soil and Plants of Polish Peat Bogs

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Abstract

Our study was carried out on three peat bogs that since the 1960s have been subjected to different degrees of anthropopression. The main objective of the research was assessment 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 concentrations of lead and cadmium in peat of Bagno Bruch (the Upper Silesian Industrial Region) exceeded the permissible levels for soils of protected natural areas. Heavy metal concentrations in plants growing in all analyzed sites show no toxic levels. Among the examined species, birch showed the highest ability to accumulate cadmium and zinc.

Keywords: peat bogs, heavy metals, anthropopression, soil, plants

Introduction

There are various types of peat bogs depending on the age, plants, and conditions that created the bog. Poland has about 51,000 peat bogs, most of them found in the northeast. The area of peatlands covers 4.1% of the entire territory and raised bogs occupy 6% of the whole area covered by peatlands [1]. The concentration of elements in the raised bogs is significantly lower when compared to the low moor because in the raised bogs' mineral compounds that originate only from atmospheric precipitation and dust deposition [2-3]. The biggest concentrations of heavy metals are found at the top layers of peat [4-5]. Since the bogs retain atmospheric pollutants, they have been used in recent years for reconstructing environmental changes [6-10]. Very high levels of heavy metals were found in raised bogs situated in the vicinity of mining and smelting areas [11-14]. Among plants commonly occurring in peatlands, mosses have been most often used for monitoring environmental contamination with heavy metals, also on a global scale [15-18]. There is scarce information on the accumulation of heavy metals by the vascular plants growing in peat bogs.

In Poland the rapid development of heavy industry and the lack or poor control of emissions has resulted in a high burden of the natural environment with air pollutants, including dust and heavy metals. In the

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last decades of the 20th century, Poland was among the most polluted countries in Europe with depositions of cadmium and lead amounting to 27 and 1,100 t year[1], respectively [19]. In 1991 the State Ecological Act was introduced, which combined liquidation and/or technological improvement of the biggest Polish industrial emitters with pro-ecological initiatives that resulted in a significant reduction of harmful substance emissions into the air [20-21]. The aim of the study was to determine the current level of accumulation of heavy metals in peat bogs subjected to different intensities of anthropopression and the concentration of heavy metals in leaves of plants growing in these areas. An attempt was also made to find the best bioindicator of heavy metal pollution.

Materials and Methods

Study Area and Studied Species

For the purpose of our research, three forest bogs were chosen. In each case, the forest floor was densely covered with several species of *Sphagnum* moss, tussocks of cotton grass (*Eriophorum vaginatum* L.), and small shrubs from the Ericaceae family dominating on hummocks. The most common species of canopy layer were Scots pines with an admixture of birch. All sites belong to protected natural areas.

Szeroki Bór peat bog (53°37′04″N, 21°38′40″E) is a main part of a wetland complex in a postglacial area of the Masurian Lakeland (NE Poland). This part of Poland is an agricultural and tourist area, free of industrial and urban heavy metal sources. The wetland complex belongs to Masurian Landscape Park. Wołosate peat bog (49°05′47″N, 22°69′53″E) is located in Bieszczady National Park (SE Poland) and was formed via paludification on an impermeable layer of Carpathian Flysch located in a valley of the Wołosatka River. It is a sparsely populated non-industrial region. Bagno Bruch peat bog (50°52′18″N, 19°04′90″E) is located in the Upper Silesia region (SW Poland) and originated from a lake established on fluvial sediments. It is a NATURA 2000 site supporting rare species of plants and animals. The Upper Silesia region has been heavily industrialized since the 19th century. Today it is an area with an enormous concentration of industry, called the Upper Silesian Industrial Region. In the vicinity of the peat bog, there is an operating steel mill in Miasteczko Śląskie. Three species were chosen for our study:

– Pine (*Pinus sylvestris* L.) is a tree common in eastern and central Europe. This species contributes 65% to the total forested area in Poland and is one of the most commonly used bioindicators of airborne pollutants.
– Birch (*Betula pendula* Roth) is one of the most popular tree species in Poland (6% of forested areas) and is a valuable alternative to pine as far as bioindication in the summer is concerned.
– Wild rosemary (*Ledum palustre* L.) is an evergreen shrub common on Polish plains and is present on dispersed sites in Polish uplands and mountains.

Sampling

Peat and mineral soil samples were collected once in October. Soil samples were collected at the edge of each peat bog. Samples were collected from each site using a hand-held twisting probe (Egner's stick). Peat and soil collected from a depth of 0-30 cm were used as material for analyses. Each time 15-20 individual samples were taken, thereby providing a mean mixed sample of about 1 kg. Dried peat and soil samples were sieved (1 mm sieve) in a laboratory and used for further analyses.

Plant material was collected in two consecutive years in July and October. Each time, samples were taken from the central part of every peat bog composite comprising leaves/needles of 5-10 random individuals from each species. In the case of *Ledum palustre*, to avoid the effect of canopy on deposition of pollutants, only plants growing in the openings were sampled. Plant samples taken for analysis were not rinsed with water. Because there was no regularity between seasons and years in the analyzed samples, we treated these data as subsequent repetitions and analyzed average results.

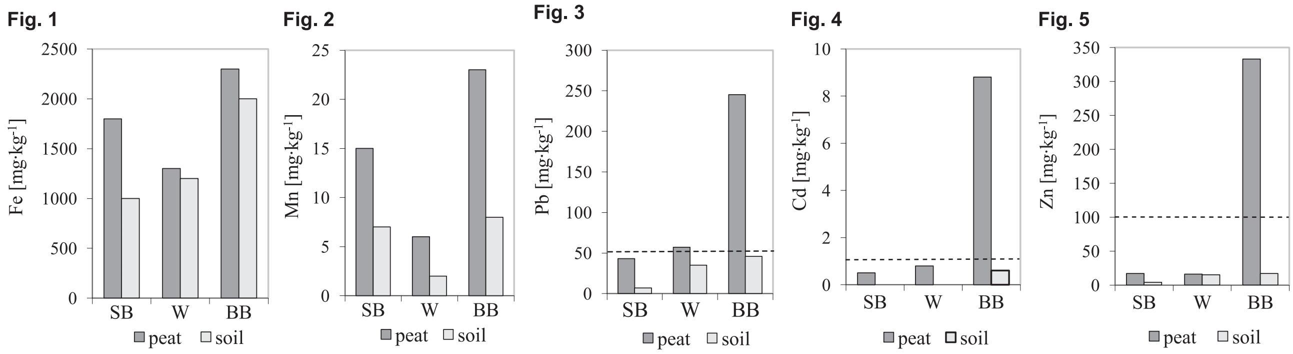
Heavy metal analyses were carried out after mineralisation using nitric acid and microwaves for plant samples and aqua regia in an open system for soil samples. Heavy metal content was established by the inductively coupled plasma (ICP) mass spectroscopy technique for plants and ICP-optical emission spectrometry for soil samples. Quality assurance and quality control was performed by analyzing the standard samples of known composition. All analyses were carried out in a Central Chemical Laboratory of the Polish Geological Institute, which possesses an AB 283 accreditation certificate.

Statistical Analyses

We used ANOVA to compare pollution profiles of the three studied locations (samples from the different plant species were compared between and within the bogs). In cases where significant interactions were found using ANOVA, post hoc analyses using LSD tests were conducted to examine which combinations of data points differed significantly ($n = 4$, $p<0.05$). In order to perform the calculation we used a STATISTICA program (StatSoft, lnc. 2011, v.10). Similar analysis was performed to compare pollution profiles of the three studied species.

Results

The highest concentration of heavy metals (several times higher than their concentrations in two other sites) was found in the peat bog of Bagno Bruch. In the peat bogs of Szeroki Bór and Wołosate the concentrations of cadmium, lead, and zinc were at similar levels. In



Figs 1-5. Contents of heavy metals (Fe, Mn, Pb, Cd, and Zn) in soil and peat on the selected peat bogs (SB – Szeroki Bór, W – Wołosate, BB – Bagno Bruch). Dotted lines indicate permissible levels [28].

all investigated sites the highest concentrations were observed for iron, zinc, and lead (Figs 1-5). A similar pattern of metal concentrations was observed for mineral soil and in all sites their concentrations were lower when compared to peat (Figs 1-5).

High differences between concentrations of heavy metals in the leaves of species collected in the same sites were recorded and the highest concentrations were found for manganese and zinc $p<0.05$ (Figs 6-10). All investigated species in Wołosate and Bagno Bruch showed a similar tendency for the accumulation of iron. A statistically significant difference ($p<0.05$ according to LSD test) in the iron concentration in leaves in comparison to other sites was found in Bagno Bruch (Fig. 6).

The highest manganese level (>500 $mg \cdot kg^{-1}$) was found in *Betula pendula* and *Ledum palustre* from Szeroki Bór. It seems that the lowest concentrations of this element were found in *Pinus sylvestris*, but this observation has not been confirmed statistically for all sites. The lowest concentration of manganese was found in *Pinus sylvestris* and *Betula pendula* from the Wołosate site <150 $mg \cdot kg^{-1}$ (Fig. 7).

Markedly the highest accumulation of lead was observed in plants from Bagno Bruch and in all species from this site the concentration of lead was at a similar level. In plants from Szeroki Bór and Wołosate only trace amounts of lead were found in leaves <2 $mg \cdot kg^{-1}$ (Fig. 8). The highest accumulation of cadmium was found in plants in Bagno Bruch, where the highest cadmium concentration occurred in *Betula pendula* leaves and the same phenomenon but with less intensity was recorded in Szeroki Bór ($p<0.05$; LSD test). In Bagno Bruch the concentration of cadmium in *Betula pendula* leaves was three times higher when compared with other species (Fig. 9). In all sites the concentrations of zinc in leaves of *Betula pendula* were several-fold higher than in other species. Zinc concentrations in *Ledum palustre* and in *Pinus sylvestris* were similar in all sites (Fig. 10).

In order to determine which species exhibits a higher tendency to bioaccumulate the selected heavy metals we used the bioaccumulation coefficient (BAC; Table 1). BAC is the relationship between the metal concentration in aboveground plant parts (foliage) to its concentration in soil. Important factors affecting the availability of heavy metals for plants are soil pH and organic matter content of soil [38]. Because an earlier work [22] showed that all the investigated peat bogs have a similar content of organic matter (about 90%) and similar pH (below 4 in the investigated surface layer), the analysis was performed in common for all examined peat bogs. It has been shown that *Betula pendula* has a significantly higher bioaccumulation ability of cadmium and zinc than other examined species. In the case of zinc the BAC factor for birch was more than five times higher when compared to pine and wild rosemary. All examined species showed a strong tendency to accumulate manganese (BAC>10). The highest capacity for bioaccumulation of manganese has been found in *Ledum palustre*.

Discussion

Because organic colloids (e.g., humic acids) are major players in the retention of heavy metals [23], peat rich in organic matter usually retains more heavy metals than mineral soil [24], and such a phenomenon was confirmed in all investigated soils (Figs 1-5). Concentrations of iron and manganese found in peat bogs of the three analyzed sites are similar to the values obtained in the raised peat bogs in northern Europe [25-26]. There are relatively slight differences between concentrations of these metals in three peat bogs and between bogs and mineral soils (Figs 1-2). This supports the conclusions drawn by Silamiķele et al. [26] – on the basis of analysis of peat samples taken in 44 representative raised bogs in Latvia – that these two metals are evidently of natural origin.

In contrast, it was found that lead and zinc determined in the Puscizna Rekowianska ombrotrophic bog in southern Poland (part of one of the largest bog complexes in Poland) demonstrate significantly higher concentrations than the material from the surrounding soil and in comparison with peat from clean regions, which indicates the anthropogenic origin of these metals [27]. A similar phenomenon was stated in our sites (Figs 3-5).

Fig. 6

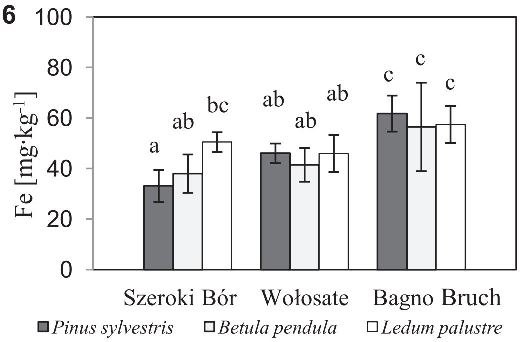
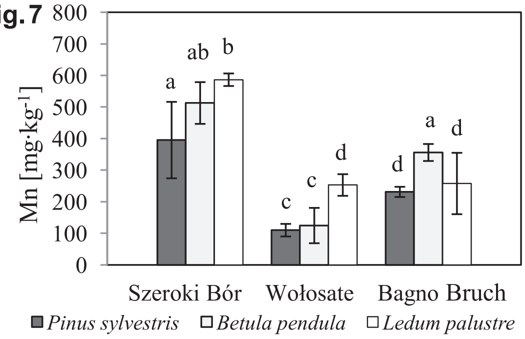


Fig. 7



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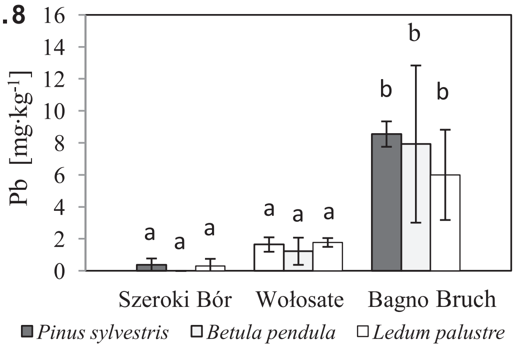


Fig. 9

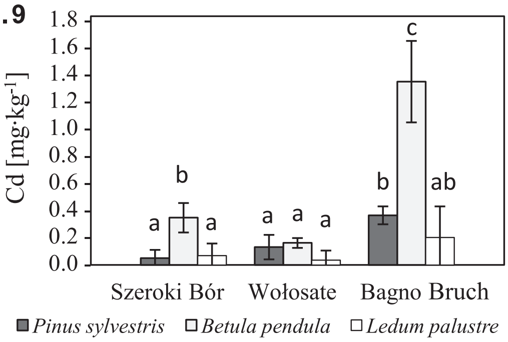
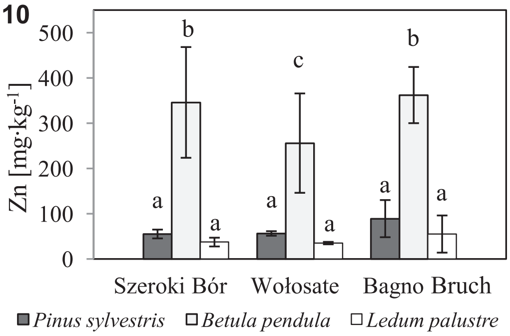


Fig. 10



Figs 6-10. Contents of heavy metals (Fe, Mn, Pb, Cd, and Zn) in plants from the selected peat bogs. Letters above bars indicate homogeneous groups according to Fisher's LSD test ($p<0.05$).

Concentrations of lead, cadmium, and zinc amounting to 245, 8.8, and 333 mg·kg^{-1}, respectively, found in the Bagno Bruch peat bog (Upper Silesia) exceed the permissible levels for soils of protected natural areas, which are 50, 1, and 100 mg·kg^{-1}, respectively [28] (Figs 3-5). The obtained results are similar to the data obtained in this site by Śmieja-Król et al. [29]. They demonstrated that concentrations of these elements in-depth profiles show similar trends, and the highest heavy metal concentrations occurred at a depth of 8-28 cm, with the concentration peaks in the layer of 10-16 cm amounting to 238 mg·kg^{-1}, 15.9 mg·kg^{-1}, and 494 mg·kg^{-1} for lead, cadmium, and zinc, respectively. It is worth noting that mutual ratios of these elements in this layer are almost the same as the ratios found in a dust fall collected in the period of 1988-92 in the region of a Miasteczko Śląskie zinc smelter [30].

The concentrations of lead in soil of more than 200 mg·kg^{-1} are considered to be of anthropogenic origin [31]. It is assumed that about 70% of lead in the environment comes from anthropogenic sources, reaching the soil with atmospheric deposition [32-33]. Lead concentrations in the peat bogs of Wołosote and Szeroki Bór exceed the average level of 25 mg·kg^{-1} for agricultural lands in Poland [34], and are close to the permissible value for the protected natural areas [28], which can be the effect of car fumes because both sites have been under intensive tourist movement for many years (Fig. 3).

In Upper Silesia 86% of soils contain more than 5 mg·kg^{-1} of cadmium, mainly due to mining and metallurgical activity, and in the areas of extraction and processing of metal ores concentrations of above 16 mg·kg^{-1} were recorded [33]. Concentrations of cadmium in the peat bogs of Wołosote and Szeroki Bór are close to the average level of this metal in Polish soils (0.5 mg·kg^{-1}) (Fig. 4) [31].

The very high level of zinc in the Bagno Bruch peat bog is a consequence of emissions from the zinc metallurgical plant located 10 km from this site (Fig. 5). The contamination of the Bagno Bruch peat bog is typical of emissions from non-ferrous metallurgical plants. In topsoil at a distance of 6.5 km from the Olkusz Zinc and Lead Smelter (southern Poland), concentrations of 90, 1.5, and 150 mg·kg^{-1} for lead, cadmium, and zinc, respectively, were recorded [35].

Concentrations of zinc in the peat bogs of Szeroki Bór and Wołosate are lower than 40 mg·kg^{-1}, which is considered geochemical background for Polish soils [30] (Fig. 5). The concentrations of lead, cadmium, and zinc in the peat bogs of Szeroki Bór and Wołosate are close to the upper limits of these metals concentrations found in surface peat cover in 26 locations across Estonia [36].

For assessing the heavy metal pool in plants the obtained results were compared to the critical limits of deficiency and toxicity provided by Marschner [37] and Kabata-Pendias [38]. The least critical content of iron ranges from 50 to 150 mg·kg^{-1}, whereas the critical toxic content is above 500 mg·kg^{-1} and depends on many factors such as, for example, the presence of other mineral

Table 1. Coefficients of heavy metals (HM) bioaccumulation – BAC (HM contents in leaves/HM contents in peat). The same letters in column indicate homogeneous groups (n = 12, p<0.05, ANOVA, post hoc Fisher's LSD test).

	Fe	Mn	Pb	Cd	Zn
Pinus sylvestris	0.03±0.007a	18±8a	0.02±0.01a	0.10±0.01a	2.0±1.1a
Betula pendula	0.02±0.01a	21±11ab	0.02±0.01a	0.30±0.1b	11±5.1b
Ledum palustre	0.03±0.006a	31±15b	0.02±0.01a	0.07±0.05a	2.0±1.1a

nutrients. A slight deficit of iron was found in leaves of all species growing in Szeroki Bór and Wołosate (Fig. 6).

The critical deficiency level of manganese amounts to 10-20 mg·kg^{-1}. There is a wide range of variation in tolerance to manganese between and within plant species [40]. Alvarez et al. [39] recorded manganese levels of up to 700 mg kg^{-1} as normal. According to Adriano [40], manganese concentrations in plants between 20 and 500 mg·kg^{-1} are normal levels, which depends to a great extent on plant species and environmental conditions, e.g., temperature. The lowest levels of manganese were found in plants from Wołosate, but these values exceeded the minimum level (20 mg·kg^{-1}). Concentrations of manganese found in leaves of *Betula pendula* and *Ledum palustre* growing in Szeroki Bór were close to a toxic level (Fig. 7). Toxicity of manganese in plants is manifested by dark spots on leaf tops plus margin chlorosis and defoliation [41]. Visual inspection of the leaves in the field did not show such symptoms.

Symptoms of the harmful effect of cadmium in plants occur at concentrations of 5-30 mg·kg^{-1} [38]. The 0.2 mg·kg^{-1} level in plants is considered to be a highly elevated concentration according to the scale proposed by Arndt [42]. The mean cadmium concentrations in spruce needles collected from all 23 Polish national parks was 0.18 mg·kg^{-1} [43]. The content of cadmium in leaves of the investigated species in all three sites are significantly below the toxicity limits (Figs 8-9). Concentrations of cadmium above 0.2 mg·kg^{-1} were found in leaves of all species in Bagno Bruch and in *Betula pendula* in Szeroki Bór (Fig. 9). The high content of cadmium in plants in the Bagno Bruch bog can be explained by the high content of cadmium deposited in peat (above the acceptable value, Fig. 4).

The critical limit of lead toxicity for plants is 30-300 mg·kg^{-1}, and a wide range of values can be contributed to the high tolerance of some species to lead (mainly those growing in contaminated areas). For example, native species *Betula pendula* and *Pinus sylvestris* have a fairly good condition and have the ability to spontaneously spread seeds under high contamination of lead [44]. Although some plants (e.g., birch, poplar, grasses) can accumulate significant amounts of lead, no higher levels of lead were found in leaves of *Betula pendula* when compared to other investigated species, which is likely caused by the place of lead accumulation in this plant (Fig. 8). Higher accumulation of lead in roots when compared to shoots were found for several species of crop plants [45-46]. It was shown that in willow (*Salix matsudana*) the meristem zone of root tips is the main site of cadmium uptake and accumulation [47].

The critical deficiency content of zinc amounts to >15-20 mg·kg^{-1} and the toxic level is 100-300 mg·kg^{-1}. In our research the content of zinc in leaves shows differences depending on plant species. The concentration of zinc in *Pinus sylvestris* needles is not toxic (does not exceed 100 mg·kg^{-1}) and in *Ledum palustre* does not exceed 50 mg·kg^{-1}. A high concentration of zinc was found in leaves of *Betula pendula*, often exceeding the critical level of toxicity (300 mg·kg^{-1}; Fig. 5). It was shown that the leaves of *Betula pendula* accumulated significantly more Zn than other species of trees, both for the trees growing in heavily polluted areas as well as for trees growing in the area of background pollution [48]. *Betula pendula* can accumulate up to several thousand mg·kg^{-1} Zn in leaves [49-50], and in the unpolluted environment they contain up to 10 times more zinc than the species characterized by normal contents.

In 1992 zinc, lead, and cadmium concentrations were examined in birch and pine leaves on ombrotrophic bogs along a spatial (southern Norway-central Norway) heavy metal deposition gradient [51]. Plant concentrations of lead and cadmium were significantly higher (3 to 4 times) in southern Norway than in central Norway, most likely because of higher root uptake in southern Norway due to distinctly higher surface soil levels of these elements from air pollution in this region. The concentrations of these elements in *Betula pendula* and *Pinus sylvestris* found in Szeroki Bór and Wołosate were very similar to the values recorded in southern Norway, which confirms the high level of long-term environmental burden of Polish territory by anthropogenic emissions.

We used BAC to indicate which species has a higher tendency to accumulate heavy metals. A value of BAC>1 shows that the plant is enriched with an element (the plant is an accumulator). BAC<1 shows that the plant excludes elements from the uptake (excluder) [52-53]. When BAC surpasses 10, those plants have the ability to hyperaccumulate elements [54]. According to the obtained results, all species mainly behaved as excluders of iron, lead, and cadmium (BACs<1). However, there are some possibilities for accumulation of metal pollution. In our research birch showed a high ability to accumulate zinc. It seems that, in the case of growth birch on a peatland, this species has the ability to accumulate significant amounts of zinc in the assimilation organs (BAC>10). In other research [55], the BAC factor for *Betula pendula* was significantly lower (1.33) than the one obtained in our research. Most probably, the results were influenced by other factors such as peat pH, contents of organic matter, and others. Both pH and redox conditions influence Mn bioavailability in soils [37]. In most acid soils at low pH (<5.5) and an increased redox potential of Mn, oxides can be easily reduced in the soil exchange sites [56], increasing the concentration of soluble Mn^{2+}[57], which is the predominant manganase form in the soil solution [40] and the most available manganase form for plants [37]. In our research all examined species showed a strong tendency to accumulate manganese (BAC>10). It seems that the strongly acidic soil environment and other factors like redox potential could play a decisive role here, but explaining the phenomenon of the great tendency to accumulate Mn in plant leaves growing on peat bogs requires additional research.

Conclusions

1. The highest accumulation of heavy metals was found in peat of Bagno Bruch, which has been affected by intensive anthropopression for many decades. It is particularly pronounced for lead, cadmium, and zinc – all of which are characteristic elements emitted during zinc processing. Despite the improvement of technological parameters of this process, the level of these metals in peat (which contains a lot of organic matter in contrast to mineral soil in this area) still exceeds the permissible level of heavy metals for natural protected areas.
2. Although heavy metals concentrations in plants growing in Bagno Bruch are markedly higher than in other sites, their levels show no toxic concentrations for plants.
3. *Betula pendula* has a higher ability to accumulate cadmium and zinc than other examined species. Moreover, in the case of zinc, birch can be hyperaccumulators of this element (BAC>10).

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