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The application of the geo-accumulation index and geostatistical methods to the assessment of forest soil contamination with heavy metals in the Babia Góra National Park (Poland)

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Abstract: The aim of this study was the application of the geo-accumulation index and geostatistical methods to the assessment of forest soil contamination with heavy metals in the Babia Góra National Park (BGNP). For the study, 59 sample plots were selected to reflect all soil units (soil subtypes) in the studied area and take into account various forms of terrain. The content of organic carbon and total nitrogen, pH, hydrolytic acidity, the base cations and heavy metals content were determined in the soil samples. The geo-accumulation index (I_{geo}) was calculated, enabling estimation of the degree of soil pollution. The tested soils are characterized by strong contamination with heavy metals, especially with lead. The concentration of heavy metals in the surface horizons of the tested soils exceeds allowable concentration. The content of heavy metals was related to the content of soil organic matter, soil acidity and altitude. Higher altitudes are dominated by coniferous tree stands, which are accompanied by acidic, poorly decomposed organic horizons. Our study has confirmed the impact of pollutants transported from industrial areas on the amount of heavy metals in soils of the BGNP.

Introduction

The occurrence of heavy metals in the surrounding environment is a current and common phenomenon of the existing civilization. A considerable portion of contaminants that are hazardous to the environment have anthropogenic sources (Schulz et al. 2006; Parrish et al. 2014), which stems primarily from the population growth and the dynamic progress of technology (Chrzan, 2013). In 2015 in Poland the total emissions of heavy metals to the atmosphere was 2584 Mg, of which over 80% were formed in the processes of combustion during the production and transformation of energy, within industry and outside of it. The intense emissions of heavy metals to air and the possibility of their transport to considerable distances resulted in the fact that heavy metals can be observed even in protected areas, i.e, in national parks (Mazurek et al. 2017; Rivera et al. 2016; Tomaškin et al. 2013). The toxic dust and gases present in the air originate primarily from industrial energy and transportation plants (Królikowski et al. 2005). Heavy metals associated with dust particles transported in the atmosphere access the soil environment with precipitation (Hvitved-Jacobsen et al. 1994). Pesticides, petroleum hydrocarbons and heavy metals such as lead, copper, chromium, cadmium, mercury and zinc are the substances most frequently responsible for the soil environment degradation process (Rosik-Dulewska et al. 2007, Bolan et al. 2004; Mench et al. 2010). According to Lasat (1999), heavy metals occur in soil in different forms: (1) as free ion metals; (2) dissolved metal complexes; (3) bound with soil organic matter; (4) as oxides, hydroxides and carbonates (5) included into structures of silicate minerals. Beyond a certain limit, heavy metals exhibit strong toxic properties and are highly hazardous to plants, animals and humans (Cicmanec, 1996). According to Kabata-Pendias (1995), the quantitative content and distribution of toxic trace elements reflects the actual status of the environment.

According to numerous studies, the soil capacity to bind heavy metals is strictly related to the pH, content of organic matter (humus type) and texture (Gerritse et al. 1984). Humus and clay minerals colloids restrict the mobility and bioavailability of trace elements by binding them (Młocek-Płóciniak, 2011). The species composition of tree stands influences the amount and quality of soil organic matter, which complexes heavy metals (Błońska et al. 2016). One of the most important factors determining the concentrations of metals in the soil and their mobility is the soil pH (Gäbler, 1997). The mobility of heavy metals is much higher in strongly acidic soil compared to the neutral and alkaline soils. Topography is also an important aspect that must be taken into account, especially when mapping heavy metal pollution in mountain areas (Chen et al. 2012). The topography was a critical aspect that controlled both the extent and direction of the pollutant transportations. It is widely known that a strong correlation between orography, amount of wet deposition and precipitation composition, and as a consequence the amount of heavy metals accumulated in soil (Fowler et al. 1998; Dore et al. 1990).

General methods of geostatistical interpolation are applied to data from random fields that meet the relevant mathematical concepts. Geostatistical interpolation methods are used where spatial data is collected and the estimated filling data is generated in the spatial gaps between actual measurements. So far, the application of geostatic methods has been used in various disciplines, especially in natural sciences (Bayraktar and Turalioglu, 2005), hydrogeology (Tonkin and Larson, 2002), mining (Richmond, 2003) and natural resources (Emery, 2005). Geostatical methods are increasingly used in relation to soil science and monitoring of changes in ecosystems due to anthropogenic influence (Reichardt and Timm, 2020; Xia et al. 2019; Lv, 2019). Geostatical methods can be used to assess the spatial distribution of heavy metals in the soil (Liu et al. 2016).

The study aim was to assess the content of heavy metals in forest soils of the Babia Góra National Park (Poland) using geo-accumulation index and geostatistical methods. The content of heavy metals was referred to the physicochemical properties of soils, geo-accumulation index, primarily the organic carbon content and pH. Variability of soil types and altitude a.s.l. were considered in the study. We hypothesized that:

(1) soil pollution with heavy metals depends on the soil properties and topography characteristics simultaneously,
(2) altitude a.s.l. determines the quality of soil organic matter and as a result the accumulation of heavy metals,
(3) estimating contaminants based on the geo-accumulation index in combination with geostatistical methods is an effective monitoring tool to determine the source of heavy metals dispersion in the environment.

Materials and methods

The study site was the Babia Góra National Park (BGNP), which was established in 1954 and is located in southern Poland, bordering with Slovakia (Figure 1). The National Park occupies the area of 3,391.55 ha, and it is surrounded by the buffer zone of 8,437 ha. The BGNP area is located at an altitude from approx. 700 m a.s.l. to the summit of Babia Góra of 1725 m a.s.l. The average annual temperature varies depending on the altitude from approx. 3°C to 13°C, and the annual rainfall is 1,225.6 mm (Obrębska-Starkel et al. 2004). The growing season in the lowest portion of the BGNP is 202 days and it is shorter in the subsequent climatic and vegetation zones (Sulikowska et al. 2017). In the lower subalpine forest it is an average of 170 days, in the upper subalpine forest 140 days, whereas in the mountain pine zone only approx. 100 days (Hess, 1965).

The BGNP is located in the Western Beskids, in the eastern part of the Żywiec Beskids. It is mostly composed of flysch formations. A considerable majority of the BGNP is occupied by Hyperdystric Cambisols (36.8%), to a lesser extent Epidystric Cambisols (13.6%), Albic Cambisols (13.5%), Podzols and other soil types (Niemyska-Łukaszuk et al. 2010). A characteristic zonation of mountainous vegetation can be distinguished in the area of the BGNP starting from the highest portions: alpine zone (1650–1725 m a.s.l.), mountain pine zone (1350–1650 m a.s.l.), subapline zone (700–1350 m a.s.l.). The national park is primarily overgrown with beech, spruce and fir forests. The *Dentario glandulosae-Fagetum*, *Luzulo nemorosae-Fagetum, Plagiothecio-Piceetum tatricum, Abieti-Piceetum* association has a considerable share in the BGNP. The *Alnetum incanae* association can be found in the vicinity of creeks and within troughs and submersion areas the *Caltho laetae-Alnetum* association is present (Holeksa et al. 2002).

The research was conducted on 59 research plots located in the Babia Góra National Park (Figure 1). Soil samples were taken from each research area for laboratory tests. Soil samples were taken from soil horizons separated from profiles during field tests. Soil samples were selected from the surface horizon (organic horizon – O), and from the underlying surface mineral horizon (humus-mineral horizon – A, or transitional AE, AB). In addition, the soil type in the order of FAO's World Reference Base for Soil Resources (WRB, 2015), altitude a.s.l., exposure were determined.

The air dried soil was sieved through a sieve with 2 mm mesh size. In thus prepared samples, the following physicochemical and chemical properties were determined (Ostrowska et al. 2001): soil pH with potentiometric method in water and in

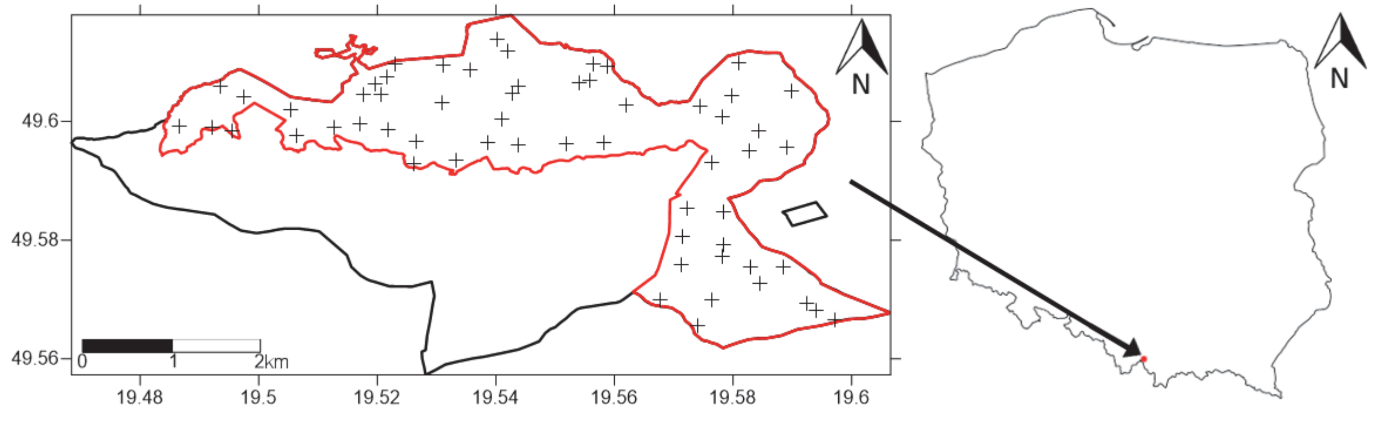

Fig. 1. Location of the study site and places of soil sampling (red line – research area; black line – area of BGPN)

1M KCl; the soil texture was determined by laser diffraction (Analysette 22, Fritsch, Idar-Oberstein, Germany), the total nitrogen and organic carbon content using the LECO CNS True Mac Analyzer (Leco, St. Joseph, MI, USA), with the calculation of the C/N ratio; alkaline cation content in 1 M ammonium acetate with sum of base cations (BC); hydrolytic acidity with the Kappen method (Hh). The concentration of cations and the content of Cd, Cr, Cu, Pb, Zn were determined by an ICP spectrometer (ICP-OES Thermo iCAP 6500 DUO, Thermo Fisher Scientific, Cambridge, U.K.). The content of Cd, Cr, Cu, Pb, Zn was determined after prior mineralization in the mixture of concentrated nitric and perchloric acids at the ratio 2:1.

ANOVA test was used to evaluate the differences between the mean values of the soil properties and heavy metals content. The Pearson correlation coefficient for the soil characteristics was calculated. Differences with $P<0.05$ were considered statistically significant. The Primary Component Analysis (PCA) method was used to assess the relationship between soil properties and heavy metal content using Statistica 13.1 (StatSoft, 2012). Surfer software (Golden Software, 2015) was used for this purpose to express spatial variability and enable to obtain map content and at the same time minimize errors of predicted values. In order to generate maps, the kriging interpolation method was used (Stein, 2012).

Moreover, the geo-accumulation index (I_{geo}) was calculated, enabling estimation of the degree of soil pollution. The geo-accumulation index (I_{geo}) enables assessment of pollution by means of a comparison between the amounts of heavy metals currently found in soils with their so-called pre-industrial amounts (Müller, 1969):

$$I_{geo} = \log_{10}\left(\frac{C_n}{1{,}5B_n}\right) \qquad (1)$$

where: Cn – mean amount of the given metal in soil, Bn – geochemical background, 1.5 – natural variations in the content of the given metal in the environment. *I*geo values ≤0 represent unpolluted soils, 0–1 represent unpolluted to moderately polluted soils, 1–2 moderately polluted soils, 2–3 moderately to highly polluted soils, 3–4 highly polluted soils, 4–5 represent highly to extremely highly polluted soils, and ≥5 extremely polluted soils (Matini et al. 2011). The backgrounds given by Kabata-Pendias (2010) were used to calculate background values for Igeo in this study: cadmium 0.45 $mg \cdot kg^{-1}$, chromium 51 $mg \cdot kg^{-1}$, copper 23 $mg \cdot kg^{-1}$, lead 28 $mg \cdot kg^{-1}$, zinc 60 $mg \cdot kg^{-1}$.

The spatial interpolation and geostatistical mapping techniques were used to develop spatial distribution maps and geo-accumulation indexes of the contents of five heavy metals studied. The most common variant of the kriging algorithm, the ordinary kriging (OK) method, was used in this research. In the selected method, the sum of weights is equal to one. This makes it possible to create an unbiased estimator which does not require prior knowledge of the stationary average of the observed values. Samples (measuring points) in the estimation area (test area) are assigned appropriate weights, called kriging coefficients (weights), in such a way as to minimize the average estimation error (kriging variance) (Stein, 2012). The variogram, which is evaluated from the data using the semi-variance equation, expresses the spatial variability of the attribute. The function of the separation distance between observations is defined as semi-variance (Matheron, 1971).

Results

The mean nitrogen and carbon content was higher in the organic horizons of the studied soils and it was 1.33 and 27.50% respectively, and in mineral horizons 0.50% and 9.01% respectively. Organic horizons were characterized by a higher mean C/N ratio, which was 20.8, and in mineral horizons 17.7 (Table 1). The studied soils of the BGNP were characterized by acidic reaction. In the organic horizons the mean pH in KCl was 3.34, and in mineral horizons the mean pH in KCl was 3.64. The mean base cations content in organic horizons of the studied soils was 14.67 $cmol(+)\cdot kg^{-1}$, and in mineral horizons 9.57 $cmol(+)\cdot kg^{-1}$. According to Kabata-Pendias (2010) admissible level of Cd amounts to 1 $mg\cdot kg^{-1}$, Cu to 30 $mg\cdot kg^{-1}$, Cr to 50 $mg\cdot kg^{-1}$, Pb to 50 $mg\cdot kg^{-1}$ and Zn to 100 $mg\cdot kg^{-1}$. Out of 59 test stands, only 10 did not show any exceedances of heavy metals. Most of the chemical properties except for pH H_2O and pH KCl showed significant differences between organic and mineral levels (Table 1).

The mean cadmium content in organic horizons was 0.96 $mg\cdot kg^{-1}$, and in mineral horizons 0.72 $mg\cdot kg^{-1}$ (Table 2). The mean chromium content in organic horizons was 1.05 $mg\cdot kg^{-1}$, whereas in mineral horizons it attained 2.53 $mg\cdot kg^{-1}$. In the case of copper and zinc, higher values were determined in the organic horizon in comparison with mineral horizon. High mean lead content was observed in the tested soils – 113.20 $mg\cdot kg^{-1}$ in organic horizons and 54.78 $mg\cdot kg^{-1}$ in mineral horizons. The calculated geo-accumulation index (Igeo) indicates contamination of the studied soils with lead (Table 2). Organic levels were characterized by statistically significantly higher content of heavy metals and geo-accumulation index in comparison with mineral levels of the soils studied (Table 2).

Table 1. Basic chemical properties of the analyzed soils

	N (%)	C (%)	C/N	pH H_2O	pH KCl	BC ($cmol(+)\cdot kg^{-1}$)	Hh ($cmol(+)\cdot kg^{-1}$)
Organic horizons	1.33± 0.39^a	27.50± 8.66^a	20.86± 4.40^a	4.22± 0.73^a	3.34± 0.85^a	14.67± 21.55^a	68.71± 31.46^a
Mineral horizons	0.50± 0.44^b	9.01± 8.39^b	17.71± 4.37^b	4.52± 0.76^a	3.64± 0.74^a	9.57± 17.32^b	25.41± 13.89^b

Mean±SD; N – total nitrogen content; C – organic carbon content; BC – sum of base cations; Hh – hydrolityc acidity; small letters in the upper index of the mean values mean significant differences between horizons

An increase of lead accumulation with the altitude a.s.l. is observed in the organic horizons of the studied soils. The remaining elements such as cadmium, chromium and copper attained similar mean content values in the distinguished altitude zones (Figure 2). In the mineral horizons of the studied soils a decrease of cadmium, copper, lead and zinc was observed with increasing altitude (Figure 3). Chromium content in the studied soils was similar in all altitude zones. The impact of vegetation becomes pronounced for the amount of metals accumulated in the studied soils. Higher mean contents of cadmium, copper and zinc in organic horizons were observed in deciduous tree stands, and lead and chromium in coniferous tree stands. In mineral horizons, the contents of heavy metals independently of the vegetation type assumed similar values. The organic horizons of Podzols were characterized by the highest lead content and high chromium content. The high Cd content was demonstrated by Histosols, and mineral horizons of Cambisols were characterized by a high Pb and Cd content.

Table 2. Average content of heavy metals and index of geoaccumulation in organic and mineral horizons of the analyzed soils

	Cd	Cr	Cu	Pb	Zn
			(mg·kg^{-1})		
Organic horizons	0.96± 0.71^{a}	1.05± 1.15^{a}	7.56± 3.42^{a}	113± 64^{a}	36.1± 24.2^{a}
I_{geo}	0.20^{a}	-5.68^{a}	-3.47^{a}	1.09^{a}	-1.59^{a}
Mineral horizons	0.72± 0.63^{b}	2.53± 1.30^{b}	4.54± 3.24^{b}	54.8± 41.2^{b}	23.2± 21.5^{b}
I_{geo}	-0.49^{b}	-3.85^{b}	-4.55^{b}	0.11^{b}	-2.66^{b}

Mean±SD; I_{geo} values ≤0 represent unpolluted soils, 0–1 represent unpolluted to moderately polluted soils, 1–2 moderately polluted soils, 2–3 moderately to highly polluted soils, 3–4 highly polluted soils, 4–5 represent highly to extremely highly polluted soils, and ≥5 extremely polluted soils; small letters in the upper index of the mean values mean significant differences between horizons

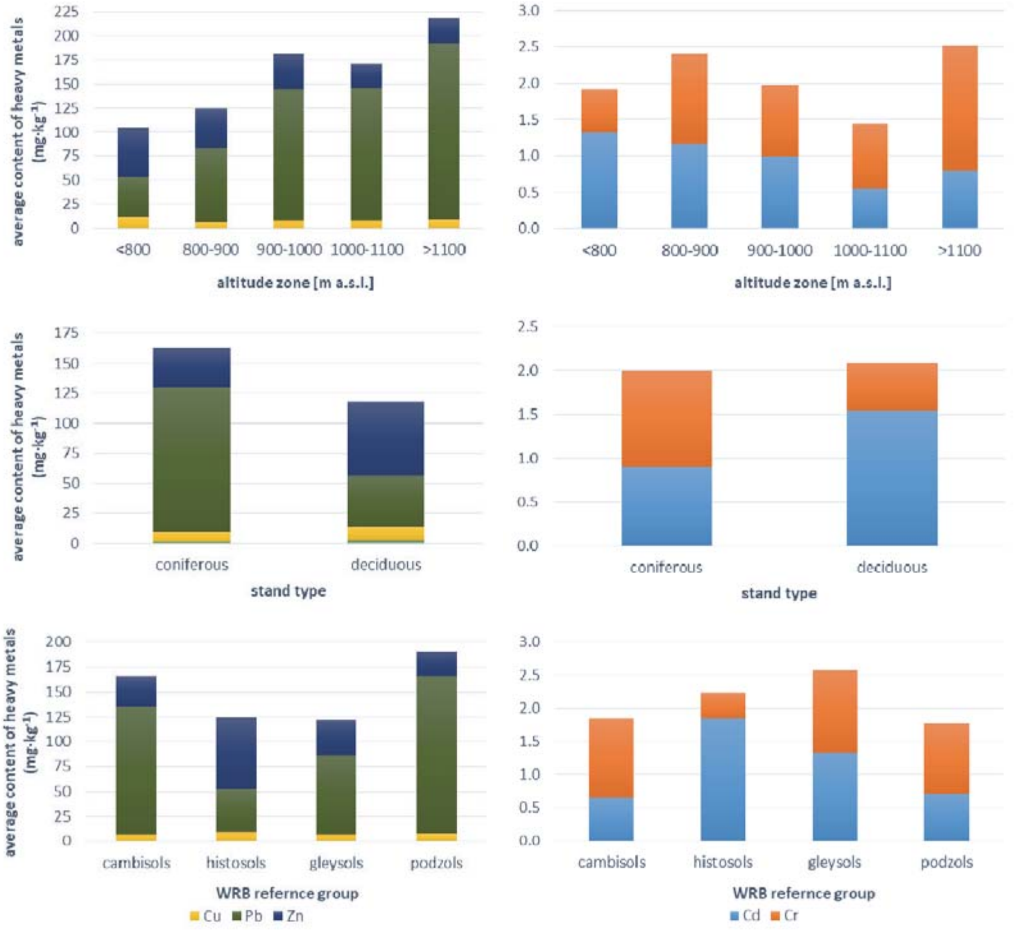

Fig. 2. The average content of heavy metals in organic horizons in relation to height classes, type of stands and type of soils

The highest cadmium content was found in the northern and eastern part of the study area (Figure 4). High amounts of cadmium were recorded in soils in the altitude range from 700 to 1000 m a.s.l. In the organic and mineral horizons of the studied soils, the highest copper contents were recorded in the northern part of the study area. High amounts of copper were recorded in soils at the altitude of approx. 700 m a.s.l. Elevated content of zinc in soils, both in organic and mineral horizons, was recorded in the north-west and east part of the study area in soils within the altitude range between 750 and 1000 m a.s.l. In organic horizons, the highest lead values were noted in the eastern part of the study area. High lead content was recorded in soils at the altitude of over 1100 m a.s.l. In the mineral horizons, high concentrations of lead were recorded in the northern portion of the studied area (Figure 4). Maps of Cd and Pb content in forest soils in terms of geo-accumulation index (Igeo) in organic and mineral horizons present concentrations in which contamination values reach moderately to heavily contaminated soils (Figure 5). Moderately to heavily contaminated soils with cadmium was found in the northern and eastern part of the study area and moderately to heavily contaminated soils with lead were recorded in the northern part of the study area.

In the case of organic horizons, a clear positive correlation between the lead content and the altitude above the sea level was observed (Table 3). A reverse relationship was recorded between cadmium and zinc content and the altitude above the sea level. The base cations content correlated positively with cadmium and zinc content, and negatively with lead content. With the increase of soil pH, the content of cadmium and zinc increased. A reverse relationship concerned lead content, the amount of which decreased with the increase of soil pH. A negative correlation between altitude above the sea level and cadmium, copper and zinc was observed in mineral horizons of the studied soils. The content of lead exhibited positive correlation with the amount of nitrogen and organic carbon. The factors 1 and 2 distinguished in the PCA for organic horizons (Figure 6) explain the total of 57.66% variance of analyzed soil properties. The first factor can be primarily associated with pH and the content of the selected heavy metals (Zn and Cd). On the other hand, the factor 2 is associated with the amount and quality of organic matter. The performed PCA confirms the relationship between lead content with altitude a.s.l., relationship between the Zn and Cd content with the pH of the studied soils and Cu and Cr content with organic matter. The factors 1 and 2 distinguished in the PCA for mineral horizons (Figure 7) explain the total of 62.33% variance of analyzed soil properties. PCA analysis confirms for mineral horizons the strong correlation between heavy metals with the studied soils pH and C and N content. The content of heavy metals in mineral horizon was negatively correlated with altitude a.s.l.

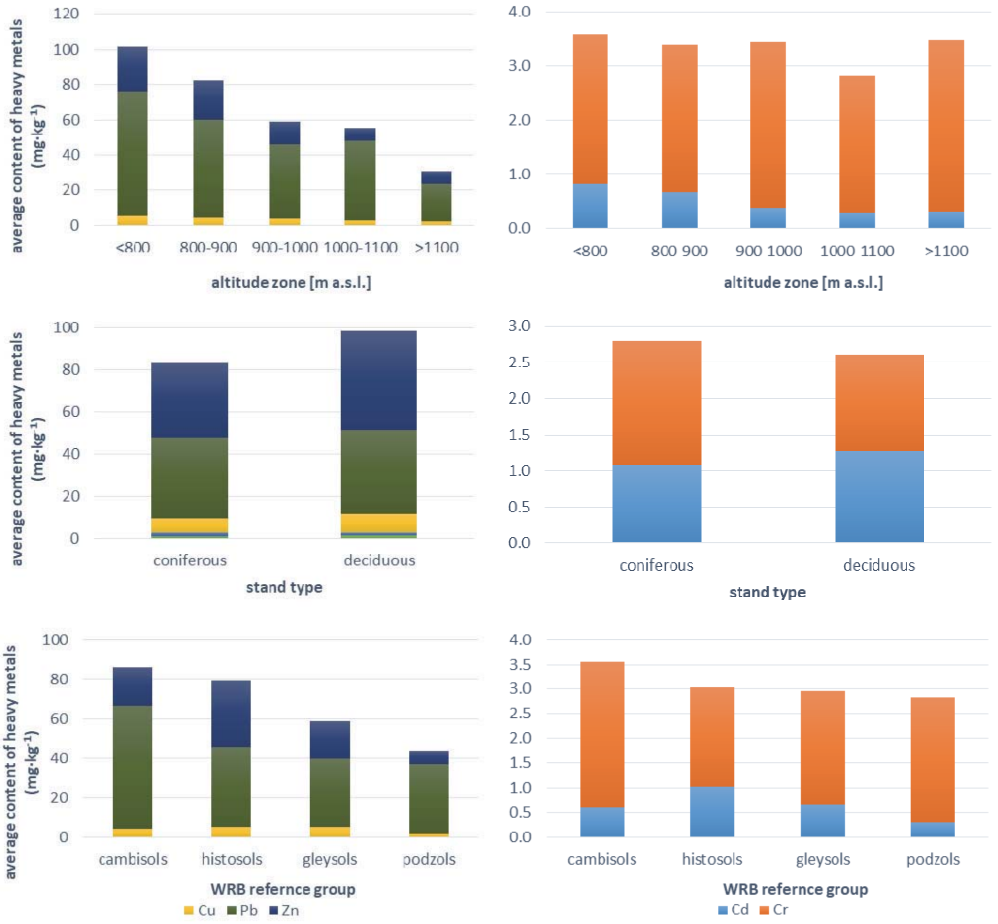

Fig. 3. The average content of heavy metals in mineral horizons in relation to height classes, type of stands and type of soils

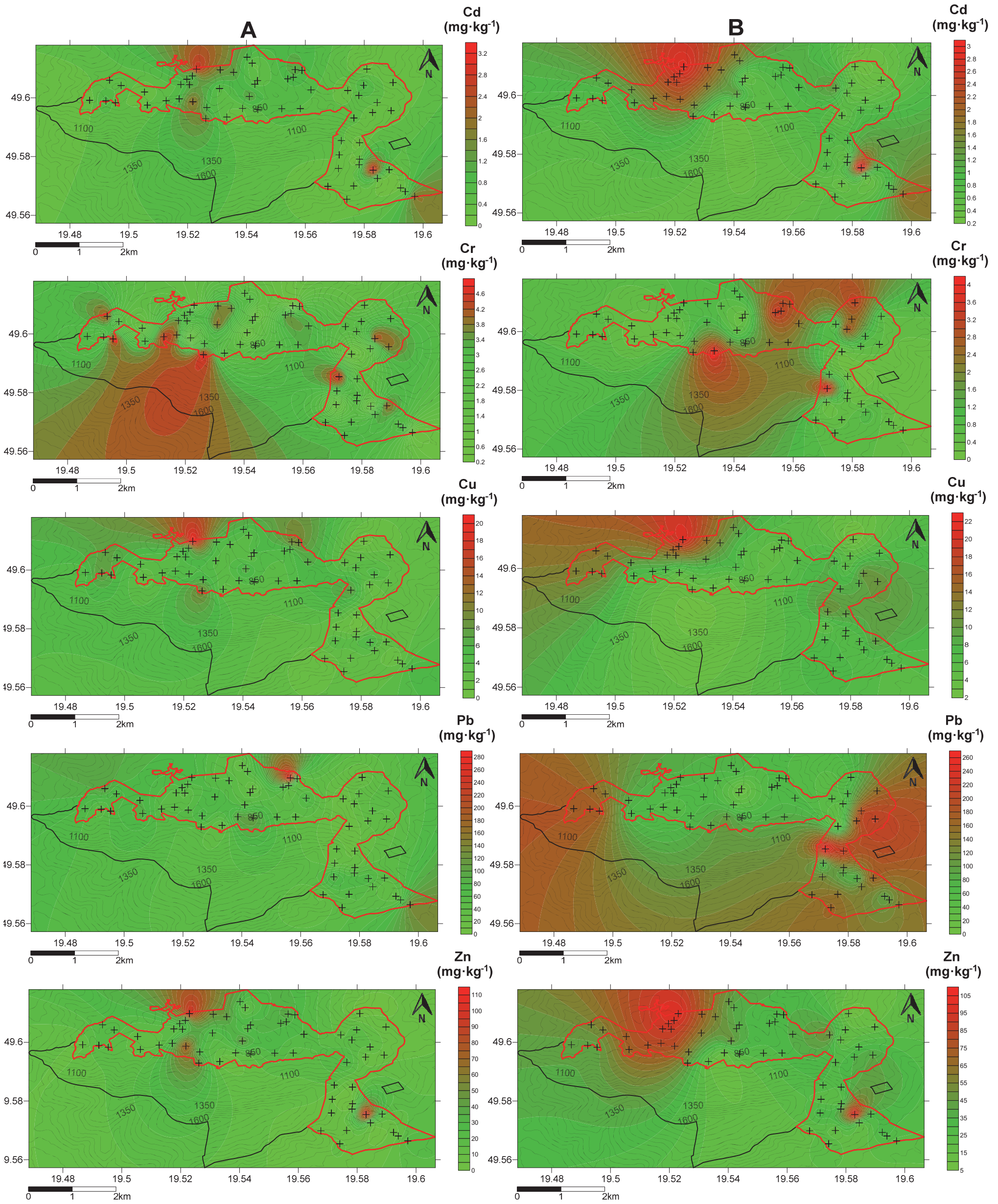

Fig. 4. Maps of spatial distribution of heavy metal (A - organic horizons; B – mineral horizons)

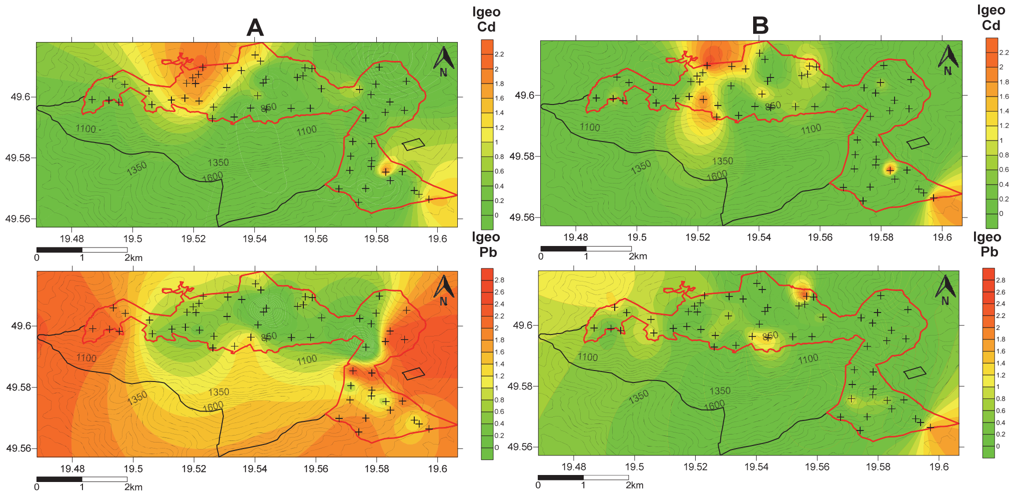

Fig. 5. Maps of Cd and Pb content in forest soils in terms of geoaccumulation index (Igeo) in organic and mineral horizons (A - organic horizon; B – mineral horizons)

Discussion

Considerable amounts of heavy metals were recorded in the soils of the Babia Góra National Park, particularly for organic horizons. The obtained results confirm the observations of other authors (Kabata-Pendias et al. 1993; Konecka-Betley et al. 1999), who recorded the highest accumulation of toxic elements for organic horizons, independently of soil type. Organic horizons of the studied soils have accumulated considerably higher amounts of heavy metals as compared with mineral horizons, this includes cadmium, chromium, copper, lead and zinc. According to Kabata-Pendias (2010), the admissible level of Cd amounts to 1 mg·kg^{-1}, Cu to 30 mg·kg^{-1}, Cr to 50 mg·kg^{-1}, Pb to 50 mg·kg^{-1} and Zn to 100 mg·kg^{-1}. The exceedances of the admissible levels were found primarily for lead. In the majority of test samples, the recorded lead concentration was higher than the admissible value. Among the 59 test sites, only 10 did not exhibit exceeded admissible levels of heavy metals. Soils of the BGNP contain slightly lower or similar amounts of heavy metals as those found for soils located in the vicinity of urban agglomerations, which are exposed to a considerably stronger influence of pollution (Wei and Yang, 2010; Morton-Bermea et al. 2009). The research of Strzyszcz (1999) and Gerszta (1987), found a similar arrangement of heavy metals in the Beskid soils based on the Igeo index, the tested soils were determined as not polluted or polluted to a minor degree. Moderate pollution (Igeo = 1–2) concerned lead in organic horizons, confirming the considerable role of organic matter in the accumulation of lead in soil (Berthelsen et al. 1994; Rademacher, 2003).

The obtained results indicate the correlation between the content of heavy metals in soils with altitude a.s.l. With the increase of altitude above the sea level, the content of lead increases in the organic horizons of the studied soils.

Table 3. Pearson correlation coefficients between the content of heavy metals and physicochemical properties of the analyzed soils

Physicochemical properties	Trace elements									
	Organic horizons					Mineral horizons				
	Cd	Cr	Cu	Pb	Zn	Cd	Cr	Cu	Pb	Zn
C	0.116	-0.309*	0.096	0.111	0.185	-0.086	-0.139	0.169	0.402*	0.014
N	0.210	-0.400*	0.328*	-0.043	0.272	0.094	-0.037	0.301*	0.424*	0.225
BC	0.436*	-0.308*	0.059	-0.536*	0.549*	-0.391*	-0.162	-0.285*	-0.037	-0.449*
$pH\ H_2O$	0.514*	-0.290	0.081	-0.581*	0.604*	0.578*	0.134	0.417*	-0.248	0.513*
pH KCl	0.519*	-0.253	0.078	-0.565*	0.619*	0.581*	0.078	0.464*	-0.210	0.489*
altitude	-0.377*	0.063	-0.101	0.607*	-0.377*	-0.534*	0.035	-0.470*	-0.256	-0.556*
sand	–	–	–	–	–	-0.411*	-0.311*	-0.439*	-0.032	-0.426*
silt	–	–	–	–	–	-0.125	-0.163	-0.161	0.229	-0.200
clay	–	–	–	–	–	-0.028	0.190	-0.140	-0.079	-0.105

N – total nitrogen content (%); C – organic carbon content (%); BC – sum of base cations (cmol(+)·kg^{-1}); sand, silt and clay content (%); * – significant at 0.05 level

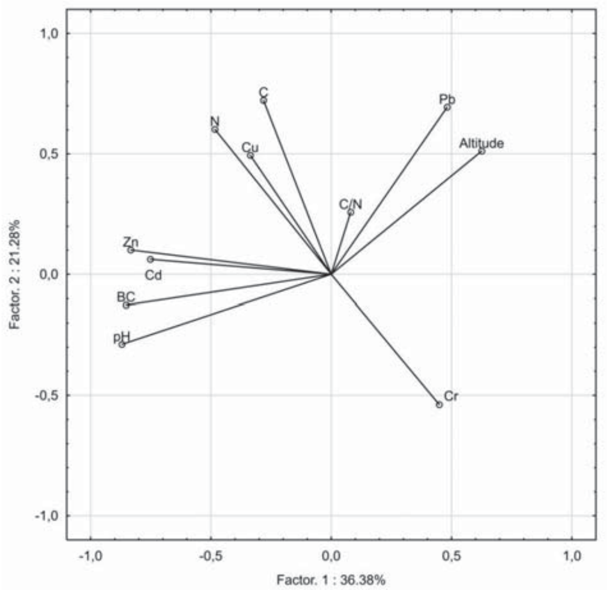

Fig. 6. Diagram of PCA with projection of variables on a plane of the first and second factor for organic horizons (N – total nitrogen content; C – organic carbon content; BC – cation exchange capacity)

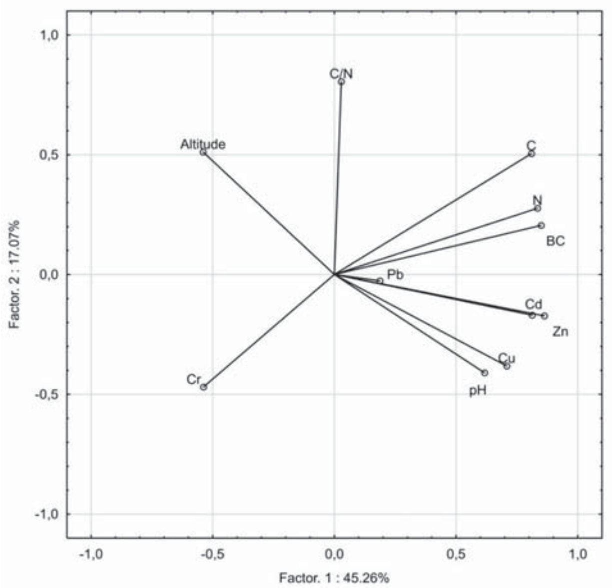

Fig. 7 Diagram of PCA with projection of variables on a plane of the first and second factor for mineral horizons (N – nitrogen content; C – carbon content; BC – cation exchange capacity)

According to Szponar et al. (2009), in mountains the mechanism of orographic pollutant movement is associated with the 'seederfeeder-effect', leading to their transport with orographic clouds up in the slope to a specific altitude and their overlapping with the pollutants originating from the trans-boundary air masses. In their study, Zwozdziak et al. (1995) demonstrated that considerably higher pollution levels were recorded on the windward slopes in the upper range of orographic winds than in the lower portions of mountains. Increase of the accumulation of heavy metals with altitude can be also associated with the increasing amount of precipitation (Zechmeister, 1995). In the West Carpathians, the average precipitation increases by approximately 100 mm with altitude increase of 100 m a.s.l. (Hess, 1965). The higher content of trace elements under coniferous tree stands predominant share of Norway spruce (*Picea abies* L.) is caused by the favorable pH of the crown throughfall. Litter under coniferous tree stands is characterized by a considerably higher acidification as compared to litter under the crowns of deciduous tree stands (Parker, 1990). Due to the adaptability of the Norway spruce (*Picea abies* L.) (Rubner, 1953) to extreme climatic conditions, the species forms tree stands in most of the study area with a cold climate. Coniferous stands with a predominance of spruce grow in areas with poor soils with a high proportion of organic matter, which affects the binding of heavy metals in the upper soil layers. According to the study of Zajączkowski (2002), spruce acidifies soil, intensifying the accumulation of pollutants in soil. According to the study of Ulrich and Matzner (1986), deciduous tree like Sycamore maple (*Acer pseudoplatanus* L.), European beech (*Fagus sylvatica* L.), Grey alder (*Alnus incana* L.) stands growing on more fertile soils, with abundant nutrients, much more efficiently reduce the harmful effect of the acidic deposition from rainfall. A particular trait of coniferous tree stands responsible for accumulation of harmful elements is the capacity to 'comb' pollutants from fog rainfall (Haase et al. 2000; Hill et al. 2002). According to Konieczyński (1982), the aerosol part of the energy pollutants emitted is often lead over zinc and earlier study on heavy metals in soils demonstrated that their mobility is largely influenced by several factors, e.g. redox potential, clay minerals content, organic matter content and pH (Scokart et al. 1983). In our study, we confirmed a correlation between the content of selected heavy metals in both organic and mineral horizons and pH and content of base cations, as observed by (Mühlbachová et al. 2005). Earlier research confirms that soil organic matter reduces the mobility and bioavailability of heavy metals through binding them (Sauvé et al. 2000). In our study, we observed a relationship between soil organic matter with Pb and Cr content.

Of note is the spatial distribution of heavy metal contents in the area of BGNP. Pollution originating from factories and plants located in the vicinity of the BGNP, including burdensome plants located on the Slovak side, may have a strong impact on the amount of heavy metals accumulated in soil. The level of zinc and lead in the fruit of rowan from the slopes of the Babia Góra Mt is only a little lower than in the material from the area of Olkusz and Kraków (Barszcz, 2004). A relatively small difference in the content of the metals mentioned above between the fruit from the Babia Góra Mt and the fruit from regions under direct influence of industry confirms that this BGNP is threatened by anthropogenic influences. According to Staszewski et al. (2012) Babiogórski, Magurski, Ojcowski and Gorczański National Parks in Poland are located on the direction of prevailing winds from the industrial regions of Košice and Prešov in Slovakia where large metallurgic plants are located. Considerable pollution with heavy metals may also be caused by residential houses heated with poor quality coal. According to Błońska et al. (2016) the most important sources of pollution around Krakow are low-stack emissions whose sources are coal combustion in individual home furnaces and traffic emissions. The distribution of the content of certain metals, in particular of lead and cadmium in the eastern part of the study area is associated with the location of traffic routes. Heavy metal accumulation in roadside soils from traffic emission is one of the significant urban environmental issues, which is critical for environmental management (Yesilonis et al. 2008; Zhang et al. 2012). Pb was the catalyst of combustion of gasoline in automobiles engines, hence soils situated near transportation routes are exposed to the accumulation of this metal (Nabulo et al. 2006; Yan et al. 2012). Flysch rocks have relatively high heavy metal contents and spatial distribution of heavy metal content in soils of the Babia Góra National Park may also be conditioned by parent rock (Šajn et al. 2013). Moreover, Pb is characterized by high affinity to organic matter (Mazurek et al. 2017). The map of geo-accumulation coefficient and the amount of heavy metals contained in BGPN soils, prepared on the basis of kriging interpolation, is a useful information base for the assessment of the content of environmental pollution. Multidimensional analysis (PCA) and correlation matrix used in this study are effective tools for source identification. However, further implementations and improvements in the use of geostatistical methods are needed to increase the effectiveness of ecosystem monitoring in terms of anthropogenic factors. According to Lark (2012), geostatical methods are a useful tool to complement soil science research.

Conclusions

1. Soils of the Babia Góra National Park are characterized by accumulation of heavy metals. The content of heavy metals, in particular of lead, exceeds the permissible pollution norms. The BGNP soil pollution with lead has been confirmed by the Igeo index.
2. The obtained results confirmed the heavy metals enrichment especially of organic horizons. The study confirmed the relationship between the content of heavy metals with acidification, C content and altitude a.s.l. We have observed a positive correlation between Pb content and altitude a.s.l. Higher altitudes are dominated by Spruce, being the main species of coniferous tree stands, which are accompanied by acidic, poorly decomposed organic horizons.
3. The method of estimating contaminants using geo-accumulation index and geostatistical methods is a useful combination for monitoring and determining the heavy metals dispersion in the natural environment under strict protection.
4. The high content of heavy metals in the soil of the Babia Góra National Park may also be conditioned by their content in the parent rocks.

5. Based on the conducted research it can be concluded that geostatical methods are an effective and complementary tool for the analysis of processes taking place in the soil environment.

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