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ORIGINAL PAPERS

CONCENTRATION AND POOLS OF TRACE ELEMENTS IN ORGANIC SOILS IN THE IZERA MOUNTAINS

Bartłomiej Glina, Adam Bogacz

Institute of Soil Science and Environmental Protection
Wroclaw University of Environmental and Life Sciences

Abstract

Concentrations of trace elements in organic soils are a result of natural accumulation or due to anthropogenic factors. A field study was carried out in May 2008 on selected sites in the Izera Mountains. Soil samples were collected from 8 profiles of organic soils. Four soil profiles were located on the plateau meadow called Hala Izerska, at the altitude of 835-850 m a.s.l. The other 4 profiles were located in the mountain range known as the Grzbiet Wysoki, at 909-990 m a.s.l. The concentration and pools of heavy metals were determined according to the elevation, depth in soil profile, content of organic matter and soil pH. The content of trace elements (Pb, Cu, Zn) was determined after wet mineralization of samples in nitric acid, using a Flame Atomic Absorption Spectrometer. Pools of trace elements were recalculated into g m^{-2} in the 0-30 cm layer of soil. The aim was to determine the influence of altitude on concentrations of trace elements in organic soils profiles. Organic soils from the Grzbiet Wysoki and Hala Izerska showed significant contamination, mainly with lead and zinc. The elements were most abundant in surface horizons. With an increasing depth into the soil profile, the content of trace elements decreased. The arithmetic means showed strong dominance of lead on zinc and copper in the examined profiles. The Grzbiet Wysoki, due to its higher location above the sea level, is more exposed to atmospheric deposition of contaminants than Hala Izerska. However, the concentration of Cu is higher in organic soils from Hala Izerska. Statistical analysis showed significant positive correlation between the Pb concentration and altitude. With an increasing altitude, the content of Pb in soil also increased. Zinc and lead correlate highly

MSc Bartłomiej Glina, Institute of Soil Science and Environmental Protection, Wrocław University of Environmental and Life Sciences, 50-357 Wrocław, Grunwaldzka 53, e-mail: bartlomiej.glina@up.wroc.pl

negatively with the depth into the soil profile. With an increasing depth, the content of these elements decreases.

Key words: soil, peat, trace elements, mountains, mountain peatlands, the Izera Mountains.

KONCENTRACJA I ZASOBY PIERWIASTKÓW ŚLADOWYCH W GLEBACH ORGANICZNYCH Z OBSZARU GÓR IZERSKICH

Abstrakt

Koncentracja pierwiastków śladowych w glebach organicznych jest wynikiem naturalnej akumulacji, lub spowodowana czynnikami antropogenicznymi. Badania terenowe wykonano w maju 2008 r. na wybranych obszarach Gór Izerskich (Hala Izerska oraz Wysoki Grzbiet). Materiał glebowy pobrano z 8 profilów gleb organicznych. Próbki do badań z Hali Izerskiej pochodziły z 4 profilów zlokalizowanych na wysokości od 835 do 850 m.n.p.m, natomiast 4 profile wykonane na Wysokim Grzbiecie występowały na wysokości od 909 do 990 m.n.p.m. Koncentrację oraz zasoby pierwiastków śladowych określono na tle wysokości nad poziomem morza, głębokości w profilu, zawartości materii organicznej oraz odczynu gleby. Zawartość Pb, Cu, Zn oznaczono po mineralizacji próbek na mokro w stężonym kwasie azotowym z użyciem aparatu AAS. Zasoby pierwiastków śladowych w glebie przeliczano na g m^{-2} w 0-30 cm warstwie gleby. Celem pracy było określenie wpływu czynnika wysokościowego na akumulację badanych pierwiastków w profilu gleb organicznych. Zawartość badanych pierwiastków śladowych (Pb, Zn, Cu) w glebach organicznych Wysokiego Grzbietu oraz Hali Izerskiej wskazuje na znaczne zanieczyszczenie tych gleb, głównie Pb i Zn. Koncentracja wszystkich analizowanych metali jest największa w poziomach powierzchniowych i z reguły maleje wraz ze wzrostem głębokości. Średnie arytmetyczne zasobów wykazały zdecydowaną dominację Pb nad Zn i Cu w profilach analizowanych gleb. Obszar Wysokiego Grzbietu ze względu na wyższe położenie jest bardziej narażony na atmosferyczną depozycję zanieczyszczeń. Koncentracja miedzi jest wyższa w profilach glebowych Hali Izerskiej. W analizie statystycznej wykazano znaczącą dodatnią korelację między koncentracją Pb a czynnikiem wysokościowym. Wraz ze wzrostem wysokości nad poziomem morza wzrastała zawartość Pb w glebie. Cynk i ołów ujemnie silnie koreluje z głębokością w profilu glebowym, wraz ze wzrostem głębokości maleje zawartość tych pierwiastków.

Słowa kluczowe: gleba, torf, pierwiastki śladowe, góry, torfowiska górskie, Góry Izerskie.

INTRODUCTION

Increased concentrations of trace elements in soil are mainly caused by anthropogenic contamination. Major anthropogenic sources of trace elements include fossil fuel combustion, non-ferrous metal production and combustion of gasoline (PACYNA et al. 2001). These contaminants can be transported over long distances. Most trace elements in terrestrial ecosystems originate from atmospheric wet and dry deposition (ANICIC et al. 2009) Organic soils are often used as references in studies of the impact of human activity on contamination with trace elements (MARTÍNEZ-CORTIZAS et. al. 1999). These soils are formed under temporary or permanent waterlogged conditions from the partial decomposition of peat-forming plants (Zaccone et al. 2007). Ombrotrophic bogs are particularly useful for assessment of the degree of trace element pollution from atmospheric deposition. This kind of peat soil is supplied with water mainly by atmospheric depositions (rain or snow) (Kvaerner et al. 2008). One of more important factors which can influence the trace element content in soils is altitude (Gerdol et al. 2006). It plays a significant role as it alters the atmospheric dry or wet deposition of trace elements.

The aim of this study was to determine influence of altitude on the trace elements concentrations in the profiles of examined organic soils.

STUDY AREA

The study was carried out in the Izera Mountains (the Western Sudetes), a mountainous region situated in southwestern Poland (Figure 1) at 50°49'- 50°51' N and 15°18'-15°29' E, with the maximum elevation of 1126 m a.s.l. The Izera Mountains lie in highland climatic regions with the longest winter duration of 110 days and snow cover duration of 116 days. The westerly and northerly Atlantic wet winds contribute to a high level of precipitation and wetness. The average air temperature is -5°C in January and 13°C in July, while the average annual precipitation is 1500 mm. The vegetation growth period lasts 175 days and starts in late April (Migoń et al. 2003). The Izera Mountains are crisscrossed by valleys of several rivers and creeks.

Fig. 1. Localization of Izera Mountains

The Izera Valley is situated between the Grzbiet Wysoki and Grzbiet Średni ranges. Geomorphological processes, affected by the temperature and hydrological regime, continue to shape the mountains. Numerous flattened peaks, often with little runoff, favor the formation of alpine-like peatlands, which in total cover nearly 300 hectares. The peatlands in the Izera Mts. are considered to be a specific type of mountain subarctic peat bogs and share many features with northernmost peat bogs, particularly those in Scandinavia (MATUŁA et al. 1997). Peatlands in the Izerska Mts. developed on granites andgneisses. The analyzed sites in the Grzbiet Wysoki represent ombrotrophic peatlands with characteristic communities of *Eriophoro vaginati-Sphagnetum recurvi* class (profile 1), *Caricetum nigrae* class (profile 3), Calmagrostis villosae-Piceetum sphagnetosum class (profile 4). Site 2 is covered by replacement communities with *Molinia caerulea*. The plant communities growing on Hala Izerska (a meadow and pasture) belong to class *Scheucherio-Caricetae fuscae* (profiles 5 and 6) or constitute a forest site with class *Oxycocco-Sphagneta* with *Pinus sylvestris* – profile 7 and *Carex acutiformis* – profile 8 (POTOCKA 1996). The examined organic soils profiles were classified as Typical sapric peat soils or Typical hemic peat soils (PTG 2011) and Sapric or Hemic Histosols according to the WRB classification (WRB 2006). Profile 1 from the Grzbiet Wysoki was classified as Peaty-Gley soils (PTG 2011) and Histic Gleysols (WRB 2006). The Izera Mountains are located in an area called the Black Triangle (crossed by the Polish, Czech and German borders). For many years, it has been heavily polluted many power plants located in Northern Bohemia, Saxony and Lower Silesia. Additionally, the long-range pollution transport form North-Western Bohemia and Eastern Saxony has aggravated the local pollution (STRZYSZCZ et al. 2001).

METHODS

Soil samples were collected with an Instorf sampler from 8 sites located on two ombrotrophic peatlands: one in the Grzbiet Wysoki (4 profiles) and the other one on Hala Izerska (4 profiles). The sampling sites lay within an elevation range from 835-850 m.a.s.l (Hala Izerska) and 909-990 m.a.s.l (the Grzbiet Wysoki). The following properties were determined in the collected soil samples: soil colour according to the Munsell Color System, ash content by peat combustion in a muffle furnace at 550°C for 6 hours, bulk density measured in undisturbed samples, organic carbon determined by dry combustion using an automatic analyzer (CS – MAT 5500), total nitrogen assayed by standard Kjeldahl technique, pH in H_2O and 1 mol dm^{-3} KCl potentiometrically at the soil : solution ratio of 1:2.5, total content of trace elements (Zn_t, $Cu_{t,}$ Pb_t,) with flame atomic absorption spectroscopy (FAAS).

The samples were digested in nitric acid (HNO_3). Pools of trace elements at the depth of 0-30 cm were calculated using formulas: metal (g m^{-2}) = a (mg kg^{-1}) · b (g cm^{-3}) · c (mm)/1000 (a – metal content, b – bulk density, c – depth). Statistica 9.0 software (StatSoft Inc., Tulsa, OK) was used to test the statistical significance of trends in changes of soil properties. For each sites, Pearson correlation coefficients were determined between the concentration of trace elements, depth, altitude, pH and soil organic matter. Differences between pools of elements in soils from Hala Izerska and the Grzbiet Wysoki were calculated using the mean standard deviation (SD) and basic analysis of variance (CV).

RESULTS AND DISCUSSION

The examined organic soils are strongly acidic. The range of pH_{KCl} values was from 2.3 to 3.8 (Table 1). The pH_{KCl} values below 4 are characteristic of ombrotrophic bogs, which are supplied with water mainly by weakly acidic precipitation (Berset et al. 2001, De la Rosa et al. 2003). The determined soil organic carbon (SOC) values ranged from 265 to 535 g kg^{-1}. The lowest SOC was observed in horizons under the moorshing process. This phenomenon is broadly reported in the literature (Sokołowska et al. 2005, Kogel-Knabner 2002). It is caused by mineralization of organic matter and its release into the atmosphere. The highest SOC was found in peat horizons consisting hemic and sapric material. Arithmetic means of the total nitrogen content in soils did not exceed 20 g kg^{-1}. Values of this parameter in all samples are estimated between 5.1-35.1 g kg^{-1} (Table 1).

Table 1

Concentrations of trace elements and some other properties of organic soils horizons

Soil horizon	Depth (cm)	Soil colors	pH_{KCl}	C-total (g kg^{-1})	N og (g kg^{-1})	Pb	Zn	Cu
						(mg kg^{-1})		
Oi	5-20* 11**	10YR 8/3*** 7.5 YR 8/3	2.3-3.4 2.8	377-480 438	11.8-26.2 17.5	15.8-207 117	13.9-134 53.7	6.4-50.5 18.5
Oe	4-18 9	10YR 8/4 7.5YR 8/4	2.3-3.2 2.7	399-510 456	5.1-20.7 14.9	42.4-246 126	12.5-58.5 33.5	1.8-35.2 12.1
Oa	7-58 29	10YR 7/4 7.5YR 4/4	2.4-3.8 3.1	322-535 451	7.8-35.1 17.1	12.0-94.9 40.1	5.8-70.4 30.2	2.7-35.9 14.0
M	10-20 16	10YR 5/4 7.5YR 6/4	2.7-3.3 2.9	265-464 391	8.0-20.7 13.6	15.0-243 96.2	24.3-122 65.5	2.2-36.4 18.8

Key: M – moorsh, O – organic, a – sapric peat, e – hemic peat, i – fibric peat,
*range (minimum-maximum), **arithmetic mean, ***soil color range

According to the Polish ground quality standards (*Ordinance*…2002), the content of trace elements in the examined soils exceeds the permissible level set for group A areas (legally protected areas), except for the zinc concentration in organic soils in Hala Izerska, which was below the maximum threshold. Generally, the highest levels of trace elements appeared in the surface horizons. With an increasing depth into the soil profile, the content of trace elements decreases. The analyzed organic soils are mostly polluted with lead. The content of this element was within a wide range of 12.0--246 mg kg^{-1}. Among the analyzed trace elements, the content of copper was significantly lower. The concentration of this element in soils did not exceed 50 mg kg^{-1} (Table 1). ETTLER et al. (1999) in their study on ombrotrophic peatlands in the Czech Izera Mountains, presented very similar concentrations of trace elements in soil.

The calculated pools of trace elements in the 0-30 cm soil layer showed significant dominance of lead above the other determined elements. The pools of Pb in soils from the Wysoki Grzbiet ranged from 3.33 to 9.46 g m^{-2}. Profile 2, localized at 990 m a.s.l., had the highest content of Pb. Soils from Hala Izerska are characterized by smaller pools of lead (Table 2). The abundance of zinc pools was estimated at 1.14 to 5.73 g m^{-2} for soils from the Grzbiet Wysoki and 1.22 to 2.87 g m^{-2} for soils from Hala Izerska. Both lead and zinc created more abundant pools in organic soils from the Grzbiet Wysoki. A reverse situation was determined for copper. Richer pools of this element were characteristic of soils from Hala Izerska (Tables 2 and 3). Profile 5 had a particularly high concentration of copper, which may have been caused by its localization in an old riverbed of the Izera River. The river transported material eroded from surrounding areas, which then settled in the riverbed (WU et al. 2011). This may indicate that the copper resources are the result of natural accumulation, not shaped by the atmospheric deposition. The results showed that altitude strongly affected the Pb concentration. Organic soils in the higher Izera Mountains contained more of this element. No such correlation was proven for the copper and zinc concentrations (Figure 2). The Grzbiet Wysoki is an orographic barrier that stops air masses, which carry pollution. Thus, higher Pb concentrations are found at at higher altitudes. ERISMAN et al. (2003) mentioned that dry or wet deposition of gases and particles was affected by factors which influenced the turbulent transport, especially wind velocity, but also by the relief and height of the land.

Statistical analysis showed a significant positive correlation between Pb concentration and altitude factor (r=0.48). As the altitude increased, so did the content of Pb in soil. Also GERDOL et al. (2006) described strong correlation between Pb concentrations and altitude. Zinc (r=-0.45) and lead (r=-0.53) negatively strongly correlated with the depth of a soil profile. The content of these elements decreases with the profile's depth. Higher concentrations of organic carbon in topsoil was mentioned elsewhere (YIN et al.

Table 2

Pools of trace elements in upper horizons of examined soils

Profile No.	Layer (cm)	Trace elements calculated (g m^{-2})					
		Pb		Zn		Cu	
1/GW	0-10	0.66	3.33	0.83	2.12	0.38	0.57
	10-20	1.25		0.65		0.12	
	20-30	1.42		0.64		0.07	
2/GW	0-10	4.62	9.46	2.32	5.73	0.69	1.17
	10-20	3.23		2.09		0.40	
	20-30	1.62		1.31		0.08	
3/GW	0-10	0.88	5.92	0.57	1.85	0.11	0.63
	10-20	3.12		0.68		0.34	
	20-30	1.92		0.60		0.18	
4/WG	0-10	2.90	7.68	0.34	1.14	0.42	0.86
	10-20	2.70		0.42		0.33	
	20-30	2.08		0.39		0.10	
5/HI	0-10	3.24	6.84	0.98	2.87	0.95	2.26
	10-20	3.24		0.98		0.95	
	20-30	0.36		0.92		0.37	
6/HI	0-10	0.28	0.76	1.25	2.65	0.54	1.02
	10-20	0.27		1.07		0.44	
	20-30	0.21		0.33		0.05	
7/HI	0-10	1.41	3.91	0.44	1.22	0.26	0.65
	10-20	1.41		0.44		0.26	
	20-30	1.09		0.33		0.14	
8/HI	0-10	0.85	2.56	0.41	1.22	0.14	0.41
	10-20	0.85		0.41		0.14	
	20-30	0.85		0.41		0.14	

Key: GW – the Grzbiet Wysoki, HI – Hala Izerska

2002). The reaction of the analyzed soils depended on the altitude and soil profile's depth (Table 4). The acidification in soil from the Grzbiet Wysoki is caused by higher precipitation at a higher altitude. There is more precipitation at higher altitude (BORUVKA et al. 2009).

Table 3

Statistical parameters of trace elements pools in examined soils

Trace element (n=4)	localization of profile	x	SD	dx	CV
Pb	GW	6.60	2.614	3.08	0.143
	HI	3.52	2.563		
Zn	GW	2.71	2.055	0.72	0.544
	HI	1.99	0.893		
Cu	GW	0.81	0.272	0.28	0.545
	HI	1.09	0.823		

Key: x – arithmetic mean, SD – standard deviation, dx – difference of arithmetic mean, CV – coefficient of variation, n – number of samples

Table 4

Coefficients of correlation between concentrations of trace elements and properties of examined organic soils

Value	Pb_t	Zn_t	Cu_t	pH	C-total
Height	0.48*	0.23	-0.21	-0.62*	0.09
Depth	-0.53*	-0.45*	-0.07	0.71*	0.18
Pb_t		0.33*	0.24	-0.29	-0.25
Zn_t			0.36*	-0.17	-0.10
Cu_t				0.13	-0.21
pH					-0.21

Key: n=37, correlation ratio significant at $^*p<0.05$

Also, some correlation was observed between the trace elements, e.g. zinc concentration is determined by lead and copper. Significant positive correlation is observed between these elements. Strong correlation was often observed between Pb and Zn of the anthropogenic origin, mainly from coal-fired power plants (Strzyszcz et al. 2001). None of analyzed trace elements showed significant correlation with organic carbon. This situation is typical of organic soils and often described in available literature (Bogacz 2010, Bogacz et al. 2011).

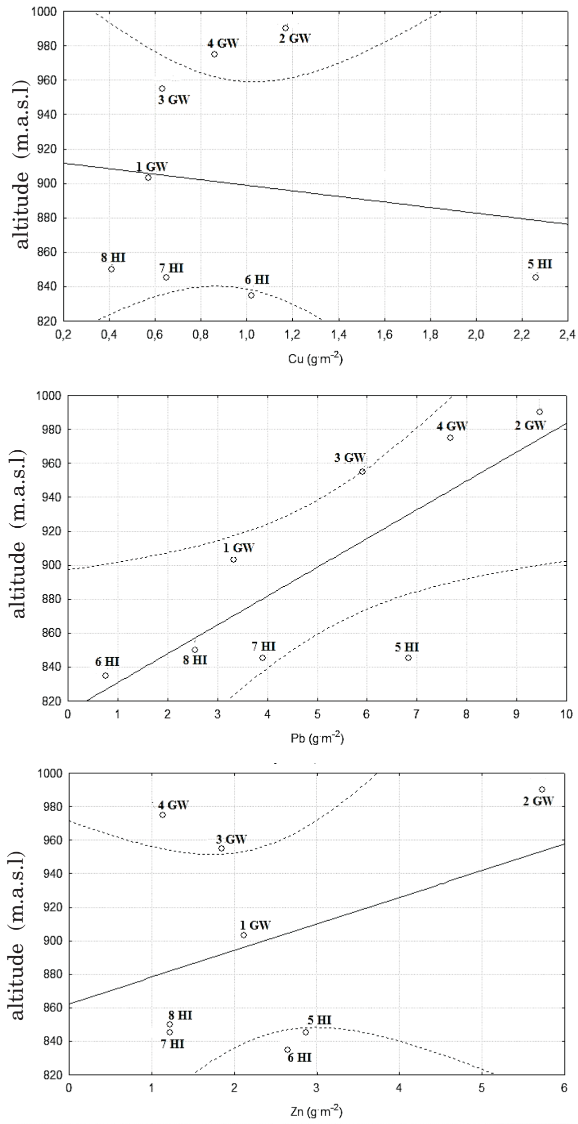

Fig. 2. Relationship between altitude and pools of trace elements

CONCLUSIONS

1. Pools of trace elements were strongly differentiated by the location of examined soils on different altitudes above sea level. The concentration of lead was particularly strongly dependent on on the altitude.

2. The highest concentrations of lead and zinc were observed in the epipedons of organic soils, which proves the anthropogenic origin of these elements and their atmospheric deposition.

3. At higher altitudes, lower values of pH were observed in soil, which suggests strong acidification of these soils.

4. The statistical analysis showed significant differences between pools of lead in soils in the Grzbiet Wysoki and Hala Izerska.

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