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ORIGINAL PAPERS

CONCENTRATION AND POOLS OF HEAVY METALS IN ORGANIC SOILS IN POST-FIRE AREAS USED AS FORESTS AND MEADOWS

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Abstract

High concentration of heavy metals in organic soils may be the result of intensive, deep-seated fires causing high temperatures. This research has been carried in four post-fire areas, located in forests or on meadows in Lower Silesia. The aim has been to determine the impact of some parameters on the content of heavy metals in soils under post-fire meadows and forests. The concentration and pool of the analyzed heavy metals were determined in soils against the background of such parameters as the depth in a horizon, organic matter content, soil colour and soil reaction. Twenty Histosol soil profiles (85 soil samples) were analyzed, representing peat-muck, muck (MtIIc1, MtIIIc1) and mineral-mucky (Me11) and on-muck soils (according to the Polish taxonomy of soils). The soils were strongly desiccated. Some physicochemical and chemical properties of pyrogenic soils were analyzed in dry samples collected into plastic bags with an Instorfu auger. Heavy metals (Zn, Cu, Pb, Ni, Cr) were determined in HCl + HNO_3. Pools of heavy metals were recalculated into g m^{-2} in 0-20 cm layers of soils and compared among forest and meadow soils. Due to intensive fires, the reaction of pyrogenic soils was slightly acid, neutral or alkaline. As a consequence of the high temperatures, a broad spectrum of soil colours was noticed. The results showed increased concentrations of heavy metals in the topmost and muddy soil horizons. The alkaline soil reaction favoured accumulation of heavy metals. Pools of heavy metals in soils were significantly lower in forest than in meadow areas, which could be attributed to different time periods which elapsed since the fires. The Hue tint of the colour of soil horizons containing ashes indicated the presence of oxidized iron forms and

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a low content of organic carbon. The accumulation of heavy metals in post-fire sites in Lower Silesia was negatively correlated with the soil's strongly acid reaction. The determined concentrations of heavy metals did not exceed the threshold values set for unpolluted soils.

Keywords: soil, peat, fire, heavy metals, valley areas, dewatering process.

KONCENTRACJA I ZASOBNOŚĆ METALI CIĘŻKICH W GLEBACH ORGANICZNYCH NA OBSZARACH POPOŻAROWYCH UŻYTKOWANYCH JAKO LASY I ŁĄKI

Abstrakt

Wysoka koncentracja metali ciężkich w glebach organicznych może być wynikiem intensywnych, wysokotemperaturowych pożarów wgłębnych. Badania prowadzono na leśnych i łąkowych obszarach popożarowych Dolnego Śląska. W glebach określono koncentrację oraz zasoby wybranych metali ciężkich na tle: głębokości w profilu, zawartości materii organicznej, barwy gleby oraz odczynu środowiska glebowego. Łącznie przeanalizowano 20 profilów płytkich gleb: torfowo-murszowych, murszowych (MtIIc1, MtIIIc1), murszowatych (Me11) i namurszowych (85 próbek glebowych). Właściwości fizykochemiczne i chemiczne gleb popożarowych oznaczono w próbkach suchych pobranych świdrem Instorf do plastikowych woreczków. Zawartość metali ciężkich (Zn, Cu, Pb, Ni, Cr) w glebie oznaczano po mineralizacji w mieszaninie $HCl+HNO_3$. Zasoby metali ciężkich w glebie przeliczano na g m^{-2} w 0-20 cm warstwie gleby i porównywano z glebami leśnymi i łąkowymi. Badania pokazały wzrost koncentracji metali ciężkich oraz ich zasoby w poziomach powierzchniowych 0-20 cm. Poziomy popożarowe gleb wykazywały odczyn lekko kwaśny, obojętny lub zasadowy. W konsekwencji temperatury pożarów można obserwować zróżnicowane spektrum kolorów gleb. Pożary na glebach leśnych i łąkowych wzbogaciły wiele poziomów w Zn, Cu, Pb, Ni, Cr. Koncentrację metali w glebach obserwowano głównie w powierzchniowych i zamulonych poziomach. Odczyn gleb sprzyjał koncentracji metali ciężkich. Zasoby metali ciężkich w glebach były wyraźnie niższe na obszarach leśnych niż łąkowych. Było to m.in. związane z czasem, jaki upłynął od zakończenia pożarów. Odcień barwy Hue w poziomach z popiołem był warunkowany intensywnym utlenianiem żelaza i niską zawartością węgla ogólnego. Gromadzenie się metali ciężkich na obszarach popożarowych Dolnego Śląska było negatywnie skorelowane z silnie kwaśnym odczynem środowiska. Nie obserwowano przekroczenia wartości granicznych metali ciężkich w przypadku gleb niezanieczyszczonych.

Słowa kluczowe: gleba, torf, pożar, metale ciężkie, obszary dolinowe, przesuszenie.

INTRODUCTION

Significant increase in the content of heavy metals is observed in ashes generated by peat fires, especially the ones causing high temperatures (ZAIDELMAN et al. 1999). The main reasons are the loss of organic matter and elevated quantities of mineral particles in ash (BANNIKOV et al. 2008). The concentration of trace elements is several-fold higher in ash than in peat, depending on analyzed trace elements (ZAIDELMAN et al. 2003, DIKICI, YLMAZ 2006).

This research has been carried out to determine the impact of some physical and chemical parameters on concentration of heavy metals (Pb, Zn, Cu, Cr and Ni) in soils of post-fire meadow and forest areas and to compare distribution of metals in the described soil horizons.

METHODS

Soil samples have been collected from two post-fire forest sites: Gromadka (GR) in Chocianów Forest Division and Mikorzyce-Górowo (MG) in Wołów Forest Division, and from two meadow sites: Lubsko (LU) and Sobin-Jędrzychów (SJ). The forest fires occurred in 1986 and 1992 and the meadow fires broke out in 2006 and 2008. In total, 20 soil profiles were analyzed and 85 soil samples were collected. Forest soil samples were collected from profiles No 9-12MG (12 years after a fire) and profiles No 1-8GR (21 years after a fire). Meadow soil samples were collected from profiles No 12-15LU (immediately after a fire) and profiles No 16-20SJ (2 years after a fire). The soil samples represented the following soil subtypes: muck, peat-muck, mineral-mucky and on-muck soils. The horizons represented strongly dried peat-muck soils and medium deep (MtIIc1 and MtIIIc1) and mineral-mucky (Me11) and on-muck soil (OKRUSZKO 1974). The peat found in post-fire sites has a distinctly high degree of organic matter decomposition (BOGACZ 2009, BOGACZ at al. 2010). In the collected soil samples, the following properties were determined: soil colour according to Munsell notation, ash content by peat combustion in a muffle furnace at 550°C for 4 hours, bulk density with 100 cm^{-3} Kopecky's metal rings, organic carbon content in a Bushi analyzer, pH in H_2O and 1 mol dm^{-3} KCl $_{(pH\ KCl)}$ potentiometrically at a 1:2.5 soil to solution ratio, total content of the heavy metals such as zinc (Zn_t), copper (Cu_t), lead (Pb_t), nickel (Ni_t) and chromium (Cr_t) with the flame atomic absorption spectroscopy (FAAS). The samples had been digested in mixed $HCl+HNO_3$. Concentrations of trace elements were analyzed in this mixture, in mg kg^{-1}. Afterwards, their pools were converted into g m^{-2} in the 0-20 cm layer of soil and compared between forest and meadow soils. For each of the investigated sites, a correlation coefficient was determined between concentration of heavy metals, pH and depth. Differences between pools of heavy metals in soil used as forests and meadows were calculated using the mean standard deviation (SD) and basic analyses of variance. Statistical analyses were made using logarithmic data with Stat-Soft Statistica software, version 8.0.

RESULTS AND DISCUSSION

The organic post-fire soils under forests and meadows were characterized by strongly acid and acid reaction in a deeper horizon, but neutral and alkaline pH in the horizons with ashes (Table 1). A study performed by ZAIDELMAN et al. (2003) on pyrogenic peat soil in Moscow region confirms this regularity. The lowest carbon content was observed in muddy horizons and those with ashes, whereas the highest one, exceeding 500 g kg^{-1} of soil, appeared in bog peat and intermediate peat horizons. Following an intensive fire, the reaction of pyrogenic soils is neutral or alkaline. As a consequences of the high temperature, a very broad soil colour spectrum, between N, 10YR and 5YR, can be observed (Table 1).

According to the Polish norms prepared for arable soils by the *Threshold quantities...* (1985), an elevated Pb content in the surface and subsurface layers of post-fire soils (ashes and horizons with ashes) occurred in some samples. Excessive metal concentrations were determined versus the Polish soil quality standards and Polish ground quality standards (*Ordinance*…2002). Generally, the highest levels of metals appeared in the topmost horizons, just a few centimetres thick, which with time might be dispersed by wind or leached by water. Fires enriched many horizons of meadow and forest soils with Zn, Cu, Cr and Ni. The highest Pb concentration was observed in the Olfh layers of litter, zinc in the thin layers of peat and litter, copper in muck and also in a thin layer of peat. The chromium content was observed mainly in ash horizons A and organic muddy horizons Om. No such regular tendencies were observed for nickel (Table 1).

Pools of lead in the analyzed forest soils layer ranged from 0.76 to 9.09 g m^{-2}. The Zn content was less varied and did not exceed 3.0 g m^{-2}. Copper, chromium and nickel were found to appear in even less diverse quantities, for example below 1.0 g m^{-2} in the 0-20 cm forest soil layer (Table 2). In post-fire meadow soils, which had been ravaged by a fire just a couple of years before, concentrations of the metals were different. Significantly higher pools of microelements, such as lead, zinc and copper as well as chromium and nickel, were observed in surface layers (Table 2).

Large quantities of organic carbon have been observed in soils under the two analyzed meadows and under forests, in layers unaffected by high- or low-temperature fires (HOGG et al. 1992). These layers were characterized by black colour 10YR 2/1. The research conducted by AFREMOV and AFREMOVA (2000) on deep peat soils implied a high carbon content, over 600 g kg^{-1} of soil, in layers affected by a low-temperature fire. An increase in the carbon content in surface layers may also be influenced by the initially low microbial activity (JASTRZĘBSKA, KUCHARSKI 2006), resulting in organic matter decomposition (TSIBART, GENNADIEV 2008). In horizons where ash suggested occurrence of fires generating temperatures over 200°C (ULERY, GRAHAM 1995),

Table 1

Heavy metal concentration and some properties in pyrogenic soil genetic horizons

Genetic horizon	Depth (cm)	Soil colors	pH_{KCl}	C-total ($g\ kg^{-1}$)	Pb	Zn	Cu	Cr	Ni
					($mg\ kg^{-1}$)				
Olfh	2-7* 4**	10YR 3/4*** 2.5YR 2.5/0	3.1-4.3 3.4	139-475 336	20.2-246 87.4	8.50-136 70.5	7.70-501 23.7	3.82-18.4 8.85	3.15-37.0 10.8
A	4-34 11	N 3/0 5YR 5/5	3.3-7.9 5.5	10.7-112 62.5	14.8-81.7 38.2	9.20-91.7 31.7	2.50-41.2 16.7	8.10-42.7 17.6	3.95-37.2 16.6
Mt	5-17 9	10YR 2/1 5Y 3/2	2.4-6.8 4.6	253-497 411	4.10-145 55.6	8.50-77.5 29.1	6.39-203 33.3	2.01-22.1 9.64	2.50-60.5 9.86
Otni	5-30 13	10YR 2/1 5YR 3/3	2.3-5.8 3.6	137-519 319	1.40-333 42.0	5.6-46.2 16.6	3.10-32.3 11.7	1.99-67.1 27.0	0.90-74.2 22.7
Otpr	13-20 18	10YR 2/1 5YR 3/1	1.7-3.5 2.6	225-415 350	1.4-8.00 6.85	7.70-32.1 19.9	4.10-28.6 14.8	5.60-8.00 7.25	21.3-76.7 51.6
O	2-16 10	N 3/0 5YR 2.5/1	4.0-6.3 5.4	171-389 268	4.97-79.4 49.8	3.51-865 297	7.91-130 50.0	2.94-46.6 21.0	1.38-33.6 15.8
O/D	8-15 11	10YR 2/1 7.5YR 4/3	3.9-5.9 4.5	55.5-109 83.9	5.23-14.8 9.54	4.25-15.0 7.66	1.50-13.0 5.72	8.40-34.2 16.1	0.40-9.00 3.48

Key: Olfh – forest litter, A – acumulation, Mt – moorsh, t – peat, tni – low peat, tpr – mediate peat, O – organic, O/D – organic/mineral, *range (minimum – maximum, **arithmetic mean, ***soil color range

Table 2

Heavy metals pools in upper horizons of pyrogenic soils in forests areas

Site No.	Layer (cm)	Heavy metals calculated (g m^{-2})									
		Pb		Zn		Cu		Cr		Ni	
1/GR	0-10	1.24		0.78		0.65		0.16		0.14	
	10-20	0.46	1.70	1.09	1.87	0.43	1.08	0.15	0.31	0.14	0.28
2/GR	0-10	0.41		0.61		0.26		0.09		0.08	
	10-20	0.35	10.76	0.29	0.90	0.54	0.80	0.27	0.36	0.13	0.21
3/GR	0-10	1.20		1.23		0.43		0.17		0.17	
	10-20	0.57	11.77	0.43	1.66	0.31	0.74	0.14	0.31	0.18	0.35
4/GR	0-10	4.82		2.77		1.06		0.38		0.23	
	10-20	0.15	14.97	0.25	3.02	0.19	1.25	0.05	0.43	0.06	0.29
5/GR	0-10	2.37		1.07		0.57		0.28		0.16	
	10-20	0.21	2.58	0.33	1.40	0.13	0.70	0.04	0.32	0.07	0.23
6/GR	0-10	1.49		1.50		0.38		0.40		0.30	
	10-20	1.95	13.44	1.01	2.51	0.50	0.88	0.59	0.99	0.64	0.94
7/GR	0-10	1.15		1.12		0.30		0.18		0.16	
	10-20	1.40	12.55	0.77	1.89	0.26	0.56	0.38	0.56	0.26	0.42
8/MG	0-10	1.65		0.82		0.30		0.28		1.40	
	10-20	1.93	3.58	1.93	2.75	0.31	0.61	0.47	0.75	2.52	3.92
9/MG	0-10	2.95		0.91		0.79		0.24		0.15	
	10-20	6.61	9.56	1.25	2.16	0.31	1.10	0.19	0.43	0.19	0.34
10/MG	0-10	1.30		0.52		0.40		0,23		0.18	
	10-20	0.09	1.39	0.55	1.07	0.74	1.14	0.01	0.24	0.41	0.59
11/MG	0-10	1.27		0.20		0.24		0.13		0.10	
	10-20	2.04	3.31	0.31	0.51	0.31	0.55	0.26	0.39	0.16	0.26

Key: GR – Gromadka, MG – Mikorzyce-Górowo

a decrease in the organic matter content was observed (Table 1). This phenomenon has been pointed out by many scientists studying post-fire soils (Zaidelman et. al. 2003, Kania et. al. 2006). It has also been confirmed by the colour of a horizon containing ashes, such as red-yellow Hue 5YR, indicating the presence of oxidized iron forms and a low content of organic carbon (Table 1).

The accumulation of organic matter determined in the analyzed post-fire sites in Lower Silesia was negatively correlated with strongly acid reaction of the soil environment (r=-0.60**, p<0.01, n=85) – Table 3. After a fire, these soils were enriched with different heavy metals in post-ash or ash horizons. This is also clearly confirmed by the correlation coefficients for the depth and concentration of Pb (r=-0.39*), Cu (r=-0.26*) and Zn (r=-0.26*) p<0.05, n=85). The Cr and Ni content in soils depends not only on their concentration in ashes but also on the intensity of mud formation in soils, a process which is often observed in deeper horizons (Tables 2 and 4). The negative correlation coefficients computed between chromium and nickel depth and concentration were not significant (Table 3). A study completed by ARKHIPOVA and KARATAIEVA (2002) on vast peat areas in Siberia confirms the above findings. Ashes generated by fires neutralize organic acids occurring in peat, mainly in surface layers, and change base saturation by adding easily soluble, alkaline substances (GYNIKOVA, SYMPILOVA 1999, KRASNOSHCHEKOV 1994).

Table 3

Coefficients of correlation between concentration of heavy meta and properties of pyrogenic soils in post-fire areas

Value	Pb_t	Cr_t	Ni_t	Cu_t	Zn_t	pH	C-total
Depth	-0.39*	0.13	0.07	-0.26	-0.26	-0.32*	-0.10
Pb_t		0.14	0.04	0.25	0.17	0.17	0
Cr_t			0.03	0.06	0.06	0.30*	-0.15
Ni_t				0.07	-0.02	0.25*	-0.05
Cu_t					0.53*	0.26*	0.08
Zn_t						0.25*	0.06
pH							-0.60*

Key: n=85, correlation ratio significant at: *p<0.05, **p< 0.01

The latter authors also emphasize a sudden decrease in the pH value, just a few years after a fire, due to migration of soil components induced by intensive precipitation and flowing water (ZAIDELMAN et al. 2003). The accumulation of new acid products of plant decomposition on the soil surface may also intensify this process (ZAIDELMAN et al. 1999). Higher pH values, resulting from neutral or alkaline reaction, are a consequence of heavy metal accumulation in post-fire soils (DIKICI, YLMAZ 2006). This is confirmed by the correlation coefficient between the reaction of a soil horizon and its depth (r=-0.32*, p<0.05, n=85) – Table 3. Many studies on heavy metal translocation in organic post-fire soils (ZAIDELMAN et al. 2003, KUTIELL, SHAVIN 1993, JOHNSTON, ELIOT 1998, LYNHAM et al. 1998) clearly indicate a high rate of metal migration, mainly during the first years after a fire. In the present study, important changes were observed in the content of heavy metals in surface layers of forest and meadow soils, and differences were noticed relative to the time lapse after a fire. These changes were mainly noticeable in the

Table 4

Heavy metal pools in upper horizons of pyrogenic soils in meadow areas

Site No.	Layer (cm)	Heavy metals calculated (g m^{-2})									
		Pb		Zn		Cu		Cr		Ni	
12/LU	0-10	2.31		5.58		1.14		0.68		0.34	
	10-20	2.05	4.36	1.12	6.70	0.53	1.67	1.21	1.89	0.36	0.70
13/LU	0-10	1.43		1.47		0.18		0.64		0.22	
	10-20	2.20	3.63	1.97	3.44	1.02	1.20	1.99	2.63	0.65	0.87
14/LU	0-10	5.34		5.30		1.63		2.24		1.07	
	10-20	4.01	9.33	3.66	8.96	1.22	2.85	3.49	5.73	1.08	2.15
15/LU	0-10	2.65		3.40		0.96		1.29		0.73	
	10-20	2.22	4.87	1.55	4.95	0.52	1.48	1.20	2.49	0.60	1.33
16/SJ	0-10	2.83		1.69		3.70		0.37		0.34	
	10-20	2.09	4.92	0.94	2.63	0.90	4.87	0.40	0.77	0.46	0.80
17/SJ	0-10	1.40		1.40		1.54		0.40		1.51	
	10-20	1.53	2.93	0.67	2.07	0.36	1.90	0.48	0.88	0.93	2.44
18/SJ	0-10	1.75		1.09		1.38		0.44		1.04	
	10-20	1.66	3.41	0.79	1.88	1.71	3.08	0.46	0.90	1.02	2.06
19/SJ	0-10	4.60		2.92		3.33		1.19		2.30	
	10-20	4.50	9.10	0.60	3.52	0.42	3.75	0.19	1.38	0.94	3.24
20/SJ	0-10	2.58		1.45		1.88		0.61		2.65	
	10-20	3.37	5.95	1.96	3.38	1.21	3.09	0.74	1.35	2.79	5.44

Key: LU – Lubsko, SJ – Sobin - Jędrzychów

Table 5

Pools of heavy metals in post fire soils used as meadowand forests

Metal (n=18)	Type of use	x	SD	dx	CV
Pb	forest	3.24	0.294		
	meadow	5.39	0.177	2.15	0.022606
Zn	forest	1.79	0.232		
	meadow	4.17	0.225	2.38	0.002537
Cu	forest	0.86	0.129		
	meadow	2.65	0.203	1.80	0.000007
Cr	forest	0.46	0.182		
	meadow	2.00	0.282	1.54	0.000025
Ni	forest	0.71	0.368		
	meadow	2.11	0.302	1.40	0.001118

Key: x – arithmetic mean, SD – standard deviation, dx – difference of arithmetic means, CV – coefficient of variation, n – number of samples case of lead, zinc and copper (Tables 2 and 4). Statistically significant differences were observed between pools of heavy metals and land use type (Table 5), a relationship which was particularly strong for Cu, but the least significant for Pb.

CONCLUSIONS

A fire causes raises the soil reaction and enlarges pools and concentration of some heavy metals, mainly in surface layers. A decrease in organic matter is also observed, especially in surface layers with ash. Generally, the threshold values set up by the norms on soil quality standard and ground quality standard (*Ordinance*…2002) were not exceeded. In a few cases, however, a slight excess in heavy metals was noticed versus the norms established by the *Threshold quantities*... (1985) for arable soils. Forest soils had a lower content and poorer pools of heavy metals in surface layers than meadow soils. This is mainly due to changes in pH, organic matter loss and a different time lapse after a fire.

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