# CONTENT OF Zn, Pb, Cd AND Ni IN PEAT-BOG AND FEN SOILS IN THE TATRA NATIONAL PARK

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A b s t r a c t: Hydrogenic soils have been considered to preserve a record amount of atmospheric deposition of heavy metals. Investigations on Zn, Pb, Cd concentrations in the peat-bog and fen soil profiles showed that the Tatra National Park has been contaminated by heavy metals, particularly cadmium. Total contents of cadmium exceeding 3 mg kg<sup>-1</sup> of soil were often found in the eutrophic fen soil surface horizons and in a depth of 30-40 cm of the peat-bog soil profiles. Concentrations of total Zn, Pb and Cd in peat-bog and eutrophic fen soils from this park area were higher than in the analogous soils from other areas of the West-Carpathians and from the lowlands of the South Poland.

Key words: heavy metals, peat-bog soils, fen soils, the Tatra National Park

#### INTRODUCTION

Condition of the natural environment of the Tatra National Park depends, to a large degree, on accumulation of heavy metals in its soils which is directly related to their contents in the parent materials and immission of industrial dust. Accumulation of many heavy metals in organic soils is favoured by their considerable affinity with organic matter. Therefore, hydrogenic and semihydrogenic soils, with high thickness in organic horizons with water retention abilities, may play such a valuable role in the detection of heavy metals in the environment [2,11,12,15].

Peat-bogs and fens in the Tatra National Park occupy small areas. The surface cores taken from the *Sphagnum* bogs are hydrologically isolated from the influence of local groundwaters and surface waters, and are fed exclusively by atmospheric deposition. Hence, they are particularly important for the diagnosing long-range air pollution threatening the environment. Peat-bogs in the Tatra Na-

tional Park have mainly developed by the accumulation of peat in the postglacial lakes and melting basins and they exist most frequently in the mountain belts [9]. Fens, unlike peat-bogs, developed in places where water flows out or are enriched by flow water. In fens, inorganic constitutents are provided both by atmospheric and hydrospheric processes. Acid fens are located mainly near the Tatra lakes in the subalpine and alpine belts [1], while eutrophic fens occupy quite small areas on the mountain glades.

The aim of the present research was to determine the state of the Tatra National Parks contamination with heavy metals on the basis of Zn, Pb, Cd and Ni concentration in the peat-bog and fen soil profiles.

### MATERIALS AND METHODS

Investigations were carried out on the soil material derived from 11 profiles situated in the peat-bogs and fens in the Tatra National Park. The peat-bogs soils were represented by 4 profiles of peat soils situated in the largest peat-bogs, located in the mountain belts, at an altitude from 1089 to 1370 m a.s.l. Fen soils (7 profiles), enumerated in the Polish Soil Systematics (1989) as peat soils and peaty gley soils, were situated at an altitude 900-1610 m a.s.l., on mountain glades (eutrophic fens) or in the subalpine belt (acid fens) (Fig. 1, Table 1).

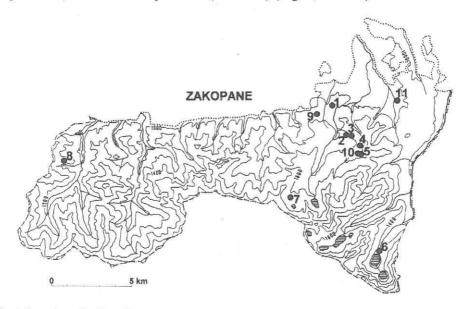


Fig. 1. Location of soil profiles in the Tatra National Park

Table 1. Location and taxonomic u	units of the soils investigated
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Profile No.	Location	Altitude (m)	Type of soil according to PTG [10]	Unit of soil according to WRB [16]
		Peat l	oogs	
1	Niżni Toporowy Staw	1089	peat soil	Dystric Fibric Histosol
2	Wielka Pańszczycka Młaka	1265	peat soil	Dystric Fibric Histosol
3	Mała Pańszczycka Młaka	1280	peat soil	Dystric Fibric Histosol
4	Wyża Pańs1089	1345	peat soil	Dystric Fibric Histosol
		Acid	fens	
5	Waksmundzka Polana	1370	peat soil	Dystric Fibric Histosol
6	Małe Morskie Oko	1420	peat soil	Dystric Sapric Histosol
7	Hala Gąsienicowa	1610	peat soil	Dystric Sapric Histosol
		Eutroph	ic fens	
8	Polana Jaworzyna	1290	peaty gley soil	Eutric Histic Gleysol
9	Sucha Polana	1115	peaty gley soil	Eutric Histic Gleysol
10	Polana Waksmundzka	1365	peaty gley soil	Eutric Histic Gleysol
11	Polana Brzanówka	900	peat soil	Eutric Sapric Histosol

The following analyses were performed in the soil samples: pH potentiometrically in H<sub>2</sub>O and 1 mol dm<sup>-3</sup> KCl, ash content at 550 °C, cation exchange capacity (CEC) by the determination of basic cations (Ca, Mg, K, Na), using for their extraction 1 mol dm<sup>-3</sup> ammonium acetate, hydrolytical acidity in 1 mol dm<sup>-3</sup> sodium acetate and total Zn, Pb, Cd and Ni contents after soil digestion in a mixture of concentrated nitric and perchloric acids according to the ASA method using an acetylene-aerial flame for the atomization.

## RESULTS AND DISCUSSION

Peat-bog soils of the Tatra Mountains are characterised by a strong acid reaction, a low ash content and a low degree of base saturation (V%) (Table 2). The results of analysis of the elementary properties of the soils investigated were similar to those of other high peat-bog soils [2,5].

The total Zn, Pb and Cd contents in the surface horizons of these soils (Tables 3 and 4) were similar to the amount of metals in the high peat-bog soils of the Niepołomice Forest [2]. The content of the above metals was considerably higher than in similar soils of the Podhale region [2] and the Jura Mountains of Switzerland [12]. The total Zn, and Cd contents was higher but the amount of Pb was lower than in the analogous soils in the Sudeten [13] (Table 3).

Table 2. Chemical properties of the soils investigated

Profile	Horizon	Depth	рН Н <sub>2</sub> О	pH KCl	Ash (%)	CEC <sup>1)</sup>	BS <sup>2)</sup>	Zn	Pb	Cd	Ni
No.		(cm) mmol (%) (+)kg <sup>-1</sup>		(%)	mg kg <sup>-1</sup>						
					Peat-bo	g soils					
	POt1	0-10	4.1	3.1	3.5	931.1	17.6	77.99	18.11	0.70	5.86
1	Ot2	30-40	4.0	3.1	5.7	619.9	5.7	176.23	61.81	4.19	12.33
	Ot3	60-70	4.1	3.3	9.9	1355.5	6.2	273.00	66.25	6.66	13.77
	POt1	0-10	3.9	2.8	2.5	696.4	9.1	61.54	73.81	0.81	3.90
2	Ot2	30-40	3.5	2.7	2.4	1173.3	4.0	78.31	122.07	5.00	5.13
	Ot3	50-65	4.0	2.8	2.4	1082.8	4.8	33.81	22.72	0.63	3.25
	POt1	0- 4	5.3	3.4	3.2	972.6	18.4	86.17	62.52	1.32	6.32
3	Ot2	4-10	3.8	3.0	9.2	1146.5	16.3	86.44	65.93	3.43	10.20
	Ot3	30-40	5.0	3.9	9.5	947.3	36.8	76.90	35.44	2.03	8.90
	Ot4	50-62	5.5	4.5	12.6	968.4	44.2	129.14	8.56	1.71	9.98
	POt1	0-10	4.5	3.2	6.7	1100.1	7.3	48.85	116.82	4.01	4.13
4	Ot2	30-40	4.2	3.4	22.4	816.8	12.0	107.68	108.40	6.01	5.98
	Ot3	60-70	4.2	3.3	38.8	722.7	11.1	35.60	76.96	1.39	7.60
					Acid fe	n soils					
5	Pot1	0-10	4.2	3.2	8.9	896.0	19.6	144.83	78.32	1.65	14.83
	Ot2	30-35	4.1	3.2	26.0	919.8	13.7	870.26	70.77	1.07	12.85
6	POt1	0-15	4.8	3.9	42.2	553.7	14.7	33.29	64.40	0.52	5.05
	Ot2	15-58	4.8	3.9	37.9	630.1	13.4	26.69	51.30	0.43	4.57
7	POt1	0-10	n.d.	n.d.	6.9	n.d.	n.d.	125.63	45.41	2.50	10.26
	Ot2	10-20	4.3	3.8	65.1	363.1	8.3	67.90	89.74	0.93	14.83
	Ot3	20-30	4.3	3.7	56.4	413.8	7.3	74.00	43.07	0.70	11.91
	Ot4	30-40	4.4	3.8	n.d.	349.6	8.0	70.05	45.27	0.67	12.49

Table 2. Continued

Profile No.	Horizon	Depth (cm)	pH H <sub>2</sub> O	pH KCl	Ash (%)	CEC <sup>1)</sup> mmol	BS <sup>2)</sup> (%)	Zn	Pb mg l	Cd	Ni
NO.		(cm)				(+)kg <sup>-1</sup>	(70)				
					Eutrophic	fen soils					
	PIt1	0-12	6.1	5.6	44.0	797.9	79.8	223.85	94.50	4.67	n.d.
8	Ot2	12-20	5.8	5.1	58.7	640.0	78.7	83.10	40.80	1.61	n.d.
	Gg	20-39	6.5	5.3	93.4	214.5	86.4	35.50	30.05	0.28	n.d.
	Cca	39-55	7.3	5.9	99.2	155.4	95.1	39.50	15.00	0.37	n.d.
	POt	0-19	6.2	5.5	64.1	707.1	81.7	338.45	113.98	8.78	9.41
9	AGg	19-37	6.4	5.6	86.4	509.0	89.1	49.15	44.01	0.22	12.51
	CGg	37-80	7.1	6.1	99.0	231.0	95.0	30.00	30.10	0.01	13.82
	C	80-99	7.5	6.6	99.5	260.9	98.1	34.70	31.40	0.01	15.66
	Aangg1	0-24	6.2	5.3	85.9	340.4	79.7	164.20	62.50	1.96	21.85
10	Aangg2	24-41	6.2	5.4	84.8	380.4	82.2	130.00	54.90	1.75	19.85
	Ot	41-61	5.9	5.1	76.9	490.8	75.3	51.97	37.52	0.51	16.55
	POt1	0-20	5.4	4.6	35.4	502.3	48.0	145.10	207.10	2.48	30.15
11	Ot2	20-55	5.0	4.4	30.1	641.8	41.7	56.60	13.87	0.96	23.99
	Ot3	55-69	4.8	4.2	39.5	651.6	42.5	53.90	20.27	0.65	31.63

<sup>1)</sup>CEC - cation exchange capacity, 2)BS - base cation saturation, n.d. - not determined

An average contents of Zn, Pb and Cd in high and transitory peat-bog soils of the Tatra National Park to a depth of 75 cm was much higher than an average content of these metals in the respective soils of the Niepołomice Forest and the Podhale [2] (Fig. 2). The highest amount of the metals investigated in the peat-bog soils of the Tatra, similarly to the soils of the Jura Mountains [12], occurred most often in the horizons at a depth of 30-40 cm. In the analogous soils of the Podhale and the Niepołomice Forest, the maximum content of metals was found in the surface horizons. Higher concentration of heavy metals in the deeper horizons of peat-bog soils may result from the atmospheric deposition during formation of these horizons [11] or from the washing-in of these metals with dissolved organic matter in the runoff water [15]. The latter idea was confirmed by Kruk and Podbielska [3]. The above authors found that an outflow of stream waters of the *Sphagnum* bog contained more Cd and Pb than an atmospheric inflow.

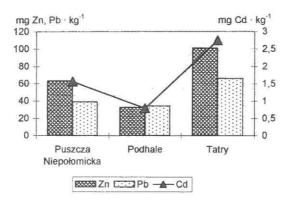


Fig. 2. An average content of Zn, Pb and Cd in the peat-bog soils to a depth of 75 cm (data from Kosiński *et el.* [2] and investigation by the present authors

Acidic fen soils were represented by 3 peat soils profiles. They were characterized by a considerably higher ash content and lower cation exchange capacity than peat-bog soils. The highest contents of Zn, Pb and Cd were found in the surface horizons of these soils and they were comparable to those occurring in the peat-bog soil subsurface horizons. In the acidic fen soils, the levels of Zn, Pb and Cd decreased with an increasing depth, and in a depth of 30-40 cm of the profiles they were lower than in the peat-bog soils (Table 2). The lowest content of the heavy metals investigated occurred in the fen soil in the Rybi Potok Valley. The soils in the above valley did not contain much Zn, Pb and Cd as they are protect against pollution by the Orla Perć and Koszysta screen.

Total Ni content in the peat-bog investigated and in the acidic fen soils was lower than an average Ni amount in the soils of the former Nowy Sącz district [14], and ranged from 3.25 to 14.38 mg kg<sup>-1</sup>.

Eutrophic fen soils were represented by 3 peaty gley soil profiles and a peat soil profile. They were characterized by a high content of ash, acid and slightly acid reaction and a far higher degree of base saturation than other soils investigated. In the above soils, total Zn, Pb and Cd content was the highest in the surface horizons where it often exceeded the values determined in the peat-bog soils and acidic fen soil surface horizons (Table 3). Eutrophic fen soil surface horizons in the Tatra National Park contained considerably higher Zn, Pb and Cd concentrations as compared to the lowland mire soils [2] and other mountain eutrophic fen soils [6-8] (Table 4).

Total Ni content in the eutrophic fen soil profiles changed irregularly. It was higher than in other soils investigated, and ranged from 9.41 to 31.65 mg kg<sup>-1</sup>.

Tal	o l e	3.	Total	levels of	zinc,	lead and	d cadmium	in surfa	e horizons	of pea	t-bog soils	
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Location	Zn	Pb	Authors		
		mg kg <sup>-1</sup>			
Puszcza Niepołomicka (2) <sup>1)</sup>	88.8; 125.1 (107.0)	70.7; 74.5 (72.6)	1.83; 2.47 (2.15)	Kosiński et al. [2]	
Kotlina Orawsko-Nowotarska (4)	48.7-60.9 (55.2)	43.6-55.9 (48.1)	1.03-1.89 (1.38)	Kosiński et al. [2]	
Karkonosze (3)	38.7-64.6 (54.4)	221.5-362.1 (281.5)	trace - 0.32	Skiba et al. [13]	
Schweizerischer Jura (3)	1.0	27.3-41.4 (32.4)	~	Shotyk et al. [12]	
Tatry (5)	48.9-144.8 (68.6)	18.1-116.8 (67.8)	0.70-4.01 (1.71)	author's investigation	

<sup>1)</sup>number of samples, (2)arithmetic mean

Table 4.	Total levels of zinc	lead and cadmium	in the surface horizons	of the eutrophic mire and fen
soils				

Location	Zn	Pb	Cd	Authors
		mg kg <sup>-1</sup>		
Kraków-Nowa Huta (2)	29.2; 394.6	51.6; 52.9	3.62; 4.29	Kosiński et al. [2]
Podgórska Wola near				
Tarnów (1)	36.3	88.2	3.67	Kosiński et al. [2]
Puszcza Sandomierska (2)	47.1; 52.2	4.3; 6.8	0.33; 1.03	Kosiński et al. [2]
Czarny Dunajec				
(Podhale) (1)	13.7; 47.0	4.0; 8.5	1.05; 1.31	Kosiński et al. [2]
Maruszyna (Podhale) (1)	241.6	50.8	1.1	Niemyska-Łukaszuk et al. [7]
Dol. Kamienicy	110.8-278.0	39.6-103.2	2.0-4.0	Niemyska-Łukaszuk et al. [6]
(Gorce) (4)	(199.1)	(78.0)	(3.2)	
Pieniny (2)	114.4; 194.1	49.2; 36.2	2.65; 7.19	Niemyska-Łukaszuk et al. [8]
Tatry (4)	145.1-338.5	62.5-207.1	1.96-8.78	
	(217.9)	(119.5)	(4.47)	author's investigation

### CONCLUSIONS

- 1. Total Zn, Pb and Cd content in the peat-bog and fen soils from the area of the Tatra National Park was higher than in the analogous soils from other areas of the West-Carpathians and from South Poland lowlands.
- 2. Total cadmium content exceeding 3 mg kg<sup>-1</sup> of soil was often found in eutrophic fen soil surface horizons and in the deeper horizons of the peat-bog profiles.
- 3. The highest total amount of Zn, Pb and Cd in the peat-bog soils of the Tatras occurred most often in the horizons at a depth of 30-40 cm. Higher concentrations of heavy metals in the deeper horizons may result from the washing-in of metals with dissolved organic matter in the runoff water.
- 4. Total Ni content in the eutrophic fen soils was considerable higher than in the peat-bog and acidic fen soils.

#### REFERENCES

- Balcerkiewicz S.: High-mountain vegetation of the five Polish Lakes Valley in the Tatra Mts. and its anthropogenic changes. Uniwersytet im. Adama Mickiewicza w Poznaniu, Seria Biologia, 25, 1-191, 1984.
- Kosiński K., Lipka K., Możdżeń M.: Contents of the heavy metals in peats (in Polish). Zesz. Nauk. AR w Krakowie, 291, Inżynieria Środowiska 15, 116-125, 1994.
- Kruk M., Podbielska K.: The differentiation of the Zn, Cu, Pb and Cd concentration in the environment of *Sphagnum* bog with humus lake (in Polish). Problemy aktywnej ochrony ekosystemów wodnych i torfowiskowych w polskich parkach narodowych. Wyd. UMCS, Lublin, 243-248, 1999.
- Mirek Z., Piękoś-Mirkowa H.: Flora and vegetation of the Polish Tatra Mountains. Mountain Research and Development, 12, 2, 147-173, 1992.
- Możdżeń M., Kosiński K.: The contents of heavy metals in the peat-bog of Puścizna Mała (Orawsko-Nowotarska Valley) (in Polish). Zesz. Nauk. AR w Krakowie, 303, Sesja Naukowa 46, 85-93, 1996.
- Niemyska-Łukaszuk J.: Forms of Zn, Pb and Cd in soils of the selected regions of the West Carpathians (in Polish). Zesz. Nauk. AR w Krakowie, Rozpr., 187, 1993.
- Niemyska-Łukaszuk J., Miechówka A., Gąsiorek M.: Zinc, lead and cadmium in the turf soils of the Podhale region (in Polish). Zesz. Probl. Post. Nauk Roln., 439, 172-176, 1997.
- Niemyska-Łukaszuk J., Miechówka A., Zaleski T.: Soils of Pieniny National Park and their threats (in Polish). Pieniny Przyroda i Człowiek, 2002.
- Obidowicz A.: Entstehung und Alter einiger Moore im n\u00f6rdlichen Teil der Hohen Tatra. Fragm. Flor. Geobot. 21, 3, 290-323, 1975.
- 10. Systematics of Polish Soils (in Polish). Roczn. Gleb., 40, 3-4, 1989.
- Shotyk W.: Natural and anthropogenic enrichments of As, Cu, Pb, Sb, and Zn in ombrotrophic versus minerotrophic peat bog profiles, Jura Mountains, Switzerland. Water, Air, Soil Pollut. 90, 375-405, 1996.
- Shotyk W., Cheburkin A.K., Appleby P.G., Frankhauser A., Kramers J. D.: Lead in three peat bog profiles, Jura Mountains, Switzerland: enrichment factors, isotopic composition, and chronology of atmospheric deposition. Water, Air, Soil Pollut. 100, 297-310, 1997.
- Skiba S., Drewnik M., Szmuc R.: Heavy metals in soils from selected regions of Karkonosz Mts (in Polish). W: Karkonoskie badania ekologiczne (red. Z. Fiszer, J. Fabiszewski). Oficyna Wyd. Instytutu Ekologii PAN, Dziekanów Leśny, 125-134, 1994.
- 14. Terelak H., Piotrowska M., Motowicka-Terelak T., Stuczyński T., Budzyńska K.: The content of heavy metals and sulphur in soils of agricultural land of Poland and the degree of their pollution with this elements (in Polish). Zesz. Probl. Post. Nauk Roln., 418, 1, 45-60, 1995.
- Urban N.R., Eisenreich S.J., Grigal D.F., Schurr K.T.: Mobility and diagenesis of Pb and <sup>210</sup>Pb in peat. Geochim. Cosmochim. Acta 54, 3329-3346, 1990.
- World reference base for soil resources. 84 World Soil Resources Reports. FAO-ISRIC and ISSS, Rome, 1998.

# ZAWARTOŚĆ Zn, Pb, Cd I Ni W GLEBACH TORFOWISK I MŁAK TATRZAŃSKIEGO PARKU NARODOWEGO

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S t r e s z c z e n i e. Gleby semihydrogeniczne i hydrogeniczne, o retencyjnej gospodarce wodnej i dużej zawartości substancji organicznej, wykorzystywane są do monitoringu zanieczyszczenia środowiska przyrodniczego metalami ciężkimi. Celem przeprowadzonych badań było określenie stanu zanieczyszczenia Tatrzańskiego Parku Narodowego metalami ciężkimi, na podstawie ich zawartości w glebach torfowisk i młak.

W materiale glebowym z 11 profili zlokalizowanych na torfowiskach wysokich i przejściowych oraz młakach kwaśnych i eutroficznych w Tatrzańskim Parku Narodowym oznaczono podstawowe właściwości gleb oraz całkowitą zawartość cynku, ołowiu, kadmu i niklu. Gleby torfowisk i młak Tatrzańskiego Parku Narodowego charakteryzowały się wyższą zawartością cynku, ołowiu i kadmu, aniżeli analogiczne gleby z innych obszarów Karpat Zachodnich i terenów nizinnych południowej Polski, co może świadczyć o ich antropogenicznym zanieczyszczeniu. Niepokojąco wysokie zawartości kadmu stwierdzono w poziomach powierzchniowych gleb młak eutroficznych oraz w poziomach podpowierzchniowych gleb torfowisk wysokich i przejściowych. Występowanie wyższych, w porównaniu z poziomami powierzchniowymi, zawartości badanych metali w poziomach podpowierzchniowych gleb torfowisk wysokich i przejściowych może świadczyć o wmywaniu ich w gląb profili wraz z substancją organiczną.

Słowa kluczowe: metale ciężkie, gleby torfowisk, gleby młak, Tatrzański Park Narodowy