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The concentration of heavy metals in soils around the wetlands of the Ina valley near Sławęcin

Koncentracja metali ciężkich w glebach mokradeł doliny Iny koło Sławęcina

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Słowa kluczowe: dolina rzeki Iny, mokradła, metale ciężkie, murszenie

Abstract

Wetlands around the upper part of the Ina valley are the area of great natural value, free from negative industrial impact. In the possible sources of contamination, we could include herbicides and artificial fertilisers from fields and meadows or municipal waste discharge from a small town Recz and local farms. The soils of wetlands, situated in the left part of the Ina valley near Sławęcin, were studied. Four characteristic profiles were made, from which soil samples were collected for laboratory analysis. In the soil samples, the content of organic matter and reaction in 1 mol KCl·dm⁻³ were determined, whereas in mineral horizons, granulometric composition and the concentration of total and exchangeable forms of heavy metals (Cd, Pb, Cu, Co, Zn, Fe). As a result of conducted studies, it was found that the soils of wetlands in the Ina valley near Sławęcin, do not exhibit contamination with heavy metals but their greater accumulation was observed in the surface muck layers than in fen peat and lower lying sediments.

Streszczenie

Mokradła w górnym odcinku doliny Iny to obszar cenny przyrodniczo i jednocześnie wolny od negatywnego oddziaływania przemysłu. Za ewentualne źródło zanieczyszczeń można przyjąć tu między innymi zanieczyszczenia z pól i łąk w postaci środków ochrony roślin oraz nawozów sztucznych, czy też zrzuty ścieków komunalnych z zabudowań wiejskich jak i niewielkiego miasta Recz. Badaniami objęto gleby mokradeł lewobrzeżnej części doliny Iny w pobliżu Sławęcina. Wykonano cztery charakterystyczne profile glebowe, z których pobrano materiał glebowy do badań laboratoryjnych. W próbkach glebowych oznaczono: zawartość materii organicznej, odczyn w 1 mol KCl·dm⁻³, w poziomach mineralnych skład granulometryczny oraz koncentrację metali ciężkich w formie wymiennej i ogólnej (Cd, Pb, Cu, Co, Zn, Fe). W wyniku przeprowadzonych badań stwierdzono, że gleby mokradeł doliny Iny koło Sławęcina nie wykazują zanieczyszczenia metalami ciężkimi, przy czym obserwuje się ich większe nagromadzenie w poziomach powierzchniowych murszowych, niż w niżej występującym torfie niskim i niżej występujących osadach.

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1. INTRODUCTION

The increase in heavy metal concentration in the environment is caused by more intensified human activity. It can be assumed that the main sources of contamination are: industry, transport and agriculture whose by-products are absorbed by bottom sediments and become a geochemical archive for the changes of environment [Kozieł, Zabłocki 2010].

The wetlands of the upper part of Ina valley are the area of great natural value, free from negative impact of industry and therefore, characterised by smaller anthropogenic pressure on the environment. However, it is not completely free from human activity. Dewatering of the Ina valley wetlands for agricultural use interrupts the stage of accumulation leading to the degradation of organic soils. As a result of decession, the formed muck layers are characterised by changeable chemical properties in relation to the parent formation, which, in turn, may cause a higher concentration of heavy metals in these layers [Becher 2011]. On the other hand, the surface soil layers are, to a greater degree, exposed to the possible contamination from fields and meadows

such as herbicides and artificial fertilisers or the discharge of waste from local farms or sewage treatment plant of Recz.

In this paper, the effects of anthropopressure on the content of heavy metals in the main types of soils of the Ina valley wetlands near Sławęcin, were assessed.

2. MATERIALS AND METHODS

Field soil studies were carried out in June 2012 in the left part of the Ina valley near Sławęcin. On the basis of field observations and preliminary soil boreholes, four objects representing the main types of soils, were designated and in each of them, one profile was made. From selected and described genetic horizons, soil samples (21) were collected for laboratory analysis. Organic matter content was determined by loss on ignition at 550°C in a microwave muffle stove (Milestone mls 1200 pyro), reaction in 1 mol KCl dm⁻³ by electrometric method, granulometric composition in mineral horizons by the method of Bouyoucosa

Table 1. Selected chemical properties, granulometric composition and content of heavy metals soluble in HCl at concentration 0.5 mol·dm⁻³

The level of genetic and grain size group name	Thickness [cm]	Losses on annealing [%]	pH in KCl	Heavy metals					
				Cd	Pb	Cu	Co	Zn	Fe
						[mg·kg ⁻¹]			
Silty soil-glial (GWmig)									
L1	0–15	17.77	6.87	0.02	15.12	3.15	8.62	2.27	26.44
L2	15–35	13.22	7.48	n.s	9.43	2.62	5.64	2.10	14.24
Lc3	35–55	16.71	7.43	n.s	4.69	3.30	5.58	2.54	18.65
Lc4	55–100	21.83	7.41	n.s	2.35	1.13	2.74	2.09	7.88
Lc5	100–200	12.50	7.56	n.s	3.21	1.08	2.65	0.59	10.28
Organic soils fibric-muck (OMi)									
OM1	0–10	79.10	6.26	0.22	25.43	0.58	1.67	0.86	22.54
OM2	10–16	81.38	6.13	0.12	21.26	0.60	1.48	0.99	14.45
OM3	16–28	89.36	6.21	n.s	3.33	n.s	1.00	0.93	5.42
OTi1	28–100	86.60	6,03	n.s	n.s	0.06	0.78	0.96	4.25
OTi2	100–200	88.45	7.19	n.s	n.s	n.s	0.78	1.06	6.00
Organic soils sapric-muck (OMa)									
OM1	0–12	18.80	6.19	n.s	14.81	1.02	1.96	1.36	13.86
OM2	12–26	22.29	6.26	n.s	7.80	1.36	1.00	0.27	6.82
OM3	26–50	54.26	6.14	n.s	3.13	1.45	0.51	0.94	5.58
OTa	50–55	44.47	6.16	n.s	2.65	0.84	0.45	0.93	4.63
A (ps)	55–80	4.17	6.69	n.s	1.12	0.14	0.25	0.14	4.24
Cg (pl)	80–100	1.44	6.34	n.s	0.85	0.23	0.28	0.19	5.20
Muck soils (CUme)									
Au1	0–14	18.67	6.65	0.18	12.15	0.71	1.48	0.91	10.03
Au2	14–24	22.16	6.44	0.11	8.22	0.93	1.00	1.01	6.86
Au3	24–34	12.31	6.45	n.s	4.05	0.52	0.70	0.78	5.42
A (pl)	34–60	7.56	6.75	n.s	n.s	0.33	0.57	0.78	4.17
Cg (pl)	60–100	1.51	6.86	n.s	1.87	0.21	0.46	0.84	3.60

Explanations: n.s. - not found (outside detectability device)

– Casagrande'a, modified by Prószyński, concentration of heavy metals (Cd, Pb, Cu, Co, Zn, Fe) in exchangeable form in 0.5 mol·dm⁻³ HCl and total in the mixture of concentrated acids HNO₃ + HClO₄, by means of atomic absorption spectrophotometer, Solar 929. In order to present the relationship between chosen properties of examined soils, correlation coefficients $r = 0.05$ were calculated using the program *Statistica 10.0 PL*.

3. RESULTS AND DISCUSSION

Field studies, conducted in the left part of the Ina valley near Sławęcín, showed that there are varying thickness of sediments of organic, mineral-organic and mineral nature. Profile I, situated very close to the riverbed, consisted of clay-organic sediments from which muddy-gley soils developed [Systematyka Gleb Polski 2011]. Profile II was composed of deep organic fibric-muck soils [Systematyka Gleb Polski 2011] formed from poorly decomposed fibric peat localised in central part of the valley. Profile III comprised shallow sapric-muck organic soils [Systematyka Gleb Polski 2011] with a thin layer of strongly decayed sapric peat (OTa 50–55 cm), which was lying on humus horizon (A 55–80 cm), built from slightly loamy sand. The profile is closed with gley parent rock developed from loose sand Cg (80–100 cm) (Table 1). Profile IV was made up of peat-mucky soils formed as a result of strong mineralisation and humification of organic matter

[Systematyka Gleb Polski 2011]. They are lying on gleyic parent rock consisting of loose sand (Cg 60–100 cm) (Table 1). Like sapric-muck soils, they are located at the edge of the Ina valley. All examined profiles I–IV have a relatively high soil reaction, especially in the case of muddy-gley soils (profile I), where only the surface layer L1 (0–15 cm) had neutral reaction (pH 6.87), whereas in lower genetic horizons, the reaction was alkaline (Table 1). Such a high reaction might have been caused by the presence of tiny calcareous shells of molluscs, precipitation of calcium carbonate or poor gleying process [Laskowski 1985]. It is worth mentioning that the surface layers of profiles under study are more acidified, which, according to [Grzywna 2014], is the evidence for the ongoing process of decession. Conducted analysis of correlation showed a significant relationship ($r = 0.50$) between pH values and the depth at which samples were taken (Table 3).

The analysed wetland soils of the Ina valley varied in the content of organic matter. The highest amount was recorded in organic fibric-muck soil (profile II), on the average, 84.98% of the whole profile, which is slightly more than in the studies on the soils of the National Park Ujście Warty [Malinowski R.20007] or in the Omulew valley [Pawluczuk, Grabowski 2012] and the Grójecka valley [Mocek *et al.* 2007]. The lowest content of organic matter indicating an intensive mineralisation process was found in profile IV, mean 12.44%. As in the case of reaction, organic matter

Table 2. Content of microelements soluble in concentrated HClO_4 and HNO_3

The level of genetic	Thickness [cm]	Heavy metals					
		Cd	Pb	Cu	Co	Zn	Fe
		[mg·kg ⁻¹]					
Silty soil-glial (GWmłg)							
L1	0–15	0.26	23.71	9.15	13.49	7.97	58.17
L2	15–35	0.13	19.23	8.13	10.65	8.61	42.68
Lc3	35–55	0.08	15.58	9.11	11.05	10.49	40.20
Lc4	55–100	0.06	7.25	4.97	6.46	8.87	26.96
Lc5	100–200	0.01	5.66	3.59	4.58	1.63	20.94
Organic soils fibric-muck (OMi)							
OM1	0–10	0.36	38.77	2.27	4.00	3.21	25.23
OM2	10–16	0.25	33.13	2.01	1.82	3.66	14.47
OM3	16–28	0.06	6.38	1.44	1.77	4.12	6.92
OTi1	28–100	0.02	n.s.	1.43	1.15	4.56	5.52
OTi2	100–200	0.03	3.27	1.85	1.48	5.44	6.62
Organic soils sapric-muck (OMa)							
OM1	0–12	0.24	23.03	2.24	4.53	6.10	20.85
OM2	12–26	0.11	10.27	2.57	3.51	1.00	11.58
OM3	26–50	0.10	17.10	2.27	3.25	0.99	13.78
OTa	50–55	0.03	4.32	1.64	2.19	1.73	7.44
A	55–80	0.01	3.49	0.51	0.37	1.59	4.48
Cg	80–100	0.03	3.46	1.59	0.47	2.18	5.49
Muck soils (CUme)							
Au1	0–14	0.22	38.77	2.27	4.00	3.21	25.23
Au2	14–24	0.12	33.13	2.01	1.82	3.66	14.47
Au3	24–34	0.05	6.38	1.44	1.77	4.12	7.55
A	34–60	0.03	2.04	1.43	1.15	4.56	4.25
Cg	60–100	0.04	3.27	1.85	1.48	5.44	6.62

Explanations: n.s. - not found (outside detectability device)

content was lower in surface layers confirming the ongoing mucking process and impoverishment in organic matter, which had been observed also by [Kaczmarek *et al.* 2010] in the studies on habitat conditions in the Noteć valley and [Kalembasa, Becher 2010] in the studies on peat-muck soils of the Liwiec valley on Siedlce upland. Negative effects of the Ina wetlands dewatering are manifested by well-developed muck horizons of organic soils (profile II - OM3 - 16–28 cm thick and profile III - OM3 - 26–50 cm thick) (Table 1).

Diverse anthropogenic activities affect the changes in the properties of wetlands and disturb their functions in the circulation of elements [Kołodziejczyk *et al.* 2009]. Analysing the obtained amounts of heavy metals soluble in the mixture of concentrated acids HNO_3 and HClO_4 (Table 2) in discussed soils, we can state that their content is within '0' degree of contamination [Kabata-Pendias *et al.* 1993] and permissible concentrations had not been exceeded [Rozporządzenie....2002]. Attention should be paid to elevated content of total and exchangeable forms of heavy metals in surface soil layers (Tables 1 and 2) in relation to lower genetic horizons. Under the conditions of humification process, these elements may become more mobile, which increases their toxicity and availability to plants [Sady, Smoleń 2004]. These relationships have been confirmed by [Kołodziejczak *et al.* 2009] for organic soils around Milicz, [Zadrozny *et al.* 2015] for the soils of Bagna Błędowskie and [Malinowski 2007] for the

soils of National Park Ujście Warty. In turn [Bogacz, Przybylska 2010], the studies on peat soils of Wrocław irrigated fields and [Ciszewski *et al.* 2004] the soils of the river Mała Panew link the elevated level of heavy metals with sewage discharge into rivers. However, our results do not confirm such a relationship since we have not observed the changes in the concentration of analysed elements with the distance from the riverbed, which may point to the transport of contamination with the river outflow into a valley. All soil profiles were characterised by varying concentration of heavy metals and their exchangeable forms were correlated with total forms (Table 3). Total form of cadmium occurred in the lowest concentration. Its amount was at the level, from 0.1 mg·kg⁻¹ in horizon Lc5 profile I and A in profile III, to 0.36 mg·kg⁻¹ in horizon OM1 profile II (Table 2). The content of the total form of this element was higher in surface layers and was decreased with depth (Table 2), which was reported also by [Kołodziejczyk *et al.* 2009], whereas the concentration of exchangeable form of cadmium (Table 2) in lower lying formations has not been detected.

Iron turned out to have the highest concentration of total forms and its level ranged from 4.48 mg·kg⁻¹ in organic sapric-muck soil to 58.17 mg·kg⁻¹ in muddy-gley soil (Table 2). In the opinion of [Niedźwiecki and Sammel 2006], elevated content of iron in surface soil layers is a consequence of mucking process and its reaction to oxygen may serve for the assessment of air–water

Table 4. Linear correlation coefficients between examined soil properties of Ina valley

Variable	Depth genetic horizons	Losses on annealing	pH in KCl	Cd ₁	Pb ₁	Cu ₁	Co ₁	Zn ₁	Fe ₁	Cd ₂	Pb ₂	Cu ₂	Co ₂	Zn ₂	Fe ₂
Depth genetic horizons	-	0.02	0.50*	-0.42	-0.62*	-0.28	-0.18	-0.18	-0.38	-0.66*	-0.62*	-0.12	-0.22	-0.06	-0.29
Losses on annealing	-	-	-0.41	0.27	0.21	-0.32	-0.21	-0.03	0.04	0.21	0.13	-0.26	-0.24	-0.13	-0.21
pH in KCl	-	-	-	-0.24	-0.23	0.45*	0.53*	0.51*	0.21	-0.25	-0.16	0.62*	0.55*	0.58*	0.49*
Cd ₁	-	-	-	-	0.75*	-0.10	-0.05	-0.08	0.42	0.73*	0.84*	-0.12	-0.05	-0.17	0.16
Pb ₁	-	-	-	-	-	0.25	0.33	0.20	0.77*	0.97*	0.87*	0.20	0.32	0.07	0.48*
Cu ₁	-	-	-	-	-	-	0.88*	0.77*	0.68*	0.30	0.31	0.94*	0.94*	0.57*	0.88*
Co ₁	-	-	-	-	-	-	-	0.82*	0.80*	0.37	0.29	0.96*	0.97*	0.71*	0.96*
Zn ₁	-	-	-	-	-	-	-	-	0.61*	0.27	0.24	0.87*	0.86*	0.91*	0.81*
Fe ₁	-	-	-	-	-	-	-	-	-	0.78*	0.64*	0.71*	0.78*	0.47*	0.86*
Cd ₂	-	-	-	-	-	-	-	-	-	-	0.89*	0.24	0.38	0.14	0.54*
Pb ₂	-	-	-	-	-	-	-	-	-	-	-	0.21	0.31	0.06	0.50*
Cu ₂	-	-	-	-	-	-	-	-	-	-	-	-	0.97*	0.75*	0.92*
Co ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	0.71*	0.97*
Zn ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.65*
Fe ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Explanations:

* correlation significant at $\alpha = 0.05$ for $n = 21$

1 - dissolvable in HCl at a concentration of $0.5 \text{ mol} \cdot \text{dm}^{-3}$

2 - dissolvable in concentrated acids HClO_4 i HNO_3

relations. Statistical analysis showed a significant relationship between exchangeable and total forms of iron and all investigated elements except exchangeable form of cadmium (Table 3).

The amount of total form of lead ranged from $2.04 \text{ mg} \cdot \text{kg}^{-1}$ in the humus horizon of muck soil to $38.77 \text{ mg} \cdot \text{kg}^{-1}$ in the horizon OM1 of organic fibric-muck soil (Table 2). These values are comparable to the results obtained by [Malinowski 2007] in organic soil of National Park Ujście Warty and [Becher 2011] in organic soils of the upper Liwiec valley. Similar to the studies of [Mocek *et al.* 2007] on the soils of Grójec valley, the concentration of lead decreased with depth, which was confirmed by statistical analysis. (Table 3). Besides, significant relationships between total lead and exchangeable cadmium and iron as well as total cadmium were detected (Table 3).

The lowest content of copper was recorded in humus horizon of organic sapric-muck soil - $0.59 \text{ mg} \cdot \text{kg}^{-1}$, and the highest in genetic horizon L1 of muddy-gley soil - $9.15 \text{ mg} \cdot \text{kg}^{-1}$ (Table 2). There was a significant correlation between total form of this element and total and exchangeable forms of Co, Zn and Fe. The concentration of cobalt was from $0.37 \text{ mg} \cdot \text{kg}^{-1}$ (A 55–80 cm) in profile III to $13.49 \text{ mg} \cdot \text{kg}^{-1}$ (L1 0–15 cm) in profile I (Table 2). Significant relationships between total cobalt and exchangeable Cu, Zn and Fe and also total Zn and Fe were also found. The level of total zinc was the lowest in genetic horizon OM3 in organic sapric-muck soil - $0.99 \text{ mg} \cdot \text{kg}^{-1}$, and the highest in the horizon Lc3 of muddy-gley soil - $10.49 \text{ mg} \cdot \text{kg}^{-1}$ (Table 2). The

total form of this element was significantly correlated with total and exchangeable form of Cu, Co and Fe.

Total levels of copper, cobalt and zinc were lower than those presented by [Mocek *et al.* 2007] in the Grójec valley or in the soils of peatland Pożary in Puszcza Kampinoska [Okolowicz 1999]. Attention should be paid to the elevated concentration of those elements in muddy-gley soil (profile I) in light of other soil profiles. This might be explained by their stronger sorbing by organic matter and clay minerals of sediments, carried by the current down the riverbed [Kabata-Pendias and Pendias 1999], which is supported by the studies of [Borowiec *et al.* 2007] on meadow habitats of the Bug valley near Dubienka.

4. CONCLUSIONS

On the basis of conducted studies on the soils of the Ina valley wetlands near Sławęcin, it was found that:

1. Content of heavy metals (Cd, Pb, Ni, Cu, Co, Zn and Fe) soluble in the mixture of concentrated acids $\text{HNO}_3 + \text{HClO}_4$ is low and therefore, the soils may be classified as the soils of natural value.
2. Surface soil layers contain higher levels of heavy metals than the deeper lying layers of organic sediments.
3. Obtained contents of heavy metals point to a barely noticeable impact of human agricultural activity on the area.

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