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HEAVY METALS AND SULPHUR IN THE SOILS OF FARMLANDS IN PROTECTED AREAS OF THE PODKARPACIE REGION

The differences in the cadmium, copper, chromium, nickel, lead, zinc, manganese, iron and sulphur content in the soils of environmentally protected and unprotected areas of the Podkarpacie Region were studied. It was shown that surface layers of soils (0–20 cm) in all kinds of land accumulate higher concentrations of cadmium and lead than the deeper layers (35–45 cm). In the Sandomierz Basin and in the Carpathian Foothills, this is also the case for zinc and sulphates. The concentration of heavy metals in the soils increases southwards. However, most soils do not display signs of contamination with the elements investigated. A contamination detected sporadically has a very local character and occurred more often in the protected areas, mainly in the northern and central parts of the region.

1. INTRODUCTION

Protected areas of the region encompass ca. 8600 km^2, which is 47.8% of this area. Parts of them are farmed. Up to the present no extensive study of heavy metal and sulphur content in the soils of the region has been published, except for a few local studies. In order to fill this gap, the concentration of Cd, Cu, Cr, Ni, Pb, Zn, Mn, Fe and S was studied in nearly 2400 soil samples from farmland soils throughout the region.

2. METHODS

The results of the analyses come from the Regional Chemical and Agricultural Station in Rzeszów. They were obtained in 1992–1997 as part of the national scheme of monitoring farmland soils [9], [10]. Although the results are a few years old, comparisons of the

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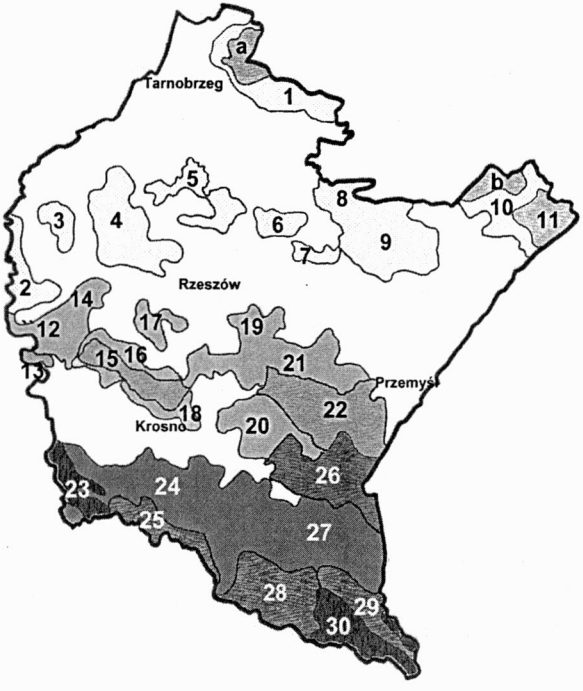
studies of the Institute of Soil Science and Plant Cultivation (IUNG) from 1995 and 2000 [5] show no significant changes in the content of heavy metals in the region.

The samples from the 0–20 cm layer were collected in a 2 × 2 km grid. Samples from the 35-45 cm depth layer were taken from every third point of the grid. The general content of the above mentioned heavy metals and sulphates was measured using standard procedures applied in this network of soil laboratories. Knowing the exact position of samples (longitude and latitude), it was possible to determine which of them were located in the protected areas, using nature protection maps [4] (figure). The results from protected and unprotected areas were compared. Evaluating the content of elements the IUNG guidelines [2] were followed, which, for the estimation of contamination levels, take into account the soil pH, as well as clay and organic matter content. The borderline concentrations indicating contamination are lower for lighter soils than for medium and heavy soils. In the latter soils, the environmental impact of the elements and their uptake by plants are smaller. This is confirmed by the indices of heavy metal transfer from soils to plants, the so-called bioaccumulation indices, calculated for over a thousand plants collected during this study in the Podkarpacie Region [6].



the Sandomierz Basin
- a PK Lasy Janowskie (no data available)
- b PK Puszczy Solskiej (no data available)
- 1 Buffer zone of PK Lasy Janowskie
- 2 Jastrząbsko-Żdżarski OChK
- 3 Przecławski OChK
- 4 Mielecko-Kolbusz.-Głog. OChK
- 5 Sokołowsko-Wilczowolski OChK
- 6 Brzóźniański OChK
- 7 Zmysłowski OChK
- 8 Kuryłowski OChK
- 9 Sieniawski OChK
- 10 Roztoczański OChK
- 11 Południoworoztoczański PK

the Carpathian Foothills
- 12 OChK Pogórza Ciężkowickiego
- 13 PK Pasma Brzanki
- 14 OChK Pogóża Strzyżowskiego
- 15 Czarnorzecko-Strzyżowski PK
- 16 Buffer zone of Czarnorz.-Strzyż. PK
- 17 Strzyżowsko-Sędziszowski OChK
- 18 Czarnorzecki OChK
- 19 Hyżniańsko-Gwoźnicki OChK
- 20 Wschodniobeskidzki OChK (northehrn part)
- 21 Przemysko-Dynowski OChK
- 22 PK Pogórza Przemyskiego

the Beskid Niski and the Bieszczady Mts.
- 23 Magurski PN
- 24 OChK Beskidu Niskiego
- 25 Jaśliski PK
- 26 PK Gór Słonnych
- 27 Wschodniobeskidzki OChK (southern part)
- 28 Ciśniańsko-Wetliński PK
- 29 PK Doliny Sanu
- 30 Bieszczadzki PN

The distribution of protected areas
Abbreviations: PK – Lanscape Park, PN – National Park, OchK – Protected Landscape Area

The significance of the results was tested using the *t*-Student test and *F*-test. The least significant differences (LSD) were calculated at an error risk not higher than 5%. The coefficients of correlation between the variables measured were also calculated. Only the signs of the correlation coefficient and significance level were included in the results section.

3. DISCUSSION OF RESULTS

The Podkarpacie Administrative Region stretches accross three distinct geographical regions of different geological structure, climate and vegetation, hence different soils as well. The variation in soils was confirmed by granulometric analysis of the samples collected (table 1). The highest proportion of sandy soils was recorded in the north of the area (Sandomierz Basin), of silty soils in the middle zone (foothills zone), and of loamy soils in the south (the Beskid Niski Mts, Bieszczady Mts, Sanocko-Turczańskie Mts). Because of this difference the element content was discussed separately for each region.

Table 1

Proportion (%) of soil types differing in granulometric content

Region	Soils			
	Sandy	Silty	Loamy	Clayey
The Sandomierz Basin	60.2	14.8	22.9	2.1
The Carpathian Foothills	10.6	72.2	13.3	3.9
The Beskid Niski and the Bieszczady Mts.	0.5	38.0	52.3	9.2

Table 2

The concentration of sulphur (SO_4–S mg·100 g^{-1}) and heavy metals (mg·100 g^{-1}) in the soil layers investigated

Region	Elements	Soil layers		Statistical significance of differences in means
		0–20 cm	35–45 cm	
The Sandomierz Basin (n = 82)	SO_4–S	1.76	1.52	*
	Cd	0.23	0.16	***
	Pb	13.5	9.0	***
	Zn	32.1	25.8	**
The Carpathian Foothills (n = 200)	SO_4–S	1.78	1.56	*
	Cd	0.37	0.26	***
	Pb	21.4	17.1	***
	Zn	46.0	42.1	***
The Beskid Niski and the Bieszczady Mts. (n = 113)	Cd	0.43	0.31	***
	Pb	26.4	21.0	***

*, **, *** Significant at the 0.05 0.01 0.001 levels of probability, respectively.

Table 3

The concentrations of sulphur and heavy metals in the surface layer of soils (0–20 cm) in the protected areas compared to the unprotected areas

Regions	Area	*n*	Clay	OM	S	Cd	Cu	Cr	Ni	Pb	Zn	Mn	Fe
			% w/w			mg·kg^{-1} soil							%
the Sandomierz Basin	Buffer zone of PK Lasy Janowskie	40	9	1.5	0.87	0.22	4.8	7.0	4.7	9.1	23.9	210	0.39
	Jastrząbsko-Żdżarski OChK	32	17	1.7	1.63	0.34	7.1	9.7	7.0	15.8	35.6	301	1.12
	Przecławski OChK	27	23	1.9	1.78	0.30	8.7	18.5	11.4	16.6	35.6	412	1.02
	Mielecko-Kolbusz.-Głog. OChK	47	12	2.0	2.13	0.26	4.9	17.7	5.2	15.4	25.0	184	0.55
	Sokołowsko-Wilczowolski OChK	23	10	2.6	1.84	0.22	7.6	16.3	5.9	14.3	22.6	224	0.69
	Brzóźniański OChK	8	13	1.5	1.84	0.17	4.3	15.9	5.9	9.6	22.4	285	0.47
	Zmysłowski OChK	4	26	1.6	1.42	0.22	4.4	26.4	9.6	16.3	26.1	289	1.02
	Kuryłowski OChK	2	10	1.3	1.17	0.16	2.4	10.3	3.1	14.9	17.5	152	0.24
	Sieniawski OChK	36	19	1.9	1.82	0.24	6.6	24.5	11.5	14.2	29.9	305	0.77
	Roztoczański OChK	30	19	1.9	1.49	0.25	5.5	20.9	8.9	13.5	21.8	302	0.69
	Południoworoztoczański PK	7	12	2.2	1.71	0.26	3.0	17.9	6.0	14.9	26.0	256	0.43
	Average for the above mentioned areas	254	**15**	**1.9**	**1.66**	**0.25**	**6.0**	**16.3**	**7.5**	**13.9**	**27.3**	**268**	**0.71**
	Average for unprotected areas	473	22	2.2	1.82	0.26	9.0	21.2	12.7	14.8	39.4	366	0.97
	Statistical significance of differences in means		***	*	NS	NS	***	***	***	NS	***	***	***

the Carpathian Foothills	OChK Pogórza Ciężkowickiego	22	35	1.4	1.54	0.29	10.3	15.1	11.7	18.6	44.8	423	1.25
	PK Pasma Brzanki	10	44	1.9	2.24	0.40	12.8	30.4	17.4	23.2	59.1	467	1.63
	OChK Pogóża Strzyżowskiego	26	30	1.5	1.70	0.30	10.7	14.9	14.6	16.1	46.2	524	1.29
	Czarnorzecko-Strzyżowski PK	36	38	2.1	2.10	0.34	11.8	34.5	21.4	23.5	52.1	506	1.48
	Buffer zone of Czarn.-Strzyż. PK	46	39	2.1	1.54	0.33	10.3	27.8	18.5	22.3	50.6	533	1.39
	Strzyżowsko-Sędziszowski OChK	22	39	1.6	1.80	0.28	9.0	31.4	16.1	16.8	46.9	406	1.14
	Czarnorzecki OChK	17	30	2.3	1.72	0.34	11.1	35.5	16.8	23.5	47.4	532	1.43
	Hyżniańsko-Gwoźnicki OChK	55	40	2.4	1.80	0.32	10.9	34.9	17.3	19.1	47.6	539	1.31
	Wschodniob. OChK (northehrn part)	26	44	2.8	1.12	0.38	15.9	27.4	27.6	19.4	62.6	556	1.86
	the Carpatian Foothills	78	37	2.4	1.29	0.37	12.8	30.2	21.1	20.2	51.2	527	1.47
	PK Pogórza Przemyskiego	100	43	2.6	1.18	0.38	14.7	31.1	23.2	20.8	50.9	509	1.61
	Average for the above mentioned areas	438	**39**	**2.3**	**1.51**	**0.35**	**12.3**	**29.5**	**19.9**	**20.3**	**50.6**	**512**	**1.46**
	Average for unprotected areas	615	34	2.4	1.84	0.28	11.3	30.7	16.4	18.3	42.3	443	1.20
	Statistical significance of differences in means		***	NS	***	**	***	NS	***	***	***	***	***
the Beskid Niski and the Bieszczady Mts.	Magurski PN	4	49	2.7	0.99	0.32	15.9	31.3	33.7	20.4	49.3	536	1.92
	OChK Beskidu Niskiego	68	50	3.4	1.68	0.49	19.7	39.2	35.4	28.4	66.0	721	2.16
	Jaśliski PK	12	48	3.4	1.35	0.44	17.1	40.4	27.9	32.0	65.5	704	2.15
	PK Gór Słonnych	43	41	3.0	1.30	0.39	14.5	32.0	25.0	24.0	59.6	561	1.83
	Wschodniob. OChK (southern part)	109	43	2.7	1.31	0.41	16.0	33.1	26.9	23.4	60.4	546	1.98
	Ciśniańsko-Wetliński PK	30	43	3.6	2.14	0.44	21.0	28.6	35.8	26.4	60.2	671	2.47
	PK Doliny Sanu	18	41	3.4	1.72	0.40	15.3	36.5	26.1	26.9	64.5	495	1.95
	Bieszczadzki PN	5	39	4.8	1.33	0.43	18.9	36.8	22.7	29.6	71.5	515	2.07
	Average for the above mentioned areas	289	**45**	**3.1**	**1.51**	**0.43**	**17.2**	**34.4**	**29.5**	**25.6**	**62.1**	**605**	**2.06**
	Average for unprotected areas	290	41	2.6	1.63	0.39	15.3	33.8	24.9	24.0	59.0	561	1.69
	Statistical significance of differences in means		***	***	NS	***	***	NS	***	**	*	NS	***
LSD between means for regions			2	0,1	n.i.	0.01	0.6	1.1	1.0	0.6	1.9	23	0.06
LSD between protected areas			5	1,0	0.51	0.06	2.6	4.6	5.1	2.9	7.5	111	0.25

Abbreviations: PK – Landscape Park, PN – National Park, OChK – Protected Landscape Area.
clay = fraction <0.02 mm; OM = organic matter; SO_4–S, mg·100g^{-1} soil.
*, **, *** $P < 0.05$, 0.01, and 0.001 levels of probability, respectively; NS = not significant.

In the whole region, the 0–20 cm depths compared to 35–45 depths have a higher concentration of cadmium and lead (table 2), as was also observed by other authors [1], [3], [11]–[13]. In the Sandomierz Basin and the foothill zone, the upper layer of soil concentrates more sulphates and zinc as well, which is obviously caused by denser population and industrial activity. As assessed by SMAL & KOT [8], agricultural practices cause less input of cadmium and lead in soils than precipitation.

Analysing data from the upper layer of soil one can see that an average sulphur content declines southwards (table 3). On the other hand, heavy metal content increases from north to south. A similar trend of cadmium and lead concentration was reported in other studies [1], [3], [11]–[13]. This does not mean that the state of soils deteriorates southwards. On the contrary, as the per cent of contaminated samples was the lowest in the south (1.8%), whereas in the rest of the area it was higher (2.2%). The reason for the higher heavy metal content in the south is a natural chemical composition of the flysh bedrock, from which most soils in the Carpathians and their foothills originated. Flysh has naturally many times higher concentration of heavy metals compared to other kinds of bedrock in the Podkarpacie Region. The studies of SKIBA and MICHALIK [7] showed that the sandstone and the shales, which build the flysh bedrock, contain similar amounts of cadmium, lead and zinc to their content in the surface layers of mountain meadows and forests of the Bieszczadzki National Park. Moreover, microscopic and spectroscopic analyses of rock outcrops confirmed a lack of contamination in the region. Only in alpine meadows of the Połonina Wetlińska, Skiba and Michalik detected small amounts of anthropogenic dust. However according to WOŹNIAK [12], the summits of the Bieszczady Mountain ranges are contaminated by cadmium and lead, whereas valleys and wind-protected slopes have lower concentrations of cadmium [13].

Protected areas of the Sandomierz Basin have a significantly lower level of copper, chromium, nickel, zinc, manganese and iron than the unprotected areas. Protected areas in the foothill zone have less sulphates than the unprotected areas in this zone, but they have more heavy metals. Also, the protected areas in the mountain zone have a higher concentration of metals than the unprotected areas of the mountains (table 3). These results are caused by the fact that in the north the soils of protected areas and parks include considerably less clays (<0.02 mm fractions) and organic matter than the unprotected areas. The reverse is true for the Carpathians and their foothills. The mentioned fractions of soils create a sorptive complex responsible for binding the metals. That is why there is a highly significant correlation ($P < 0.001$) between the concentration of all the metals studied and the content of loam and organic matter. On the other hand, human influence is clear as far as the concentration of sulphates is concerned, which is the highest in the unprotected parts of the foothill zone.

Although the concentration of most heavy metals in farmland soils of the region is higher than in the north and center of Poland, most of the land has a natural (0°) or, only sometimes, slightly heightened (I°) concentration of the elements studied [5], [9].

Weak (II°) or sporadically medium contamination with heavy metals (III°) and anthropogenic contamination with sulphur (IV°) was detected in 6.4% of samples. It was commoner in the unprotected (4.2%) than in the protected areas (2.2%). The proportion of contaminated samples coming from national parks, landscape parks and areas of protected landscape was very low everywhere (0.7% in the Sandomierz Basin, 0.6% in the Carpathian Foothills and 0.9% in the mountains). This indicates that the contamination is low and has a local character.

4. CONCLUSIONS

1. The near-surface layer of soil in the whole study area is richer in cadmium and lead than the deeper layer of soil. In the Sandomierz Valley and the Carpathian Foothills this also applies to zinc and sulphates.

2. Most farmland in the Podkarpacie Region is not contaminated by heavy metals, and their content depends mainly on natural factors and increases southwards.

3. The sulphate content in the foothill zone is higher outside the protected areas.

4. Weak or medium contamination with heavy metals and anthropogenic contamination with sulphur has an insular character and occurs mainly in unprotected areas.

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METALE CIĘŻKIE I SIARKA W GLEBACH UŻYTKÓW ROLNICZYCH OBSZARÓW CHRONIONYCH WOJEWÓDZTWA PODKARPACKIEGO

Analizowano różnice zawartości kadmu, miedzi, chromu, niklu, ołowiu, cynku, manganu, żelaza i siarki w glebach obszarów chronionych i niechronionych województwa podkarpackiego. Wykazano, że warstwy powierzchniowe (0–20 cm) wszystkich gruntów gromadzą więcej kadmu i ołowiu niż głębsze (35–45 cm), a w Kotlinie Sandomierskiej i pasie pogórzy – także więcej cynku i siarczanów. Stwierdzono, że w miarę przesuwania się z północy na południe w glebach wzrasta stężenie metali ciężkich. Mimo to zdecydowana większość gleb nie wykazuje zanieczyszczenia badanymi pierwiastkami, a stwierdzane sporadyczne przypadki mają charakter punktowy i w większym stopniu dotyczą terenów niechronionych, zwłaszcza w części północnej i środkowej województwa.