Acta Agrophysica, 2001, 51, 221-230

HEAVY METALS PHYTOAVAILABILITY IN THE SOILS OF THE ECOLOGICALLY ENDANGERED REGIONS IN THE PROVINCE OF TARNÓW

F. Gambuś, M. Rak, J. Wieczorek

Department of Agricultural Chemistry, Agricultural University of Cracov
Al. Mickiewicza 21, 31-120 Kraków, Poland

A b s t r a c t. The present paper reviews content and phytoavailability of heavy metals (Cd, Cu, Ni, Pb, Zn) in the soils of seven selected regions in the former Tarnów province, considered to be particularly endangered by contamination by these metals. One hundred soil samples were collected, 50 from the 0-10 cm layer and 50 from the 40-50 cm layer and mixed meadow sward from the same places.

Most of the examined soil samples had a natural heavy metal content with the exception of a few samples containing higher amounts of Cd, Ni, and Zn. A strong correlation between heavy metal content and soil sorptive capacity and the organic matter content and the level of soil fraction with particle diameter of <0.02 and <0.002 mm was observed. Analysis of heavy metals in plants revealed that the limit values of Cd and Zn content were exceeded only occasionally together with reduced fodder quality of the investigated sward.

K e y w o r d s: heavy metals, contamination, phytoavailability, soils, plants.

INTRODUCTION

Soil physico-chemical properties, including heavy metal content, are determined in a natural way and by anthropogenic factors. Parent rock is a natural source of heavy metals in the soil as well as the flux of their natural cycle between various environmental elements enriched by volcano eruptions, large forest fires and other factors of similar type [12]. Anthropogenic contamination is caused mostly by the emission of metalliferous dust into atmosphere by industry and an increasing number of motor vehicles when solid and liquid fuels are burned. Soil chemical degradation is also caused by sludge introduction into soil together with other waste products, mineral fertilisers - mainly calcium and phosphorus and some pesticides [3,5,7,10]. Plants uptake heavy metals mainly by their root system. They can also assimilate large amounts from dust descending from atmosphere onto leaf blades. The amount of heavy metals absorbed by leaves depends both on the intensity of dust pollutant emission and on the leaf surface and shape. The most important factors influencing phytoavailability of heavy metals present in the soil are as follows: (i) concentration of potentially available forms of these metals in the soil, (ii) metal concentration in the soil solution and their proportions which influence the processes of synergism or antagonism, (iii) sorptive and desorptive soil properties and soil pH, (iv) characteristics of plant species and varieties, and their stage of growth.

The aim of this paper was to evaluate content and phytoavailability of some heavy metals (Cd, Cu, Ni, Pb, Zn) in the soils of seven selected regions of the former Tarnów province considered to be especially endangered by contamination with these metals.

MATERIALS AND METHODS

Seven regions localised along the E-40 road from Bochnia to Dębica were subjected to the present investigation. In mid September of 1997, one hundred soil samples were collected, 50 from the 0-10 cm layer and another 50 from the 40-50 cm layer and plants from the same sites. The sites selected for the sampling were in the region of strong anthropopressure related to the industrial plant of this region such as: Polifarb in Dębica, Plastics Work in Pustków and Nitrogen Works in Tarnów, large dumping grounds (Tarnów-Krzyż and Bochnia-Krzyżanowice) and also with traffic intensification on the E-40 road (Pogórska Wola). The region of Żyraków was selected as a control free from significant sources of pollution.

To standardise the analysis results and to facilitate their interpretation, investigations were conducted mostly on the sodded soils covered with permanent mixed sward. Only two research points were localised on arable land. A perennial grassland with intact soil reflects the state of anthropogenic contamination of the upper layer better than arable land and facilitates comparison of this state with the subsoil layer [9].

In the soil samples, basic physico-chemical soil properties were determined as well as the total level of the heavy metals after soil dissolution in the mixture of concentrated nitric and perchloric acids. Soil reaction (pH) was determined potentiometrically and hydrolytic acidity (Hh) as well as base exchangeable capacity (BEC) by the Kappen's method. From the latter two values, cation exchangeable capacity (CEC) was calculated as well as the index of saturation of the sorptive complex with the base cations (V). Organic matter content was determined by the Tiurin's method by means of oxidation with potassium dichromate, and the granulometric composition by the (areometric) Bouyoucos-Casagrande's method as modified by Prószyński. The plant material analysed (50 samples) was composed mostly of swards from grasslands and barren land and only in 2 sites (in Żyraków) maize leaves were analysed. The plant samples were incinerated dry and the heavy metal content in the solution obtained after dissolving ash in the diluted nitric acid (1:2) and in the solution obtained after soil dissolution was determined by the AAS method.

Statistic analysis of the results was conducted according to the computer programme Statgraphics 2.6 and Excel 97.

RESULTS AND DISCUSSION

The statistic data presented in Table 1, describing the physico-chemical properties of the examined soils, indicate a great variation in the controlled characteristics. The values of variation coefficients inform about the highest variation in the occurrence of the fraction with the particle diameter <0.002 mm and cation exchangeable capacity (CEC), including both its components: hydrolytic acidity (Hh) and base exchangeable capacity (BEC). The values of variation coefficients of these characteristics in the both layers of all examined soil samples range from 59 to 94 %. The differences in the organic matter content (particularly in the 40-50 cm layer) and the occurrence of the particles with the diameter <0.02 mm in the soil were less pronounced. The reaction of the soil (pH_{KCl}) ranged greatly and in the upper layer amounted from 3.5 to 6.9 and in the 40-50 cm layer from 3.8 to 7.1.

High acidification of a lot of the examined soil samples, often both in the upper layer and subsoil (it is particularly true for the light soils and the soils with low organic matter content), may increase absorption of many heavy metals by plants, even when their content in the soil is low [2,6,8]. Evaluation of the heavy metal levels in the 0-10 cm and 40-50 cm layers of the investigated soils was based on the limits proposed by Kabata-Pendias *et al.* [11]. Most of the investigated samples had a natural heavy metal content (Table 2). Only 5 samples collected from the 0-10 cm layer contained "increased" cadmium amounts, 3 - nickel and 13 - zinc. Increased amounts of heavy metals were also found in 3 samples of the subsoil (taken from the 40-50 cm layer) with regard to nickel and 4 to zinc. According to Kabata-Pendias *et al.* [11], it is possible to

T a b l e 1. Physico-chemical properties of the 0-10 and 40-50 cm soil layers in the investigated regions in the Tarnów province

Locality of sampling Value	pH_{KCl}	Sorption capacity*				Organic matter (%)	Fraction content (%)	
		Hh	BEC	CEC	V		<0.02	<0.02
		(cmol(+)kg^{-1})			(%)		mm	mm
Layer 0-10 cm (mean value)								
Dębica (n=12)	4.8	5.4	25.7	31.1	80	5.3	49	25
Pustków (n=3)	4.2	5.4	6.3	11.7	50	3.3	11	5
Żyraków (n=5)	4.6	5.0	12.2	17.2	71	3.9	32	12
Bochnia-Krzyżanowice (n=9)	5.1	4.5	23.7	28.3	83	4.4	52	18
Tarnów-Krzyż (n=6)	4.9	4.5	6.9	12.3	50	3.9	23	20
Tarnów-Mościce (n=7)	4.7	5.6	16.5	22.1	73	5.1	44	15
Pogórska Wola (n=8)	4.8	6.8	14.0	22.9	50	9.4	20	10
All samples (n=50)								
Minimum	3.5	0.4	1.5	8.0	19	1.7	8	3
Maximum	6.9	19.9	54.8	74.7	98	36.1	74	49
Mean	4.8	5.4	17.8	23.4	70	5.3	37.1	15.5
Coefficient of variation (%)	20	67	74	60	29	92	47	59
Layer 40-50 cm (mean value)								
Dębica (n=12)	5.1	2.7	25.4	28.1	86	1.8	51	27
Pustków (n=3)	4.6	3.6	2.5	6.1	40	1.2	12	4
Żyraków (n=5)	4.4	3.1	9.1	12.6	70	1.1	31	13
Bochnia-Krzyżanowice (n=9)	5.1	3.3	17.0	21.1	81	1.6	56	22
Tarnów-Krzyż (n=6)	4.4	3.0	3.9	6.9	54	0.9	20	6
Tarnów-Mościce (n=7)	5.0	3.3	12.1	15.8	75	2.0	47	17
Pogórska Wola (n=8)	5.0	2.5	2.8	6.1	46	2.0	22	11
All samples (n=50)								
Minimum	3.8	0.3	0.4	2.5	10	0.4	5	1
Maximum	7.1	8.3	53.5	56.1	98	4.2	79	50
Mean	4.9	3.0	13.1	16.4	69	1.6	38.6	16.5
Coefficient of variation (%)	20	59	94	75	30	50	54	70

*Hh - hydrolytic acidity; BEC - base exchange capacity; CEC - cation exchange capacity; V - 100 BEC, CEC.

grow any field cultures on these soils, excluding or reducing vegetable production for children. The presented evaluation of the heavy metal content in the province of Tarnów confirms the results obtained by the Regional Agrochemical Station in

Table 2. Total heavy metal contents of the 0-10 and 40-50 cm soil layers in the investigated regions in the Tarnów province

Locality of sampling Value	Cd	Cu	Ni	Pb	Zn
	Layer 0-10 cm (mean value)				
Dębica (n=12)	0.55	19.2	27.7	35.1	89.9
Pustków (n=3)	0.33	3.8	4.3	13.8	26.8
Żyraków (n=5)	0.45	10.9	17.4	17.9	54.9
Bochnia-Krzyżanowice (n=9)	0.70	20.8	37.3	28.9	95.9
Tarnów-Krzyż (n=6)	0.44	5.0	5.6	18.4	41.4
Tarnów-Mościce (n=7)	0.44	16.7	29.9	27.6	78.3
Pogórska Wola (n=8)	0.72	11.4	9.4	29.8	81.0
	All samples (n=50)				
Minimum	0.20	3.0	2.7	12.4	15.7
Maximum	1.85	31.4	60.7	66.6	144.7
Mean	0.55	14.4	21.7	27.1	74.8
Coefficient of variation (%)	48	58	73	44	42
	Layer 40-50 cm (mean value)				
Dębica (n=12)	0.31	18.1	29.1	22.9	68.8
Pustków (n=3)	0.18	2.4	3.8	8.8	17.9
Żyraków (n=5)	0.22	8.5	17.3	11.6	43.9
Bochnia-Krzyżanowice (n=9)	0.46	21.6	42.8	23.4	83.2
Tarnów-Krzyż (n=6)	0.43	3.7	5.1	12.7	35.1
Tarnów-Mościce (n=7)	0.34	15.0	28.6	22.8	68.4
Pogórska Wola (n=8)	0.18	4.1	7.0	11.0	31.0
	All samples (n=50)				
Minimum	0.02	1.0	1.1	3.0	7.1
Maximum	0.64	35.9	65.6	38.1	122.2
Mean	0.32	12.5	22.4	17.9	55.7
Coefficient of variation (%)	54	76	79	50	53

Kraków [1] supervised by the Institute of Soil Science and Plant Cultivation [13]. They found out that 78.9 % of soils in the Tarnów province have a natural content and others have an "increased" heavy metal content. The heavy metal content of the investigated plant material varied considerably (Table 3). Taking into consideration evaluation criteria for the heavy metal content of fodder plants proposed by Kabata-Pendias *et al.* [11] only in a few samples, cadmium and zinc occurred in excessive amounts. An admissible cadmium content was exceeded in three plant samples collected in the vicinity of the E-40 road in Pogórska Wola, in both maize samples grown in Żyraków, in two sward samples from Dębica and in one

T a b l e 3. Heavy metal contents in the plants of the investigated regions in the Tarnów province

Locality of sampling Value	Mean value (mg kg^{-1} d.m.)				
	Cd	Cu	Ni	Pb	Zn
Dębica (n=12)	0.34	5.89	3.55	4.07	35.7
Pustków (n=3)	0.34	3.02	1.48	4.33	49.5
Żyraków (n=5)	0.82	4.85	3.62	3.24	48.3
Bochnia-Krzyżanowice (n=9)	0.48	6.41	4.15	6.00	40.8
Tarnów-Krzyż (n=6)	0.33	3.96	2.00	4.84	40.6
Tarnów-Mościce (n=7)	0.26	4.22	2.38	4.69	32.3
Pogórska Wola (n=8)	0.46	5.10	2.52	4.97	78.9
	All samples (n=50)				
Minimum	0.11	0.35	0.68	0.71	15.3
Maximum	2.50	9.03	7.61	7.97	250.4
Mean	0.42	5.10	3.01	4.67	45.5
Coefficient of variation (%)	91	38	51	28	75

from Pustków. Fodder quality deterioration due to the zinc content exceeding limits, was observed only in two cases. Zinc content slightly exceeded limits in a maize sample from Żyraków and 2.5-times in one sward sample from Podgórska Wola.

An excessive accumulation of heavy metals in the examined plants was found only in the case of cadmium and zinc. Their availability for plants strongly depends on the soil reaction [2,4]. Since the above cases were observed not in the soils with the highest cadmium and zinc content but in the most acidified soils, it can be assumed that liming of these soils should prevent plants from an excessive absorption of these metals, and hence from the worsening of fodder quality.

A statistic data analysis, conducted separately for each soil layer, showed a strong linear correlation between heavy metal content and other soil properties (Table 4). Concentration of the investigated heavy metals in the upper soil layer was strongly, positively correlated with CEC and BEC. Correlation coefficients for this interdependence amounted to 0.61-0.83 and were statistically significant with the significance level $p = 0.001$. Apart from cadmium, accumulation of the examined metals in the soil was also strongly correlated with the level of the soil fraction with the particle diameter <0.02 and <0.002 mm. Cadmium, lead and zinc content correlated with the level of organic matter in the soil. Soil reaction had the lowest effect on the concentration of the examined metals. In the case of subsoil (40-50 cm layer), correlation between the level of the examined metals and its physico-chemical soil properties was similar as in the 0-10 cm layer. Only the cadmium

Table 4. Correlation coefficients (r) between total heavy metal contents of the soils and properties of the investigated soil layers

Soil properties	Cd	Cu	Ni	Pb	Zn
		Layer 0-10 cm			
pH_{KCl}	0.24	0.15	0.19	0.17	0.26
Hh	0.34*	0.08	-0.04	0.26	0.13
BEC	0.71***	0.67***	0.60***	0.75***	0.78***
CEC	0.77***	0.64***	0.54***	0.78***	0.78***
V	0.35**	0.52***	0.61***	0.40**	0.55***
Organic matter	0.77***	0.17	0.07	0.57***	0.42**
Fraction <0.02 mm	0.27	0.76***	0.82***	0.52***	0.71***
Fraction <0.002 mm	0.23	0.67***	0.58***	0.56***	0.62***
		Layer 40-50 cm			
pHKCl	0.04	0.31*	0.25	0.14	0.12
Hh	0.11	-0.21	0.12	0.30	0.28*
BEC	0.20	0.81***	0.70***	0.72***	0.71***
CEC	0.21	0.79***	0.71***	0.69***	0.69***
V	0.27	0.63***	0.64***	0.54***	0.58***
Organic matter	0.22	-0.02	0.37**	0.61***	0.50***
Fraction <0.02 mm	0.43**	0.09	0.87***	0.84***	0.89***
Fraction <0.002 mm	0.31*	0.07	0.74***	0.81***	0.81***

r significant at: *p=0.05; **p=0.01; ***p=0.001.

content of this soil layer was not significantly correlated with the soil physico-chemical properties. The above metal content was only weakly correlated with the soil granulometric composition. Interaction between the heavy metal content of the soil and accumulation of these metals in the plants growing on these soils, was characterised by much lower values of correlation coefficients than described above (Table 5). Only the relation between nickel and cooper concentration in the soil and plants was described by a statistically significant value of the linear correlation coefficient (with $p = 0.01$). For both metals this value amounted to $r = 0.42$. In the case of other metals, these coefficients were close to zero.

An equation of multiple regression synthetically presents heavy metal content of the soil and plants with regard to the effect of various soil properties on the metal availability for plants [4]. To determine the above equation, a step-by-step method was used, taking into consideration analysis of heavy metal content of the examined soil and plant samples and the soil physico-chemical properties. The regression Eq. (1), describing zinc content in plants (Zn_P) on the basis of various soil properties, has the biggest prognostic value. Zinc content of the soil is not included in this equation, while accumulation of cadmium

Table 5. Correlation coefficients (r) between the total heavy metal levels in the investigated soils and plants

Metal	Cd	Cu	Ni	Pb	Zn
		Layer 0-10 cm			
Cd	-0.04	0.33*	0.14	0.37	-0.04
Cu	0.14	0.42**	0.38**	0.23	0.14
Ni	0.05	0.24	0.42**	0.19	-0.24
Pb	-0.15	0.26	0.17	0.23	-0.11
Zn	0.01	0.38*	0.35*	0.24	-0.05
		Layer 40-50 cm			
Cd	-0.06	0.24	0.13	0.26	-0.18
Cu	-0.09	0.04	-0.10	0.08	-0.10
Ni	0.05	0.24	0.45**	0.17	-0.24
Pb	-0.15	0.09	0.28*	0.08	-0.32
Zn	-0.03	0.26	0.42**	0.19	-0.28*

r significant at: *p=0.05; **p=0.01.

(Cd_S), cooper (Cu_S) and Nickel(Ni_S) in the soil are taken into account together with the level of the soil fractions with the particle diameter <0.02 mm (F1) and its CEC.

$$Zn_P = 59.44 + 39.39(Cd_s) + 6.18(Cu_s) - 1.29(Ni_s) - 1.47(F_1) - 1.75(CEC) \quad (1)$$

The coefficient of determination for this equation is equal to $R^2 = 0.62$. The equation (2) with $R^2 = 0.23$ has much lower prognostic value and describes the nickel content of meadow sward (Ni_P) on the basis of its content in the upper soil layer (Ni_S) and its pH_{KCl} (pH).

$$Ni_P = 4.74 + 0.05(Ni_s)\ \ 0.60(pH) \quad (2)$$

In the case of the three other metals (Cd, Cu and Pb), the equations of multiple regression describing interactions between plant metal content and soil properties, were characterised by very low values of the coefficients of determination, fluctuating between 0.04 and 0.12. It means that other factors, not taken into account in the present investigations, influenced their content in the meadow sward. In this case, varied species composition of the examined meadow sward and a flactuating proportions of dicotyledonous plants in this sward have the top priority.

CONCLUSIONS

1. Most of the examined soils had a natural heavy metal content. Only few samples collected in Pogórska Wola near the E-40 road, in the vicinity of Polifarb

Works in Dębica and in the region of dumping grounds and Nitrogen Works in Tarnów, had an increased cadmium, nickel or zinc content.

2. Heavy metal content of plants collected from grasslands varied greatly, but only in a few samples excessive amounts of cadmium and nickel were found and reduced fodder quality.

3. Statistic analysis showed a strong linear correlation between the total heavy metal content of the soil and sorptive capacity, organic matter content and the soil granulometric composition.

4. Among the metals taken into consideration in the present experiment, only the zinc content in sward can be calculated with a good probability on the basis of the equation of multiple regression, taking into consideration various soil properties. In the case of other metals, the functions determined described only less than 20% of variability, which means that other factors, not taken into consideration in the present experiment, influence phytoavailability of heavy metals.

ACKNOWLEDGEMENTS

The authors thank prof. K. Mazur who offered the possibility to use some results of soil and plant analysis presented in the paper.

REFERENCES

1. **Anonym:** The Regional Chemical and Agricultural Station in Kraków: The organisation and realization of the experiments were included in the ecological monitoring of the Tarnów province in 1992-1994 Kraków, 1994.
2. **Blume H.P., Brümmer G.:** Prediction of heavy metals behaviour in soil by means of simple field tests. Ecotox. Environ. Safety, 22, 164-174, 1991.
3. **Curzydło J., Gambuś F., Mundała P.:** Heavy metals content of arable soils around the T. Sendzimir steelworks in 1987-1994. Zesz. Probl. Post. Nauk Roln., 456, 71-81, 1995.
4. **Gambuś F.:** The influence of soil reaction on solubility of heavy metals in soil and their availability to plants. Zesz. Probl. Post. Nauk Roln., 456, 71-81, 1998.
5. **Gambuś F., Curzydło J., Mundała P., Szwalec A.:** Changes in heavy metals contents in plants grown in the vicinity of T. Sendzimir Ironworks in 1983-1994. Zesz. Nauk. AR Kraków, 319, Rolnictwo 34, 61-70, 1997.
6. **Gambuś F., Gorlach E.:** The influence of manure, straw and brown coal on phytoavailability of heavy metals. Zesz. Nauk. AR Szczecin, 172, Rolnictwo, 62, 131-137, 1996.
7. **Gorlach E.:** Heavy metals as a factor threatening to soil fertility. Zesz. Probl. Post. Nauk Roln., 421a, 113-122, 1995.
8. **Gorlach E., Gambuś F.:** The effect of liming, adding peat and phosphorus fertilization on uptake of heavy metals by plants. Pol. J. Soil Sci., XXIV/2, 199-204, 1991.

9. **Gorlach E., Gambuś F.:** The contents of heavy metals in meadow soils and plants of north-west region of Kraków province within the range of emission of zinc and lead works. Acta Agr. et Silv., ser. Agr., 33, 61-72, 1995, (Polish).

10. **Gorlach E., Gambuś F.:** Phosphorus and multicomponent fertilizers as a source of soil pollution by heavy metals. Zesz. Probl. Post. Nauk Roln., 448a, 139-146, 1997.

11. **Kabata-Pendias A., Motowicka-Terelak T., Piotrowska M., Terelak H., Witek T.:** The evaluation of the contamination level of soils and plants by heavy metals and sulphur. Wyd. IUNG, P(53), Puławy, 1993.

12. **Kabata-Pendias A., Pendias H.:** Biogeochistry of Trace Elements. PWN, Warszawa. 1993.

13. **Terelak H., Piotrowska M., Motowicka-Terelak T., Stuczyński T., Budzyńska K.:** 1995. The content of heavy metals and sulphur in soils of agricultural lands of Poland and degree of their pollution with these elements. Zesz. Probl. Post. Nauk Roln. 418, 45-60, 1995.