

DISTRIBUTION OF CADMIUM AND ZINC IN DIFFERENT FRACTIONS OF GLEY-AMPHIGLEY SOIL

Lepomir COGA – Mirjana HERAK CUSTIC – Tomislav COSIC – Milan POLJAK – Marko PETEK

Faculty of Agriculture, University of Zagreb

Introduction

Cadmium (Cd) availability mostly depends on the plant genetic traits, the form in which Cd is found in soil, and the concentration of antagonistic elements, primarily zinc (Zn) (Smilde et al., 1992). Like other heavy metals in soil, cadmium can be found in the exchangeable, carbonate, organic, oxide and residual fractions (Kim and Ferguson, 1991). Contrary to previous views that soil Cd is to a large extent adsorbed on organic matter (Kushizaki, 1977), recent investigations indicate that adsorption of Cd onto organic matter is not significant owing to the low Cd affinity for forming complexes with organic matter (Davis, 1984). Major part of Cd is in the exchangeable fraction, which is in dynamic balance with Cd from soil solution, and in the oxide fraction, which is particularly notable in contaminated acid soils (Nemeček et al., 1998). Long-term application of phosphorus fertilizers, produced from crude phosphates and containing rather large amounts of Cd may also lead to an increase of soil Cd and its accumulation in plants (Daniel and Gyori, 2000). The objective of this study was to determine, using the sequential extraction method, the distribution of Cd and Zn in different fractions of untreated soil (control) and in soil treated with Cd and Zn. Treatments with Cd and Zn were aimed at simulating potential soil pollution by Cd, and the influence of Zn on reducing the harmful effects of Cd.

Material and methods

Distribution of Cd and Zn between fractions was monitored in the period from 1997 to 1999 on drained gley-amphigley soil (Kapelna-Donji Miholjac): pH_{KCl} 6.7, humus 2.6 %, plant available phosphorus 91 mg $\text{P}_2\text{O}_5 \text{ kg}^{-1}$ and potassium 89 mg $\text{K}_2\text{O kg}^{-1}$, total cadmium 0.72 mg Cd kg^{-1} , total zinc 43.9 mg Zn kg^{-1} . Test crops included maize (1997), winter wheat (1998) and winter barley (1999). Uniform fertilization was applied in all three years: 170 kg N ha^{-1} , 100 kg $\text{P}_2\text{O}_5 \text{ ha}^{-1}$ and 150 kg $\text{K}_2\text{O ha}^{-1}$. The trial comprised three treatments with three replications: control Cd0Zn0 (0.0 mg Cd kg^{-1} 0.0 mg Zn kg^{-1}), Cd2Zn4 (2.0 mg Cd kg^{-1} and 4.0 mg Zn kg^{-1}) and Cd2Zn0 (2.0 mg Cd kg^{-1} and 0.0 mg Zn kg^{-1} soil). Cadmium was applied in the form of cadmium sulphate ($3\text{CdSO}_4 \times 8\text{H}_2\text{O}$), and zinc in the form of zinc sulphate ($\text{ZnSO}_4 \times 7\text{H}_2\text{O}$). Average soil samples were taken five times a year (20, 60, 90 120 and 150 days post treatment), and metal distribution between fractions was determined by the method after Tessier et al. (1979). Exchangeable Cd and Zn (F1) were extracted in 1 mol dm^{-3} MgCl_2 (pH 7). Cadmium and zinc bound to carbonates (F2) were extracted with 1 mol dm^{-3} NaOAc (pH 5). Cadmium and zinc bound to Fe and Mn oxides (F3) were extracted in 0.04 mol dm^{-3} $\text{NH}_2\text{OH} \times \text{HCl}$ in 25 % v/v acetic acid. Cadmium and zinc firmly bound to organic matter and sulphides (F4) were extracted in 30 % H_2O_2 (pH 2) and in 3.2 mol dm^{-2} NH_4OAc in HNO_3 , at room temperature. Residual Cd and Zn (F5) were determined by digestion in a mixture of

HCl:HNO₃ = 3:1. Cd and Zn concentrations in soil were determined by atomic absorption spectrometry (PU 9100X, AAS). Impact of applied Cd and Zn on their concentrations in soil was investigated by the analysis of variance, while the relations between Cd and Zn concentrations and sampling time were found with the aid of regression analysis.

Results and discussion

In all trial years, significantly larger amounts of total Cd and Zn were recorded in treatments with Cd and Zn compared to the control treatment (Cd0Zn0) fertilized with NPK fertilizers only (Table 1).

Table 1. Analysis of variance and treatment means for Cd and Zn concentrations in soil

		Cd		Zn	
		0-30 cm			
Source	df	F			
Year, Y	2	15.68	**	29.63	**
Treatment, T	2	12026.30	**	1590.57	**
Ctrl vs trt [†]	1	24052.10	**	3176.72	**
Y x T	4	7.97	**	3.59	**
Treatment		Mean concentration (mg kg ⁻¹)			
Cd0Zn0		0.71		44.25	
Cd2Zn4		2.79		45.76	
Cd2Zn0		2.78		43.94	

Table 2. Coefficients of regression of Cd concentration and sampling time

	Treatment*		
Fractions	Cd0Zn0	Cd2Zn4	Cd2Zn0
F1		-6.57	-6.63
F2		0.25	0.3
F3		4.86	4.29
F4	0.1	0.26	0.29
F5	-0.08	nl	0.58

*all values are multiplied by 10³

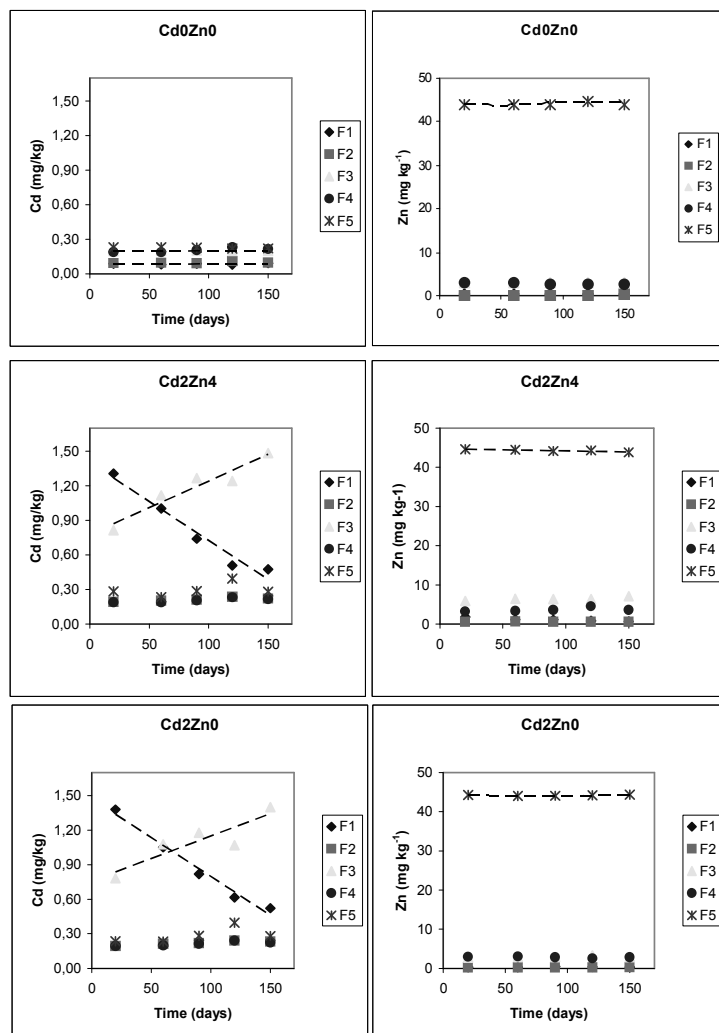
*empty cells – no regression

*nl – nonlinear regression

Results of regression analysis (Table 2) show that there is a relationship between sampling time and Cd concentration in particular fractions in treatments with Cd whereas no such relationship was found in the control treatment. As the trend of Cd and Zn distribution did not differ greatly in trial years, only average values of Cd and Zn in different fractions are presented for the studied period 1997-1999 (Graph 1). In the control treatment, the largest amount of Cd was found in fractions F3 and F5, while in treatments involving Cd application it was most abundant in fractions F1 and F3. The highest Cd concentration (46.9-49.7 % of total Cd) in fraction F1 was recorded 20 days post treatment, and the lowest (17.3-19.6 % Cd) during the last sampling 150 days after treatment. Progressive decrease in exchangeable Cd in soil with increasing the time interval treatment-sampling, regardless of the source of pollution, was recorded by Brams and Anthony, (1988). In contrast to fraction F1, Cd concentration in fraction F3 increased with prolongation of the time interval treatment-sampling. During the first sampling in fraction F3, 28.1 to 29.2 % of total Cd was bound while 52.7 to 55.3 % of total Cd was bound after 150 days. The high proportion of Cd in fraction F3 can be associated with oxido-reduction processes. Through valency change, manganese and iron participate in oxidation and reduction processes. The highest proportion of Cd in fractions F1 (19.8 %) and F3 (22.3 %) was also recorded by Makovnikova (2000) in 13

representative soil types of Slovakia. Jeng and Singh (1993) established that cultivated soils in Norway averagely contain 47 % total Cd in F1, 33 % in F3, 4 % in F2, and only 5 % in fraction F4.

Graph 1. Distribution of Cd and Zn in fractions (mg kg^{-1}) in dependence on sampling time and treatment, in the plough layer (0-30 cm,) 1997-1999



In contrast to Cd, the highest level of Zn was found in fraction F5, regardless of the trial treatment, and the lowest in fractions F1 and F2. Lower participation of Zn in fraction F1 can be related to the soil cation exchange capacity of more intensive binding of basic cations, including zinc, at a soil reaction over pH 5.5. The obtained results are in agreement with the results of a number of other researchers. Singh et al. (1991)

determined 73 to 88 % total Zn bound in fraction F5, and only 4 % in fraction F1. This was corroborated by the results achieved by Leštan and Grčman (2001). In polluted soils of Mežica (Slovenia), these authors determined 0.36 to 3.88 % total Zn in fraction F1, and 33 to 68 % in fraction F5.

Conclusions

Research results show significant differences in Cd distribution in dependence on the degree of soil pollution and sampling time. The greatest changes in cadmium concentration were recorded between fractions F1 and F3. Relatively small quantities of exchangeable cadmium in the control treatment provide evidence that the effects of agrochemical agents on environmental pollution are negligible compared to other sources of pollution.

References

- Brams E. – Anthony W.: 1988. Residual cadmium in a soil profile and accumulation in wheat grain – Plant and soil. 109, 3-8 pp.
- Daniel P. – Gyori Z.: 2000. Effect of cadmium on the development of maize plants. *Novenytermeles*. 49 (4):405-412 pp.
- Davis R.D.: 1984. Cadmium-a complex environmental problem, part I. – *Experientia* 40, 177-234 pp.
- Jeng A.S. – Singh B.R.: 1993. Partitioning and distribution of cadmium and zinc in selected cultivated soils in Norway – *Soil Science*. Vol. 156, No. 4, 240-250 pp.
- Kim N.D. – Ferguson J.E.: 1991. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *Sci. Total Environ.* 105: 191-209 pp.
- Kushizaki M.: 1977. Studies on soil pollution by cadmium, a heavy metal – *JARQ*. Vol. 11, 2, 89-94 pp.
- Leštan D. – Grčman H.: 2001. Speciation of lead, zinc and cadmium in contaminated soils from Mežica valley. *Biotechnical Faculty, University of Ljubljana – Kmet.* 77-2, 205-214 pp.
- Makovnikova J.: 2000. Relations between some soil parameters and available contents of cadmium, lead, copper and zinc – *Rostl. Vyr.*, 46 (7):289-296 pp.
- Nemček J. – Podlešakova E. – Pastuszkova M.: 1998. Use of the sequential analysis for the assessment of trace elements bonds in soils – *Rostl. Vyr.*, 44, (5):203-207 pp.
- Singh A. – Goyal – Gupta A.P.: 1991. Effect of cadmium and farm yard manure on the concentration and uptake of zinc by wheat in texturally different soils – *Crop Research (HISAR)* 4 (2): 199-205 pp.
- Smilde K.W. – Van Luit B. – Van Driel W.: 1992. The extraction by soil and absorption by plants of applied zinc and cadmium – *Plant and soil*. 143 (2), 233-238 pp.
- Tessier A. – Campbell P.G.C. – Bisson M.: 1979. Sequential extraction procedure for the speciation of particulate trace metals – *Anal. Chem.* 51: 844-851 pp.