ON THE FATE OF CADMIUM IN THREE DIFFERENT SOILS FROM THE DANUBIAN LOWLAND (SLOVAKIA)

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Abstract: The use of phosphate fertilizers and sewage sludge results in pollution of field soils with cadmium. To predict the cadmium transport in soil, knowledge of the forms of cadmium bonds with soil particles is necessary. Two radioactive tracer techniques were used to estimate the forms of cadmium bonds with the particles of the loamy sand soil from Kalinkovo, loamy soil from Macov, and clay soil from Jurová. Cadmium partitioning between the soil particles < 0.01 mm, easily mobile in soil macropores, and the soil particles > 0.01 mm was estimated with the modified batch technique. It was found that cadmium – soil contact lasting one-minute resulted in the 35.55%, 32.12%, and 48.12% of cadmium being adsorbed on soil particles < 0.01 mm of the soils from Kalinkovo, Macov, and Jurova, respectively. An increase in the contact time of Cd with the soil resulted in a drop in the cadmium sorption on particles < 0.01 mm, and therefore, in a drop in the potential cadmium transport via soil macropores to deeper depths of the studied soils. The modified Tessier sequential analysis served to the chemical description of that partitioning. It was found from the results of this analysis made after 1-day, 1-month, 3-month, and 6-month contact of Cd with the soil that the drop in the exchangeable sorbed fraction of cadmium was accompanied with an increase in the irreversibly sorbed fraction of cadmium.
Keywords: cadmium, soil, sorption, radiotracer, Tessier sequential analysis

DAS SCHICKSAL DES KADMIUMS IN DREI VERSCHIEDENEN BODEN AUS DEM DONAUTIEFEBENE (SLOWAKEI)

Zusammenfassung: Die Verwendung der Phosphatdünger und Abfallschlämme resultiert in Kontamination des Bodens mit Kadmium. Für die Prognose des Kadmiumtransportes in Boden sind die Kenntnisse der Bindungsform des Kadmiums mit Bodenpartikeln notwendig. Für die Bestimmung der Bindungsform des Kadmiums mit Partikeln des lehmig-sandigen Bodens aus Kalinkovo, des Lehmboden aus Macov und des tonigen Bodens aus Jurová wurden zwei isotopentracer Methoden appliziert. Die Kadmiumverteilung zwischen Bodenpartikeln <0.01 mm, die in Makroporen leicht mobil sind und Bodenpartikeln >0.01 wurde mit Hilfe von modifizierten Batch-Technik. Es wurde festgestellt, dass 1 Minute langer Kadmium-Boden Kontakt resultierte in 35.55%, 32.12% und 48.12% Adsorption des Kadmiums an Bodenpartikeln <0.01 mm aus Kalinkovo, Macov und Jurová. Der Anstieg der Kadmium-Boden Kontaktzeit resultierte in einen Rückgang der Sorption des Kadmiums an Bodenpartikeln <0.01, und daher in einen Rückgang des potentiellen Kadmiumtransportes durch Makroporen in die tieferen Bodenpartien. Die modifizierte Tessier Sequenzanalyse nutzte man für die chemische Beschreibung dieser Verteilung. Den Resultaten dieser Analyse, durchgeführt nach 1-Tag, 1-Monat, 3-Monate und 6-Monate langen Kadmium-Boden Kontakt nach wurde festgestellt, dass der Rückgang der austauschbaren sorptionfähiger Fraktion des Kadmiums war mit einem Anstieg der irreversibel sorbierten Fraktion des Kadmiums begleitet.
Schlüsselworte: Kadmium, Boden, Sorption, Isotopentracer, Tessier Sequenzanalyse

1. Introduction

Cadmium is one of the most toxic metals with carcinogenic and teratogenic impacts. Application of phosphates, fungicides and wastewater sludge are main sources of cadmium contamination of soils (Kováčová, 2000) and rivers (Pekárová and Velísková, 1998) in agriculturally utilized catchments. Cadmium transport in agricultural soils is influenced by many factors, e.g. tillage practices, duration of the cadmium – soil interaction, soil type and layering, water flow and solute transport distribution between the macropore and matrix domain, rain/irrigation intensity, total and active $CaCO_3$ content, organic matter content, as well as pH value of the soil solution.

It has been assumed that the movement of heavy metals requires the metal to be in the soil solution. For that reason, physical mixture through ploughing of the soil surface during repeated cultivation is the main factor which contributes to an increase in the concentration of heavy metals beneath the zone of application (Navarro-Pedreno et al., 2003). This is true for soil profiles under conventional tillage, but in the soils with conservation- or no-tillage management, the chemicals adsorbed on the soil particles < 0.01 mm can bypass much of the soil matrix via macropores (Jacobsen et al., 1997; Laegsmand et al., 1999).

Our attention was focused on the Danube Lowland which is a large (1260 km²) agriculturally utilized area situated in the south-west part of Slovakia, with shallow (0.5–3 m) underlying aquifer containing about 10 km³ of freshwater. In the last decade, an increase of groundwater vulnerability to cadmium has been noticed in this area due to the synergic effect of: (i) the transition from Soviet phosphate fertilizer (from the Kola peninsula) with a small amount of cadmium (1–3 mg Cd.kg⁻¹ of fertilizer) to African phosphates with 18–24 mg Cd.kg⁻¹ of fertilizer, (ii) reduced number of agrotechnical operations resulting in the formation of macropore systems as a network for preferential flow, (iii) inappropriate irrigation practice with a fast application of the necessary volume of water when the irrigation rate exceeds the saturated hydraulic conductivity of the soil matrix, and (iv) the climate change when heavy rainstorms can occur after the prolonged dry periods.

The first objective of this study was to estimate the share of cadmium adsorbed on soil particles < 0.01 mm of three different field soils from the Danubian Lowland. This portion of cadmium is potentially mobile in soil macropores (particle facilitated transport). The second objective of the study was to determine the individual forms of cadmium in the soil samples from the Danubian Lowland where a rapid macropore flow of water and cadmium was observed in our previous study (Lichner, 1998). Both the share of cadmium adsorbed on soil particles < 0.01 mm and the individual forms of cadmium in the soil samples were treated as related to a duration of cadmium – soil interaction.

2. Material and methods

The study was undertaken on light, medium heavy, and heavy soils in the Danubian Lowland. The light soil occurs in Kalinkovo [loamy-sand soil, Calcaric Fluvisol (FAO, 1998)]. The medium heavy soil occurs in Macov [loamy soil, Calcari-Haplic Chernozem (FAO, 1998)]. The heavy soil occurs in Jurová [clay soil, Calcari-Mollic Fluvisol (FAO, 1998)]. Basic characteristics of the soils studied were estimated by Fulajtár et al. (1998) and they are presented in Table 1. The quality of humus is assessed by the ratio of humic acids to fulvic acids content (HA/FA).

Sorption and desorption experiments were undertaken using radioactive tracer techniques. The radioactive tracer technique is based on the fact that stable and radioactive isotopes of a chemical element have the same physical and chemical properties, and therefore, they are subjected to the same impacts in the soil – water – solute system. But ease and speed of the radioactive tracer activity (proportional to concentration) measurement is an advantage of this technique in comparison with common analytical methods.

The sorption S of cadmium on all the soil particles was estimated by the conventional batch technique (Selim et al., 1992; Čipáková et al., 2002). Each sorption experiment involved 10 g of dry soil, passed through a 2-mm sieve before use, 40 ml of distilled water, and radioactive cadmium [109]Cd (in the form of $CdCl_2$) with a concentration of 50.9 mg.l⁻¹ and specific activity a_0. Soil, water and cadmium mixture was placed into a 100-ml polyethylene

bottle and shaken for 5 s. Then, a 5-ml sample of eluate was taken 1 min after shaking, centrifuged, and the specific activity a of the [109]Cd in aqueous phase was measured using a multi-channel gamma-spectrometer. The cadmium sorption S on the soil particles was calculated from the equation:

$$S = (a_0 - a)/ a_0. \tag{1}$$

A similar procedure was used for the 2-, 3-, 5-, 10-, 30-, and 60-min duration of cadmium – soil interaction.

Table 1. Agrochemical characteristics of studied soil samples (Fulajtár et al., 1998).

Studied soil	Kalinkovo	Macov	Jurová
≥ 0.25 mm (%)	6.04	0.86	1.54
0.25–0.05 mm (%)	55.77	36.14	11.35
0.05–0.01 mm (%)	22.48	28.84	27.84
0.01–0.001 mm (%)	10.22	19.94	37.32
≤ 0.001 mm (%)	5.49	14.22	21.92
≤ 0.01 mm (%)	15.71	34.16	59.27
Illite (%)	60–80	60–80	50–70
Chlorite (%)	10–20	10–20	10–20
Smectites (%)	5–10	10–20	10–20
Calcite (%)	2–5	2–5	2–5
Dolomite (%)	1–3	1–3	1–2
Quartz (%)	2–5	1–3	1–3
pH (H_2O)	7.8	8.0	8.6
pH (KCl)	7.4	7.7	7.4
$CaCO_3$ (%)	27	26	16
C_{ox} (%)	0.78	1.38	2.20
Humus (%)	1.35	2.38	3.79
HA/FA	0.62	1.58	1.77

The sorption S' of cadmium on the soil particles < 0.01 mm, which did not settle on the bottom of a polyethylene bottle within one minute after shaking, was estimated by the modified batch technique (Lichner and Čipáková, 2002). Each sorption experiment involved 10 g of dry soil, passed through a 2-mm sieve before use, 40 ml of distilled water, and radioactive cadmium [109]Cd (in the form of $CdCl_2$) with a concentration of 50.9 mg.l^{-1} and specific activity a_0. Soil, water, and cadmium solution was placed into a 100-ml polyethylene bottle and shaken for 5 s. Then, a 5-ml sample of solution was taken 1 min after shaking, and the specific activity a' was measured with a multi-channel gamma-spectrometer. In this sample the [109]Cd occurs in aqueous phase and also adsorbed on the soil particles < 0.01 mm. The cadmium sorption S' on the soil particles < 0.01 mm was:

$$S' = (a' - a)/a_0. \tag{2}$$

A similar procedure was chosen for the 2-, 3-, 5-, 10-, 30-, and 60-min durations of cadmium – soil interaction, with one change: 1 min before taking the sample of eluate the mixture was shaken for 5 s. According to Stokes law:

$$v = l/t = 2 g r^2 (\rho_s - \rho_w)/9 \eta \tag{3}$$

(where: v – velocity of the soil particle in water, l – length of the soil particle path in water, t – time of the soil particle path in water, g – acceleration of gravity, r – radius of the soil particle, ρ_s – density of the soil-water mixture, ρ_w – density of water, η – dynamic viscosity of water) it was calculated that all the soil particles > 0.01 mm would settle on the bottom of the bottle

within 1 min. It should be noted that all sorption experiments were carried out in duplicate, and arithmetic means of S and S' are presented.

In the desorption phase of experiments, the modified Tessier sequential extraction method (Palágyi et al., 1991) was used where two steps were added to the original method (Tessier et al., 1979): extraction with redistilled water (step 1), and extraction with 2M HNO_3 (step 8). Individual extraction agents and corresponding cadmium fractions isolated from soil components are shown in Table 2 (Navarčík et al., 1997).

Table 2. Individual extraction agents and corresponding cadmium fractions isolated from soil components (Navarčík et al., 1997).

Step	Reagent Composition	Action time /hour/	Isolated fraction
1	Redistilled water (pH=5.5)	1	Water-soluble
2	1M $MgCl_2$ (pH=7)	1	Exchangeable
3	0.025 M $Na_4P_2O_7$	1	Bound to humic acids
4	1M NaOAc+HOAc (pH= 5) where HOAc=CH_3COOH	24	Bound to carbonates
5	0.04 M $NH_2OH.HCl$	24	Bound to Fe/Mn
6	30 % H_2O_2 + HNO_3 (pH=2)	24	Organically bound and bound to sulphates
7	2M HNO_3	24	Residue, soluble in mineral acid
8	1 M NaOH	24	Residue, soluble in hydroxide
9			Insoluble rest

The results from the different extractions were combined according to the three-component model (Almas et al., 2000) as follows: the water-soluble fraction equals to the fraction isolated in step 1, the reversibly sorbed (exchangeable) fraction equals to the fraction isolated in step 2, and the irreversibly sorbed fraction of cadmium equals to a sum of the fractions isolated in steps 3–9. Their partitioning is based on the fact that plant uptake of metal ions occurs primarily through soil solution, and that the transfer of water-soluble cadmium into the irreversibly sorbed fractions can go through the reversibly sorbed (exchangeable) fraction only (and vice versa).

3. Results and discussion

The results of the conventional batch technique showed that cadmium – soil contact lasting for one-minute resulted in 96.61%, 95.78%, and 97.83% of the cadmium being adsorbed on all particles of the soils from Kalinkovo, Macov, and Jurová, respectively. The results of the modified batch technique showed that cadmium – soil contact lasting for one-minute resulted in 35.55%, 32.12%, and 48.12% of cadmium being adsorbed on soil particles < 0.01 mm of the soils from Kalinkovo, Macov, and Jurová, respectively (Čipáková et al., 2002). Drop in the share of cadmium sorbed on particles < 0.01 mm with an increase in the duration of cadmium – soil contact, presented in Figure 1, can be explained by the aging effect, i.e. by the transfer of cadmium from the reversibly sorbed into irreversibly sorbed sites.

This suggests that during the first rain or irrigation event following phosphate application, nearly all of the cadmium dissolved in water should be adsorbed on soil particles of the studied soils. In accordance with the findings of Jacobsen et al. (1997), cadmium adsorbed on particles < 0.01 mm, and mobilised by erosive impact of rain or irrigation could be transported via soil macropores. This particle- (Jacobsen et al., 1997) or colloid-facilitated transport (Laegsmand et al., 1999) of cadmium could be the cause of deep penetration of cadmium into the soil profile. Camobreco et al. (1996) presented similar results on the organically complexed heavy metals transported via soil macropores.
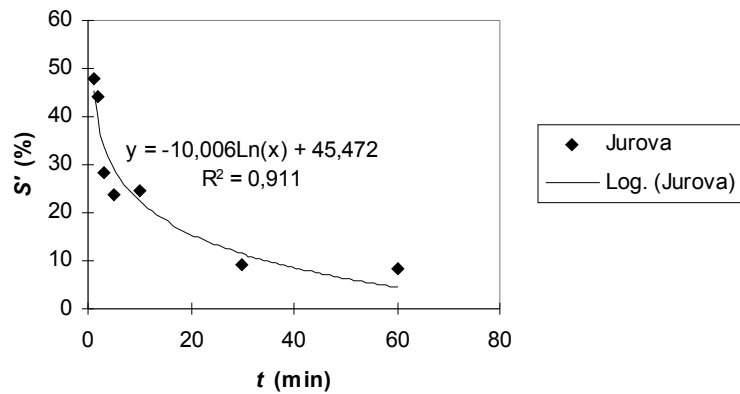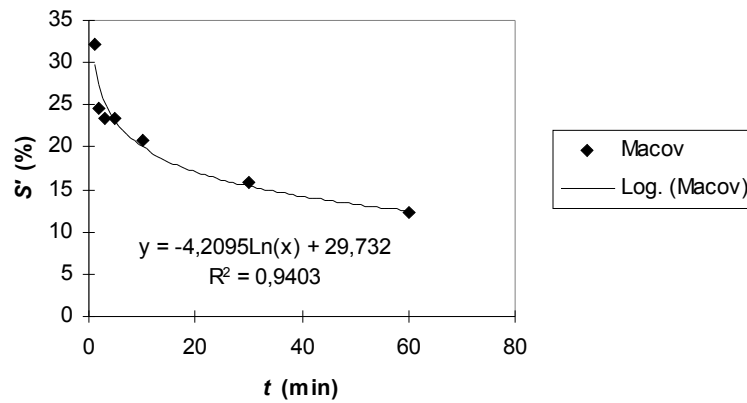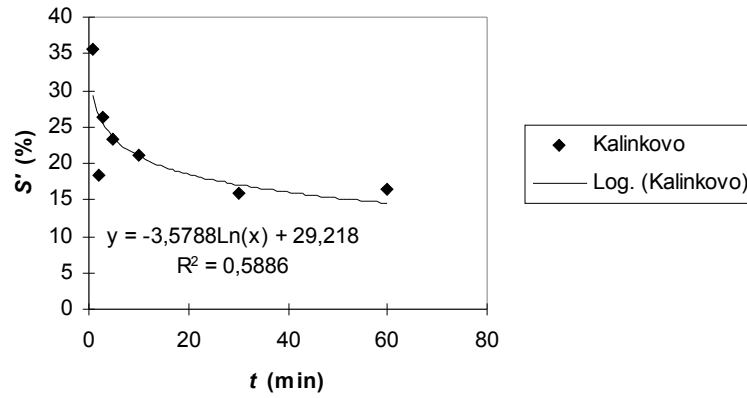
Figure 1. Sorption S' of cadmium on soil particles < 0.01 mm versus the duration t of contact between cadmium and soil.

The results of desorption experiment are presented in Table 3. Similar decrease in the reversibly sorbed fraction with duration of contact between cadmium and soil can be seen as in the case of the fraction of cadmium sorbed on soil particles < 0.01 mm. On the

other side, similar increase in the irreversibly sorbed fraction with duration of contact between cadmium and soil can be seen as in the case of the fraction of cadmium sorbed on soil particles > 0.01 mm in all the three soils.

Table 3. Individual extraction agents and corresponding cadmium fractions isolated from soil components (Navarčík et al., 1997).

Site	Fraction	Duration t of contact between cadmium and soil			
		1 day	1 month	3 months	6 months
Kalinkovo	Water-soluble	0.74	0,47	0,41	0,40
	Reversibly sorbed	39.43	30.27	21.67	13.33
	Irreversibly sorbed	59.83	69.26	77.92	86.27
Macov	Water-soluble	1.42	0.68	0.41	0.86
	Reversibly sorbed	29.30	25.40	14.77	11.56
	Irreversibly sorbed	69.28	74.92	84.82	87.58
Jurová	Water-soluble	5.00	0.23	0.23	0.70
	Reversibly sorbed	20.30	26.41	10.45	10.51
	Irreversibly sorbed	74.70	73.36	89.32	88.79

Since the bioavailability and mobility of the cadmium is related to its existing species, its speciation is increasingly attracting more attentions. Generally, soils include various components differing in sizes (sand, silt, clay) and chemical composition (silicate minerals, carbonates, hydrous oxides of Fe, Mn, and Al, organic matter). Soils contain very small clay particles in conjunction with larger aggregates stuck together with humified organic matter. Some soils consist larger nodules of iron oxides or calcium carbonate. This physical and chemical heterogeneity affects substantially the sorption of cadmium in soils.

The obtained results suggest that the rapid surface sorption reactions are followed by a subsequent slow transfer of the cadmium into soil fractions with tendency towards irreversibility. Increasing degree of irreversibility during cadmium sorption on goethite was attributed previously to slow diffusion into the solid phase (Gerth et al., 1993). McBride (1989) hypothesized that the metals may slowly diffuse into extremely small pores of particle aggregates, which probably displays a high degree of nonreversibility.

4. Conclusion

The results suggest that during the first rain or irrigation event following phosphate application, nearly all of the cadmium dissolved in water should be adsorbed on soil particles of the studied soils. Subsequently, the cadmium adsorbed on particles < 0.01 mm, and mobilised by erosive impact of rain or irrigation could be transported via soil macropores. Owing to the aging effect, increase in both the irreversibly sorbed fraction of cadmium and the fraction of cadmium sorbed on soil particles > 0.01 mm with duration of contact between cadmium and soil was registered in all the three soils.

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