

Cadmium distribution coefficients and Cd transport in structured soils

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ABSTRACT

In the case of cadmium transport via soil macropores, the short-term duration of an interaction between the reactive solute in aqueous phase and soil, as well as cadmium precipitation or adsorption on particles $< 10^{-5}$ m should be taken into account. Two distribution coefficients are proposed for predicting the cadmium transport in a structured soil: the matrix distribution coefficient K_{dm} , equal to the equilibrium distribution coefficient K_d^{eq} and estimated using the conventional batch technique, and the macropore distribution coefficient K_{dm} , estimated using the modified batch technique. It was found that the conventional approach (using the coefficient K_d^{eq} only) would underestimate a penetration of the part of Cd transported in the macropores about 255-times in the loamy-sand soil in Kalinkovo, 20-times in the loam soil in Macov, and 122-times in the clay soil in Jurová in comparison with the approach proposed in this study.

Keywords: cadmium; distribution coefficient; penetration; structured soil

The content of cadmium in some agricultural soils is increasing due to the use of phosphate fertilizers, fungicides, sewage sludge and atmospheric deposition from industrial sources (Olek and Filipek 1998). Adsorption of Cd onto the soil components is dependent on many factors, e.g. the content of humic acids (Barančíková et al. 1997), organo-clay complexes (Bolton and Evans 1996), oxides of Fe, Al, and Mn (Camobreco et al. 1996), calcium carbonate (Balík et al. 1999), as well as the soil surface charge (Babejová et al. 2001) and pH values (Bolton and Evans 1996). If several heavy metals are present in soil, competitive adsorption should be taken into the account (e.g. Slaboň and Čelková 1997).

Knowledge of the total content of cadmium in soils provides only a limited information when considering its toxic effects, and therefore, some measure of availability and mobility is required. Partitioning based on the degree of Cd association with soil components is made using various modifications of the sequential selective extraction procedure (e.g. Jeng and Singh 1993, Navarčík et al. 1994, Borůvka et al. 1997, Almas et al. 2000, Makovníková 2000). At the lowest degree of association, the easily soluble and exchangeable forms are obtained which can be mobile and bioavailable. High share of Cd in the above-mentioned forms is contained in Podzols and Dystric Cambisols, low share is characteristic for Haplic Chernozems, Rendzina and Chernozems (Makovníková 2000). Drop in the bioavailable forms (immobilization) of cadmium can be achieved by an addition of calcium hydroxide (Bielek et al. 1998), calcium carbonate (Balík et al. 1999), humic acids (Barančíková et al. 1997, Kolář et al. 1998), zeolite, Al-montmorillonite, and gravel sludge (Lothenbach et al. 1998).

Share of the easily soluble and exchangeable Cd forms decreases with an increase in the Cd-soil contact time as it

was found by Navarčík et al. (1994) for three soil types and two Cd-soil contact times (1 and 180 days), and by Almas et al. (2000) for another soil type and seven Cd-soil contact times (0.5, 1, 3, and 24 hours, 1 week, 1 month, and 1 year). The long-term change (it may not be the drop only) of the bioavailable forms of contaminants in soil is called aging by some authors (e.g. Tagami and Uchida 1998).

It has generally been assumed that heavy metals are immobile in managed agricultural soils. This assumption was supported by the conventional laboratory leaching studies in packed soil columns where infiltrating water travelled through the entire soil matrix. Based on the above-mentioned results, transport of cadmium in soil is predicted using the convective-dispersion equation where the retention of cadmium is assessed with the distribution coefficient K_d^{eq} that describes the partitioning of Cd between a solid and an aqueous phase in equilibrium. The distribution coefficient K_d^{eq} is estimated using a batch technique where the soil-solution sample is equilibrated for 18–48 hours (e.g. Buchter et al. 1996, Barančíková et al. 1997, Kováčová 2000). This approach badly underestimates the Cd penetration in the structured soils, as it was presented in our previous study on the cadmium transport in a loam soil under meadow (Lichner 1998) where a deep Cd penetration up to 60 cm was observed. Using the equilibrium distribution coefficient K_d^{eq} and convective-dispersion equation, it was predicted that all the Cd would remain in the 10-cm top layer. In spite of that prediction, it was found that more than 40% of Cd penetrated deeper than predicted. It was confirmed in the recent studies that water, solutes, and chemicals adsorbed on the soil particles $< 10^{-5}$ m can bypass much of the soil matrix via macropores (Camobreco et al. 1996, Jacobsen et al. 1997, Laegsmand et al. 1999).

Table 1. Particle size distribution of the top layer (0.1–0.2 m) of soils used in this study (Fulajtár et al. 1998)

Site	Sand (%)		Silt (%)		Clay (%)	
	≥ 0.25 mm	0.25–0.05 mm	0.05–0.01 mm	0.01–0.001 mm	≤ 0.001 mm	≤ 0.01 mm
Kalinkovo	6.04	55.77	22.48	10.22	5.49	15.71
Macov	0.86	36.14	28.84	19.94	14.22	34.16
Jurová	1.54	11.35	27.84	37.32	21.92	59.27

For this reason, a conventional approach to the Cd transport prediction should be re-evaluated and maybe abandoned in the case of macropore flow in structured soils where the two-domain (macropore and matrix domain) approach should be used in modelling the Cd transport (e.g. Vogel et al. 2000). Retention of cadmium in the matrix domain can be easily assessed using the matrix distribution coefficient $K_{dm} = K_d^{eq}$. In the macropore domain with up to four orders of magnitude higher water velocity and less amount of sorption sites in comparison with the matrix domain, duration of the Cd-soil interaction is in the order of minutes (Alaoui et al. 1997). In addition to the Cd in aqueous phase, Cd adsorbed on the particles $< 10^{-5}$ m or precipitated can be mobilized by erosional impact of rain or irrigation and transported through the soil macropores (Jacobsen et al. 1997, Laegsmand et al. 1999).

The aim of this study was to estimate the distribution coefficient K_{dm} that would serve to predict the reactive solute transport through the surface-vented macropores better than the equilibrium distribution coefficient K_d^{eq} .

MATERIAL AND METHODS

Soil samples were taken in the top layer of three various structured soils in the Danubian Lowland. The light loamy-sand soil [Eutric Fluvisol (FAO 1997)] was sampled in Kalinkovo, the medium heavy loam soil [Calcari-mollic Fluvisol (FAO 1997)] in Macov, and the heavy clay soil [Calcari-mollic Fluvisol (FAO 1997)] in Jurová. Particle size distribution and selected chemical properties of the top layer (0.1–0.2 m) of the soils in this study are shown in Tables 1 and 2 (Fulajtár et al. 1998). Quality of humus is assessed with a ratio of the humic acids to fulvic acids content (HA/FA).

The distribution coefficient K_d was estimated with the conventional batch technique (Selim et al. 1992, Čipáková and Mitro 1997) using radioactive cadmium ^{109}Cd .

Each sorption experiment involved $m = 10$ g of dry soil, passed through a 2-mm sieve before use, $V = 40$ ml of distilled water, and cadmium ^{109}Cd (in the form of CdCl_2) with concentration of 50.9 mg.l^{-1} and specific activity a_0 . The soil, water, and cadmium solution were placed into a 100-ml polyethylene bottle and shaken for 5 sec. Then 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 multichannel spectrometer gamma with Ge/Li detector. The measurements lasted for 10–60 minutes depending on the measured specific activity. The Cd sorption S on all the soil particles, and the distribution coefficient K_d were calculated from the equations:

$$S = (a_0 - a)/a_0 \quad (1)$$

$$K_d = (V/m) (a_0 - a)/a \quad (2)$$

where: m – mass of the dry soil sample, V – volume of the solution used in the sorption experiment.

The same procedure was chosen for the 2-, 3-, 5-, 10-, 30-, and 60-min duration of the Cd-soil interaction.

The distribution coefficient K_d' was estimated with the modified batch technique. 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 concentration of 50.9 mg.l^{-1} and specific activity a_0 . The soil, water, and cadmium solution were placed into a 100-ml polyethylene bottle and shaken for 5 sec. Then, 5-ml sample of solution (where ^{109}Cd in aqueous phase and that adsorbed on the soil particles $< 10^{-5}$ m occur) was taken 1 min after shaking, and the specific activity a' was measured for 90 seconds using a multichannel spectrometer gamma with Ge/Li detector. Cadmium sorption S' on the soil particles $> 10^{-5}$ m and the distribution coefficient K_d' were calculated as follows:

$$S' = (a_0 - a')/a_0 \quad (3)$$

$$K_d' = (V/m) (a_0 - a')/a' \quad (4)$$

Cadmium sorption S'' on the soil particles $< 10^{-5}$ m is:

$$S'' = (a' - a)/a_0 \quad (5)$$

Table 2. Selected chemical properties of the top layer (0.1–0.2 m) of soils used in this study (Fulajtár et al. 1998)

Site	pH (H_2O)	pH (KCl)	CaCO_3 (%)	C_{ox} (%)	Humus (%)	HA/FA
Kalinkovo	7.8	7.4	27	0.78	1.35	0.62
Macov	8.0	7.7	26	1.38	2.38	1.58
Jurová	8.6	7.4	16	2.20	3.79	1.77

Table 3. Sorption of cadmium on all the particles (S), on the particles $> 10^{-5}$ m (S'), and on the particles $< 10^{-5}$ m (S'') of the topsoils used depending on the Cd-soil contact time

Time of Cd-soil contact (min)		1	2	3	5	10	30	60
Loamy-sand soil Kalinkovo	S (%)	96.61	96.97	97.56	98.74	98.86	99.19	99.75
	S' (%)	61.06	78.62	71.18	75.36	77.74	83.2	83.23
	S'' (%)	35.55	18.35	26.38	23.38	21.12	15.99	16.52
Loam soil Macov	S (%)	95.78	96.26	95.84	96.93	96.95	97.17	97.20
	S' (%)	63.66	71.69	72.40	73.57	76.06	81.29	84.90
	S'' (%)	32.12	24.57	23.44	23.36	20.89	15.88	12.30
Clay soil Jurová	S (%)	97.83	98.18	98.27	97.94	98.67	99.21	99.18
	S' (%)	49.71	54.15	69.78	74.10	74.10	90.19	91.02
	S'' (%)	48.12	44.03	28.49	23.84	24.57	9.02	8.16

Similar procedure was chosen for the 2-, 3-, 5-, 10-, 30-, and 60-min duration of Cd-soil interaction with one change that 1 min before taking the sample of eluate the mixture was shaken for 5 s. It was calculated according to the Stokes law:

$$v = l/t = 2gr^2(r_s - r_w)/9\eta \quad (6)$$

where: v – velocity of the soil particle in water, l – path, t – time, g – acceleration of the gravity, r – radius of the soil particle, r_s – density of the soil-water mixture, r_w – density of water, η – dynamic viscosity of water, that all the soil particles $> 10^{-5}$ m would settle on the bottom of bottle in 1 min.

RESULTS AND DISCUSSION

All the above-mentioned sorption experiments were carried out in duplicate, and arithmetic means of the cadmium sorptions S , S' and S'' , as well as distribution coefficients K_d and K_d' are presented in Tables 3 and 4, respectively, for the Cd-soil contact times equal to 1, 2, 3, 5, 10, 30, and 60 min. As each triplet (Table 3) or couple (Table 4) of results represents a sorption experiment with a separate soil sample, a few deviations from the trend of sorption and K_d' can be attributed to the variability of soil properties.

It was found that more than 35% of Cd was adsorbed on the particles $< 10^{-5}$ m of the loamy-sand soil from Kalinkovo, more than 32% on the particles $< 10^{-5}$ m of the loam soil from Macov, and more than 48% on the particles $< 10^{-5}$ m of the clay soil from Jurová for the Cd-soil

interaction lasting 1 min (Table 3). The percentage of Cd adsorbed on the particles $< 10^{-5}$ m decreased with an increase in contact time, with two exceptions only (for 2 and 3 min in Kalinkovo, and for 5 and 10 min in Jurová) when an increase of percentage was observed (Figure 1). Similar decrease of the exchangeable Cd fraction was observed by Navarčík et al. (1994) and Almas et al. (2000) but for much longer Cd-soil contact.

For the shorter contact times (1 to 10 min), the percentage of Cd adsorbed on the particles $< 10^{-5}$ m of the clay soil from Jurová was higher in comparison with the loamy-sand soil from Kalinkovo and the loam soil from Macov. It could be expected with regard to the content of particles $< 10^{-5}$ m (Table 1). But for the longer contact times (30 and 60 min), the percentage of Cd adsorbed on the particles $< 10^{-5}$ m of the clay soil from Jurová was lower in comparison with the loamy-sand soil from Kalinkovo and the loam soil from Macov. It should be noticed that after the 30-min and 60-min Cd-soil interaction, 9.0 and 8.2% of cadmium only was adsorbed on the particles $< 10^{-5}$ m forming $> 59\%$ of all the particles in the soil from Jurová. Competition could be responsible for the above-mentioned decrease in the percentage of Cd adsorbed on clay particles composed of mainly illites and chlorites (Čurlík, personal communication). The Cd ions in the surface fluid layer of clay particles are retained by electrostatic attraction to the charged surface unless they exchange with other cations in solution (in this case probably with Ca). Then the Cd ions can be adsorbed on another soil particles.

Table 4. Impact of the Cd-soil contact time on the distribution coefficients K_d and K_d'

Time of Cd-soil contact (min)		1	2	3	5	10	30	60
Loamy-sand soil Kalinkovo	K_d (cm ³ .g ⁻¹)	114.0	128.0	159.9	313.5	346.9	489.8	1596
	K_d' (cm ³ .g ⁻¹)	6.27	14.71	9.88	12.23	13.97	19.81	19.85
Loam soil Macov	K_d (cm ³ .g ⁻¹)	90.79	103.0	92.15	126.3	127.1	137.3	138.9
	K_d' (cm ³ .g ⁻¹)	7.01	10.13	10.49	11.13	12.71	17.38	22.49
Clay soil Jurová	K_d (cm ³ .g ⁻¹)	180.3	215.8	227.2	190.2	296.8	502.3	483.8
	K_d' (cm ³ .g ⁻¹)	3.95	4.72	9.24	11.4	11.4	36.77	40.54

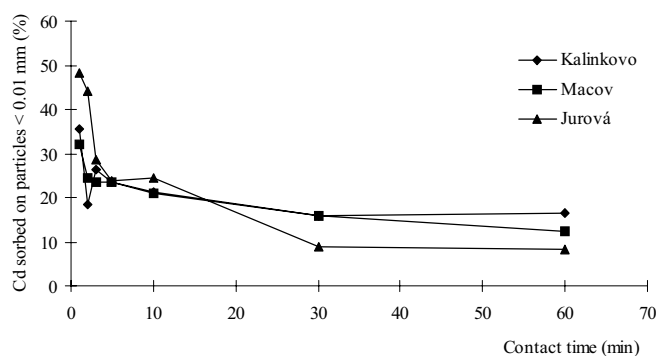


Figure 1. Share of the cadmium adsorbed on the particles $< 10^{-5}$ m vs. time of the Cd-soil contact for the topsoils from Kalinkovo, Macov and Jurová

In this study, the distribution coefficient K_d for 60-min lasting Cd-soil contact was set to be equal to the matrix distribution coefficient K_{dm} , and the distribution coefficient K_d for 1-min lasting Cd-soil contact was set to be equal to the macropore distribution coefficient K_{dm} (Table 4). It was found that using the coefficient K_{dm} instead of K_d would underestimate a penetration of the part of Cd transported in the macropores about 255-times in the loamy-sand soil in Kalinkovo, 20-times in the loam soil in Macov, and 122-times in the clay soil in Jurová.

Measurements of the partition of water and solutes between the macropore domain and the matrix domain (Lichner and Houšková 2001), as well as estimation of a probability of the rain with intensity higher than $k_s = 2 \text{ mm} \cdot \text{hr}^{-1}$ and duration more than 1 hr made by Faško from 10-year observations (Lichner et al. 1999) gave evidence that macropore flow can appear 24-times, on the average, in the south-western Slovakia during vegetation season. This flow can be the cause of rapid Cd transport from the soil surface to the depth well below the root zone.

The modified batch technique is presented to estimate the distribution coefficient K_{dm} that would serve to predict the reactive solute transport (in aqueous phase and that adsorbed on soil particles $< 10^{-5}$ m) through the surface-vented macropores. The distribution coefficients K_{dm} and K_{dm} are proposed for predicting the cadmium transport in a structured soil using a two-domain model.

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ABSTRAKT

Distribuční koeficienty kadmia a Cd transport ve strukturních půdách

Použití konvenčního postupu (konvektivně-disperzní rovnice a rovnovážný distribuční koeficient K_d^{eq}) značně podhodnocuje hloubku vniku kadmia ve strukturní půdě. Při rychlém transportu v makropórech totiž nedochází k rovnovážnému rozdělení a v makropórech se kromě rozpuštěných látek mohou pohybovat i látky vysrážené nebo sorbované na částice $< 10^{-5}$ m. Proto navrhuje použití dvou distribučních koeficientů pro popis transportu Cd ve strukturní půdě: maticového distribučního koeficientu K_{dm} , měřeného pomocí konvenčního sorpčního experimentu, a makropórového distribučního koeficientu K_{dM} , měřeného pomocí modifikovaného sorpčního experimentu. Zjistili jsme, že použití konvenčního postupu by podhodnotilo hloubku vniku části Cd pohybující se v makropórové doméně asi 255krát pro hlinitopísčitou půdu v Kalinkově, 20krát pro hlinitou půdu v Macově a 122krát pro jílovitou půdu v Jurové v porovnání s navrženým postupem. Překvapující je i zjištění, že na půdních částicích $< 10^{-5}$ m, které tvoří > 59 % částic jílovité půdy v Jurové, se adsorbovalo jen 8–9 % Cd pro 30–60 min trvající kontakt Cd s půdou.

Klíčová slova: kadmium; distribuční koeficient; penetrace; strukturní půda

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