

Parameterisation and modelling of cadmium transport in soils under conditions of climate change

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Abstract Cadmium penetration into a sandy-loam soil during the field ponded infiltration at Kráľovska lúka site in Southern Slovakia was observed in a controlled experiment using a radioactive tracer technique. Quite deep ^{115m}Cd penetration (65 cm beneath the soil surface) gives evidence of the particle-facilitated transport of cadmium through preferential pathways, when more than 40% of the applied cadmium moved deeper than 10 cm. Adsorption of cadmium on all the soil particles, the particles >0.01 mm and the particles <0.01 mm were estimated in laboratory batch tests using the radioactive tracer technique, and the distribution coefficients were calculated for both the matrix and preferential flow domains. Speciation of cadmium in the studied soil was estimated using the modified Tessier sequential extraction procedure. Data from the field experiment were used to calibrate the dual-continuum model S1D Dual. The model will be used for predicting cadmium penetration into the soil in Kalinkovo, Macov and Jurová during a simulated heavy-rain event.

Key words: *batch test; cadmium; distribution coefficient; dual-continuum system; macropores; particle-facilitated transport; preferential flow; radioactive tracer; sorption; Tessier sequential extraction procedure; vadose zone*

Introduction

Cadmium is one of the most toxic metals with carcinogenic and teratogenic impacts. The main source of Cd pollution in agricultural soils is the extensive application of mineral phosphorous fertilizers, fungicides and sewage sludge (Horn et al., 2003). Cadmium is bound to permanently charged surfaces of clay minerals, to surfaces of hydroxyl groups along the edges of clay particles, to phyllosilicate clays (Bolton, Evans, 1996), to Fe and Al (hydr)oxides, and to phenol and carboxyl groups of soil organic matter (Eriksson, 1989). Factors that influence cadmium mobility in agricultural soils are 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 CaCO₃ content, organic matter content, as well as pH value of the soil solution (e.g. Andreini, Steenhuis, 1990; Camobreco et al., 1996).

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 that 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 preferential paths. The preferential paths for water flow and solute transport in the unsaturated zone of soil are the hydrologically effective (= surface vented) macropores: biopores (e.g. earthworm, ant, and root holes), inter-aggregate pores, and desiccation cracks (Andreini, Steenhuis, 1990; Czarnes et al., 2000).

Our attention was focused on the Danubian Lowland which is a large (1260 km²) agriculturally managed area situated in the south-west of Slovakia, with a shallow (0.5–3.8 m deep) underlying aquifer containing about 10 km³ of freshwater. In the last ten years, the risk of deep penetration of cadmium into the soils, and shallow groundwater pollution has increased in this region due to:

- (i) substitution of Soviet phosphate fertilizers (from the Kola Peninsula) with a small amount of cadmium (1–3 mg Cd kg⁻¹) by African phosphates with 18–80 mg Cd kg⁻¹,
- (ii) reduced number of agricultural operations resulting in the formation of macropore systems,
- (iii) inadequate irrigation practices resulting in the ponding infiltration of water, and
- (iv) much of the precipitation occurring (as a result of climate change) in a small number of rain events with

extremely high rainfall intensity which can occur at any time during the vegetation season.

Preferential flow effects, which may trigger colloid-facilitated transport, develop in structured soils when macropore network is connected to the soil surface and when the rainfall or irrigation intensity is greater than the infiltration capacity of the soil matrix. In the research study related to the Danubian Lowland, Lichner et al. (1999) found that major rainstorms capable of generating macropore flow occur in average 24 times during the growing season (from April to October). Torrential rainstorms, following long lasting periods without precipitation, represent a weather pattern that may become rule rather than exception in Central Europe in the period of global warming that we might be experiencing.

The main objective of our research related to the cadmium transport is the improved prediction of the Cd movement in response to rainstorm events. The SID Dual model was calibrated using data from the standard double ring ponded infiltration experiment at Kráľovská lúka site, and will be used to predict cadmium penetration into the soil in Kalinkovo, Macov and Jurová during a simulated heavy-rain event.

Material and methods

The experimental sites at Kráľovská lúka, Kalinkovo, Macov and Jurová are located in the Danubian Lowland. The soil at Kráľovská lúka meadow near Bodíky is classified as Calcaric Fluvisol (WRB, 1998). From the point of view of texture it is graded as loam. The soil at Kalinkovo site is classified as Calcaric Fluvisol (WRB, 1998). From the point of view of texture it is graded as sandy loam. The soil at Macov site is classified as Calcari-Haplic Chernozem (WRB, 1998). From the point of view of texture it is graded as loam. The soil at Jurová site is classified as Calcari-Mollic Fluvisol (WRB, 1998). From the point of view of texture it is graded as loam. Chemical properties of the top layer (0.1–0.2 m) of studied soils are presented in Table 1. An example of the hourly and daily precipitation amounts measured in this region in the course of heavy rain events at two meteorological stations is presented in Table 2.

Table 1 Properties of the top layer (0.1–0.2 m) of studied soils

Site	Cox (%)	Humus (%)	pH(H ₂ O)	pH(KCl)
Kráľovská lúka (Bodíky)	2.16	3.72	7.73	7.25
Kalinkovo	0.78	1.35	7.8	7.4
Macov	1.38	2.38	8.0	7.7
Jurová	2.20	3.79	8.6	7.4

The transport of cadmium was measured during a standard double ring ponded infiltration experiment

by means of a radioactive tracer technique. The experimental setup is shown in Fig. 1. The probe, used to determine Cd concentrations, consists of a duralumin tube (inner diameter of 8 mm, outer diameter of 12 mm), in which the Geiger-Müller detector (with the length of 21 mm and the diameter of 6.3 mm) and the analog interface unit, connected to a nuclear analyzer with a coaxial cable, can be lowered to any desired depth (up to 1.5 m). Four tubes were inserted into the soil vertically from the soil surface inside the inner ring of the infiltrometer, and the cone soil seal was made of a clay-loam soil for each vertical probe. The function of the sealing design was tested by a dye tracer test (Alaoui et al., 1997). Owing to its small size the Geiger-Müller detector can be considered as a point detector, and the standard deviation in the number of counts, n , for a single measurement is \sqrt{n} (IAEA, 1975).

Table 2 The hourly and daily precipitation amounts during heavy rain events measured at two meteorological stations in the southwest of Slovakia

Date	Bratislava – Koliba			Pezinok – Myslénice
	6.7.1997	7.7.1997	8.7.1997	10.7.1999
Hours	(mm)	(mm)	(mm)	(mm)
0–1	0	1.9	2.3	0
1–2	0	3.1	1.3	0
2–3	0	2.7	2.4	0
3–4	0	2.7	2.3	0
4–5	0	1.8	2.3	0
5–6	0	2.8	2.2	0.2
6–7	0	4.1	2.0	0.4
7–8	1.8	3.0	2.0	0.2
8–9	6.8	2.8	1.5	0
9–10	2.0	3.5	2.2	0
10–11	1.9	2.7	0.8	0
11–12	3.6	2.9	1.1	2.4
12–13	5.1	5.0	2.8	1.0
13–14	5.6	6.6	1.2	0
14–15	4.0	5.0	0.7	49.7
15–16	3.9	5.0	0.9	40.9
16–17	3.7	3.3	0.1	36.5
17–18	3.4	3.9	0.1	11.5
18–19	2.8	3.1	0	3.0
19–20	2.5	2.6	0	1.0
20–21	2.2	1.9	0	2.0
21–22	2.5	1.8	0	2.7
22–23	2.4	1.6	0	0
23–24	1.5	1.6	0	0
Daily Precipitation Amount	55.7	75.4	28.2	151.5

The experiment was carried out at the end of the 17-day period without precipitation. Prior to the measurements, first 30 cm of the topsoil root layer was removed and the surface was leveled. As a result, the grass cover did not influence the cadmium fate, and the preferential

paths were formed mainly by the earthworm burrows. The removal of the top layer was motivated by the difficulties associated with the parameterization of this highly organic horizon for modeling purposes. Next, the infiltration rings and the detector probes were installed. Then, 2 cm of water containing the radioactive tracer $^{115m}\text{Cd}^{2+}$ (with the half-life of 43 days and activity less than 10 MBq) and carrier CdCl_2 (with cadmium concentration about 2 mg l^{-1}) was allowed to infiltrate into the soil (which corresponded to 8-minute lasting Cd pulse). After that, another 14 cm of clean water was supplied to the soil surface in small doses (to keep the water level in the infiltration rings at an approximately constant level), and the infiltration was terminated 110 minutes after the beginning of the infiltration. Finally, the distribution of cadmium in the soil profile was determined by measuring the counting rate along the detector probes at selected depths.

The counting rate recorded by the detector is directly proportional to the activity of the radioactive tracer (IAEA, 1975), in this case to the mass of radioactive cadmium occurring in a cylindrical volume with the radius of a few centimeters (the half-thickness of the contributing volume for the sandy loam soil and ^{115m}Cd is about 1 cm). Multiple measurements can be done to determine the distribution of the tracer along the probe. In our case, the measurement levels were chosen in the depth from 15 cm to 65 cm to be 10 cm apart (with additional measurements in the depth of 0–10 cm to estimate the contribution of matrix flow). The relative concentration of cadmium at any level can be derived from the corresponding counting rate f as follows

$$c_j = \frac{f_j}{\sum_{i=1}^N f_i} \quad j = 1, 2, \dots, N \quad (1)$$

where N is the total number of measurement levels.

The relative mass S of cadmium sorbed on all the soil particles was estimated by the conventional batch technique (Selim et al., 1992). Each sorption experiment involved $m = 10 \text{ g}$ of dry soil, passed through a 2-mm sieve before use, $V = 40 \text{ ml}$ 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 relative mass S of cadmium sorbed on the soil particles and the distribution coefficient for matrix domain K_{Dm} were calculated from the equations:

$$S = (a_0 - a) / a_0 \quad (2)$$

$$K_{Dm} = (V/m) (a_0 - a) / a \quad (3)$$

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

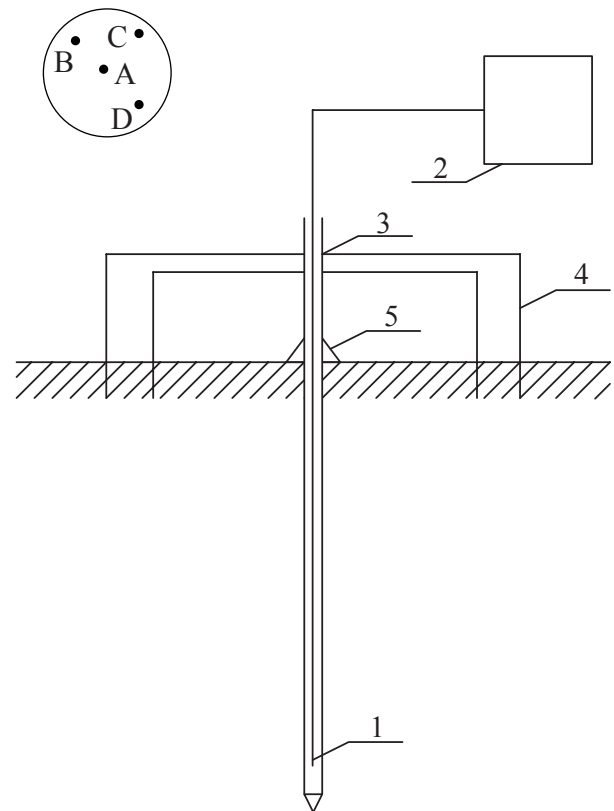


Fig. 1 Schematic of the field experiment setup: 1 – Geiger-Müller detector, 2 – nuclear analyzer, 3 – duralumin tube, 4 – double ring infiltrometer, 5 – seal made of clay-loam soil. The attached schematic depicts the location of the probes inside the inner infiltration ring (A, B, C and D).

The relative mass S' of cadmium sorbed on the soil particles $< 0.01 \text{ mm}$, which did not settle on the bottom of a polyethylene bottle within one minute after shaking, was estimated by the modified batch technique (Lichner, Čipáková, 2002). Each sorption experiment involved $m = 10 \text{ g}$ of dry soil, passed through a 2-mm sieve before use, $V = 40 \text{ ml}$ 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 were 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 $< 0.01 \text{ mm}$. The relative mass S' of cadmium sorbed on the soil particles $< 0.01 \text{ mm}$ and the distribution coefficient for preferential flow domain K_{Df} were calculated from the equations:

$$S' = (a' - a) / a_0 \quad (4)$$

$$K_{Df} = (V/m) (a_0 - a') / a' \quad (5)$$

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:

$$v = l/t = 2 g r^2 (\rho_s - \rho_w) / 9 \eta \quad (6)$$

(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.

The speciation of cadmium in studied soils was estimated using the modified Tessier sequential extraction procedure (Tessier, 1979; Palágyi et al., 1991). In this modification two steps were added to the original procedure: extraction with distilled water (step 1), and extraction with 2M HNO₃ (step 7). Each extraction procedure involved 10 g of dry soil, and 40 ml of extraction reagents (Table 3). Owing to an ease and speed of radioactive tracer techniques, speciation of the radioactive cadmium ¹⁰⁹Cd was estimated in the procedure.

The 1D Dual is a dual-continuum model, which is based on the dual-permeability approach and allows for the simulation of preferential flow effects such as the macropore transport with the domain specific sorption.

Using the concept of Gerke and van Genuchten (1993a) the variably saturated flow in a dual-continuum system can be described by means of two coupled Richards' equations:

$$C_f \frac{\partial h_f}{\partial t} = \frac{\partial}{\partial z} \left(K_f \left(\frac{\partial h_f}{\partial z} + 1 \right) \right) - \frac{\Gamma_w}{w_f} \quad (7)$$

$$C_m \frac{\partial h_m}{\partial t} = \frac{\partial}{\partial z} \left(K_m \left(\frac{\partial h_m}{\partial z} + 1 \right) \right) + \frac{\Gamma_w}{w_m}$$

where the subscripts m and f denote the matrix domain and the preferential flow domain (henceforward abbreviated to “PF-domain”), respectively. In the above equations:

h is the pressure head (m), K is the hydraulic conductivity (m s⁻¹), C is the differential water capacity (m⁻¹), z is the vertical coordinate assumed to be positive upward (m), and Γ_w is the transfer term (s⁻¹), which controls the exchange of water between the flow domains. The terms w_m and w_f are the volume fractions of the matrix domain and the PF-domain, respectively, with $w_m + w_f = 1$.

The water transfer between the matrix and the PF-domain is assumed to be proportional to the pressure head difference between the domains through the first-order transfer term:

$$\Gamma_w = \alpha_w (h_f - h_m) \quad (8)$$

where α_w is the water transfer coefficient. This coefficient was closely examined by Gerke and van Genuchten (1993b). Based on their evaluation, following formulation was suggested by Ray et al. (2004):

$$\alpha_w = \alpha_{ws} K_{ar} \quad (9)$$

where α_{ws} is the water transfer coefficient at saturation and K_{ar} is the relative unsaturated hydraulic conductivity of the interface between the matrix and the PF-domain. The value of K_{ar} fluctuates between 0 and 1 depending on the degree of saturation near the interface.

Similarly to the water flow, the dual-permeability solute transport can be described by means of two coupled advection-dispersion equations (Gerke and van Genuchten, 1993a):

$$\frac{\partial R_f \theta_f c_f}{\partial t} + \frac{\partial q_f c_f}{\partial z} - \frac{\partial}{\partial z} \left(\theta_f D_f \frac{\partial c_f}{\partial z} \right) = - \frac{\Gamma_s}{w_f} \quad (10)$$

$$\frac{\partial R_m \theta_m c_m}{\partial t} + \frac{\partial q_m c_m}{\partial z} - \frac{\partial}{\partial z} \left(\theta_m D_m \frac{\partial c_m}{\partial z} \right) = + \frac{\Gamma_s}{w_m} \quad (11)$$

where c is the solute concentration (kg m⁻³), θ is the soil water content (m³ m⁻³), D is the coefficient of hydrodynamic dispersion (m² s⁻¹), q is the water flux (m s⁻¹), Γ_s is the solute

Table 3 Sequence of extraction steps in the modified Tessier sequential extraction procedure

Step	Reagent composition	Time (hr)	Isolated fraction
1	Re-distilled water (pH = 5.5)	1	Water-soluble
2	1M MgCl ₂ (pH = 7)	1	Exchangeable
3	0.025 M Na ₄ P ₂ O ₇	1	Bound to humic acids
4	1M NaOAc + HOAc (pH = 5)	24	Bound to carbonates
5	0.04 M NH ₂ OH.HCl	24	Bound to Fe/Mn
6	30 % H ₂ O ₂ + HNO ₃ (pH=2)	24	Organically bound and bound to sulfates
7	2M HNO ₃	24	Fraction dissolved in mineral acid
8	1 M NaOH	24	Fraction dissolved in hydroxide
9			Residue

HOAc = CH₃COOH

transfer term ($\text{kg m}^{-3} \text{s}^{-1}$). Formally identical set of equations can be formulated for a dimensionless concentration. In that case, the solute transfer term receives the unit of s^{-1} .

The linear equilibrium sorption is incorporated through the retardation factor R (-), which is directly related to the distribution coefficient K_D ($\text{m}^3 \text{kg}^{-1}$)

$$R_i = 1 + \frac{\rho_i}{\theta_i} K_D \quad i = f, m \quad (12)$$

ρ is the solid phase bulk density (kg m^{-3}). The adsorption is domain specific, which means that different retardation factors may be used for each of the two domains (i.e., R_f for the PF-domain and R_m for the matrix).

The solute transfer term Γ_s is defined as the mass flux of solute being transported from one domain to the other, and is expressed as:

$$\Gamma_s = \Gamma_w c_i + \alpha_s (c_f - c_m) \quad (13)$$

In case that water flows from the PF-domain to the matrix domain: $c_i = c_p$, for the flow in the opposite direction: $c_i = c_m$. The first term on the right hand side defines the advective exchange of solute due to the movement of water, Γ_w , from one domain to the other because of the water pressure difference between the domains. The second term accounts for the diffusive exchange of solute due to the concentration difference. The rate of the diffusive exchange is controlled by the solute transfer coefficient, α_s .

In analogy to the water transfer coefficient, the solute transfer coefficient can be expressed as

$$\alpha_s = \alpha_s \theta_n \quad (14)$$

where α_{ss} is the solute transfer coefficient at saturation, and θ_{ar} is the relative degree of saturation of the interface between the matrix domain and the PF-domain.

The respective solute concentrations in the two domains are related by

$$\theta c = w_f \theta_f c_f + w_m \theta_m c_m \quad (15)$$

where c is the composite concentration and θ is the composite water content of the soil, which is determined by

$$\theta = w_f \theta_f + w_m \theta_m \quad (16)$$

No rainfall had occurred for 17 days before the infiltration experiment, so that the soil profile was quite dry. Since the initial distribution of the soil water content in the soil profile was not measured, the soil water flow simulation was started at a time corresponding to 17 days before the beginning of the infiltration experiment with the initial condition defined as so called “field capacity condition”

(i.e., fully saturated soil profile left to drain freely for 48 hours). Then the soil profile was allowed to dry for 17 days by grass transpiration and free drainage, and the final soil water content distribution was used as the initial condition for the subsequent simulation of the infiltration experiment. For the duration of the experiment, the constant pressure head condition was prescribed at the top boundary to represent the ponded soil surface during the infiltration. The free drainage condition (unit hydraulic gradient) was used as the lower boundary condition.

The initial condition for the transport of cadmium was a solute-free soil profile. The upper boundary condition for the Cd transport was set as 8-minute lasting pulse of Cd at the concentration equal to the fictitious value of 1. The exact Cd concentration in the water entering the soil surface during the infiltration experiment was not measured, therefore, only relative concentrations and masses could be evaluated. A zero concentration gradient at the depth of 1 m was set as the lower boundary condition.

Results and discussion

The results of the radioactive tracer $^{115\text{m}}\text{Cd}^{2+}$ measurements, performed during the field ponding infiltration experiment, are summarized in Fig. 2. The figure shows the distribution of counting rate with depth at the end of infiltration, i.e., after 110 minutes since the beginning of infiltration. The results provide evidence of a relatively deep breakthrough of cadmium. Trace concentrations were detected as deep as 65 cm, while more than 40% of applied cadmium moved deeper than 10 cm, due to preferential flow.

The results of the conventional batch tests showed that as early as 1 minute after the start of adsorption 99% of cadmium had been adsorbed on soil particles in all the studied soils. The relative mass S of cadmium adsorbed on all the particles during 60-minutes lasting Cd-soil contact, the relative mass S' of cadmium adsorbed on the soil particles < 0.01 mm during 1-minute lasting Cd-soil contact, and the distribution coefficients for matrix K_{Dm} and preferential flow K_{Df} domains are presented in Table 3 for all the studied soils. The distribution coefficients will be used for two-domain modelling of the cadmium transport in studied soils.

Fig. 3 provides comparison of the measured and simulated distributions of cadmium in the soil profile at the end of the infiltration experiment. The dual-permeability model under the Scenario 1, in which no transfer of cadmium between the flow domains is considered, significantly overestimates the measured Cd penetration. Scenario 2, in which the Cd transfer between the domains is enabled, provides very good agreement between measured and simulated Cd masses. According to the model, 32% of the total Cd amount moves below the 10 cm depth. The dual-permeability model reveals Cd residua down to 75 cm beneath the surface, albeit in negligible concentrations (below 10^{-5} of applied concentration).

Table 3 The relative mass S of cadmium adsorbed on all the particles during 60-minutes lasting Cd-soil contact, the relative mass S' of cadmium adsorbed on the soil particles < 0.01 mm during 1-minute lasting Cd-soil contact, and the distribution coefficients for matrix K_{Dm} and preferential flow K_{Df} domains

Site	Kráľovská lúka	Kalinkovo	Macov	Jurová
S (%)	99.32	99.75	97.20	99.18
S' (%)	65.55	61.06	63.66	49.71
K_{Dm} (cm ³ .g ⁻¹)	654	1596	138.9	483.8
K_{Df} (cm ³ .g ⁻¹)	2.01	6.27	7.01	3.95

The model, calibrated on the results of cadmium penetration during the field ponding infiltration experiment at Kráľovská lúka (Boďiky) will be used again for predictions of cadmium penetration into the soil in Kalinkovo, Macov and Jurová during a simulated heavy-rain event (Table 2).

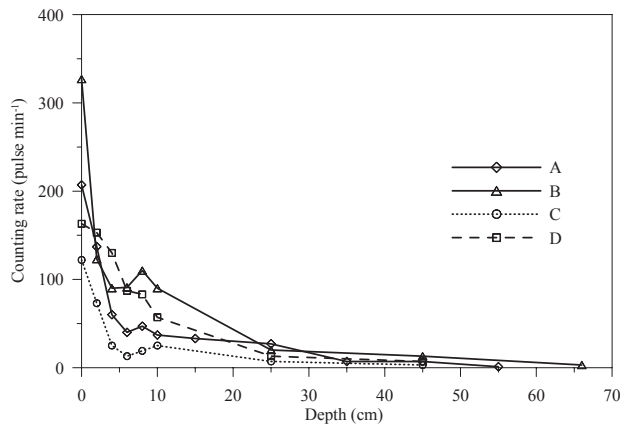


Fig. 2 Results of the tracer experiment performed with the radioactive isotope of cadmium ^{115m}Cd²⁺. The individual graphs show counting rates measured at different depths along the four inserted detection probes (cf. Fig. 1).

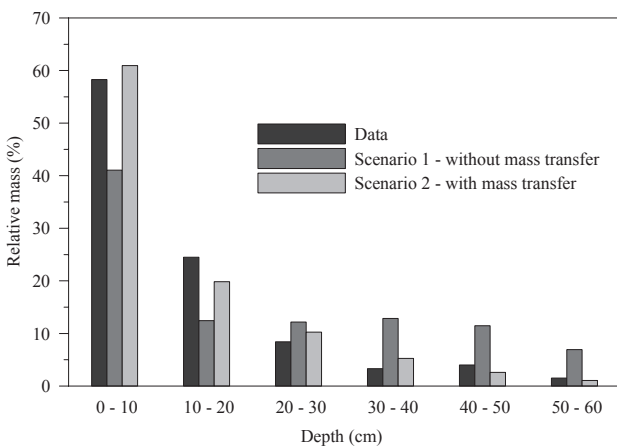


Fig. 3 Comparison of the measured masses of cadmium, obtained from the field tracer experiment with the corresponding masses simulated by the dual-continuum model (Scenario 1 and Scenario 2)

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