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Abstract

Human health has been potentially threatened by cadmium (Cd) contained in sewage irrigation water. Previous studies of Cd transport in soils were mainly conducted using small soil cores with pH values less than 6. The objectives of this study were to determine the parameters of the convection-dispersion equation (CDE) for Cd transport in relatively larger columns with neutral and alkaline soils, and to investigate the parameters' variability with depth. The soil columns were 50 cm in length and 12.5 cm in diameter. Ceramic suction lysimeters were buried at depths of 2.5, 7.5, 17.5, 27.5, and 37.5 cm to abstract soil solution. Cd concentration in the soil solution samples were subsequently analyzed to obtain breakthrough curves (BTCs). Equilibrium and nonequilibrium models in CXTFIT program were used to estimate parameters of the CDE. The results suggested that both equilibrium and non-equilibrium models performed well in modeling Cd transport. The hydrodynamic dispersion coefficient (D) ranged from 0.18 to 10.70 $cm^2 \, h^{-1}$, showing large differences among different depths. The retardation factor (R_d) ranged from 25.4 to 54.7 and the standard deviation of R_d value was lower than 30% of the mean value. Precipitation coefficient (R_p) decreased consistently with increasing depth, varying from 1.000×10^{-10} to $0.661 \, h^{-1}$. Sensitivity tests showed that D was less sensitive than R_d. These results would be helpful in understanding the transport and retention of Cd in non-acidic soils.

Keywords
convection-dispersion equation (CDE), CXTFIT, dispersion, retardation, sewage effluent irrigation

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Modeling Cadmium Transport in Neutral and Alkaline Soil Columns at Various Depths[*1]

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ABSTRACT

Human health has been potentially threatened by cadmium (Cd) contained in sewage irrigation water. Previous studies of Cd transport in soils were mainly conducted using small soil cores with pH values less than 6. The objectives of this study were to determine the parameters of the convection-dispersion equation (CDE) for Cd transport in relatively larger columns with neutral and alkaline soils, and to investigate the parameters' variability with depth. The soil columns were 50 cm in length and 12.5 cm in diameter. Ceramic suction lysimeters were buried at depths of 2.5, 7.5, 17.5, 27.5, and 37.5 cm to abstract soil solution. Cd concentration in the soil solution samples were subsequently analyzed to obtain breakthrough curves (BTCs). Equilibrium and nonequilibrium models in CXTFIT program were used to estimate parameters of the CDE. The results suggested that both equilibrium and non-equilibrium models performed well in modeling Cd transport. The hydrodynamic dispersion coefficient (D) ranged from 0.18 to 10.70 cm^2 h^{-1}, showing large differences among different depths. The retardation factor (R_d) ranged from 25.4 to 54.7 and the standard deviation of R_d value was lower than 30% of the mean value. Precipitation coefficient (R_p) decreased consistently with increasing depth, varying from 1.000×10^{-10} to 0.661 h^{-1}. Sensitivity tests showed that D was less sensitive than R_d. These results would be helpful in understanding the transport and retention of Cd in non-acidic soils.

Key Words: convection-dispersion equation (CDE), CXTFIT, dispersion, retardation, sewage effluent irrigation

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INTRODUCTION

Irrigation using secondary treated sewage effluent has been widely applied in areas with limited agricultural water resources (Crook and Surampalli, 1996; Maeda *et al.*, 1996; Murtaza *et al.*, 2010). Nutrients contained in sewage water can increase the yield of crops (Feng *et al.*, 2003), but pollutants brought into the cropland from irrigation are of environmental concern (Bahri, 1999; Qi *et al.*, 2003). Sewage water may contain heavy metals which have been detected in the crop grains (Feng *et al.*, 2002, 2003). In the suburban areas of Beijing, sewage is the main medium carrying cadmium (Cd) into cropland, and cadmium was found to be the most hazardous metal in sewage irrigated areas (Hu *et al.*, 2010; Murtaza *et al.*, 2010).

Cadmium transport and accumulation in soils are closely related to soil texture and pH (Shaheen and Tsadilas, 2010). Studies have focused on sandy soils or acid soils with pH values less than 6, in which heavy metals leach readily (Selim *et al.* 1992; Allen *et al.* 1995; Seuntjens *et al.*, 2001; Liu *et al.*, 2006). However, neutral and alkaline soils are common in northern China where sewage effluent irrigation has been widely adopted. A non-acidic environment enhances the precipitation and adsorption of heavy metals in the soil; thus a high percentage of Cd is trapped by the topsoil rather than being leached into shallow groundwater.

Recently the chance of acid rain occurrence in northern China has been increasing (Zhao and Hou, 2010). If acid rain falls on soil with a high content of heavy metals, the heavy metals can be leached into soil water quickly and will have a hazardous effect on the environment. There is an urgent need to investigate Cd transport in northern China's neutral and alkaline soils.

Fate and transport of Cd involve processes with complex physical-chemical reactions including oxidation-reduction, precipitation and dissolution, and surface and solution phase complexation (Selim *et al.*, 1992). Deterministic models based on the convection-dispersion equation (CDE) have been built to describe the transport of solute in the soils. Hinz and Selim (1994), Filius *et al.* (1998) and Selim *et al.* (1992) applied the CDE model to simulate Cd transport in soil columns under acidic environmental conditions. Mathialagan and Viraraghavan (2002) predicted the adsorption and transport of Cd in perlite using the CDE model. Overall, the CDE model has been widely used to investigate the transport processes of Cd.

The retardation factor (R_d) and hydrodynamic dispersion coefficient (D) are the two main parameters for CDE models. R_d can be derived from partition coefficients *via* batch experiments and soil physical properties such as bulk density and porosity. Zhang *et al.* (2000) obtained partition coefficients for Cd adsorption in seven soils in China with pH values ranging from 4.85 to 8.70, and it was found that a linear Freundlich adsorption model reasonably represented the data. However, most batch experiments for Cd adsorption were restricted to acidic soils or soils with the pH controlled to be less than 6. Also, in the batch experiments the ratio of mass of water to soil was arbitrarily chosen as 10:1 (Selim *et al.*, 1992), 25:1 (Neal and Sposito, 1986) or 100:1 (Allen *et al.*, 1995), which leads to large discrepancies between predicted values and observed data by using a CDE (Allen *et al.*, 1995). Values of D can be determined by transport experiments with inert chemicals such as tritium (Selim *et al.*, 1992).

Besides laboratory experiments, R_d and D values can be obtained by fitting breakthrough curves (BTCs). CXTFIT, a computer program that has been used to estimate CDE parameters in steady state one-dimensional flow (Toride *et al.*, 1999), has been successfully used to fit R_d and D values for Cd transport in soil columns (Kookana and Naidu, 1998; Pang *et al.*, 2002). Most Cd breakthrough curves have been evaluated by analyzing Cd concentration in the out-

flow leachate from small soil cores with inner diameter around 6 cm and length about 10 cm. In small soil cores, side-wall boundary conditions affect soil water flow more than in larger columns which can better mimic field conditions. Therefore, there is a need to model Cd transport in relatively larger soil columns under non-acidic environments. The objectives of this study were: i) to determine the parameters in CDE equations for Cd transport in neutral and alkaline soils by fitting the breakthrough curves obtained from relatively larger soil columns; and ii) to investigate the variability of the parameters at different depths.

MATERIALS AND METHODS

Soils were sampled from 0–100 cm depth at three sewage effluent irrigation areas, Beitiantang, Wudian and Yongledian, in the suburban areas around the City of Beijing. Soils were uniformly mixed and air dried, then passed through a 2-mm sieve. Soil texture was analyzed by the hydrometer method in the Soil Analysis Lab, China Agricultural University. Contents of heavy metals and organic matter (OM) in the soils were measured by a Hitach F70000 fluorescence spectrometer for Hg (detection limit 1×10^{-10} mol L^{-1}), an Agilent 7 500 CX inductively-coupled plasma mass spectrometer for Cd and Pb (detection limit 10 and 0.1 nmol mol^{-1}, respectively), and a Hatch2O carbon dioxide meter for OM (detection limit 1.25 mg L^{-1}). Electrical conductivity (EC) and pH values were obtained using an Accumet Handhold pH/mv/ion meter for the mixture of 10 g soil and 50 mL distilled water.

Four acrylic columns were built, two for the soil from Beitiantang (noted as sandy loam column 1 and 2), and one for each of the soil from Wudian (silt loam column) and Yongledian (loam column). Each column was 55 cm long, with inner diameter of 12.5 cm (outer diameter 13.5 cm) and an outlet at the bottom for free drainage (Fig. 1). Gravel was placed at the bottom 10 cm of each soil column, above which was a 12.5 cm diameter plastic plate with small holes which facilitated a free drainage. Soils were adjusted to a gravimetric water content of 100 g kg^{-1} before being repacked into the columns. Sandy soil from Beitiantang was packed at a dry bulk density of 1.68 g cm^{-3} while soils from Wudian and Yongledian were packed at a density of 1.40 g cm^{-3} in the acrylic columns. The bulk densities were close to field conditions. The soils were packed with a 5-cm depth layer at a time. In each soil column,

five ceramic suction lysimeters were buried during the soil packing procedure to extract soil water solution at 2.5, 7.5, 17.5, 27.5 and 37.5 cm depths below the soil surface. The method used in this study to extract soil water solution was described in detail by Feng *et al.* (1995). After the soil columns had been saturated from the bottom to top using tap water, the water supply was switched from the bottom to the top. After 3 pore volumes of drainage outflow, the water flow in the soil columns reached steady state with an upper boundary condition of constant head.
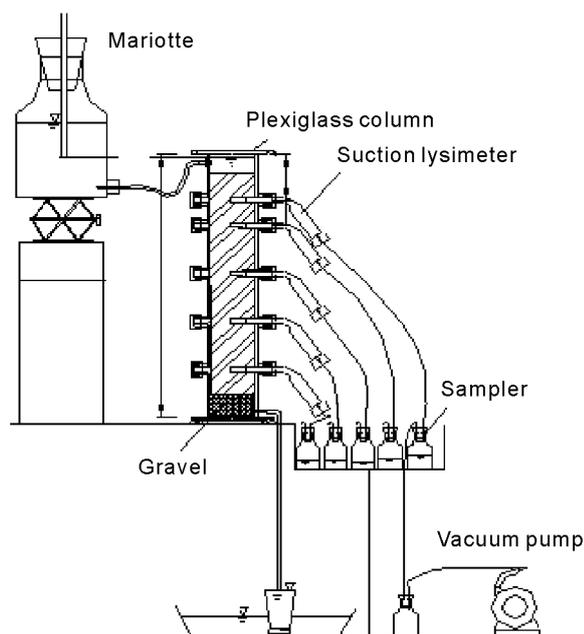

Fig. 1   Cadmium transport experiment configuration.

When the flow of the tap water reached the steady state, the tap water flow was stopped, and cadmium (CdCl$_2$·5H$_2$O, with a degree of purity of 99.9%) dissolved in tap water at a concentration of 400 mg Cd L^{-1} was introduced into the top of all soil columns subsequently. Soil solution was extracted at each of the five depths with a ceramic suction lysimeter and a vacuum pump. The input solution at the top of each column was also sampled at the same time. The sampling time interval was 4 hours in the first 24 hours and 12 hours thereafter. Cadmium concentration in the solution was analyzed by the plasma mass-spectrometer. The Cd solution samples were acidified to pH < 2 before analysis because precipitation occurred in some samples after a month's storage. The experiment lasted for 209 hours (around 9 days).

The steady outflow rate was measured to calculate the water flux (q, cm h^{-1}). Porosity was estimated by the known soil column bulk density and mineral particle density (2.65 g cm^{-3}). The value of saturated volumetric water content (θ_s) was assumed equal to porosity. Pore water velocity (v, cm h^{-1}) was calculated by:

$$v = q/\theta_s \tag{1}$$

According to the experimental conditions, assumptions were made as follows: 1) adsorption and precipitation occurred in the soil columns; and 2) Freundlich linear model (Henry model) was effective for the Cd adsorption in the 3 soils (Zhang *et al.*, 2000). The governing equation is:

$$R_d \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - R_p C \tag{2}$$

where C is the Cd concentration in the soil solution (mg L^{-1}), R_p is the first order precipitation coefficient (h^{-1}), x is the depth variable (cm), and t is the time variable (h).

The low initial Cd content (less than 0.2 mg kg^{-1}) in the soil was considered negligible in relative to the Cd concentration in the input solution, so the initial condition was set as zero:

$$C(x,t)|_{t=0} = 0 \tag{3}$$

The ponded Cd solution concentration was the upper boundary of the equation:

$$C(x,t)|_{x=0} = C_0 \tag{4}$$

where C_0 is the Cd concentration of the solution sampled from the top of the soil column (mg L^{-1}). During the whole experimental period, the Cd concentration in the drainage outflow was extremely low (less than 0.01 mg L^{-1}) relative to the input concentration, so the lower boundary was approximated as:

$$C(x,t)|_{x\to\infty} = 0 \tag{5}$$

The CXTFIT program (Version 2.1) was used to fit the parameters R_d, D and R_p. During the parameter estimation, pore velocities were fixed to the measured values, and the average Cd concentration in the solution sampled on the top of the column was considered the input concentration C_0. The initial Cd concentration in the soil profile prior to adding Cd solution was set to be zero according to Eq. 3. Initial values of R_d and D were estimated by:

$$R_d = \frac{\rho K}{\varphi} + 1 \tag{6}$$

$$D = \alpha v \qquad (7)$$

where ρ is the soil bulk density (g cm^{-3}), φ is the porosity (cm^3 cm^{-3}), K is the partition coefficient of linear adsorption model (cm^3 g^{-1}), and α is the dispersivity (cm). Zhang *et al.* (2000) studied the partition coefficients for 7 soils among which 3 soils had the similar soil texture and pH value with the soils used in this experiment. The K derived by Zhang *et al.* (2000) were used to estimate the initial R_d input for the Cd transport equation. The initial α (0.15 cm) was selected from the successful prediction of nitrogen transport and transformation in sandy loam soil column by Feng (1993). The start value for the iteration of precipitation coefficient was set to be 0.1 h^{-1}. Parameters were estimated without constraints. Root mean squared error (RMSE), coefficient of determination (R^2), and coefficient of variation (CV) between predicted and observed Cd concentration were used to evaluate goodness of the CDE fitting.

RESULTS AND DISCUSSION

Soil properties

Soil texture, initial contents of heavy metals, and other soil properties are shown in Table I. Background contents of Cd ranged from 0.106 to 0.160 mg kg^{-1},

which were negligible compared to the concentration of Cd input solution. The organic matter (OM) content increased in the order of sandy loam < silt loam < loam.

Saturated soil water content and pore water velocity are included in Table II. Pore water velocity in sandy loam soil columns was 5 to 7 times higher than in silt loam and loam columns. The high pore water velocity in sandy loam soil columns could be explained by the high hydraulic conductivity which is attributed to high sand content (Rawls *et al.*, 1982). Since all soil columns shared the same water reservoir (a Mariotte bottle), water head was the same for each soil column.

Breakthrough curves

Cadmium breakthrough curves (BTCs) in sandy loam, silt loam and loam soils are shown in Fig. 2. The measured Cd concentration in the solution ponded on the top of each soil column varied from 294 to 406 mg L^{-1}, mostly less than 400 mg L^{-1}. The reason was that precipitation occurred both in the Mariotte bottle and in the solution on the top of the soil columns. The averaged concentrations were 347, 353, 334 and 337 mg L^{-1} for sandy loam column 1, sandy loam column 2, silt loam column, and loam column, respectively. During the 209-hour experiments, there was no appreciable Cd detected at the 37.5 cm depth in any

TABLE I

Selected properties of the three soils used in this experiment

Sampling location	Sand	Silt	Clay	Texture[a]	Cd	Hg	Pb	OM[b]	pH	EC[c]
	%				mg kg^{-1}			%		mS cm^{-1}
Beitiantang	66.1	23.9	10.1	Sandy loam	0.106	0.015	18	0.34	7.8	29.7
Wudian	32.9	50.6	16.5	Silt loam	0.160	0.098	24	1.17	8.0	29.8
Yongledian	36.1	42.6	21.3	Loam	0.114	0.291	24	2.08	7.0	29.6

[a] According to USDA textural triangle; [b] Organic matter; [c] Electrical conductivity.

TABLE II

Saturated volumetric soil water content (θ_s), pore water velocity (v) and initial input of CXTFIT program

Soil column	θ_s	v	Initial input[a]		
			D	R_d	R_p
	cm^3 cm^{-3}	cm h^{-1}	cm^2 h^{-1}		h^{-1}
Sandy loam 1	0.366	5.42	0.81	41	0.1
Sandy loam 2	0.366	7.59	1.38	41	0.1
Silt loam	0.472	1.07	0.16	369	0.1
Loam	0.472	1.06	0.16	301	0.1

[a] D = dispersion coefficient; R_d = retardation factor, initial R_d values were changed to 50 for silt loam and loam soils; R_p = precipitation coefficient.

soil column. Cadmium was detected earlier at 2.5, 7.5 and 17.5 cm depths in sandy loam column 2 than in sandy loam column 1. At the depths of 7.5, 17.5 and 37.5 cm, breakthrough curves in sandy loam column 2 were steeper that those in the column 1. This might suggest that these two columns might not be packed with an identical density.
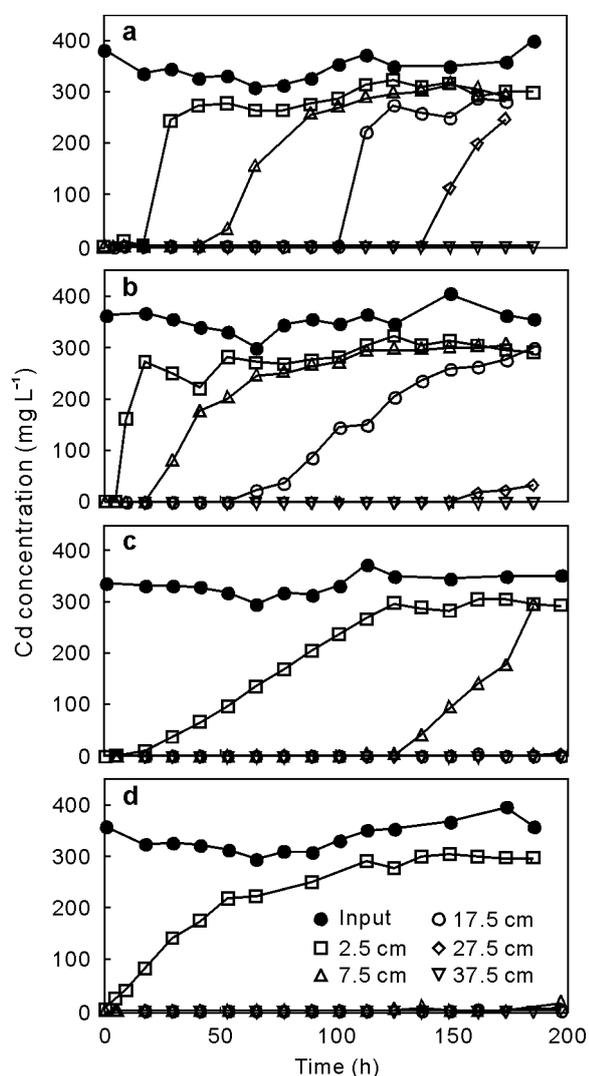

Fig. 2   Breakthrough curves (BTCs) of Cd at different depths in (a) sandy loam soil column 1, (b) sandy loam soil column 2, (c) silt loam soil column and (d) loam soil column.

Breakthrough velocity of Cd was related to pore water velocity and soil texture. At the same depth of each soil column, sandy loam soil presented the highest breakthrough velocity, followed by silt loam and loam. Clay, which is negatively charged, showed a high capability of retaining Cd. The pore velocities of silt loam and loam were close, but the breakthrough curves at 7.5 cm of the two columns were quite different. At the

depth of 7.5 cm, measured Cd concentration was 293 mg L^{-1} at hour 197 in the silt loam while no appreciable amount of Cd was detected in the loam column. This could be attributed to about 30% higher content of clay in the loam soil from Yongledian.

Fitted parameters

Three parameters, D, R_d and R_p, were fitted by an equilibrium model using CXTFIT for each breakthrough curve. Initial input data for each soil column are included in Table II. Difficulties arose when estimating parameters for silt loam and loam columns with initial R_d values as large as 369 or 301. Results were unreasonable since the fitted parameters were 7.80×10^{20} cm^2 h^{-1}, 1.00×10^{-10}, and 1.30×10^{23} h^{-1} for D, R_d and R_p of silt loam column at $x = 7.5$ cm, respectively. This indicated that the K values adopted from Zhang *et al.* (2000) were not valid for silt loam and loam soils used in this study. Initial R_d values for silt loam and loam soils were then revised to 50 by using the fitted R_d values in the sandy loam soil as a reference. Fitted BTCs are shown in Fig. 3.

Fitted parameters, D, R_d and R_p, and statistical factors, RMSE and R^2, are listed in Table III. An extremely low D value (2.30×10^{-10} cm^2 h^{-1}) was obtained when fitting the breakthrough curve at the depth of 17.5 cm in sandy loam soil column 1. It is unknown why the slope of this breakthrough curve was so steep, similar to a piston flow mode. We speculated that the soil around the suction lysimeter was disturbed by the ceramic suction lysimeter when applying vacuum at hour 113, which may lead to a local macropore flow. A dispersion coefficient, 0.738 cm^2 h^{-1}, thereby was fixed to estimate R_d and R_p using the average of the D values at 2.5 and 7.5 cm depths. Neither R_d, R_p, RMSE nor R^2 changed much (within $\pm 10\%$) when compared to those parameters from previous fitting.

Fitted dispersion coefficients (D) ranged from 0.18 to 10.70 cm^2 h^{-1}, generally lower than the D values from acidic soils in Liu *et al.* (2006) and Hinz and Selim (1994). The variability of D with depth in each soil column was fairly large. The standard deviation (SD) with depth was 0.54, 5.05, and 0.27 cm^2 h^{-1} in the sandy loam column 1, sandy loam column 2, and silt loam column, respectively. There was no consistent trend in D with respect to monitored depth. However, in sandy loam column 1 and column 2 containing the same sandy soil, the soil column with a higher pore water velocity tended to have a higher dispersion coef-
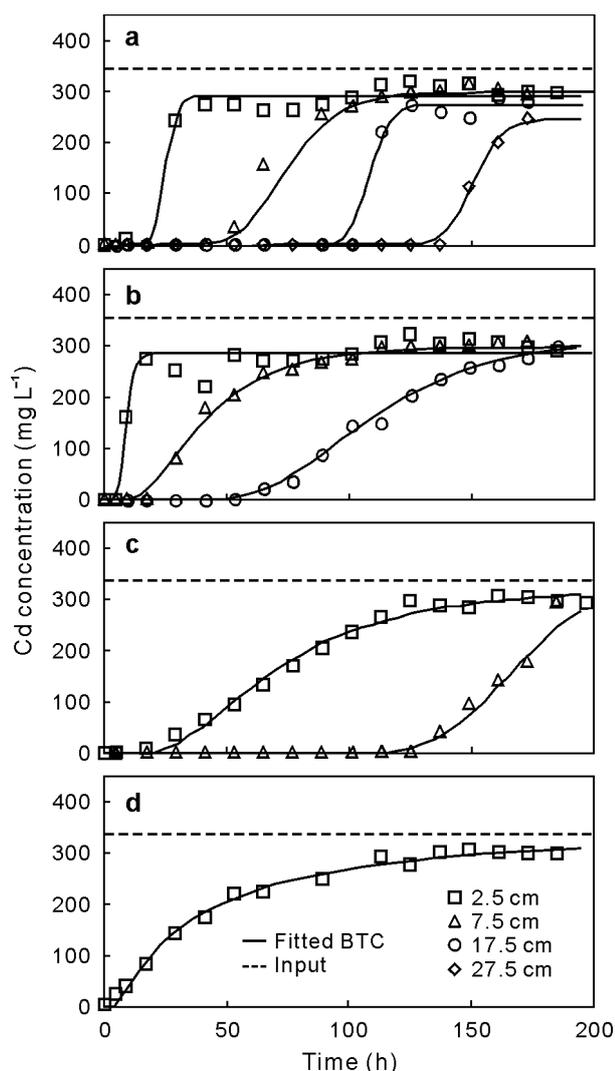
Fig. 3   Predicted breakthrough curves (BTCs) of Cd by the equilibrium model of CXTFIT program for (a) sandy loam soil column 1, (b) sandy loam soil column 2, (c) silt loam soil column, and (d) loam soil column.

ficient. Retardation factors (R_d) ranged from 24.5 to 54.7 for all BTCs with a consistent decreasing trend in the sandy loam column 1. The CV values for R_d were 29%, 30% and 26% of the mean value in the three columns, respectively. These percentages were much lower than those of dispersion coefficient.

The fitted first order precipitation coefficient R_p ranged from 1.000×10^{-10} to 0.661 h^{-1}, consistently decreasing with an increase of depth. In the sandy loam soil column 1, R_p from 0 to 2.5 cm depth was 0.373 h^{-1}, 2.5 times higher than that from 0 to 7.5 cm and 4.2 times higher than that from 0 to 17.5 cm. In the silt loam and loam soil columns, R_p was close to 0 at the two depths. Coefficient of determination (R^2) of every fit was > 0.94, and the root mean square error (RMSE) varied from 25.1 to 5.8 mg L^{-1}, which

were within 15% of the mean values of observed breakthrough curves. The high R^2 and low RMSE values indicated that the predicted concentrations matched the observed data well.

Sensitivity of D and R_d

The standard deviation in Table III indicated that fitted D values showed a higher variability than R_d, because the CV ranged between 0.76 and 1.10 for D values, while CV values were between 0.26 and 0.30 for R_d. The breakthrough curve of sandy loam soil column 1 at a depth 7.5 cm was selected to analyze the sensitivity of D and R_d. The values of D and R_d for this BTC were 1.3 cm^2 h^{-1} and 50.4, respectively. In the first trial, D changed from 1.0 to 2.0 cm^2 h^{-1} with an interval of 0.5 cm^2 h^{-1}while R_d and R_p in Table III were unchanged. Simulated breakthrough curves based on the D values of 1.0, 1.5 and 2.0 cm^2 h^{-1} are shown in Fig. 4a. RMSE values of these three curves were 10.3, 9.6 and 12.2 mg L^{-1}, which were within 20% of the RMSE values of 10.3 mg L^{-1} from the best fit scenario in Table III. In the second trial, the same procedure was used to test the sensitivity of R_d of this breakthrough curve. R_d changed from 45 to 55 with an interval of 5 while other input parameters for this breakthrough curve in Table III were not changed. The simulated Cd breakthrough curves are shown in Fig. 4b. RMSE values of these three curves were 20.6, 9.4 and 16.6 mg L^{-1}, respectively, on ave-
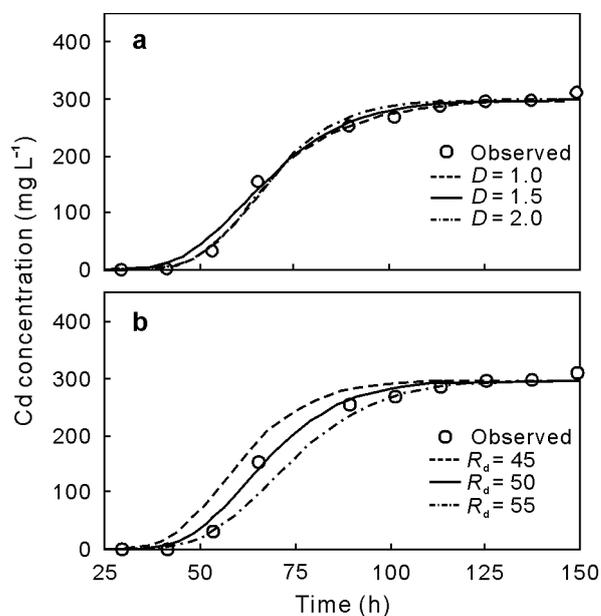

Fig. 4   Fitted Cd breakthrough curves of sandy loam soil column 1 at 7.5 cm deep with (a) different dispersion coefficients (D) and (b) different retardation factors (R_d).

TABLE III

Fitted dispersion coefficient (D), retardation factor (R_{d}), precipitation coefficient (R_{p}), root mean square error (RMSE) and coefficient of determination (R^2) by the equilibrium model of CXTFIT program with modified input concentration of Cd (C_0) and pore water velocity (v)

Depth	D	R_{d}	R_{p}	RMSE	R^2
cm	cm^2 h^{-1}		h^{-1}	mg L^{-1}	
		Sandy loam soil column 1 ($C_0 = 347$ mg L^{-1}; $v = 5.42$ cm h^{-1})			
2.5	0.177	54.7	0.373	18.1	0.981
7.5	1.300	50.4	0.108	10.3	0.995
17.5	0.738[a]	33.7	0.072	14.2	0.989
27.5	0.287	29.8	0.068	5.8	0.995
Mean (SD[b])	0.491 (0.54)	42.2 (12.24)	0.155 (0.15)	12.08 (5.25)	0.990 (0.01)
		Sandy loam soil column 2 ($C_0 = 353$ mg L^{-1}; $v = 7.59$ cm h^{-1})			
2.5	0.979	27.9	0.661	25.1	0.941
7.5	10.710	50.2	0.176	9.8	0.995
17.5	8.230	51.0	0.056	9.0	0.995
Mean (SD)	6.640 (5.05)	43.0 (13.11)	0.289 (0.32)	14.6 (9.06)	0.977 (0.03)
		Silt loam soil column ($C_0 = 334$ mg L^{-1}; $v = 1.07$ cm h^{-1})			
2.5	0.485	35.3	0.021	12.1	0.991
7.5	0.109	24.5	1.000×10^{-10}	15.1	0.972
Mean (SD)	0.297 (0.27)	29.9 (7.64)	0.021 (0.01)	13.6 (2.17)	0.982 (0.01)
		Loam soil column ($C_0 = 337$ mg L^{-1}; $v = 1.06$ cm h^{-1})			
2.5	3.721	36.5	1.000×10^{-10}	10.3	0.992

[a] D value for the sandy loam soil column 1 at 17.5 cm was not fitted value but fixed by the average of D values at 2.5 and 7.5 cm in the same column; [b] Standard deviation.

rage 51% higher than the RMSE value of 10.3 mg L^{-1} in Table III.

Fitting with different C_0 and R_p

The precipitation coefficient decreased dramatically with depth which indicated that much more precipitation occurred in the top soil layers. Note that in this experiment input Cd solution was exposed to the air and visible precipitation appeared both in the Mariotte bottle and on the top of soil columns. Because the input solution samples were not filtered and they were acidified in sampling bottles before analysis, it is possible that the input solution was overestimated since it might include Cd precipitation. Therefore, the input solution concentration of each soil column was adjusted to be equal to the maximum concentration detected at 2.5 cm. Thus the input concentrations were changed from 347, 353, 337 and 334 mg L^{-1} to 317, 323, 305 and 305 mg L^{-1} for sandy loam column 1, sandy loam column 2, silt loam column and loam column, respectively. The same fitting procedure was followed to estimate the parameters D, R_{d} and R_{p}.

The fitted parameters are shown in Table IV. The D, R_{d}, and statistical factors (RMSE and R^2) changed little after the input concentration of each column was modified to the maximum Cd concentration detected at the 2.5 cm depth. Precipitation coefficient generally decreased by more than 50% for most breakthrough curves compared with the results in Table III though an exception occurred at the 7.5 cm depth in sandy loam column 1.

Since the precipitation coefficients in the silt loam and loam soil columns were found to be close to 0 in Table III, Cd precipitation in these two soils might be negligible. All the breakthrough curves were fitted again with the assumption that $R_{\mathrm{p}} = 0$ and the results are included in Table IV. For the silt loam and loam columns, D and R_{d} decreased slightly when using the assumption of no precipitation and the RMSE values were generally improved. For example, for the BTC at 2.5 cm in silt loam column RMSE reduced from 12.8 to 12.4 mg L^{-1}. However, for the sandy loam soil columns 1 and 2, RMSE increased and R^2 decreased after eliminating the precipitation component. These results indicated that including the precipitation coefficient component improved the performance of CXTFIT when fitting BTC of Cd in the coarser textured soils with high flow rates.

TABLE IV

Fitted dispersion coefficient (D), retardation factor (R_d), precipitation coefficient (R_p), root mean square error (RMSE) and coefficient of determination (R^2) by the equilibrium model of CXTFIT program with modified input concentration of Cd (C_0) and pore water velocity (v)

Depth	With precipitation in soils					Without precipitation in soils ($R_p = 0$)			
	D	R_d	R_p	RMSE	R^2	D	R_d	RMSE	R^2
cm	cm^2 h^{-1}		h^{-1}	mg L^{-1}		cm^2 h^{-1}		mg L^{-1}	
	Sandy loam soil column 1 ($C_0 = 317$ mg L^{-1}; $v = 5.42$ cm h^{-1})								
2.5	0.176	54.6	0.176	18.1	0.981	0.319	55.6	28.2	0.951
7.5	1.510	58.8	1.890	10.3	0.996	1.994	53.0	13.7	0.992
17.5	0.738	33.7	0.042	14.2	0.989	0.738	34.2	27.8	0.955
27.5	0.287	29.8	0.049	5.8	0.995	0.746	31.0	10.2	0.984
	Sandy loam soil column 2 ($C_0 = 323$ mg L^{-1}; $v = 7.59$ cm h^{-1})								
2.5	0.970	27.6	0.386	25.1	0.941	41.200	106.0	31.3	0.902
7.5	10.400	48.6	0.082	9.8	0.995	17.600	56.7	12.6	0.991
17.5	8.150	50.4	0.017	9.0	0.995	9.290	51.8	8.8	0.994
	Silt loam soil column ($C_0 = 305$ mg L^{-1}; $v = 1.07$ cm h^{-1})								
2.5	0.401	33.0	1.000×10^{-10}	12.8	0.990	0.384	32.6	12.4	0.990
7.5	0.095	24.0	1.000×10^{-10}	18.3	0.959	0.075	23.3	13.5	0.978
	Loam soil column ($C_0 = 305$ mg L^{-1}; $v = 1.06$ cm h^{-1})								
2.5	1.820	21.5	1.000×10^{-10}	12.9	0.988	1.670	20.6	12.2	0.988

Depth variability of fitted parameters

Very close or identical dispersion coefficients were reported at multiple depths of one soil column when fitting nonreactive chloride (Toride *et al.*, 1999). However, this may not be the case for Cd transport in neutral and alkaline soils. For most of the breakthrough curves, fitted D, R_d and R_p ranged from 0.1 to 10 cm^2 h^{-1}, from 20 to 60, and from 0 to 2 h^{-1}, respectively. Although there was no consistent trend of D or R_d for any soil column with respect to depth, R_p was usually found to decline with increasing depth.

Nonequilibrium model

Although repacked soils are usually considered homogenous media, both physical and chemical nonequilibrium models have been applied to describe the transport of heavy metals in repacked soil columns (Pang *et al.*, 2002; Hutchison *et al.*, 2003). The nonequilibrium model is based on the theory that the water contained in soil pores is composed of two regions: mobile region where the water is relatively mobile and immobile region where the advection is minimal. The nonequilibrium model of CXTFIT was used in this study to investigate the performance of a nonequilibrium model on BTC fitting for Cd transport. Fitted parameters are included in Table V. Comparing the statistical factors from the nonequilibrium model to those from Table III, neither RMSE nor R^2 values changed significantly. P values in a two-tail t-test were 0.70 and 0.42 for RMSE and R^2, respectively, when comparing the equilibrium and nonequilibrium models, respectively, which indicates that there was no significant improvement in modeling Cd transport using the nonequilibrium model. The variability of D and R_d with respect to depth increased in every soil column compared with the equilibrium model. For example, R_d in sandy loam column 1 ranged from 29.8 to 54.7 in the equilibrium model but from 29.6 to 120 in the nonequilibrium model. Overall, it suggested that the equilibrium model was adequate for modeling the transport process of Cd in this study.

Sewage effluent irrigation implications

This Cd transport experiment, with surface ponding and free drainage in relatively larger soil columns, can better mimic a field irrigation scenario than small cores penetrated by pumped solutions. The breakthrough curves suggest that people should be more cautious when applying sewage containing Cd into sandy soils. In this study, the penetration of the Cd front was more than 4 times faster in sandy loam soil than silt loam and loam soils. Groundwater under sandy loam soils which has accepted sewage effluent irrigation in southwestern Beijing is prone to be contaminated by trace metals. This study also showed

TABLE V

Dispersion coefficient (D), retardation factor (R_d), partitioning variable (β), transfer coefficient (ω), precipitation coefficient in the mobile region (R_p1), precipitation coefficient in the immobile region (R_p2), root mean square error (RMSE) and coefficient of determination (R^2) fitted by two-region physical nonequilibrium model of CXTFIT program with modified input concentration of Cd (C_0) and pore water velocity (v)

Depth	D	R_d	β	ω	R_p1	R_p2	RMSE	R^2
cm	cm^2 h^{-1}					h^{-1}	mg L^{-1}	
				Sandy loam soil column 1 ($C_0 = 347$ mg L^{-1}; $v = 5.42$ cm h^{-1})				
2.5	0.107	120.0	0.429	0.130	1.000×10^{-5}	0.048	14.0	0.991
7.5	1.300	50.4	0.999	100.000	0.015	0.005	11.7	0.995
17.5	0.033	34.2	0.999	59.280	0.008	0.006	9.9	0.996
27.5	0.229	29.6	0.999	1.000×10^{-7}	0.015	1.000×10^{-7}	8.0	0.993
				Sandy loam soil column 2 ($C_0 = 353$ mg L^{-1}; $v = 7.59$ cm h^{-1})				
2.5	0.495	36.4	0.726	0.042	0.085	1.000×10^{-7}	24.6	0.954
7.5	2.120	49.8	0.653	0.094	0.021	1.000×10^{-7}	7.0	0.998
17.5	8.230	95.6	0.533	0.004	0.000	5.100×10^{-13}	10.2	0.995
				Silt loam soil column ($C_0 = 334$ mg L^{-1}; $v = 1.07$ cm h^{-1})				
2.5	0.036	32.2	1.000×10^{-4}	3.550	0.019	0.017	9.4	0.996
7.5	0.113	113.4	0.217	1.000×10^{-7}	1.000×10^{-7}	1.000×10^{-7}	21.6	0.955
				Loam soil column ($C_0 = 337$ mg L^{-1}; $v = 1.06$ cm h^{-1})				
2.5	1.850	25.7	1.000×10^{-4}	7.720	0.001	0.019	9.2	0.995

that for silt and loam soils, large quantities of Cd accumulated in the top soil layers, which may be harmful to human beings and wildlife when exposed to sewage irrigated fields. To reduce Cd leaching into deeper soil layers or groundwater, irrigation should be managed to reduce ponding depth and pore water velocity in soil profiles.

CONCLUSIONS

Parameters for describing Cd transport process were fitted by equilibrium and nonequilibrium models of CXTFIT at multiple depths of neutral and alkaline columns (50 cm in length and 12.5 cm in diameter) with soils from sewage irrigated regions in Beijing, China. The deterministic equilibrium model from CXTFIT was adequate for modeling Cd transport for the non-acidic soils used in this study. The dispersion coefficients ranged from 0.18 to 10.70 cm^2 h^{-1}, revealing high depth variability but low sensitivity to the breakthrough curves. Retardation factors ranged from 25.4 to 54.7 and the CV values was lower than 30% for different depths of each soil column. Precipitation coefficient decreased with increasing depth, and overall the value varied from 1.000×10^{-10} to 0.661 h^{-1}. These parameters can serve as references for estimating Cd accumulation in soils and transport to groundwater in China's sewage irrigated cropland, which is important for evaluating environmental impacts of sewage

effluent irrigation. Although the larger columns can better mimic field irrigation scenarios, the experiment using larger column encountered some problems such as oxidation of Cd soil solution due to its exposure to the air. The other limitation of this study is that the BTCs were obtained from disturbed soils which may need adjustment such as adding macropore effect when applied to field conditions.

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