

# Study on the mechanism of transport of heavy metals in soil in western suburb of Beijing<sup>\*</sup>

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**Abstract** Researchers are paying more and more attention to the adsorption and transport of heavy metals in soil. In this study, laboratory experiments were performed to investigate the characteristics of adsorption and transport of mercury in soils of different locations in the western suburb of Beijing. To characterize the adsorption mechanism of mercury in soil, adsorption isotherms were determined through a batch experiment. Soil column experiments were performed in saturated soil under steady-state flow at a specific water head. The breakthrough curves (BTC) for the tracer (bromine) and mercury were obtained after continuous input. Moreover, two solute transport models [convection-dispersion equation model (CDE) and two-site non-equilibrium model (TSN)] were used to simulate heavy metal movement in soil on a laboratory column scale. According to the simulating results, we explored which model is more adapted to simulate the movement of heavy metals in saturated soil in the western suburb of Beijing.

**Key words** heavy metal; pore-water velocity; retardation factor; two-site non-equilibrium model

## 1 Introduction

Incorporation of potentially toxic metals (e. g. Cd, Cu, Cr, Pb, Hg, As, Se, Zn, Ni) into soils either through sewage-sludge irrigation or some other sources of pollution (e. g. atmospheric deposition, application of agri-chemicals) has posed a great threat to the environment and human health (Teng Yanguo et al., 2002, 2004). The metals may be accumulated in food chain or may be leached out of soils to pollute groundwater supplies. Of these potentially toxic metals, Hg is considered one of the most hazardous from an environmental viewpoint. Thus the concern about soil and water pollution has emphasized the necessity of understanding the factors controlling the retention and release of Hg in soil.

The most important physico-chemical process affecting the behavior of metals is the sorption of metals from the liquid phase onto the solid phase. Sorption of metals by soils is strongly influenced by various soil characteristics. For example, some studies have shown that the sorption of metals by soils tends to increase

with increasing pH (Gerriste and van Driel, 1984; Naidu et al., 1994), organic matter (Gerriste and van Driel, 1984), cation exchange capacity (Buchter et al., 1989), and the contents of iron (Elliott et al., 1985) and manganese (Stahl and James, 1991) oxides. According to Jessberger et al. (1997), batch tests provide a quick method of estimating the maximal contaminant retention capacity of soil. The BET (batch equilibrium test) is also used to determine the partitioning/distribution coefficient parameter ( $K_d$ ). The determination of  $K_d$  is also important, as it indicates the retention of contaminants by soil solids.

In this paper laboratory experiments were performed to investigate the adsorption and transport of mercury and lead in soils of different locations in the western suburb of Beijing. To characterize the adsorption mechanism of mercury in soil, adsorption isotherms were determined through the batch experiment. Soil column experiments were performed in saturated soil under steady-state flow at a specific water head. Moreover, two solute transport models [convection-dispersion equation model (CDE) and two-site non-equilibrium model (TSN)] were used to simulate heavy metal movement in soil on a laboratory column scale. According to the simulating result, we explored which model is more adapted to simulate the movement of heavy metals in saturated soil in the western suburb of Beijing.

## 2 Material and methods

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## 2.1 The two-site non-equilibrium (TSN) model

The equations are given below:

$$R \frac{\partial C}{\partial t} + \frac{\varphi}{\theta} \left( \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \right) = D \frac{\partial^2 C}{\partial \chi^2} - V \frac{\partial C}{\partial \chi} \quad (1)$$

$$\frac{\partial S_1}{\partial t} = f K_d \frac{\partial C}{\partial t} \quad (2)$$

$$\frac{\partial S_2}{\partial t} = \alpha [ (1-f) K_d C - S_2 ] \quad (3)$$

$$R = 1 + \frac{\varphi}{\theta} K_d \quad (4)$$

where  $C$  is the solute concentration in solution ( $M/L^3$ );  $t$  is the time after injection (T);  $\chi$  is the transport distance (L);  $V$  is the pore-water velocity ( $L/T$ );  $D$  is the dispersion coefficient ( $L^2/T$ );  $\varphi$  is the bulk density of the soil ( $M/L^3$ );  $R$  is the retardation factor;  $K_d$  is the partition coefficient for linear sorption ( $L^3/M$ );  $\alpha$  is the rate of mass transfer ( $T^{-1}$ ); and  $f$  is the fraction of instantaneous sorption sites;  $\theta$  is the porosity of the soil ( $L^3/L^3$ );  $S_1$  is the sorbed concentration on instantaneous sites ( $M/M$ );  $S_2$  is the sorbed concentration on kinetic sites ( $M/M$ ).

## 2.2 The convection-dispersion equation model (CDE) (Bachmat and Bear, 1964)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial Z^2} - V \frac{\partial C}{\partial Z} - \frac{\rho}{n} \frac{\partial S}{\partial t} \quad (5)$$

$$S = K_d C \quad (6)$$

where  $C$  is the solute concentration in solution;  $t$  is the time;  $n$  is the porosity of the soil;  $Z$  is the transport distance;  $\rho$  is the bulk density of the soil;  $S$  is the sorbed concentration on soil;  $D$  is the dispersion coefficient;  $V$  is the pore-water velocity;  $K_d$  is the partition coefficient of the soil. The units are the same with the parameter of the TNS model.

Here, Eq. (5) is presented below:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial Z^2} - V \frac{\partial C}{\partial Z} \quad (7)$$

where  $R$  is the retardation factor, which is defined as:

$$R = 1 + \frac{\rho}{n} K_d \quad (8)$$

## 2.3 The two-region non-equilibrium (TRN) model

In the TRN model it is assumed that the liquid phase can be partitioned into mobile and immobile regions. The two-region solute transport model is given below (Van Genuchten and Wagenet, 1989):

$$\begin{aligned} (\theta_m + f \rho_b K_d) \frac{\partial C_m}{\partial t} &= \theta_m D_m \frac{\partial^2 C_m}{\partial \chi^2} - \nu \theta_m \frac{\partial C_m}{\partial \chi} \\ &- \alpha (C_m - C_{im}) \end{aligned} \quad (9)$$

$$[\theta_{im} + (1-f) \rho_b K_d] \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (10)$$

The subscripts  $m$  and  $im$  stand for the mobile region and the immobile region, respectively.  $f$  is the fraction of sorption sites of the mobile region to all sorption sites; and  $\alpha$  is a first order mass transfer coefficient ( $T^{-1}$ ).

In this paper, the parameters may be estimated from the column breakthrough curve data using the computer program CXTFIT (Toride et al., 1999) because the three models are included in the program. The program solved the inverse problem by fitting mathematical solution of the theoretical transport models to experimental results.

## 3 Experimental

The material used in the laboratory columns was taken from the western suburb of Beijing [DBW (Dong Beiwang) and CJJC (Xijiao Jichang)]. The physical and chemical characteristics of soil are given in Table 1.

Table 1. Physical and chemical characteristics of soil

Sample No.	Composition (%)			Organic carbon content (g/kg)	Cation exchange capacity (cmol/kg)	pH (S:W=1:5)	Bulk density (g/cm <sup>3</sup> )	Saturated moisture content (cm <sup>3</sup> /cm <sup>3</sup> )
	Sand grain	Silt	Clay					
DBW	51.2	29.6	19.2	17.13	14.424	8.24	1.27	0.489
XJJC	47.4	32.8	19.8	19.53	13.715	8.17	1.29	0.457

The columns used were chlorinated polyethylene tubes measured at 33 cm in length and 9 cm in internal diameter. The columns were packed to saturate condi-

tions. Flow was supplied from the bottom of each column to remove any entrapped air and to minimize the possibility of preferential flow. The bottom cap consis-

ted of an chlorinated polyethylene plate with small holes, covered with fine meshes to distribute the inflow.

The experiments were done at normal temperature ( $20 \pm 1^\circ\text{C}$ ). Distilled water was used as the water source. In order to examine the influence of water velocity on metal transport, the high and low heads, 125 cm and 88 cm in length, respectively, were applied to the columns. Firstly, in order to gain the coefficient of permeability, the columns were flushed with distilled water at the desired head. Then, a continuous pulse of chemical solution, containing  $\text{Hg}^{2+}$  and  $\text{Br}^-$  ions, was injected into the columns until the ratio between metal inflow and outflow-concentration was less than 5%. Then the pulse was stopped after four samples were gained. The ion  $\text{Br}^-$  was used as a conservative tracer to independently estimate pore-water velocity and dispersion, and to examine any physical non-equilibrium process in the experimental system. Samples were frequently taken from the outflow, particularly during the period of rapid concentration change. The  $\text{Hg}^{2+}$  samples were acidified and analyzed on a polarized Zeeman atomic absorption spectrophotometer.  $\text{Br}^-$  samples were analyzed using a spectrophotometer. In this paper, the focus of discussion is put on the Hg movement in soil.

#### 4 Parameter estimation

The two-region model incorporated in the CXTFIT program was applied to the  $\text{Br}^-$  data to examine any physical non-equilibrium process in the system. All water in the system was essentially mobile, the program suggested to us the equilibrium model for the  $\text{Br}^-$  data. Hence the CDE model was used for the  $\text{Br}^-$  data to estimate the pore-water velocity ( $V$ ) and dispersion coefficient ( $D$ ). As only two parameters are optimized in the equilibrium model, the  $V$  and  $D$  results can be determined uniquely. Then, by holding  $V$  and  $D$  constant for the metal Hg, the values of  $R$  for the metal were optimized using the two-site model of the CXTFIT program.

It should be noted that the  $R$ -values derived from the CXTFIT program correspond to the  $K_d$  values for linear isotherms [Eq. (4)]. However, sorption is generally not linear for heavy metals (Pang and Close, 1999; Hinton and Close, 1998). For solutes with non-linear isotherms to be used in the CXTFIT program, Van Genuchten (1981) introduced two linearization methods. These two methods allow us to obtain an equivalent  $K_d$  value. However, as we did not actually determine the isotherms of the metals in this study, the calculation of  $K_d$  and its corresponding nonlinear pa-

rameters was hence not carried out. Therefore, the retardation factor,  $R$ , is the only parameter used herein to express the relative sorption capacity of soil.

### 5 Results and discussion

#### 5.1 $\text{Br}^-$

Under different water heads, all  $\text{Br}^-$  BTCs are shown in Fig. 1. The breakthrough time was affected mainly by pore-water velocity except the properties of soil. This is further supported by the results obtained from the two-region model, suggesting that all water in the columns was essentially mobile and the equilibrium model should be used for analyzing the  $\text{Br}^-$  data. The parameter values for the  $\text{Br}^-$  calculated from the CDE model are listed in Table 2, including effective porosity and disparity. These parameters are used in the TSN model.

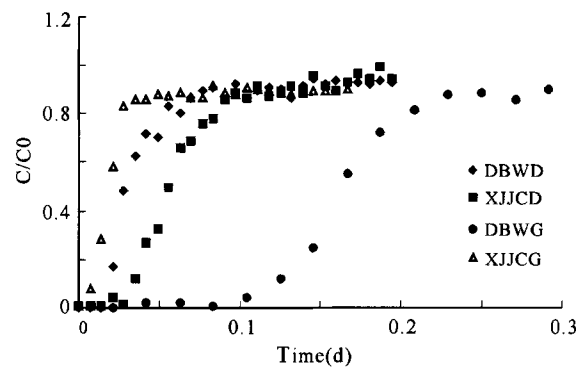


Fig. 1. Breakthrough curve of  $\text{Br}^-$ , DBWD (Dong Beiwang) at the low head; XJJCD (Xijiao Jichang) at the low head; DBWG (Dong Beiwang) at the high head; XJJCG (Xijiao Jichang) at the high head.

#### 5.2 Hg breakthrough curve

Figure 2 shows the observed and model-simulated BTCs of  $\text{Hg}^{2+}$  in the DBWD column by the CDE and TSN models. Other BTCs are omitted. Comparison of the experimental results shows that the TSN model is more perfect than the CDE model. Figure 3 shows the BTCs of Hg at two different pore water velocities in Xijiao Jichang and Dong Beiwang. The pore-water velocity of Dong Beiwang is bigger under the high water head, whereas the pore-water velocity of Xijiao Jichang is smaller under the high water head, depending on the characteristics of soil. The decisive factor affecting the retardation factor is not the head but pore water velocity. Table 2 lists parameter values for the  $\text{Hg}^{2+}$  derived from the curve fitting and calculated from the model-derived parameters, including retardation factor. From the results, it is obvious that pore water velocity is neg-

atively correlated with the retardation factor. This has also been reported by other authors (Ptacek and Gillham, 1992; Pang Liping et al., 2002). The velocity dependence of retardation factor is an indication of non-equilibrium conditions. The negative *R-V* correlation could be explained in terms of the retention time of metals in the columns. At the low flows, longer retention time of the metals in the columns permits more

complete sorption. Contrast to the retardation factor derived from the batch experiment, the retardation factors derived from the column experiment are small. The pore-water velocity would affect the transport of metals evidently. The *R* of the CDE model displays a big difference from the retardation factor derived from the batch experiment. So, the TSN model is more suitable than the CDE model for application in this study.

Table 2. The parameters derived from the CDE and two-region models

Condition	Parameter	Pore water velocity (m/d)	Effective porosity ( <i>n</i> )	Saturated moisture content ( $\theta_s$ ) (cm <sup>3</sup> /cm <sup>3</sup> )	Disparity ( $\alpha$ ) (cm)	Retardation factor from experimental data	Retardation factor from CDE model	Retardation factor from TSN model
XJJC	Low head	0.462	0.397	0.457	0.75	332.44	13.3	320
	High head	6.501	0.394	0.457	0.89	334.96	4.89	233
DBW	Low head	3.443	0.313	0.489	0.55	156.79	5.2	127
	High head	0.825	0.375	0.489	0.69	187.65	17.4	187

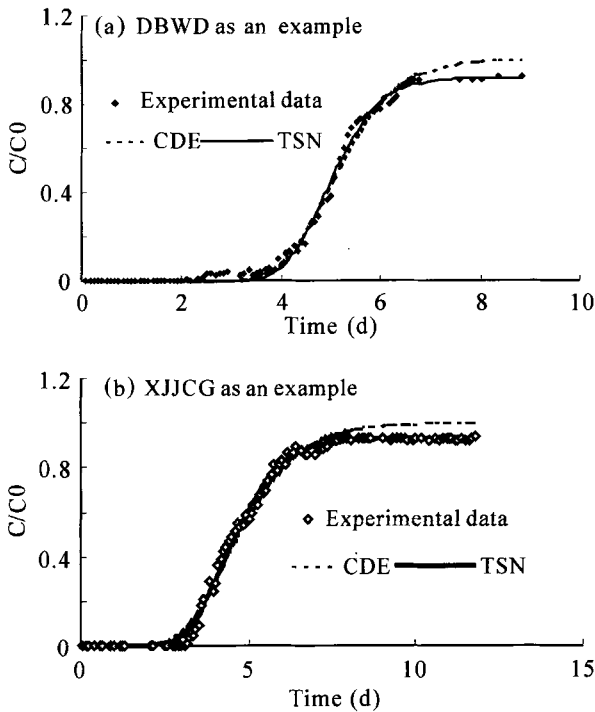


Fig. 2 (a). Observed and CXTFIT-simulated concentration breakthrough curves of Hg (II), taking DBWD as an example; (b) observed and CXTFIT-simulated concentration breakthrough curves of Hg (II), taking XJJC as an example.

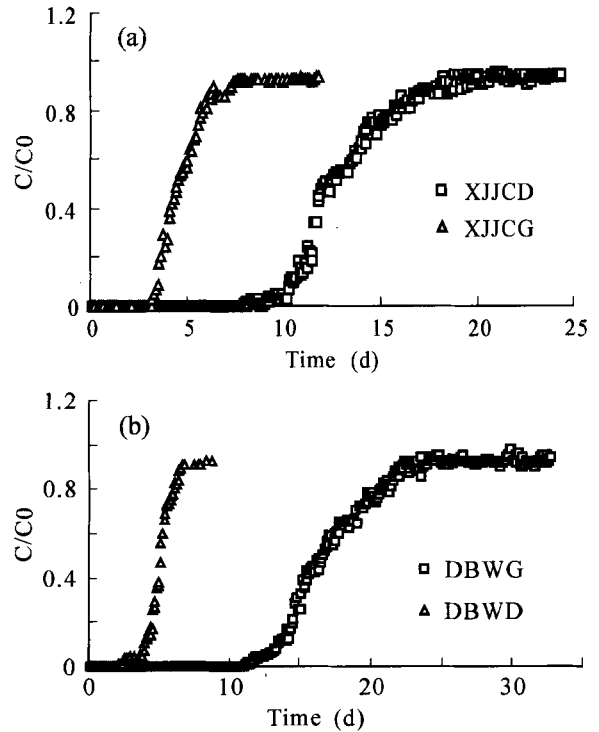


Fig. 3 (a). XJJC breakthrough curves at different pore-water velocities; (b) DBW breakthrough curves at different pore-water velocities.

### 6 Conclusions

This study deals with the metal sorption in uniformly packed columns, where physical non-equilibrium effects are minimal, so metal sorption is affected by chemical non-equilibrium phenomenon. The study describes the effect of pore-water velocity on the chemical

non-equilibrium transport of Hg. The higher the pore-water velocity is, the smaller the retardation factor will be. This paper offers the heavy metal transport model for the soil from the western suburb of Beijing. We can use this model to predict the transport rules of heavy metals in soil in the western suburb of Beijing so as to rehabilitate the polluted soil.

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