



## Investigation of the transport and fate of Pb, Cd, Cr(VI) and As(V) in soil zones derived from moderately contaminated farmland in Northeast, China

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### ARTICLE INFO

#### Article history:

Received 6 January 2009

Received in revised form 2 May 2009

Accepted 5 May 2009

Available online 15 May 2009

#### Keywords:

Heavy metal

Soil zones

Transport

Column leaching tests

Breakthrough curves

Selective sequential extraction

Solvent extraction

### ABSTRACT

Some farmland in Shenyang had been irrigated with industrial wastewater since 1962. Although wastewater irrigation was ceased in 1992, soil had been heavily polluted by heavy metals, especially by Cd. For better understanding processes of soil-heavy metal interactions, in particular, the mobility and retention mechanism of heavy metal in soil, a study on the transport and fate of heavy metals in soil zones from Shenyang suburb was carried out by column leaching tests in laboratory. Breakthrough curves of Pb, Cd, Cr(VI) and As(V) fitted by Thomas model and Yoon–Nelson model. The results of fitted breakthrough curves showed that transport rates of the four heavy metals in the soil zones followed the order: Cr(VI) > As(V) > Cd > Pb, which indicated that Cr(VI) was much more mobile, and Pb was comparatively unmovable. Cr in effluents and As were almost entirely Cr(VI) and As(V), respectively, and no Cr(III) and As(III) was ever detected during the leaching tests. The contents of Pb, Cd, Cr and As in leached soils decreased in the order of Pb > Cd > Cr > As, which suggested that adsorption ability of soil to Pb was greatest and to As was least. The methods of selective sequential extraction and solvent extraction were used to determine the fractions of Pb, Cd, Cr, As and the valent states of Cr, As [Cr(VI) or Cr(III), As(V) or As(III)] in original soils and in leached soils. After leaching tests, the relative and absolute concentrations of exchangeable, carbonate, Fe–Mn oxide and organic fraction of each element were all increased, which enhanced the potential mobility and risk of Pb, Cd, Cr and As to soil/groundwater system. The relative concentrations of Cr(III) and As(III) in different depth of the soil zones after leaching tests were increased by about 6.0% and 5.6%, respectively. Cr(III) and As(III) tended to be adsorbed by soils, which reduced the mobility of them into groundwater.

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### 1. Introduction

Trace elements from anthropogenic activities, such as industrial wastes, mining activity, agricultural production and atmospheric disposition from burning fossil were commonly discharged into environment [1]. Impact of trace toxic elements on the environment should be concerned in order to minimize their threat to soil/groundwater system. Soil serves many important functions in our society, particularly for agriculture production. It is thus of extreme importance to protect soil resource and ensure its sustainability.

Environmental hazards derived from trace toxic elements were close linked to the mobility and distribution of these elements in soil [2]. The mobility of trace elements in terms of leachability depended not only on total concentrations of elements in soil but also on soil geochemical properties and environmental factors [3,4].

The transport of trace elements in the soil zones had received considerable attention, since even a slow transport of heavy metals (eg. Pb, Cd, Zn and Cu) through the soil zones might result in increased contents of heavy metals in groundwater [5,6]. Recently, Cr(VI) and metalloid As(V) with high aqueous solubility brought public health concern since the anionic forms were considered mobile. Numerous studies were performed to assess the transport behavior of Cr and As in the soil zones [3,4].

However, to assess environmental impact of heavy metal, the knowledge of the total concentration of a specific trace element without considering its speciation was not sufficient, because the mobility and toxicity of trace element in contaminated soil were greatly controlled by its chemical speciation [7]. Determination of valent state of heavy metal (e.g., As and Cr) was also very important, since their toxicity and mobility were associated with oxidation/reduction state [3,4]. Trace elements distributed among many components of soil solids and associated with them in different ways. The mobility and bioavailability of trace elements in solid samples were generally evaluated by selective sequential extraction. A large number of selective sequential extraction methods had

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**Table 1**  
Physical and chemical properties of the soils used in this experiment.

Soil	Depth (cm)	pH	Sand (%)	Silt (%)	Clay (%)	BD (g/cm <sup>3</sup> )	TOC (%)	EC (μs/cm)	CEC (mmol/kg)
I	0–20	7.07	18	58	24	1.346	14.300	28	157.06
	20–40	7.21	26	52	22	1.336	6.940	42	160.00
	40–60	7.20	38	45	17	1.326	5.235	51	137.24
II	0–20	7.02	23	51	26	1.531	10.74	105	135.49
	20–40	6.95	31	48	21	1.583	9.077	75	119.65
	40–60	6.99	41	41	18	1.594	1.563	77	100.55

TOC: total organic carbon; BD: bulk density; EC: electrical conductivity; CEC: cation exchange capacity.

been reported, but many of which were modified on the basis of the five-step sequential extraction technique, developed by Tessier et al. [8]. By this technique, trace element were classified into five fractions: exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter and residual.

The studied area is situated within the suburb of Shengyang, which is major heavy industrial production base in the region for several decades. Increased contaminants may pose substantial threat to the local agriculture, as contaminants may enter and accumulate in soils through many approaches [9,10]. In Shenyang, some areas irrigated by wastewater with heavy metals more than 10 years ago had been heavily polluted by Cd and slightly polluted by Zn and Cu, in light of the China Environmental Quality Standards [11], and the dominant fractions of Cd were exchangeable and carbonate fractions, which represent up to 43% and 35% of the total amount of Cd, respectively [12]. Contamination of agricultural soils may cause long-term environmental and healthy risk. The presence of trace toxic elements in the farmland has imposed a need for better understanding the processes of soil–trace element interactions, in particular, the mobility and retention mechanism of trace element in soil [13]. A research about trace toxic elements in agricultural soil in Shenyang suburb, China could provide valuable and insightful information for other regions in China. The main objectives of the study were to evaluate the downward transport of metallic Pb, Cd, Cr(VI) and metalloid As(V) in the soil zones and to evaluate the risk of the four heavy metals to soil/groundwater system, according to chemical fractions of the four elements and valent states of Cr and As. Some conclusions obtained from this work are significant for understanding the transport and fate mechanism of heavy metal in soil zones

## 2. Materials and methods

### 2.1. Collection and preparation of soil sample

Soils with number I and II used in this study were sampled from two sites within contaminated farmland in Northeast China. Site I (123° 29. 352′ E, 42° 04. 001′ N) was situated in the neighborhood of a chromium waste disposal. Residual materials produced in industrial production containing chromium with great concentration were disposed for about 50 years. Leachate from the disposal had restrained the growth of corn plants covering the site. Soil II (125° 05. 839′ E, 43° 53. 503′ N) was sampled in the farmland on the left bank of a river seriously contaminated mainly by industrial wastewater. The farmland had been irrigated with the wastewater from the river for long-time. Although wastewater irrigation was already prohibited, heavy metal pollution (especially Cd) of the agricultural soil had been serious.

Soils were sampled from three layers as 0–20 cm, 20–40 cm and 40–60 cm in a profile. In the laboratory, soil samples were air-dried and passed through a 2 mm nylon sieve to remove large debris, stones and pebbles. Soil I was used for Cr(VI) and As(V) leaching tests and Soil II was used for Pb and Cd leaching tests. Some basic physicochemical properties of the soils are shown in Table 1.

### 2.2. Soil column leaching tests

Each column has an inner diameter of 18.5 cm, a length of 60 cm. Three sections of column with length of 20 cm represented for soil layers of 0–20 cm, 20–40 cm, 40–60 cm from top to bottom in column, respectively. The three separated sections can be well jointed, sealed and can also be separated again for soil sampling after the leaching tests. Each section has a small hole drilled on the tube sidewall for collecting effluents at different time.

Before leaching tests, soils were saturated with distilled-deionized water (dd H<sub>2</sub>O) at ionic strength of 0.01 mol/L CaCl<sub>2</sub> for 24 h. Four soil columns were leached with the solution containing 100 mg/L Pb, 100 mg/L Cd, 10 mg/L Cr(VI) and 10 mg/L As(V), respectively (pH 6.0) by dilution of Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (all analytical grade reagent) stock solution with dd H<sub>2</sub>O. The flow rate was adjusted to be 2.8 ml min<sup>-1</sup>. At different leaching time, the effluents were collected for concentration measurement of each heavy metal.

After the tests, the four columns were separated, extruded (~20 cm each). All soils from the specified depth range were thoroughly mixed, dried, ground. Soil samples before and after tests were analyzed for element concentration using acid digestion method according to the standard, GB15618 [14]. The concentrations of Pb and Cd in the extracts were measured using flame atomic adsorption method or graphite furnace atomic adsorption method (AAS 700 equipped with GFAAS, PerkinElmer, USA). The method for determining As and Cr concentration will be introduced in Section 2.4.

### 2.3. Determination of fractions of the four heavy metals and valent states of chromium and arsenic

The method of selective sequential extraction could provide valuable information of element portioning in soils, sludge, and sediments and also provided an estimation of their mobility [15]. In this study, the selective sequential extraction technique of Tessier et al. [8] was used to analyze the chemical fractions of Pb, Cd, Cr and As in soils before and after tests (double samples). A minor modification of the selective sequential extraction was used for determination of exchangeable Cr and As in soils [16]. For quality control, reagent blanks, replicates were incorporated in the analysis to detect contamination and assess error. The analytical results showed that there was no sign of contamination and the average deviation of analysis were generally <4%. The overall recovery ratios of Pb, Cd, Cr and As (the sum of the five fractions to the total element concentration) were around 81–104%.

Generally, chromium presents in the forms of Cr(VI) and Cr(III) in environment. Cr(VI) is both highly soluble and toxic to plants and animals, yet Cr(III) is relatively insoluble and less toxic [17]. Cr(VI) can be reduced to Cr(III) in soil under favorable conditions. It is generally recognized that As(V) was the major species in oxidized acidic environment, but the most stable and predominant form was As(III) [18]. As(III) was greatly toxic, while potential mobility of As in soil was related to As(V) [19]. In this study, Cr and As valence

**Table 2**  
Fractions of the four heavy metals by selective sequential extraction and valent state of chromium and arsenic by solvent extraction.

Selective sequential extraction	Extractants	Solvent extraction	Extractants
Exchangeable fraction	Pb and Cd were extracted with 1 mol/L MgCl <sub>2</sub> (pH 7.0), Cr and As were extracted with 1 mol/L KCl and 0.1 mol/L KH <sub>2</sub> PO <sub>4</sub>	Cr(VI)	0.28 mol/L Na <sub>2</sub> CO <sub>3</sub> + 0.5 mol/L NaOH
Carbonate-bound fraction	1 mol/L NaOAc adjusted to pH 5.0 with HOAc	As(V) and As(III) (without changing its speciation)	10 mol/L HCl
Fe–Mn oxide fraction	0.04 mol/L NH <sub>2</sub> OH·HCl in 25% (v/v) HOAc		
Organic fraction	30% H <sub>2</sub> O <sub>2</sub> + 3.2 mol/L NH <sub>4</sub> OAc in 20% HNO <sub>3</sub>		
Residual fraction	HNO <sub>3</sub> + HClO <sub>4</sub>		

were determined using solvent extraction methods developed by Bank et al. [4] and Chappell et al. [20], respectively. The methods of selective sequential extraction and solvent extraction were listed in Table 2

The concentration of Cr(VI) in extraction solution was measured by 1, 5-diphenyl carbonize spectrophotometer method [14] using a WFJ2-7200 Spectrophotometer (Unico (Shanghai) Instruments Co., Ltd, China). Total Cr were analyzed using an acid digestion method according to the China standard, GB15618 [14] and measured by GFAAS, it was assumed that the total Cr was composed of Cr(VI) plus Cr(III). Thus, the Cr(III) in each sample was calculated as Eq. (1):

$$\text{Cr(III)} = \text{total Cr} - \text{Cr(VI)} \quad (1)$$

As species (As(V), As(III)) was determined by flow injection hydride generation atomic adsorption spectrometry with variable sodium tetrahydroborate concentrations [21].

#### 2.4. Statistical analysis

Successful description of column tests requires prediction of the breakthrough curves for the effluents. The Thomas equation [22], as shown in Eq. (2) was widely used for describing breakthrough curve.

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{(K_T(q_0 m - c_0 V))/Q}} \quad (2)$$

where  $C_t$  is element concentration in the effluent (mg/L);  $C_0$  is initial concentration of element (mg/L);  $K_T$  is Thomas rate constant (mL/(min mg));  $q_0$  is maximum amount of element that can be absorbed by soil (mg/g);  $m$  is mass of the adsorbent (g);  $V$  is effluent volume (L);  $Q$  is flow rate (mL/min).

Yoon and Nelson [23] developed a relatively simple model to describe the adsorption and breakthrough of adsorbate vapors or gases with respect to activated charcoal. This model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson equation regarding to a single component system is expressed as:

$$\frac{C_t}{C_0} = \frac{e^{(K_{YN}t - \tau K_{YN})}}{1 + e^{(K_{YN}t - \tau K_{YN})}} \quad (3)$$

where  $K_{YN}$  is rate constant (L/h);  $\tau$  is time required for 50% adsorbate breakthrough (h) and  $t$  is sampling time (h).

Here, BTCs were fitted by nonlinear least squares fitting using Microcal Origin (Version 6.1). The regression was performed until  $X^2/\text{DOF}$  was not reduced (the fitting converged) or  $X^2/\text{DOF}$  did not change in 10 iterations (the fitting did not converge), where  $X^2/\text{DOF}$  was used to represent the deviations of the theoretical curves from the experimental data.

### 3. Results and discussion

#### 3.1. Transport rate of Pb, Cd, Cr(VI) and As(V) in the soil zones

The results obtained from soil column leaching tests are shown in the form of breakthrough curves fitted by the Thomas model and the Yoon–Nelson model (Fig. 1 and Fig. 2). Each regressed curves indicated that they were all well fitted with  $R^2$  ranging from 0.828 to 0.992 (Table 3). The relative concentrations ( $C_t/C_0$ ) of the four elements in leachates were increased with leaching time and effluent volume. An apparent plateau in the breakthrough curve ( $C_t/C_0$  0.8–1.0) appeared for each element in different sampling depth except Pb and Cd at 60 cm depth, which showed that the soils almost reached saturated adsorption to the four elements. In later period of tests, the columns for Pb and Cd leaching tests were blocked and leachates could not be collected, so Pb and Cd in effluents at 60 cm sampling depth had not reached apparent plateau of breakthrough curves.

As shown in Fig. 1 and Fig. 2, steep breakthrough curves were obtained for Cr(VI) because of its lesser adsorption capacity by soil. Breakthrough point for Cr(VI) leaching appeared at 5 h, 30 h and 60 h for the sampling depth of 20, 40, 60 cm, respectively and maximum concentration in effluents appeared at 40 h, 96 h, 320 h, respectively. The high mobility of Cr(VI) posed a risk of groundwater contamination of Cr(VI).

Compared with Cr(VI), breakthrough point of As(V) was significantly delayed, which appeared at 23 h, 95 h and 140 h for the sampling depth of 20 cm, 40 cm, 60 cm, respectively. The time needed to reach an apparent plateau of breakthrough curves ( $C_t/C_0 \sim 1.0$ ) was nearly 900 h, 1500 h and 3000 h longer for the sampling depth of 20 cm, 40 cm, 60 cm, respectively. However, for Pb and Cd, the concentration in leachate increased more slowly and the breakthrough point appeared later (about several hundred to several thousand of hours) than that of Cr(VI) and As(V).

The fitted values of  $K_T$  and  $q_0$  are presented in Table 3. With the depth of soil zones increased, the values of  $K_T$  decreased and  $q_0$  was almost constant for each element. The predicted and experimental value of  $q_0$  (soil capacity) obtained for each element showed negligible difference. The modeled values of  $\tau$  were in agreement with the measured values, which indicated that data of column tests were well fitted by the Yoon–Nelson model. According to values of  $K_T$  (presenting the rate of pollutants transport), the rates of the four elements transport in the soil zones followed the order: Cr(VI) > As(V) > Cd > Pb. Heavy metal adsorption in soil was mainly affected by soil character, metal ion property. The differences of physical and chemical properties of two soils used in this experiment (as shown in Table 1) were not obvious, so differences in mobility and accumulation of the four elements in the soil zones were mainly related to their properties [24]. Positively charged Pb and Cd were adsorbed by negative sites on the soil surface. Anionic Cr(VI) and As(V) could be only adsorbed by goethite, FeO(OH), aluminum oxides and other soil colloids with positively charged surface sites [25]. Soil surfaces were normally negatively charged, so Pb and Cd were adsorbed greatly [26].

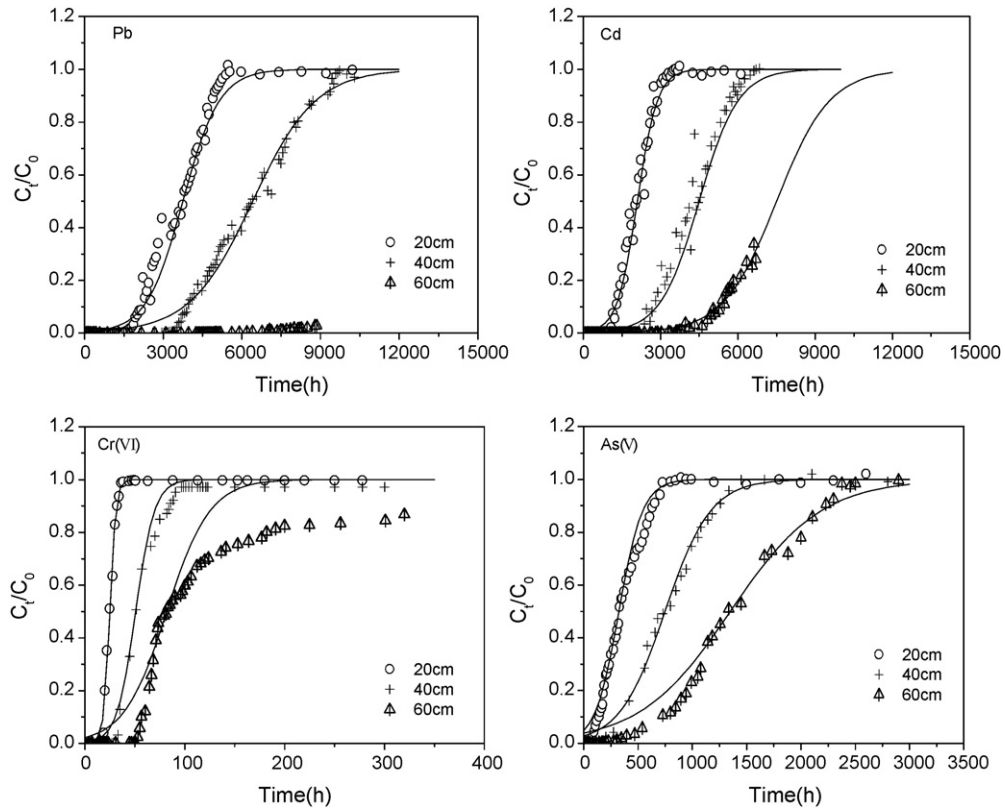


Fig. 1. The experimental data and predicted breakthrough curves obtained according to the Yoon and Nelson model for Pb, Cd, Cr(VI) and As(V) leaching tests.

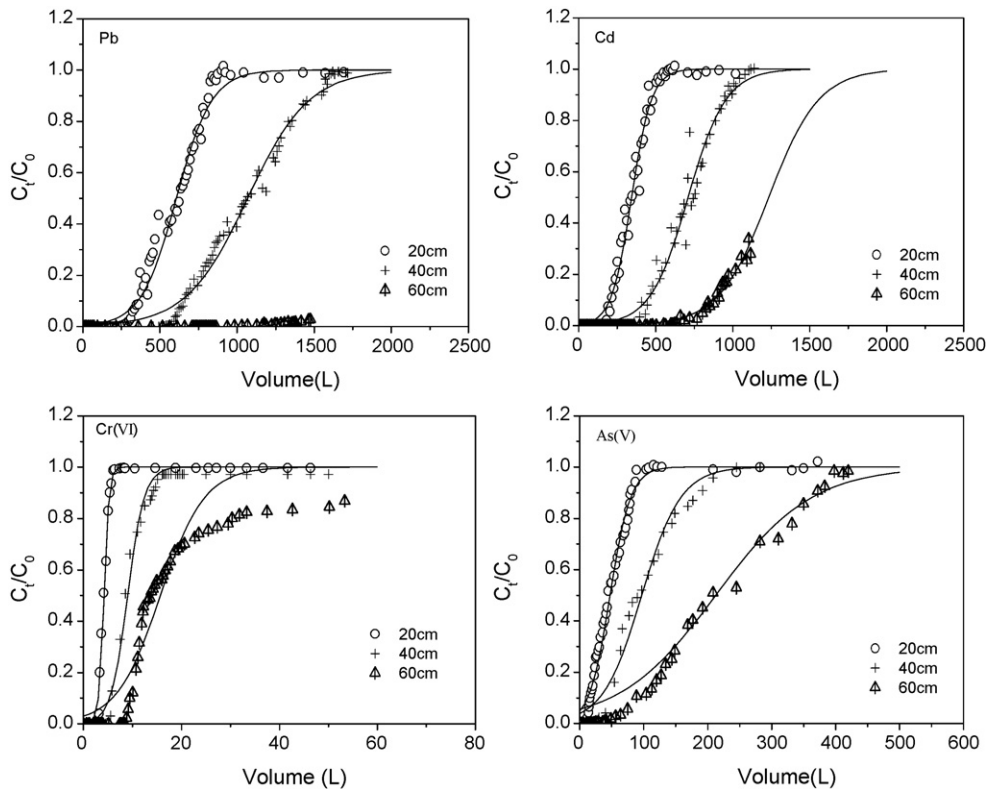


Fig. 2. The experimental data and predicted breakthrough curves obtained according to the Thomas model for Pb, Cd, Cr(VI) and As(V) leaching tests.

**Table 3**  
Parameters predicted from the Thomas model and the Yoon–Nelson model for Pb, Cd and Cr(VI) and As(V) leaching tests.

Heavy metal	Depth (cm)	$C_0$ (mg/L)	The Thomas model				The Yoon–Nelson model			
			$K_T$ (ml/(mg min))	$q_{0,theo}$ (mg/g)	$q_{0,exp}$ (mg/g)	$R^2$	$K_{YN}$ (L/h)	$\tau_{0,theo}$ (h)	$\tau_{0,exp}$ (h)	$R^2$
Pb	20	100	0.24	12.13	10.48	0.986	0.0014	3644	3750	0.985
	40	100	0.14	10.68	10.36	0.988	0.0008	6423	6400	0.987
	60	100	–	–	–	–	–	–	–	–
Cd	20	100	0.43	6.875	5.467	0.988	0.0026	2063	2100	0.989
	40	100	0.23	7.107	5.367	0.984	0.0013	4264	4500	0.972
	60	100	0.17	8.225	4.965	0.973	0.0010	7439	–	0.972
Cr(VI)	20	10	537	0.0084	0.0112	0.992	0.326	25	24	0.992
	40	10	165	0.0090	0.0122	0.989	0.108	54	50	0.985
	60	10	62	0.0105	0.0100	0.892	0.047	91	82	0.849
As(V)	20	10	17.3	0.095	0.179	0.988	0.0092	348	325	0.982
	40	10	9.16	0.097	0.181	0.975	0.0048	760	780	0.992
	60	10	3.71	0.142	0.183	0.804	0.0024	1351	1300	0.828

Effluent Cr was entirely Cr(VI), and no Cr(III) was ever detected during leaching tests. Lack of effluent Cr(III) suggested that Cr(III) transport in the soil zones was of minor importance, most likely because soil was efficient sorbent for Cr(III), which was in agreement with the findings of Jardine et al. [17]. Likewise, no As(III) was detected in the effluents.

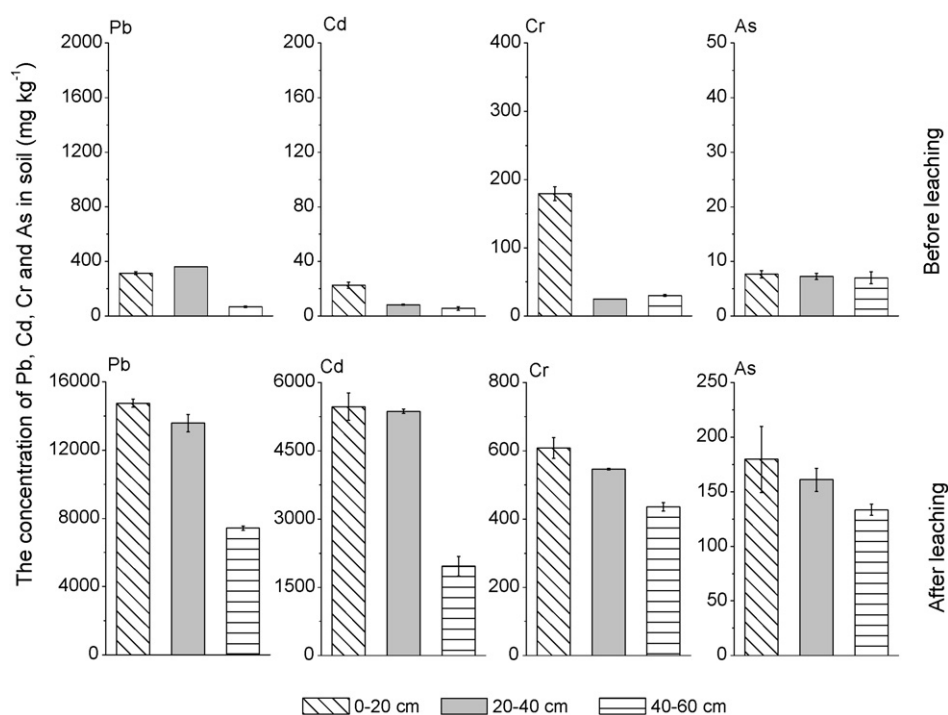
### 3.2. Element concentrations in soils before and after column tests

The element levels in the soils before and after tests are presented in Fig. 3. Element concentrations in the soil zones decreased with depth. For original soils, high levels of Cr and Cd in soil I and high levels of Cd and Pb in soil II were found in the studied sites. In accordance with the Environmental Quality Standard for Soils [14], the original two soils were found moderately or heavily contaminated with one or more of the four elements. Collectively, the findings suggested that trace toxic elements had been accumulated in the soils due to the emissions of pollutants into the studied area in recent years.

As shown in Fig. 3, the concentrations of Pb, Cd, Cr and As were increased dramatically after leaching tests. The concentration of each element was decreased slightly with depth of the soil zones, which might due to the lower contents of clay particle, TOC and CEC in deeper soil zones. Concentrations of the four elements in soils were all higher remarkably than the third level of the Environmental Quality Standard for Soils [14]. Due to different adsorption abilities of soil to different characteristic elements [27], there were great variations of each element concentration in soils, and which followed the order of Pb > Cd > Cr > As.

### 3.3. Element fractions in soils before and after column tests

The chemical fractions of Pb, Cd, Cr and As in soils before and after column leaching tests are shown in Fig. 4. For the original soils, Fig. 4 showed that Pb and As were associated dominantly with the residual fractions, followed by the organic fractions. In general, the exchangeable and carbonate-bound Pb and As accounted <7% of the total Pb and As, respectively. A significant fraction of Cr in the soils was bound in the residual phase, and other four fractions accounted



**Fig. 3.** Total contents of Pb, Cd, Cr and As in soils before and after column tests.



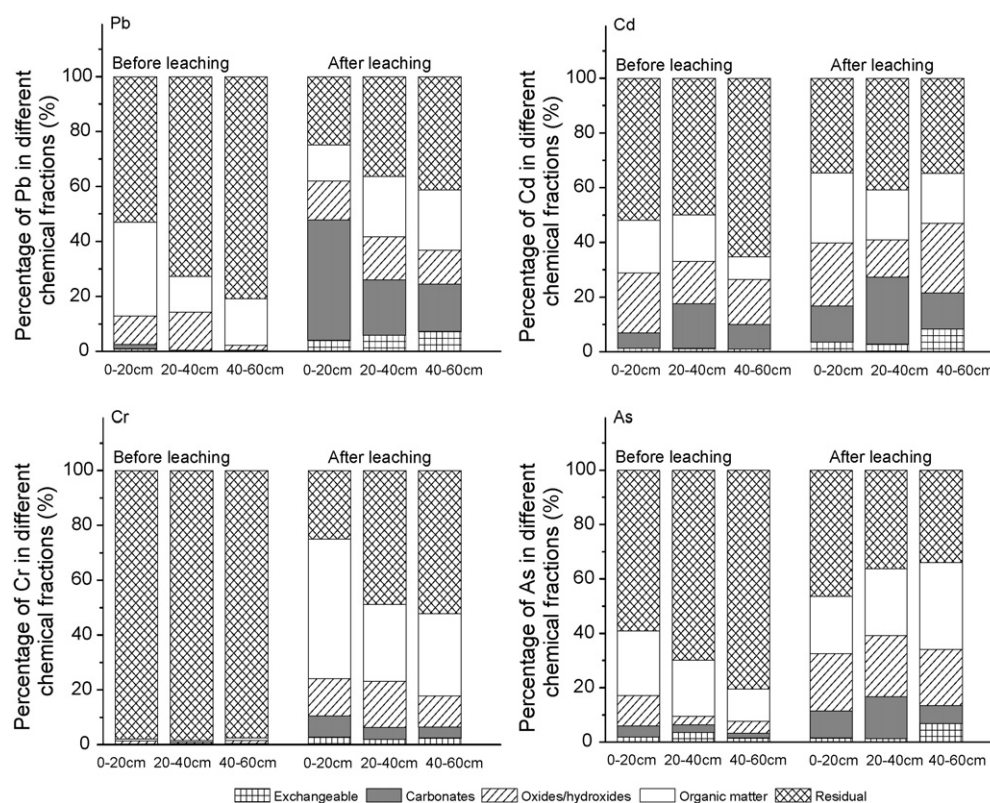


Fig. 4. Variation of the percentage of Pb, Cd, Cr and As in different fractions with soil depth before and after column tests.

<3% of the total Cr. Some studies showed that Cr was mostly presented in residual fraction of soil at the horizon or profile scale [28] and widely considered to have a very low geochemical mobility [29]. Cd in soils was mainly associated with the residual fraction, secondarily with the Fe–Mn oxides fraction, followed by organic fraction and carbonate fraction. The percent of exchangeable Cd in the soils was very low.

As the results show, there are some variations in the proportions of the four elements in five fractions after tests. As shown in Fig. 4, the relative concentrations of other four fractions of the elements except residues were all increased. Because leaching time was greatly shorter than the time for soil-heavy metal interactions under the natural condition, it was very difficult for heavy metals from anthropogenic activities to enter in the firm mineral crystal lattice in soil to form the residual fraction during such a short time. After entering soil, a part of heavy metals were in the form of exchange fraction, and with time increased, exchangeable fraction would be adsorbed, mineralized by soil and transformed to be other fractions. Considering the absolute concentration, the five fractions of each element were all increased due to element addition into the soils. For Pb, the carbonate fractions were increased greatly. The primary mechanism for Pb retention in clay soils was through precipitation of the metal ions with carbonates and amorphous oxides or hydroxides [30]. Yong and Phadungchewit [31] proved that the presence of carbonates in soil contributed significantly to the adsorption capacity of soil. The increase of each non-residual fraction except exchangeable fraction (average 1%) for Cd was almost equivalent (average 5%). For Cr, the relative concentrations of the organic and Fe–Mn oxide fractions were significantly increased, especially the organic fraction (average 36%). Likewise, through studying the fractions of heavy metal in sandy and loessial soils, Han and Banin [32] found that, after its addition to the soil, Cr was bound to the organic matter fraction. The organic matter, Fe–Mn oxide and carbonate fraction of As were increased obviously.

Lund and Fobian [33] found that As was retained by organic matter and Fe, Al and Mn oxides in contaminated industrial sites.

The exchangeable fraction was the first to be brought into solution and is considered to be easily available for plant uptake. The carbonate fraction was susceptible to pH change. The Fe–Mn oxide fraction was unstable under low Eh conditions. The organic fraction could be degraded under oxidizing conditions and the residual fraction was not bioavailable since it was not expected to be solubilized over a reasonable period of time on natural conditions [8]. For the four trace elements, the exchangeable fractions with high bioavailability and mobility were increased averagely about 1.2–5.4%, which indicated the increase of direct risk of Pb, Cd, Cr, and As to soil/groundwater system. The amounts of non-residual fractions represent the amounts of potentially active trace elements [34]. In general, the high proportion of trace elements in non-residual fractions of the soils may suggest great contribution of anthropogenic elements. The non-residual fractions of Pb, Cd, Cr, and As in the soil zones after leaching tests averaged 65.87%, 63.32%, 58.00% and 61.14%, respectively. The non-residual fractions of Pb, Cd, Cr, and As in the original soils averaged 31.23%, 44.40%, 20.43% and 35.90%, respectively. The increase of non-residual fractions elucidated the increase of potential risk of Pb, Cd, Cr, and As to soil/groundwater system.

#### 3.4. Transformation of oxidation and reduction states of chromium and arsenic before and after column tests

Redox of Cr was governed by many factors including aeration reactions, soil moisture content, wetting and drying, iron and manganese status, microbial activity, organic matter, pH and availability of electron donors and acceptors [35]. In this study, although Cr was introduced into soils as  $\text{Cr}_2\text{O}_7^{2-}$ , under long-term water saturated conditions, the proportions of Cr(III) in different depth of soil profiles were increased by about 6.0% percent after column leaching

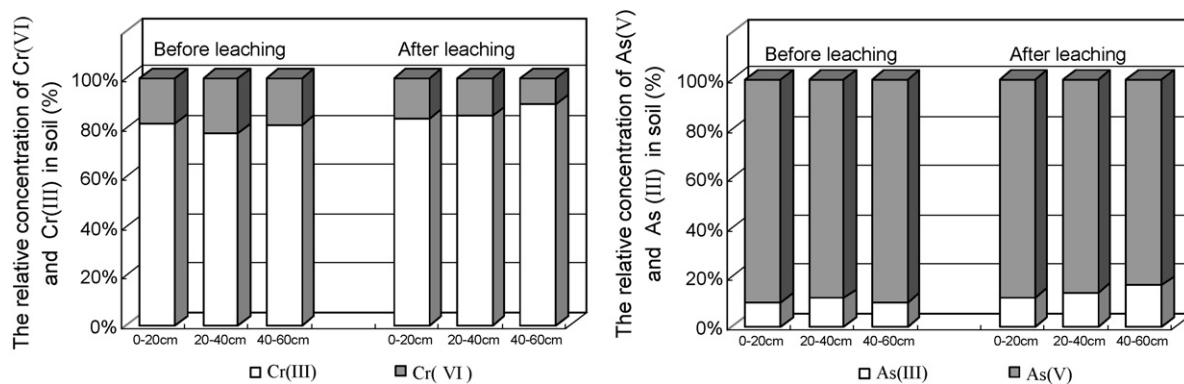


Fig. 5. The relative concentration of Cr(VI), Cr(III) and As(V), As(III) in soil before and after column tests.

tests (Fig. 5). Considering the absolute mass, the concentrations of Cr(III) were increased by about 400 mg/kg, which suggested that Cr(III) was precipitated from solution after hundreds of hours of reaction. The reduction of Cr(VI) in large scale reduced its mobility and toxicity.

As was introduced into soils as pentavalent arsenic ( $\text{HASO}_4^{2-}$ ), but water saturated conditions would also promote the reduction of As. As shown in Fig. 5, the proportions of As(III) in different depth of soil profiles after tests were increased by about 5.6%, and the absolute concentrations of As(III) had about 20 mg/kg increase. Valent states of arsenic investigated by Ng et al. [36] on arsenical pesticide contaminated soils showed that As(III) components were 0.32–56% in nine composite samples of surface and subsurface soils. In acidic soils (average pH of 5.3) contaminated by mine tailings, Howell et al. [37] found that arsenite was present in a large proportion in aerobic soils (up to 45% of total arsenic). According to the standard electrode potential ( $\varphi^0$ ) of redox reaction,  $\varphi^0$  of Cr(VI) redox (+1.33 V) was greater than that of As(V) (+0.56 V), so under the same condition, the degree of Cr(VI) reduction was significantly more than that of As(V). The increased Cr(III) and As(III) tended to be adsorbed by soils, which reduced the movement of them into groundwater.

#### 4. Conclusions

Soil column leaching tests were carried out in order to investigate transport and fate of Pb, Cd, Cr(VI) and As(V) in soil zones derived from farmland. The results showed that the retention of Pb, Cd in soils were very great and the retention of Cr, As were comparatively lesser, which followed the order of  $\text{Pb} > \text{Cd} > \text{Cr} > \text{As}$ . According to the breakthrough curves, the transport rate of the four trace toxic elements in the soil zones decreased in the order of  $\text{Cr(VI)} > \text{As(V)} > \text{Pb} > \text{Cd}$ . The results of selective sequential extraction showed that bioavailable exchangeable-fractions and active non-residual fractions of the four metals after leaching tests were increased, which elucidated the increased direct and indirect risk of Pb, Cd, Cr, and As to soil/groundwater system. Under long-time water saturated condition, the reduction reactions occurred for Cr(VI) and As(V), and the degree of Cr(VI) reduction was significantly more than that of As(V). The reduction reduced the transport of Cr(VI) and As(V) into groundwater and also changed their toxicity.

#### Acknowledgements

The authors are grateful to the financial support provided by the National Basic Research Program of China under Grant No. 2004CB418505.

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