Fractions distribution of arsenic and cadmium in arable land soils in vicinity of mining area

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Toxicity heavy metals in soil to ecological system were determined by chemical associations. It is significant to identify the distribution of heavy metals in arable land soil, due to the reflection of the bioavailability of heavy metals to crops, especially to the area of high anthropogenic heavy metals input. Sequential extraction procedures were applied to define As and Cd into six fractions, including water soluble (WS), exchangeable (EX), carbonate-bound (AC), Fe & Mn oxided-bound (OX) and residual (RES), in arable land soil of iron deposit area. The arable land soil of mining area was contaminated by As and Cd either or both, the average concentrations of As and Cd were 59.44 and 1.403 mg kg^{-1}, respectively. The ratio of residual fraction was the topped among the six fractions of these two contaminants. The total ratio of liable fractions (AC, OX, OC) of As and Cd were 11.8% and 27.1%, and it was mainly determined by the processes of weathering of soil parent materials. The fractions of WS and EX in soil were related to the anthropogenic input of them.

INTRODUCTION

Mining is a mainly source of heavy metals into the environment. Mine tails and wastewaters, which cause the surrounding environment being severely contaminated by heavy metals, are created during the mining exploitation processes [1-3]. Availability, mobility, toxicity and potential ecological risk of heavy metals are determined by the chemical forms, so-called fractions [4-6]. For the purpose of estimating the bioavailability and toxicity of soil heavy metals, it is necessary to determine their chemical forms associated with different phases of soils along with the total contents. And the knowledge of how they partition among the various geochemical phases allows for a better insight into the mechanisms of retention and release involved in the process of migration and decontamination [7.8].

In order to separate the trace elements associated with the different phases, selective chemical reagents has been used, which include weak acids, chelating agents or reducing agents combined with acids [7.9.10]. One step extractions are widely used for different phases extracting due to the fact they are easy to perform, rapid and clearly show the different pollution levels of soils and sediments. Sequential extraction procedures (SEPs) provide detailed information of the differentiation of several association forms of heavy metals in soils [4.7.8.11].

And SEPs can evacuate the disadvantage of one step extractions that no potential bioavailability of heavy metals for plants can be obtained [12]. SEPs are widely applied to assess mobility and characterize the fractionation of heavy metals in sediments, soils and waste materials [4.11.13.14]. Therefore, the current study was to report on the total contents and the fractions extracted by SEPs of As and Cd in arable land soil of Shilu iron deposit area of Hainan, and identify the mainly influence factors of non-residual fractions of As and Cd in soil.

MATERIALS AND METHODS

Study area

Shilu area, which in Western Hainan Island, is very rich in mineral deposits. It is one of the most important iron ore cluster area in China. Mining in Shilu can be traced as early as three centuries ago. Along with several large scale iron mines a lot of small scale mines scattered in the area. Owing to poor mining waste management practices water and soils in the area have been contaminated by mining exploration.

Sampling and analysis

Soil samples were collected from upper 20 cm in arable land of vicinity of mine tailings. To avoid local variability, six samples within a 10 meters diameter of each sample site

were mixed into one sample in the field. A total of 16 soil samples were obtained. The soil samples were air-dried at room temperature, crushed and passed through 2 mm nylon mesh sieve for soil pH and sequential extraction of As and Cd analysis. Ten grams of soil sample was ground to pass through 0.25 mm nylon sieve for organic matters (OM) and cation exchange capacity (CEC) analysis, and 0.149 nylon sieve for soil As, Cd, Ca, Si and K analysis.

The soil pH was measured using a glass electrode, at 1:5 (w/v) ratio of soil: water. After oxidized by $K_2Cr_2O_7$, the concentration of OM in soil was measured by the titration method. The CEC was determined by the Kjeldahl distillation and titration method, after extracted with NH_4OAc. The total contents of As was determined by atomic fluorescence (AFS), Cd was measured by atomic absorption spectrometry (AAS), and Si, Ca and K were measured by ICP-AES, after digesting samples with analytically HNO_3 and $HClO_4$ [15].

The sequential extraction procedure was six-step method which proposed by Ma and Rao (Table 1) [14]. 2.5g of soil was extracted in a 100 ml polythene centrifuge tube with the corresponding extracting solution, and the samples were agitated by reciprocating shaker. The procedure was outlined in sequential order as Table 1. After each successive extraction, separation was done by centrifuging at 5000 rpm for 30 min. Supernatants were filtered with 0.45 μm microfiltration membrane and the concentrations of As and Cd were measured.

Table 1. Procedure for the sequential extraction of As and Cd in soil. [†] 0.25g of the residue from step 5 was digested on electric heating plate with analytically HNO_3 and $HClO_4$.

| Phase/Association	Abbr.	Step	Operational definition
Water Soluble	WS	1	25ml DO-H_2O, 75rpm, 60 min
Exchangeable	EX	2	25ml 1 M $MgCl_2$ (pH 7.0), 75 rpm, 60 min
Carbonate-bound	AC	3	25ml 1M NaOAc (adjusted to pH 5.0 with HOAc), 75 rpm, 60 min
Fe & Mn Oxided-bound	OX	4	50ml 0.25M $NH_2OH \cdot HCl$, 75rpm, 60 min
Organic-bound	OC	5	3ml 0.02M HNO_3, 8ml 30% H_2O_2, digestion 180 min at 85±2°C 20ml 3.2M HOAc/3.2M HNO_3, digestion 600 min at 25±5°C
Residual	RES	6	Acid mixture [†]

Statistical analysis

All statistical analyses were performed using SAS 9.00. Analysis of variance was applied to assess significant different parameters, and the confidence interval for the Student t-test was calculated at $\alpha=0.05$. Factor analysis was applied to investigate the accumulations and distribution of fractions of As and Cd in study soil.

RESULTS AND DISCUSSION

Total contents of As and Cd in soils

Both of concentrations of these two contaminants in soils varied widely. The variations of elements contents in soils reflected the natural differences in soil genesis and the degree of anthropogenic emission. According to China's Environmental Quality Standard for Soils (GB15618-1995), the arable land soil was contaminated by one or both of As and Cd in study area (Figure 1). Due to the study area very rich in mineral deposits, the soil parent materials had relatively higher contents of heavy metals [16]. And the irrigation water for agriculture land of this area was polluted by the mining activities, which made the heavy metals accumulated on the soils in study area. Rodríguez et al. indicated that the drainage

was considered as one of the main effects causing the dispersion of pollution in mining area [17].
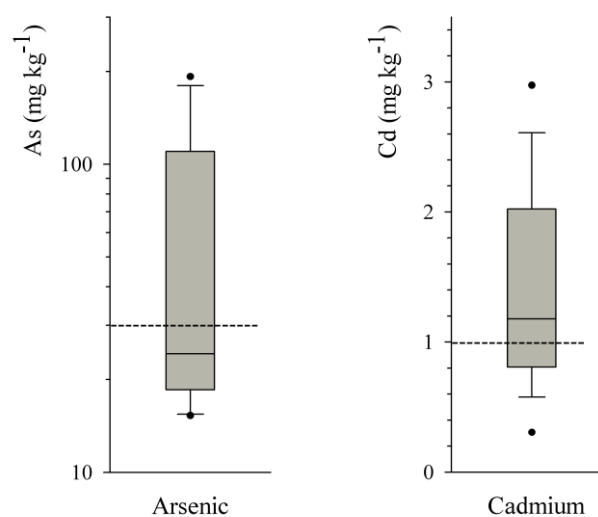
Fig. 1. Contents distribution of As and Cd in soil. ------Threshold of third grade, As 30 mg kg^{-1}, Cd 1 mg kg^{-1} (GB15618-1995).

Fractions of As and Cd in soils

The differences between total amounts and the sum of the extracted phases were As (2.9 ± 1.2)% and Cd (3.3 ± 2.8)% of the total of the selected soil samples. This indicated that the sequential

extraction procedure and analysis techniques seemed satisfactory and practical for arable land soil of study area. Arsenic was mostly concentrated in the residual fraction (Figure 2), with the percentage of total As in the residual fraction ranging from 80.3% to 95.8%, and the average contents of residual fraction As was 50.75 mg kg^{-1}. Among the non-residual fractions, the OX fraction contained a majority content of total non-residual As in soil, partly reflecting that As tends to form OX fraction once it was in soils [18-19]. The concentration of WS fraction As was only 1.21 mg kg^{-1}, however, the ratio of this fraction only lower than RES and OX fractions. This partly attributed to that anthropogenic input of As in arable land by irrigation water, which was contaminated by heavy metals during the mining exploring processes.

The ratio of Res fraction Cd was (54.8 ± 16.2)%, which is significantly higher than other fractions (Figure 2). Among the non-residual fractions Cd in soil, the concentration of EX fraction was the highest, which was 0.742 mg kg^{-1}. The high percentage of EX fraction Cd indicated that the high potential ecological risk of Cd in study area, this may be due to the anthropogenic input Cd was mainly the EX fraction. The ratio of AC, OX and OC fractions Cd were 9.5%, 13.6% and 4.0%, respectively.

Influence factors of fractions of As and Cd in soils

The residual fractions of heavy metals in arable land soil are unlikely to be released during cropping processes. However, the WS, EX, AC, OX and OC fractions are labile and hence more available for crops and plants [20]. Due to WS and EX fractions of As and Cd are most easily to be available for crops or plants, only the AC, OX, and OC fractions of these two contaminants were taken into account

for labile fractions, which can cause potential risks to crops and human health. The contents of labile fractions of As and Cd were positive correlated with the total contents of them in soil (Figure 3). And this indicated that the concentration of labile fractions of these two elements can accumulated as the arable land soil were polluted by As and Cd.
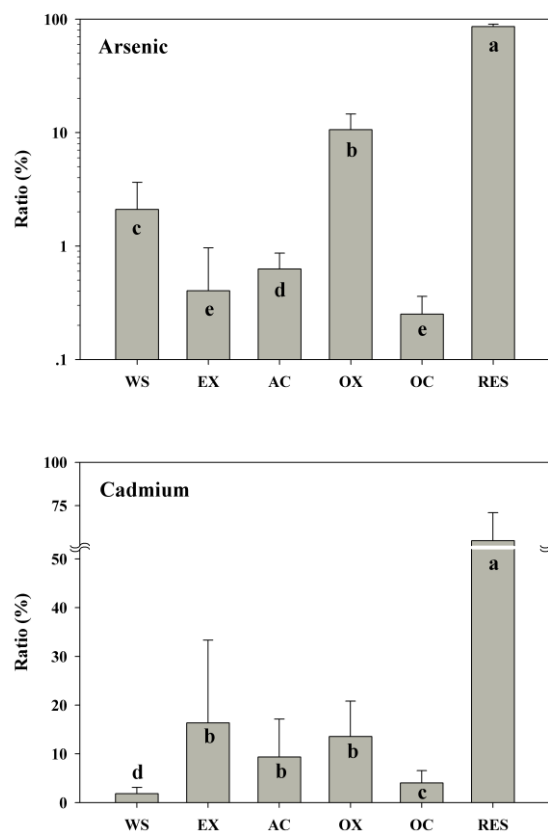
Fig. 2. The fractions distribution of As and Cd in soil. Columns with the different letters were significantly different (Sig.<0.05).
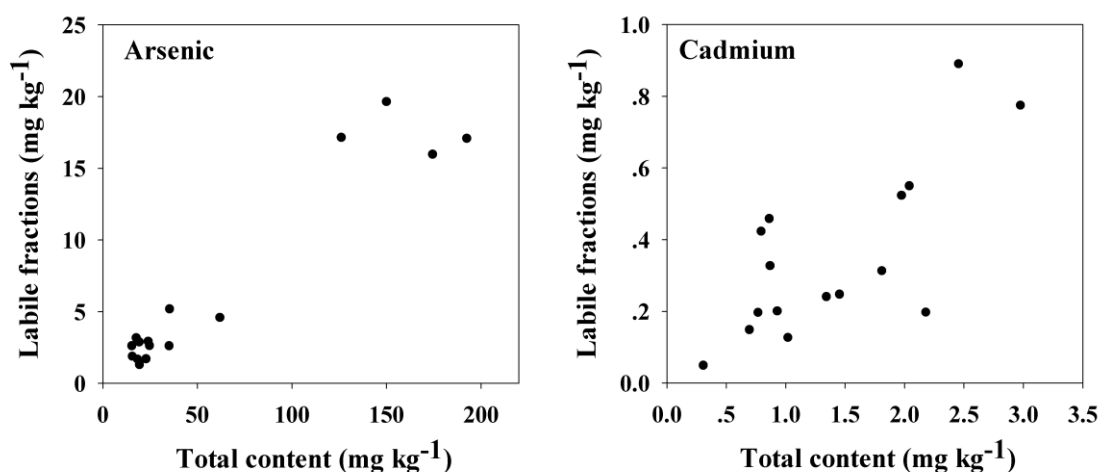
Fig. 3. Labile fractions of As and Cd with total contents in soil.

Due to both of anthropogenic input level and soil properties affected the distribution of soil As and Cd fractions, the non-residual fractions contents of these two elements cannot totally determined by their total contents in soils. Factor analysis (FA) was applied for soil properties and the proportions of total contents in the non-residual fractions of As and Cd by evaluation of principal components and computing the eigenvectors. Three factors with eigenvalues higher than 1 (before and after Varimax normalized rotation) were extracted. The results of FA were presented in Table 2. The first three factors account for 75.1% of total variance. The high communality estimates suggested that the high portion of variance was explained by the first three factors.

Table 2. Statistical results of factor analysis.

		Factor 1	Factor 2	Factor 3	Communality estimates
pH		0.855	0.312	0.017	0.83
OM		0.004	0.839	-0.091	0.71
CEC		0.365	0.826	-0.039	0.82
SiO_2		-0.752	-0.529	0.020	0.85
K_2O		0.812	0.362	-0.107	0.80
CaO		0.896	0.229	0.007	0.86
Ratio of $As_{(Ws+Ex)}$		0.062	-0.197	0.920	0.89
Ratio of $Cd_{(Ws+Ex)}$		-0.438	0.058	0.619	0.58
Ratio of labile fractions As		0.678	-0.151	-0.339	0.60
Ratio of labile fractions Cd		0.741	-0.014	-0.183	0.58
Initial	Eigenvalues	4.88	1.41	1.22	
	% of variance	48.84	14.10	12.18	
After Rotation	Eigenvalues	4.10	2.01	1.40	
	% of variance	40.99	20.13	14.01	

Factor 1 explained 40.99% of total variance with a high positive loading from soil pH, K_2O, CaO, Ratio of labile fractions of As and Cd, and high negative loading from SiO_2. Factor 1 may explain the processes of weathering of soil parent materials. During the weathering processes, the metallic cations were released from soil parent materials and labile fractions of As and Cd were accumulated. Factor 2, which had the high positive loading from Organic matters, CEC and moderate positive loading from soil pH, K_2O and CaO, and moderate negative loading from SiO_2, was considered as the second stage of the formation of soil from parent material, pedogenesis. During the pedogenesis processes, contents of organic matters, CEC and some metallic cations were increased, while soil SiO_2 content was decreased. The fractions distribution of As and Cd have not significant relationship with Factor 2 in this study. Factor 3 was considered present the anthropogenic input of As and Cd in soil, since it had high positive loading from Ratio of $As_{(Ws+Ex)}$ and $Cd_{(Ws+Ex)}$ and negative loading from Ratio of labile fractions of As and Cd. The As and Cd were accumulated in arable land soil mainly as WS and EX fractions, since the irrigation water of study area were contaminated by mining and smelting activities. The concentration increasing of WS and EX fractions will affect the ratio distribution of fractions.

The weathering processes were the main determined factors of labile fractions ratio of total As and Cd contents in soil. However, the main influence factors of WS and EX fractions ratio of these two contaminants in soil were the anthropogenic input. Although the concentrations of $As_{(WS+EX)}$ and $Cd_{(WS+EX)}$ were quite lower, both of WS and EX fractions of them were highly available for crops and plants [9.20]. So, the potential ecological risk, which shed by anthropogenic input As and Cd, should not be ignored.

CONCLUSION

The arable land soil in vicinity of mining area was contaminated by As and Cd, and the contents of As and Cd in study soil were 59.44 and 1.403 mg kg^{-1} respectively. Both of As and Cd were mainly distributed in residual fraction, and the ratio of their labile fractions (AC, OX, OC) was determined by the processes of weathering of soil parent materials. The mainly influence factor of WS and EX fractions, which were highly available for crops and plants, were anthropogenic input. Therefore, measures should be taken to control the anthropogenic emission of As and Cd in vicinity of mining area.

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