

Spatial distribution of chromium in soils contaminated by chromium-containing slag

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Abstract: To evaluate the metal chromium (Cr) contamination of soil at a chromium-containing slag site by ferrochromium production, the contaminated sites, under slag heap, in the vicinity of slag heap and arable soils near the outlet of sewer channel, and unpolluted site 5 km away from one ferroalloy plant in Hunan Province, China, were selected. The concentrations of total Cr and water soluble Cr in bulk soil samples and profile depth samples were determined. The results show that the soils in the vicinity of slag heap have the highest total Cr content followed by the soils under the slag heap and near the outlet of sewer channel of the factory. The mean concentrations of total Cr in the top soils at above three contaminated locations exceed the critical level of Secondary Environmental Quality Standard for Soil in China by 3.5, 5.4 and 1.8 times. In most Cr polluted soils, total Cr has a relative accumulation in soil depth of 40–60 cm, but this trend is not found in unpolluted soils. The average concentrations of water soluble Cr (VI) in top soils under slag heap and in the vicinity of slag heap are 176.9 times and 52.7 times higher than that in the uncontaminated soils, respectively. However, water soluble Cr (VI) contents in soils near sewer channel are all low and the values are close to that in the uncontaminated soils. Although water soluble Cr (VI) content in soil profiles decreases with soil depths, it in soils under slag heap maintains a high level even at a depth of 100–150 cm. The results imply that the transportation of Cr (VI) can result in a potential risk of groundwater system in this area.

Key words: total Cr; water soluble Cr (VI); chromium-containing slag heap; soil contamination; Cr contamination

1 Introduction

Chromium (Cr) is one of the most common metal contaminants in soil because of its use in ore refining, production of steel and alloys, metal plating, tanneries, wood preservation, and pigmentation. In soil environment, the most stable oxidation states of chromium are Cr (III) and Cr (VI). Cr (III) is considered to be an essential trace element for the functioning of living organisms, while Cr (VI) is toxic and carcinogenic to humans via inhalation for long exposures[1–2]. Furthermore, Cr (VI) is easily soluble and mobile and Cr (VI) in soils can be leached into surface water or groundwater, and taken up by plants. The concentration of Cr (VI), as low as 0.5 mg/kg in solution and 5 mg/kg in soils can be toxic to plants[3]. Hence, Cr (VI) incurs a significant risk to human health when released into the

soil environment. Chromium-containing slag is the final by-product of the smelter of ferrochromium. Obviously chromium-containing slag heap is a potential point source for soil pollution. Moreover, the residence time of chromium in soils is estimated to be 10^3 – 10^4 years.

Chromium accumulates in soils mostly as the result of chromium-containing waste discharge. China is one of the major countries to produce chromate. The accumulated amount of chromium-containing slag discharged from metallurgical and chemical industries over a span of the more than 30 years was more than 6 million tons, and 200–300 thousand tons are being discharged annually[4]. Most Cr industry operations lack appropriate disposal facilities, and hence, chromium-containing slag has become a serious problem as a contaminant in soils. It is reported that the accumulated soils polluted by chromium-containing slag reached up to 12 500 thousand tons and this value will increase because

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continuous leaching out of the Cr (VI) in chromium slag can cause sustainable contamination to its near environment. Chromium-containing slag is one of the most hazardous solid wastes because of its high content of dissolvable Cr (VI). The Hunan Ferro-Alloy Plant in China used chromium ore to produce chromate since 1966. As a consequence, large amounts of solid waste, i.e. slag, have been directly heaped on the ground without any measure to prevent leaching, resulting in the heavy metal Cr contamination of soil nearby.

Many studies on soil contamination of heavy metal from industrial sites were reported[5–6]. However, transverse and lengthways soil contamination levels around a pollution source were inadequate, especially, no literature was found to investigate the degree of chromium contamination in soils under the chromium-containing slag heap. In an attempt to evaluate the contamination severity of Cr by chromium-containing slag at a ferro-alloy plant in Hunan Province, China, and to investigate the Cr transportation into subsoil and their vertical distribution, the total Cr and water soluble Cr (VI) in bulk soil and soil profiles were studied.

2 Experimental

2.1 Site description

Soil samples were taken from chromium-containing slag sites and the vicinity area at a ferro-alloy plant in Hunan Province at latitude 27°75'N, and longitude 112°50'E, China. The region is sub-tropic warm-moist climate. The average annual temperature is 17 °C. Monthly mean temperatures range 29.7 °C in July to 4.1 °C in January. The average annual precipitation is 1 300 mm.

The slag was produced during the process of chromium ore. The slag site is an enclosed area of 500 m×10 m. The volume of slag accounted for 90 000 m³ and the total amount of 117 000 t. The slag was initially deposited on soil without leaching protection from 1960's. The soils in the study was Haplic Acrisol.

2.2 Soil sampling

The samples of the uncontaminated soils (control

site) were collected from locations 5 km away from the ferro-alloy plant. 10 soil bulk samples were collected from topsoil (0–20 cm) in spring of 2007. At the same time, 3 soil profiles, taken from 4 depths (0–20 cm, 20–40 cm, 40–60 cm and 60–100 cm) were investigated to assess the vertical distribution patterns.

In order to assess the contaminations of Cr (VI) in soils from chromium-containing slag, the contaminated sites, under the slag heap, in the vicinity of slag heap and the arable soils near the outlet of sewer channel of the factory, were chosen. 3, 5 and 23 bulk soil samples (0–20 cm) were taken from sites under slag heap, in the vicinity of slag heap and near the sewer channel, respectively. 3, 2 and 4 soil profiles were taken from sites under slag heap, in the vicinity of slag heap and the arable soils near the outlet of sewer channel of the factory. In soil profile, soil cores were carefully separated into 0–20, 20–40, 40–60, 60–100 and 100–150 cm depth. In the vicinity of slag heap, the two soil profiles were at distances of 50 m and 100 m from the slag heap, and soil cores were collected only at depths of 0–20 cm, 20–40 cm, 40–60 cm, 60–100 cm because of their high groundwater levels. All bulk soil samples and soil cores at each depth were air-dried and passed through 0.26 mm polyethylene sieve prior to chemical analysis. The main physical and chemical properties of these tested soils are presented in Table 1.

2.3 Analytical methods

Total Cr in soil was determined by wet digestion method. 300 mg of homogenized soil samples was put into a 50 mL polytetrafluoroethylene crucible. Then 10 mL 68% HNO₃ +5 mL 1:1 H₂SO₄ +5 mL 47% HF were added into samples and heated around 230 °C until the solution became grey. After slightly cooling, 3 mL of 1:1 HCl was added into samples to make all compounds dissolved. The digested solution was transported into a 50 mL flask and 5 mL 10% NH₄Cl solution was added. The solution was added to 50 mL with distilled water and filtered. The concentration of Cr in the filtered solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The water soluble Cr(VI) was determined by adding

Table 1 Some physical and chemical properties of tested soil

Soil type	<i>n</i>	pH (1:1)	OM/(g·kg ⁻¹)	CEC/ (cmol·kg ⁻¹)	Particle size distribution/%		
					>0.01 mm	0.01–0.001 mm	<0.001 mm
Under slag heap	3	9.75±0.23	8.1±1.0	7.9±1.1	59.2±9.1	21.6±4.2	19.2±3.6
In vicinity of slag heap	5	9.62±0.28	8.9±1.3	8.6±2.1	57.1±10.3	20.1±3.6	22.8±4.2
Near sewer channel	23	6.86±0.30	32.7±11.1	14.3±2.1	35.1±11.3	25.3±5.6	39.6±12.2
Control site	10	6.58±0.21	34.5±13.1	15.3±2.6	37.6±10.4	27.4±6.8	35.0±10.3

n is the number of samples; OM means organic material; and CEC means cation exchange capacity.

50 mL deionized water to 10 g soil samples and shaking for 1 h. After filtration, the soluble Cr (VI) in the filtrate was determined by using 1, 5-Diphenyl- carbohydrazide spectrophotometric method.

All the samples were analyzed in three replicates. The quality control of analytical accuracy was carried out by reagent blanks and referred soils (Chinese Standard ESS-3).

3 Results and discussion

3.1 Horizontal distribution of total Cr and water soluble Cr (VI)

3.1.1 Total Cr in soils contaminated by chromium-containing slag

The contents of total Cr in topsoil at different locations are presented in Table 2. The contents of total Cr in soil show substantial variations according to the distance from the chromium slag site. The total Cr in soils under slag heap ranged from 1 248.4 to 2 130.3 mg/kg. The total Cr contents in soils near slag heap were in the range from 656.1 to 3 500.1 mg/kg, with the mean value of 2 239.5 mg/kg. The mean content of total Cr in the soils near the sewer channel was 995.3 mg/kg, ranging from 208.6 to 6 207.6 mg/kg. The total Cr in the soils of control site was from 90.0 to 117.5 mg/kg with minor variation.

In comparison with control site values (Table 2) in the unpolluted soils, the mean values of total Cr in the contaminated soils were much higher. The contents of total Cr in the soils under the slag heap, in the vicinity of slag heap and near the sewer channel were 15, 21 and 9 times higher than that of the control site, respectively. In comparison with the critical value of Secondary Environmental Quality Standard for Soil in China (total Cr $\leq$ 350 mg/kg) (National Environmental Protection Agency of China, 1995), the mean contents of total Cr in the soils under the slag heap, in the vicinity of slag heap and near the sewer channel exceeded the critical value by 3.5, 5.4 and 1.8 times, respectively. Total Cr contents in all the samples under the slag heap and in the vicinity of slag heap were all higher than the critical value without exception. Near the sewer channel, the content of total Cr

in 22 soil samples exceeded the standard limit of Cr and the highest value was 18 times the standard limit. These results show that there is serious pollutions, resulting from the chromium-containing slag in the studied areas. For the selected three locations, in the vicinity of slag heap the soil had the highest contaminant level, followed by that under the slag heap, while near the sewer channel the soil had the lowest contaminant level.

Most researches focused on the comparisons of contamination severity in soils around the contaminant sources. The results that total Cr concentrations decreased with distance increasing from the contaminating sources were reported in previous literatures[7–9], which were in agreement with our study. The observation that no direct relationship was apparent between the soil chromium content and the distance from the slag heap was also reported by LOYAUX-LAWNICZAK et al[10]. However, no literature was documented to investigate the contaminant severity under the slag heap due to the difficulty of sampling. In this study, the total Cr contents in soils under the slag heap were slightly lower than that in the vicinity of slag heap. This is because total Cr in surface soils under the slag heap is mainly from natural leaching and mobility from the chromium-containing slag. However, total Cr enriching in the topsoil in the vicinity of slag heap can be attributed to runoff, leaching and diffusing of Cr (VI) released from chromium-containing slag.

Generally, high Cr load of soils may increase uptake by plants and cause adverse effects to ecosystems, animal and human health if consumed in foodstuff [11–12]. Because soil samples from sites near the sewer channel were paddy soils, it was reasonable to assume that the high amount of total Cr in this farmland was likely to lead to food chain contamination. These facts revealed that the metal chromium discharged from the ferro-alloy plant posed a significant risk to soil environment.

3.1.2 Water soluble Cr (VI) in soils contaminated by chromium-containing slag

Water soluble Cr (VI) contents at different sampling

Table 2 Horizontal distribution of total Cr and water soluble Cr(VI) in topsoil (mg/kg)

Sampling site	n	Total Cr				Water soluble Cr(VI)			
		Mean	Min.	Max.	S.D.	Mean	Min.	Max.	S.D.
Under slag heap	3	1 589.3	1 248.4	2 130.3	473.5	123.8	49.5	252.7	112
In vicinity of slag heap	5	2 239.5	656. 1	3 500.1	1 413.5	36.9	0.5	101.8	38.9
Near sewer channel	23	995.3	208.6	6 207.6	1 643.1	0.6	0.2	1.7	0.3
Control site	10	104.9	90.0	117.5	13.9	0.7	0.1	1.1	0.5

n is number of samples; S.D means standard deviation.

sites are also shown in Table 2. The average soluble Cr (VI) content in the soils under slag heap was 123.8 mg/kg with the highest value of 252.7 mg/kg and the lowest 49.5 mg/kg. The average content of water soluble Cr (VI) in the soils in the vicinity of slag heap was 36.9 mg/kg, ranging from 0.5 to 101.8 mg/kg. The average contents of water soluble Cr (VI) under slag heap and in the vicinity of slag heap were higher than that in the unpolluted soils (control site) by 176.9 times and 52.7 times, respectively. However, the water soluble Cr (VI) contents in all the soils near the sewer channel showed a low value that was close to that in control site. The results further show that the slag site at the ferro-alloy plant was heavily polluted by chromium. Moreover, it was noted that the content of water soluble Cr (VI) was the highest in the soils under the slag heap.

Although water soluble Cr (VI) content in the soil near the sewer channel was low, the total Cr content was still higher than the critical level of Secondary Environmental Quality Standard for Soil in China. Cr (III) can be converted to Cr (VI) in the presence of MnO_2 [13]. Other forms of Cr such as exchangeable Cr, carbonate-bonded Cr can also be transformed to water soluble Cr (VI) when soil characteristics including pH, organic matter were changed [14]. It should be pointed out that small content of water soluble Cr (VI) in soils near the sewer channel may still pose potential health risks.

3.2 Vertical distribution of total Cr and water soluble Cr (VI) in soil profiles

3.2.1 Distribution of total Cr in soils profiles

The vertical distribution of total Cr in the soil profiles are shown in Figs. 1–4. Under slag heap, the total Cr contents in profile 1 and profile 3 gradually increased with soil depth increasing within 60 cm depth, thereafter, their values declined again. The results implied that the total Cr accumulated at 60 cm depth. It probably contributed to immobilization of Cr by more Fe and Mn compounds. However, the higher Cr concentration was found at the depth of 20–40 cm in profile 2. There was no consistent distribution pattern of total Cr in soil profiles in the vicinity of slag heap since the limited number of profiles (Fig. 2). Near the sewer channel, the distribution of total Cr in profiles 6, 7, 8 and 9 showed a decrease trend with decreasing depths, indicating the Cr pollutant from chromium-containing slag was immobilized in the top soils as compared with the heavily polluted soils under slag heap and in the vicinity of slag heap (Fig. 3). The variation of total Cr concentrations in unpolluted soil profiles (profile 10 and profile 11) is not distinct except for profile 12 where relatively higher total Cr accumulations were found in surface depth (Fig. 4). In general, the mean total Cr contents in different soil

depths under slag heap are in the following order: 40–60 cm (2 236.8 mg/kg) > 20–40 cm (2 210.9 mg/kg) > 0–20 cm (1 589.3 mg/kg) > 60–100 cm (1 258.4 mg/kg) > 100–150 cm (623.1 mg/kg). Similar order was observed in soil profiles in the vicinity of slag heap. These observations clearly indicated a strong retention of Cr in middle soil depth at the chromium-containing slag sites of the ferro-alloy plant (Under slag heap and in the vicinity of slag heap). The vertical distribution of total Cr in soil profiles in the vicinity of slag heap found in previous literatures showed an accumulation towards intermediate depth soil [5, 9, 15–17]. MORGADO attributed the observed leaching and a slight accumulation of Cr in intermediate depth primarily to iron compounds in retaining the element at depth [9]. This was because Cr exists in oxidation states of Cr(III) and Cr(VI) [8] and in the presence of Fe(III) in geological environments, the solubility of Cr(III) is ubiquitously controlled by the solid solution $(\text{Cr, Fe})(\text{OH})_3$ [18–19]. In this study, the tested profile soil is derived from quaternary red earth in the southern China, in which iron-manganese nodules often aggregate in the intermediate depth soil [20]. This can be the reason for accumulation of total Cr in intermediate depth soils under the slag heap and in the vicinity of slag heap. Similar results were obtained by BHATTACHARYA that a significant metal enrichment could also be noted in the Fe and Mn-rich bottom sediments of the stream [8].

However, the vertical distribution profiles near the sewer channel showed different patterns of total Cr as compared with that under slag heap and in the vicinity of slag heap, presenting the highest concentrations in the topsoil and rapid decrease with depths. These variations were probably due to land use pattern and an anthropogenic influence. Near the sewer channel was cultivated fields, where fertilizers and organic manure were often applied, resulting in the accumulation of organic matter in topsoil. This may be an important reason of high enrichment of total Cr in topsoil near the sewer channel. A high content of organic matter indicated the accumulation of the metals due to the formation of metal-organic complexes [8]. Similar findings were obtained by BALASOIU et al who showed that chromium retention was stronger in organic than in mineral soil material [21]. Various authors reported that the accumulation of total Cr in contaminated soils may vary according to the quantity of organic matter in the soils because chromium can be adsorbed by organic matter [15, 17].

In addition, our results also showed that Cr can be leached out from the soil, and its content in one sample at a depth of 150 cm under slag heap even reached up to three times as high as the critical level of Secondary Environmental Quality Standard for Soil in China (Table

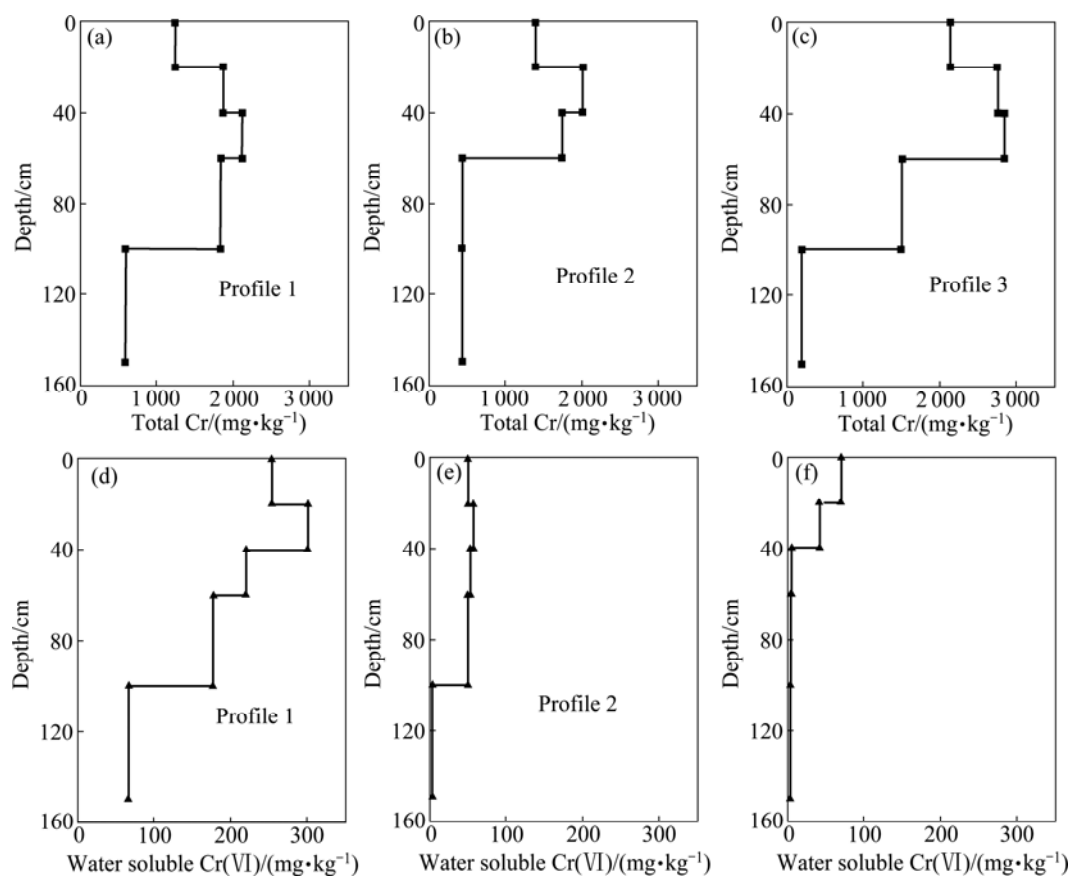


Fig.1 Distributions of total Cr and water soluble Cr (VI) in soil profiles under chromium-containing slag heap

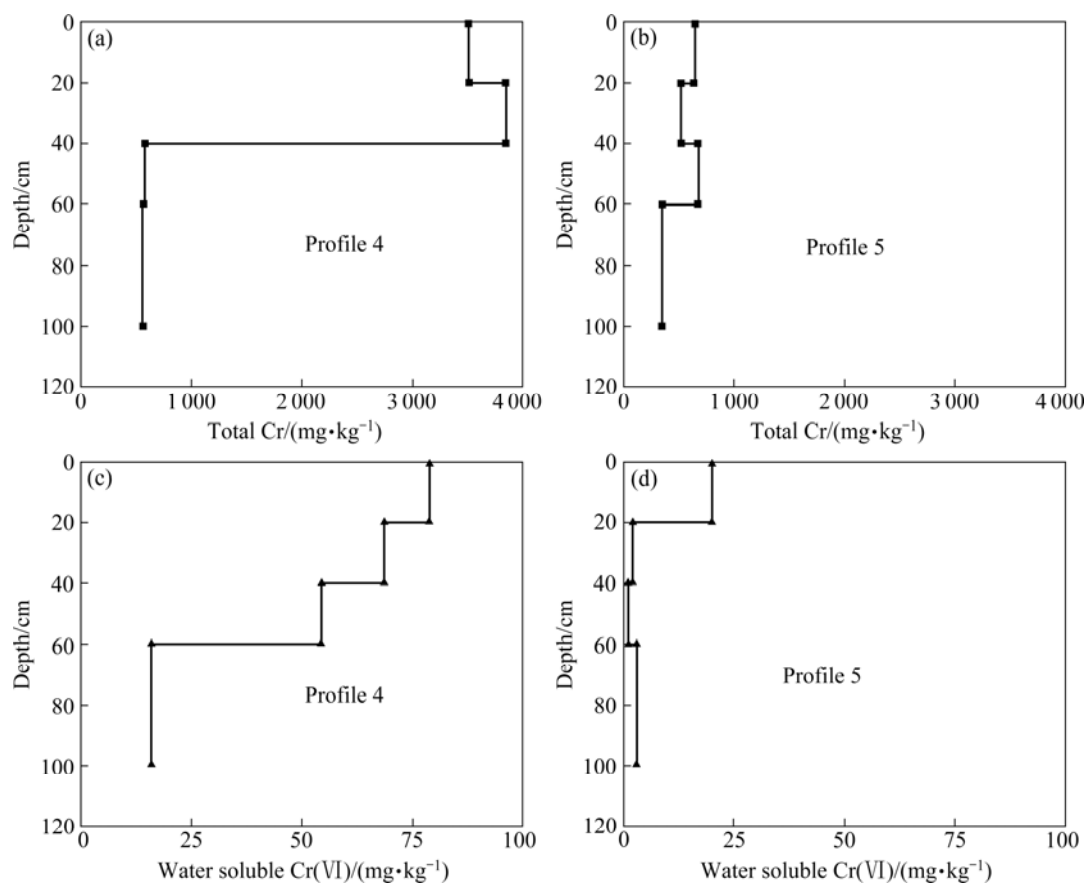


Fig.2 Distribution of total Cr and water soluble Cr (VI) in soil profiles in vicinity of chromium-containing slag heap

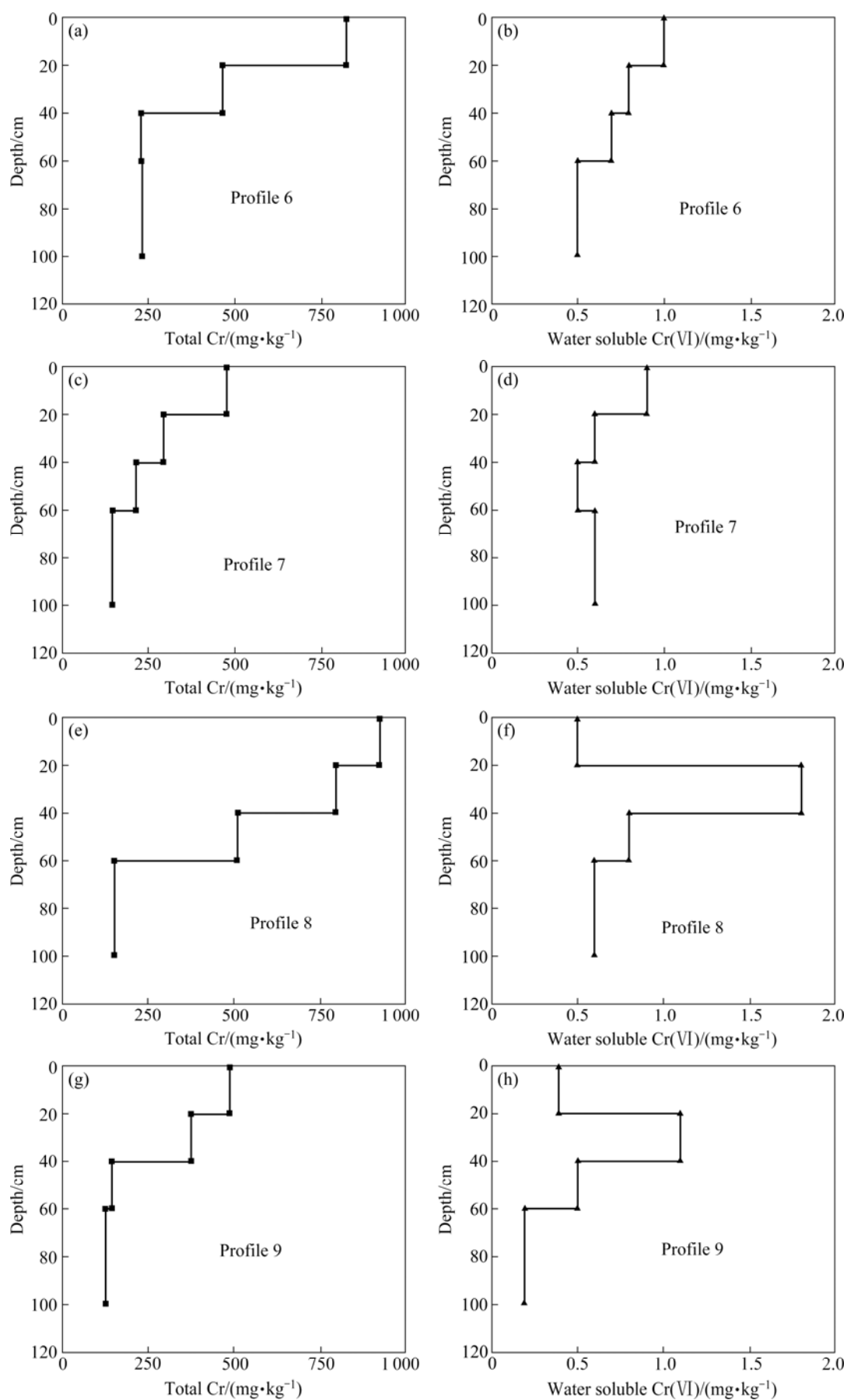


Fig.3 Distribution of total Cr and water soluble Cr (VI) in soil profiles near sewer channel of manufactory

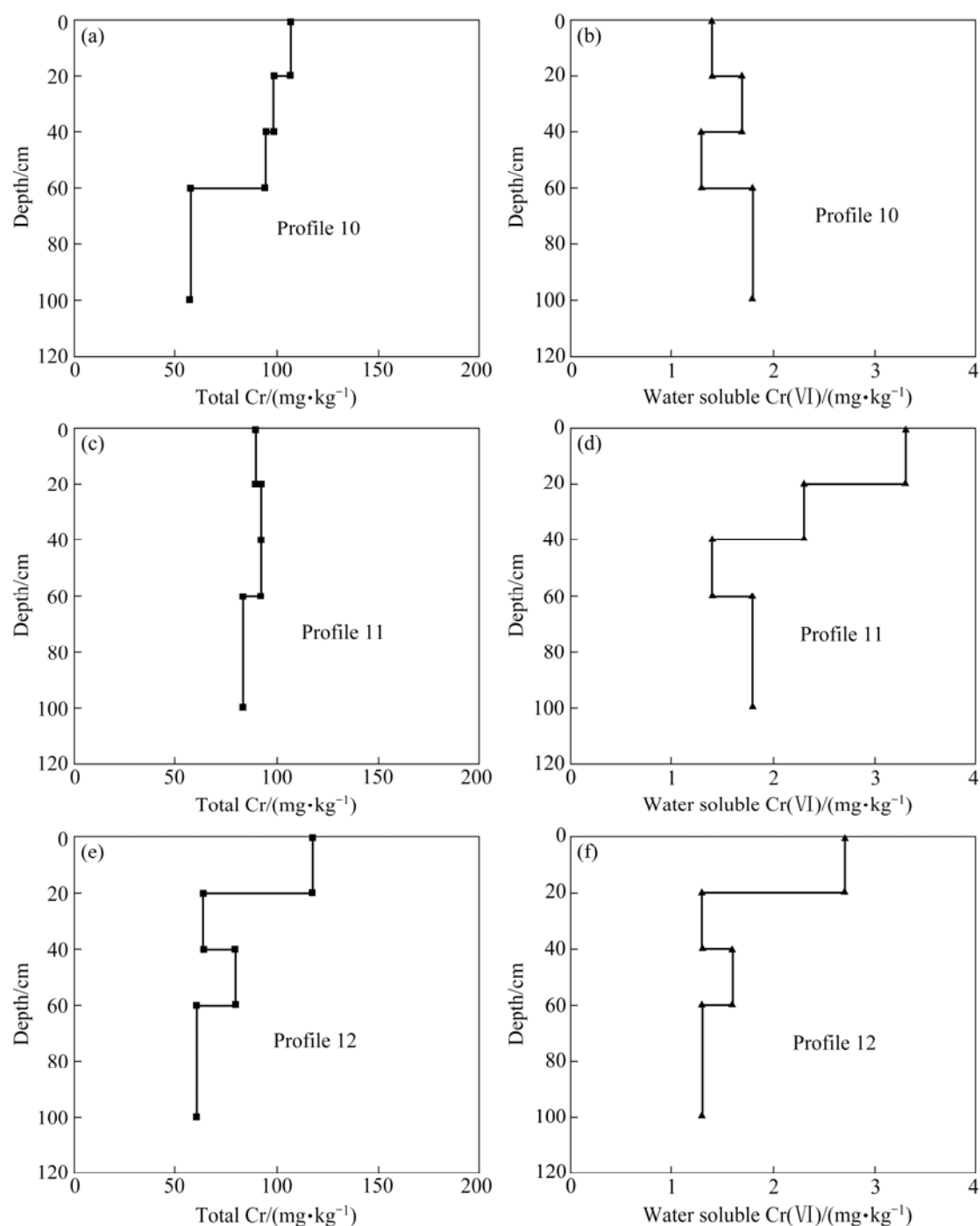


Fig.4 Distributions of total Cr and water soluble Cr (VI) in soil profiles at uncontaminated site

2 and Fig.1). Actually, the total Cr contents in each depth of soil profile under the slag heap and near slag heap were much higher than the critical level of Secondary Environmental Quality Standard for Soil in China. The average total Cr content of each depth in profile soil was 2–6 times as high as the standard limit. Unlike sites under slag heap and in the vicinity of slag heap, the mean contents below the depth of 40 cm near the sewer channel were in the range of the standard limit, only the Cr content of samples in surface soil (0–20 cm) and

subsurface soil (20–40 cm) were higher than the standard limit (Table 2). Significant differences in mean concentrations of each depth among three locations indicated that the degree of pollution followed the order: under the slag heap > in the vicinity of slag heap > near the sewer channel. These results further elucidated that chromium from the slag heap can migrate in the subsoil, although soil was responsible for the retention of chromium. The results implied that there existed a significant potential for chromium to be a serious threat

to groundwater system. Our observations are in agreement with previous reports[22–23].

3.2.2 Distributions of water soluble Cr (VI) content in soil profiles

The water soluble Cr (VI) in profile 1 and profile 2 under the slag heap increased with depths increasing within 40 cm (Fig.1), and then the contents decreased again. The content of water soluble Cr (VI) in the soils of profile 3 showed minor variation except for surface depth (0–20 cm) where water soluble Cr (VI) content was much higher than that in other depths (Fig.1). The water soluble Cr (VI) content in each depth of profile 4 and profile 5 in the vicinity of slag heap (Fig.2) revealed similar patterns with a decrease trend with depths increasing. Water soluble Cr (VI) contents of each depth in all profiles near the sewer channel showed very low values, which were close to control site concentrations (Fig.3 and Fig.4).

The mean water soluble Cr (VI) contents in each soil depth are listed in Table 3. At all sampling locations the mean water soluble Cr (VI) content in soil profiles decreased with soil depth increasing. However, water soluble Cr (VI) content in each soil depth under slag heap was much higher than that in the vicinity of slag heap followed by near the sewer channel and control sites. These findings indicated that under slag heap and in the vicinity of slag heap the soils were heavily polluted by chromium from chromium-containing slag heap. Furthermore, water soluble Cr (VI) in soils under the slag heap maintained a high level even at a depth of

100–150 cm, indicating a substantial release and migration of water soluble Cr (VI) from the chromium-containing slag heap. The transportation of Cr (VI) can result in a potential risk of groundwater system in this area.

4 Conclusions

The total Cr content in polluted sites varied substantially at a ferro-alloy plant in Hunan Province, China, and Cr contamination severity depends on the distance from the slag heap. The total Cr contents in soils under the chromium-containing slag heap, in the vicinity of slag heap and near the sewer channel of ferro-alloy plant were higher than the critical level of Secondary Environmental Quality Standard for Soil in China by 3.5, 5.4 and 1.8 times, respectively. Total Cr had a relative accumulation in soil depth of 40–60 cm.

The average water soluble contents under slag heap and in the vicinity of slag heap were 176.9 times and 52.7 times higher than that in the unpolluted site, respectively. Water soluble Cr (VI) content decreased with soil depth increasing in the most polluted soils, but it can transport to the depth of 100–150 cm under the slag heap. Therefore, there is a potential risk of Cr contamination for groundwater in this area. Although water soluble Cr (VI) content in soils near the sewer channel of the factory is similar to control site value, the total Cr still maintained high level, implying the Cr contamination in those soils cannot be neglected.

Table 3 Vertical distribution of total Cr and water soluble Cr in soil profiles(mg/kg)

Sample depth/cm	Statistical parameter	Under slag heap (n=3)		In vicinity of slag heap (n=2)		Near sewer channel (n=4)		Control site (n=3)	
		Total Cr	Water soluble Cr (VI)	Total Cr	Water soluble Cr (VI)	Total Cr	Water soluble Cr (VI)	Total Cr	Water soluble Cr (VI)
0–20	Mean	1 589.3	123.8	2 078.1	49.4	679.2	0.7	104.9	2.5
	Min.	1 248.4	490.5	6 560.1	20.0	479.9	0.4	900.0	1.4
	Max.	2 130.3	252.7	3 500.1	78.8	922.9	1.0	117.5	3.3
	S.D.	4 730.5	112.0	2 011.0	41.6	228.2	0.3	130.9	0.9
20–40	Mean	2 210.9	132.7	2 183.8	35.4	484.1	1.2	84.8	1.8
	Min.	1 872.4	400.2	5 250.3	20.2	297.2	0.6	63.4	1.3
	Max.	2 756.2	300.8	3 842.3	68.6	796.0	1.8	98.4	2.3
	S.D.	4 760.8	145.8	2 345.5	46.9	219.2	0.6	18.7	0.5
40–60	Mean	2 236.8	910.2	635.9	27.8	276.8	0.6	89.0	1.40
	Min.	1 724.1	300.0	584.8	10.2	149.2	0.5	79.8	1.30
	Max.	2 852.2	218.5	687.0	54.4	509.6	0.8	95.1	1.60
	S.D.	5 710.0	112.9	720.3	37.6	159.3	0.2	80.1	0.15
60–100	Mean	1 258.4	760.2	746.2	90.6	166.1	0.7	67.5	1.6
	Min.	4 480.9	200.1	557.7	30.2	129.0	0.5	57.9	1.3
	Max.	1 503.2	176.4	934.7	15.9	234.7	1.2	83.7	1.8
	S.D.	7 190.0	900.0	266.6	80.9	460.9	0.3	14.1	0.3

n is number of samples, and S.D. means standard deviation.

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