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Migration and transfer of chromium in soil-vegetable system and associated health risks in vicinity of ferro-alloy manufactory

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Abstract: Study was carried out to analyze the distribution and migration patterns, soil-to-plant transfer and potential health risks of chromium in soil-vegetable system in areas near a ferro-alloy manufactory in Hunan province. The results show that soils near sewer outlet, sewer channel and in control area are averaged 2 239.5, 995.33 and 104.9 mg/kg, respectively. The total Cr has a relative accumulation in soil depth of 200−400 mm near the sewer outlet, mainly enriches in the surface layer (0−200 mm) near the sewer channel and decreases gradually in unpolluted soils. The differential concentration level of enrichment between layers is little. The results also indicate that the three vegetables of celery, lettuce and Chinese cabbage are able to convert the potentially toxic Cr (VI) species into the non-toxic Cr (III) species, and the chromium contents in the edible parts of the vegetables are averaged 11.95 mg/kg. The transfer factors of the three vegetables follow the order: Chinese cabbage > lettuce > celery. The estimated total daily intake of chromium substantially exceeds the dietary allowable value, which may pose health risks to local population.

Key words: heavy metal; chromium; migration; transfer factor; health risk; soil; vegetable

1 Introduction

Chromium is a common heavy-metal contaminant in soil, groundwater and sediments. Cr-contaminated site has been found at 1036 of the 1591 National Priority List sites identified by the United State Environmental Protection Agency [1]. China is one of the major countries to produce chromate [2]. Most Cr industry operations lack appropriate facilities to dispose Cr-containing wastewater and to deposit chromate ore processing residue. Hence, Cr pollution in soils has become a serious problem [3]. Usually, Cr occurs in two forms: Cr (III) and Cr (VI). Chronic exposure to Cr (III) may result in liver, kidney or lung damage. Cr (VI) is highly toxic to biota and has been determined to be a human carcinogen by inhalation [4].

Wastewater irrigation is a widespread practice in the world and is known to contribute significantly to the heavy metals contamination in soils. In China, although the wastewater treatment capacity is 35.785×10^6 t/d, only 40% total wastewater discharged is treated [5], and some of the un-treated wastewater from industries and communities is used for land irrigation [6]. Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation and leachate discharge, may not only result in soil contamination, but also lead to elevated heavy metal uptake by crops, and thus affect food quality and safety [7−8]. Cr is released into the environment as a result of human activities, including wastewater discharges and leachate released from chromate ore processing residue in electroplating, leather tanning and textile industries. Ingesting Cr-contaminated vegetables can cause stomach upsets and ulcers, convulsions, kidney and liver damage [1].

Food chain contamination is one of the major routes for the entry of heavy metals into animal and human system, and consumption of vegetables is one of the most important pathways by which heavy metals enter the food chain [9]. Heavy metal accumulation in vegetables depends upon plant species. The uptake efficiency of heavy metals is evaluated by either plant

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uptake or soil-plant transfer factors [10]. However, previous relative studies of heavy metal accumulation in plants have been mainly focused on arsenic, cadmium and other metals [11−12]. For Cr, previous studies focused more on the effect of Cr deficiency on human health [13]. Recently, concern about Cr as an environmental pollutant has been escalating [14]. Due to its build up to toxic levels in the environment as a result of mining industry, industrial or municipal wastewater reuse for irrigation and other activities [15]. However, researches on the transfer dynamics of Cr in the soil-plant systems under field condition that assess plant uptake of Cr are scanty. Evidences indicate that consumers are at risk when agricultural product contains excess of toxic elements [16]. Therefore, an additional insight into chromium uptake, accumulation and assessment of human health risks associated with Cr-contaminated soils is still needed.

Hunan province (central south China) is regarded as the heartland of nonferrous mining. In a long period, the emissions of Cr in Hunan province ranked first in China. Therefore, the aim of this study is to investigate Cr contents of soil and vegetables in the vicinity of a ferro-alloy manufactory in Hunan province, analysis the vertical distribution and migration of chromium in soil profiles and estimate the soil-to-plant transfer of chromium, evaluate the potential health effect of chromium polluted soil on local population through vegetable consumption.

2 Materials and methods

2.1 Site description and sampling

Soil and vegetable samples were taken near a ferro-alloy manufactory in Hunan province (27°75′N, 112°50′E). This manufactory was established in 1960's and generated 11 700 t of chromate ore processing residue and a huge amount of wastewater without proper leaching protection and disposal. The leachate and wastewater were discharged into a sewage outlet that flew through an arable area (vegetable field). The soil in this study was classified as Haplic Acrisol.

Surface soil samples (0−200 mm in depth) were collected near a sewage outlet, vegetable cultivation fields near a sewage channel and a control area about 5 km away from the ferro-alloy plant. At each site, soil was randomly sampled and bulked together to form a composite sample. The samples were air-dried and passed through a 0.26 mm polyethylene sieve. Sub-samples were used to measure the physical and chemical properties according to standard procedures (Table 1). Two, four and three soil profiles were taken from locations near the sewage outlet, near the sewage channel and in the control area, respectively. The nine undisturbed one-meter soil profiles were carefully sectioned at 200 mm intervals (0−200 mm, 200−400 mm, 400−600 mm and 600−1 000 mm, respectively).

Three waste water samples were also collected near the sewage outlet. 50 mL waste water sample was acidified with ultra-pure concentrated 6 mol/L nitric acid to pH<2 before chemical analysis.

In addition, three common grown vegetables, celery (*Apium graveolens*), Chinese cabbage [*Brassica compestris L. ssp. pekinensis (lour) Olsson*] and lettuce (*Lactuca sativa L*) were also collected from the same sites near the sewage channel and control area where the soils were collected. Fresh vegetable samples were washed with deionized water to remove visible soil particles and airborne pollutants. Then, absorbent paper was used to remove surface water of vegetables. After about 10 min, the fresh mass of edible parts of every vegetable samples were determined. The vegetable samples were then dried in an oven at 60 °C until constant mass. The dry mass were also determined and the samples were subsequently powdered using a pestle and mortar, and sieved through muslin cloth.

2.2 Analytical methods

For the total Cr concentrations, 300 mg homogenized soil samples were put into a 50 mL polytetrafluoroethylene crucible. Then 10 mL 68% HNO_3+5 mL 98% H_2SO_4+5 mL 47% HF were added into samples and heated at 230 °C until the solution became grey. After slightly cooling, 3 mL 1:1 HCl was added into the samples to make all compounds dissolved. The digested solution was transported into a 50 mL flask and 5 mL 10% NH_4Cl solution was added. The solution was added to 50 mL distilled water and filtered, and the concentration of total 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 50 mL deionized water to 10 g soil samples and then shaked for 1 h. After filtration, the water soluble Cr (VI) was determined by using 1, 5-diphenyl-carbohydrazide spectrophotometric method [17]. All the samples were analyzed in three replicates. The quality control of analytical accuracy was carried out by reagent blanks and standard reference soil (China Standard ESS−3, 98.0 mg/kg), which demonstrated that the results were in the guarantee value ((96.4±2.5) mg/kg).

The waste water sample was digested with 15 mL HNO_3 and 20 mL $HClO_4$ (70%). Then, 6 mol/L HCl was added to the digested solution to measure 50 mL in volume and then filtrated. The waste water sample was then analyzed for chromium content by UV spectrometric technique.

For vegetable samples, 2.0000 g powdered sample was digested with 5 mL concentrated Analar HNO_3 at 160 °C. After cooling down, the suspensions were filtered and the filtrate was adjusted to 50 mL with double deionized water. Thereafter, concentrations of Cr in the digested samples were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and UV spectrometric technique. A reagent blank and standard reference plant material (GBW07603 from the National Research Center for Standards in China) were included to verify the accuracy and precision of the digestion and subsequent analysis procedure.

2.3 Soil-plant transfer factor

The transfer factor (F) between plants and soil was defined as the ratio between Cr levels in plants and soil (unitless) as

$$F=\frac{C_{\text{plant}}}{C_{\text{soil}}} \tag{1}$$

where C_{plant} and C_{soil} represent the Cr concentration in the extracts of plants and soils on dry mass basis, respectively.

2.4 Daily intake of chromium from vegetables

The daily intake of Cr (D, mg/d) from vegetables was determined as

$$D=C_{\text{metal}}\times C_{\text{factor}}\times V_{\text{di}} \tag{2}$$

where C_{metal}, C_{factor} and V_{di} represent the Cr concentrations in vegetables (dry mass basis, mg/kg), conversion factor and daily intake of vegetables (kg/d), respectively. The conversion factor (C_{factor}) was used to convert fresh green vegetable mass to dry mass. Previous literatures [10, 18] always used the C_{factor} of 0.085 for all kinds of vegetables. In this study, the difference of C_{factor} between the three vegetable species (celery, Chinese cabbage and lettuce) was considered, which was defined as the ratio between dry mass and fresh mass. The average daily vegetable intake for local populations was considered to be 0.345 kg/(person·d) [19]. The habitual consumption of vegetables in the study area was inquired by a 100-item semiquantitative food frequency questionnaire. Participants were asked to report their frequency of consumption of 15 common vegetables during the year preceding the start of the study. Participants could indicate their consumption frequency by choosing one of six categories ranging from “never or less than once per month” to “three to seven times per week.”

3 Results and discussion

3.1 Soil characteristics and chromium distribution

As shown in Table 1, soils near sewer channel and in control area have quite similar organic matter contents, suggesting that there is little difference of fertilizer levels in the two vegetable cultivation areas. Also, cation exchange capacity (CEC) values show little discrepancy between the two fields. The organic matter contents and CEC values near the swear outlet are the lowest. Table 1 also shows that the soil pH near the swear outlet is the highest and the average pH of the soils near the sewer channel is higher than that of the control field.

Cr (VI) concentration of waste water samples collected near sewage outlet is averaged 6.63 mg/L, which is 13 times higher than that of the maximum permit concentration (0.5 mg/L) in China. Across the study area, a wide range (90−6 207.6 mg/kg) of soil Cr concentrations are observed, as listed in Table 2. Results presented in Table 2 also show that the total Cr

Table 1 Physical and chemical properties of soil samples

Sampling site	Number of samples	pH	Organic material content/(g·kg^{-1})	Cation exchange capacity/(mol·kg^{-1})	Particle size distribution/%		
					＞0.01 mm	0.01−0.001 mm	0.001 mm
Near sewer outlet	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 area	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

Table 2 Concentrations of Cr in surface soils at three sampling sites (mg/kg)

Sampling site	Number of samples	Total Cr			Water soluble Cr(VI)		
		Minimum	Maximum	Mean ± SD	Minimum	Maximum	Mean ± SD
Near sewer outlet	5	656.1	3 500.1	2 239.5 ±1 413.5	0.5	101.8	36.9 ±38.9
Near sewer channel	23	208.6	6 207.6	995.3 ±1 643.1	0.2	1.7	0.6 ±0.3
Control area	10	90.0	117.5	104.9 ±13.9	0.1	1.1	0.7 ±0.5

SD: Standard deviation

concentrations near the sewer outlet (2 239.5 mg/kg) are significantly higher than that near the sewer channel and in the control soils (995.3 and 104.9 mg/kg, respectively), indicating that the chromium containing wastewater leads to substantial buildup of Cr in the area. Compared the Cr content with the critical limit in China's soils (200 mg/kg, respectively), it is quite clear that serious pollution occurs near the sewage outlet and channel.

3.2 Migration of chromium in soils

Figure 1 shows the vertical distribution of total Cr and water soluble Cr (VI) in the three areas. The mean total Cr concentrations in different soil depths near the sewer outlet are in the order: 200−400 mm (2 183.8 mg/kg)>0−200 mm (2 078.1mg/kg)>400−1 000 mm (691.05 mg/kg), which indicates a strong retention of Cr in the middle soil depth in this field. The leaching and a slight accumulation of Cr in intermediate depth may be attributed to iron compounds in retaining the element at depth [20]. The tested profile soil is derived from quaternary red earth and iron-manganese nodules often aggregate in the intermediate depth soil, which leads to Cr enrichment [21]. In addition, the solubility of Cr(III) is ubiquitously controlled by the solid solution (Cr, Fe)$(OH)_3$ in the presence of Fe(III) in the study area [22]. Therefore, it is reasonable that total Cr accumulates in intermediate depth soils near the sewer outlet.

However, vertical distribution profiles near the sewer channel shows different patterns of total Cr as compared with that near the sewer outlet. The total Cr is significantly higher at 0−200 mm of the soil surface, and decreases rapidly in the following several depths, indicating that the contamination is restricted to the soil surface in the area. Under natural condition, the distribution of metals in soil profiles is mainly inherited from the parent materials and pedogenic movement when no extraneous metals enter. However, the input and re-distribution of heavy metals from anthropogenic sources become the major factor affecting their distribution patterns in soils. In this study, the significant enrichment of total Cr in the surface soil layers near the sewer channel clearly evidences the influence of waste water irrigation. In addition, the distribution pattern may also due to the application of fertilizers and organic manure in the surface soil of cultivated fields that near the sewer channel. The formation of metal-organic complexes leads to the accumulation of metals in soils with high content of organic matter and chromium retention is stronger in organic than in mineral soil material [23]. The absorption of chromium by organic matter in the surface soil is also found in control area. However, unlike near the sewer outlet and sewer channel, total Cr contents in control area decrease gradually in the following depths.

In all soil profiles, water soluble Cr (VI) concentrations decrease with depth. In addition, water soluble Cr (VI) concentration in each soil depth follows the order: near the sewer outlet > near the sewer channel > control sites, which indicates that soils near the sewer outlet are heavily polluted by chromium. It is also found that chromium from the surface layer can migrate in the subsoil, although soil is responsible for the retention of chromium. The results imply that there exists a significant potential for chromium to be a serious threat to groundwater system, especially in areas near the sewer outlet.

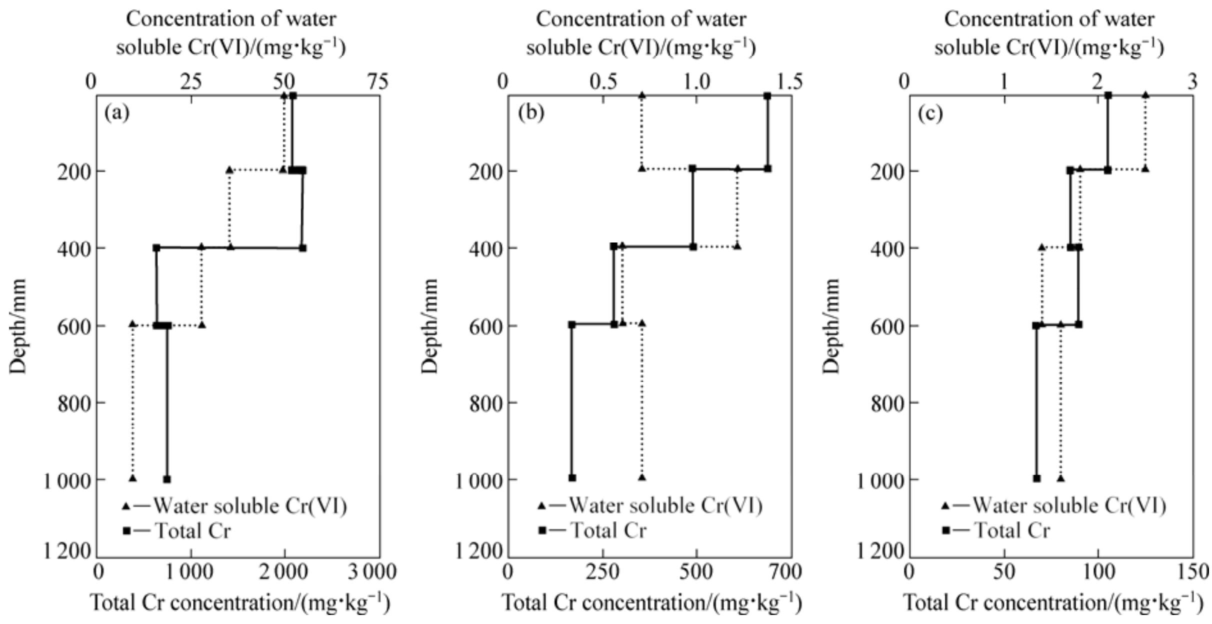

Fig. 1 Vertical distribution of total Cr and water soluble Cr(VI) in soil profiles near sewer outlet (a), sewer channel (b) and in control area (c)

3.3 Bioaccumulation of chromium in vegetables

In all vegetable samples tested, it is able to detect only Cr (III) species. No Cr^{6+}, Cr^{5+} or Cr^{4+} species are detected in any of the crops examined. These results suggest that plant tissues are able to convert the potentially toxic Cr (VI) species into the non-toxic Cr (III) species.

The Cr concentrations in all plant samples exceed the maximum permissible limit of 0.5 mg/kg, on a dry mass basis. Chromium contents in the edible parts of the three different vegetables are listed in Table 3. The plant Cr concentrations near sewer channel are averaged 11.1 mg/kg (range: 2.1−18.8 mg/kg). In addition, the average content of plant Cr in control area of 12.8 mg/kg (range: 1.0−26.6 mg/kg) is similar to that near the sewer channel. There are three possible reasons for the interpretation why plant Cr contents have little difference between the two areas. One possible reason is the effect of organic matter (OM). Some literature [24] holds the opinions that the metals combined with organic matters are difficult to be taken by plants. However, soil Cr uptaken by plants is an interesting area, and Ref. [24] has illustrated that the organic-binding Cr can be easily decomposed by anaerobic metal-reducing bacteria and then be absorbed by plants. The soils near the sewer channel and in control area have quite similar OM contents. The second possible reason is that although the total soils Cr near the sewer channel are higher than that in control area, a majority of soils Cr near the sewer channel are Cr(III) and the water soluble Cr (VI) content between the two areas is similar (averaged 0.7 and 0.6 mg/kg, respectively). Cr (III) is adsorbed 30−300 fold more strongly to soil clay minerals than Cr(VI) and difficult to be adsorbed by plants [25]. Similar results were also reported by ZAYED et al [14]. The third reason might be the self-adjusting of plants, which plays an important role on sequestering the metals in their roots. The self-adjusting of plants makes only small amounts of Cr be translocated to the up-ground parts of vegetable crops. Therefore, it is reasonable that Cr concentrations in the up-ground parts of vegetable near the sewer channel are similar to that in the control field. In addition, this would imply a great daily intake and health risk of Cr in control area, which should be taken into consideration.

Table 2 lists different vegetables varied in their ability to accumulate Cr in their tissues. The trends of Cr concentrations in different vegetables are in the order: Chinese cabbage>lettuce>celery. Of the edible portions, Chinese cabbage appears to bio-accumulate the highest concentrations of Cr. Similar results were reported by ZAYED and TERRY [26], they found that out of eleven different plant species, *Brassicaceae* family (i.e. cabbage, cauliflower and kale) accumulated the most Cr in their tissues. Indeed, studies conducted by KUMAR et al [27] clearly showed that Brassica species had an unusual ability to take up heavy metals such as Pb, Cr, Cd, Ni, Zn and Cu from root substrates and concentrate these metals in their tissues. The result shows that lettuce is also high Cr-accumulator in the study area. The amount of metal ingested by human beings is straightly related to alimentary habits and their content in foodstuff. The vegetable contamination in the study area is at its highest in two of the predominant dietary vegetables, Chinese cabbage and lettuce. Therefore, it is strongly suggested that the alteration of vegetable structure in the Cr contaminated area can reduce health risks of human being exposure to Cr contamination.

3.4 Soil-plant transfer factor

Soil-plant transfer factor (TF) is one of the key components of human exposure to metals through food chain. TF values of Cr for three most common vegetables in uncontaminated soils and contaminated soils are shown in Fig. 2. The transfer factor of celery, lettuce and Chinese cabbage follows the order: Chinese cabbage>lettuce>celery. The experimental results also show that the TF values differ significantly between locations and vegetable species. The results indicate that the TF values of all three vegetables decrease with increasing metal contamination in soil. According to CUI et al [28], the TF difference among locations may be related to soil properties. The mean pH of the contaminated soils is higher than that of the control soils. The difference of soil pH is little in the control area (ranged from 5.3 to 6.0). However, it is found that soil pH is very variable near the sewer channel (ranged from 4.5 to 7.9), which indicates a somewhat heterogeneous feature in this site. Moreover, Cr concentrations near the sewer channel have high coefficient of variation (CV) as high as 165.1, which is significantly higher than that in the control area (14.5). The diversity of soil pH and CV

Table 3 Cr concentrations in edible parts of vegetables (mg/kg)

Vegetable	Number of samples	Near sewer channel			Control area		
		Minimum	Maximum	Mean ± SD	Minimum	Maximum	Mean ± SD
Celery	10	2.1	9.3	6.5 ± 3.0	1.0	14.2	7.3 ± 5.7
Chinese Cabbage	10	12.0	17.8	14.9 ± 2.1	11.1	23.9	15.8 ± 5.0
Lettuce	10	6.3	18.8	11.8 ± 4.5	8.1	26.6	15.2 ± 7.2

SD: Standard deviation

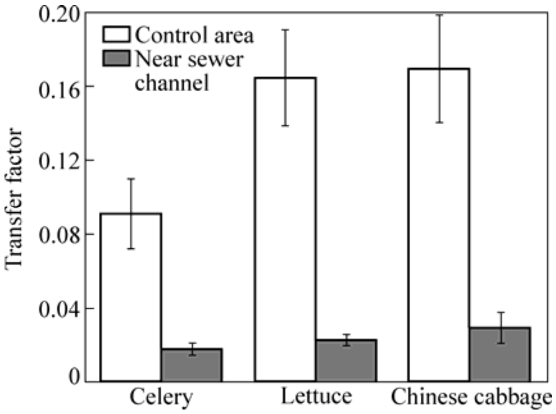

Fig. 2 Transfer factor values of Cr for three common vegetables in different locations

may be related to soil properties, which consequently controls the availability and uptake of Cr for plants. Additionally, as mentioned earlier, vegetables in control soils grow well and the Cr concentration in the edible part of plant is at a similar level to or slight higher than that grown on contaminated soils. However, corresponding Cr contents of soils are much higher than those of the control soil, and hence the TF values of vegetables grown on contaminated soils decrease.

3.5 Daily intake of chromium and associated health risks

Daily intake of Cr (DIC) is very important for estimating the level of exposure and observing the health risk of vegetable ingestion. According to the food frequency questionnaire, celery, Chinese cabbage and lettuce account for 25%−35% of the total consumption of vegetables for local residents and 30% is used in our research. It is found that the intake ratio of celery to lettuce to Chinese cabbage is around 1: 4: 5. In addition, C_{factor} values of all plant samples are calculated, and the average C_{factor} values of celery, lettuce and Chinese cabbage (0.078 7, 0.037 8 and 0.088 5, respectively) are used for DIC calculation.

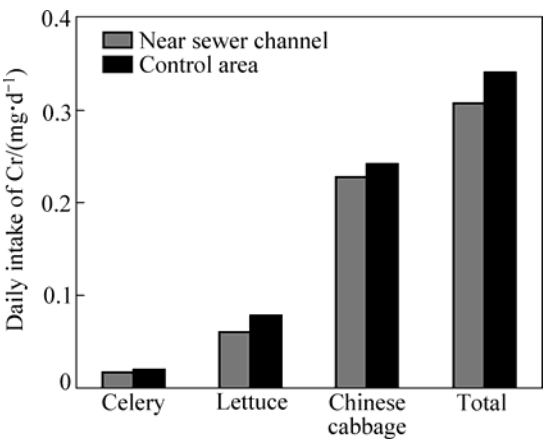

Fig. 3 Daily intake of chromium from vegetable ingestion in different areas

The total DICs from the three vegetable species for local residents are estimated in the present work, which are 0.31 and 0.34 mg/d near the sewer channel and in control area, respectively. In addition, results in Fig. 3 show that the high DIC values are from Chinese cabbage consumption (averaged 0.23 mg/d), and the low values are from celery ingestion (averaged 0.018 7 mg/d). The estimated total DIC (ranged from 0.16 to 0.41 mg/d) is higher than the dietary allowable value (0.025−0.030 mg/d for male and 0.015-0.020 mg/d for female) recommended by Food and Nutrition Board [29]. Moreover, the estimated total DIC values of vegetables are higher than most of the values that reported in previous literature [30], which mainly ranges from 0.006 to 0.03 mg/d. Therefore, the Cr pollution may pose health risks to local population and the risks of the three vegetables ingestion follow the order: Chinese cabbage>lettuce>celery.

Furthermore, there are also other sources of Cr exposures (e.g. dermal contact, ingestion of contaminated soils, drinking of contaminated ground water, showering and cleaning using polluted surface or ground water), which are not taken into account in this study. Therefore, chromate ore processing as a pollution source of Cr in the study area must be considered more seriously.

4 Conclusions

1) The average values of total Cr concentrations in soil near the sewer outlet, near the sewer channel and in control area are 2 239.5, 995.33 and 104.9 mg/kg, respectively. Total Cr near the sewer outlet has a relative accumulation in the intermediate depth soil. However, the total Cr near the sewer channel mainly increases in the surface layer and decreases gradually in unpolluted soils. Additionally, the water soluble Cr (VI) concentrations in all soil profiles decrease with soil depths.

2) Chromium contents in the edible parts of vegetables are averaged 11.95 mg/kg, which exceed the maximum permissible limit. The transfer factor of celery, lettuce and Chinese cabbage follows the order: Chinese cabbage>lettuce>celery.

3) The estimated total daily intake of Cr has substantially exceeded the dietary allowable value. The Cr pollution may pose health risks to local population. In addition, the health risks from consumption of celery, lettuce and Chinese cabbage follows the order: Chinese cabbage>lettuce>celery.

References

[1] Agency for Toxic Substances and Disease Registry. Toxicological profile for chromium [R]. Atlanta, GA, U.S.: Dept of Health and Human Services, Public Health Service, 2000.

[2] HUANG Shun-hong, PENG Bing, YANG Zhi-hui, CHAI Li-yuan, XU You-ze, SU Chang-qing. Spatial distribution of chromium in soils contaminated by chromium-containing slag [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(3): 756−764.

[3] FELTER S P, DOURSON M L. Hexavalent chromium- contaminated soils: Options for risk assessment and risk management [J]. Regulatory Toxicology and Pharmacology, 1997, 25(1): 43−59.

[4] USEPA. Integrated risk information system: Chromium (VI) [EB/OL]. [2010−10−10]. http://www.epa.gov/iris/.

[5] MUCHWEI M, BIRKETT J W, CHINYANGA E, ZVAUYA R, SCRIMSHAW M D, LESTER J N. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health [J]. Agriculture, Ecosystems & Environment, 2006, 112(1): 41−48.

[6] KHAN S, CAO Q, ZHENG Y M, HUANG Y Z, ZHU Y G. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China [J]. Environmental Pollution, 2008, 152(3): 686−692.

[7] SONG Jie, GUO Zhao-hui, XIAO Xi-yuan, MIAO Xu-feng, WANG Feng-yong. Environmental availability and profile characteristics of arsenic, cadmium, lead and zinc in metal-contaminated vegetable soils [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(3): 765−772.

[8] SUN Hong-fei, LI Yong-hua, JI Yan-fang, YANG Lin-sheng, WANG Wu-yi, LI Hai-rong. Environmental contamination and health hazard of lead and cadmium around Chatian mercury mining deposit in western Hunan Province, China [J]. Transactions of Nonferrous Metals Society of China, 2010, 20 (2): 308−314.

[9] SIPTER E, ROZSA E, GRUIZ K, TATRAI E, MORVAI V. Site-specific risk assessment in contaminated vegetable gardens [J]. Chemosphere, 2008, 71(7): 1301−1307.

[10] RATTAN R K, DATTA S P, CHHONKAR P K, SURIBABU K, SINGH A K. Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—A case study [J]. Agriculture, Ecosystems & Environment, 2005, 109(3−4): 310−322.

[11] CHEN Huai-man. Heavy metal contamination in soil-plant system [M]. Beijing: Science Press, 1996: 32−36. (in Chinese)

[12] HOUGH R L, YOUNG S D, CROUT N M J. Modelling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm [J]. Soil Use Manage, 2003, 19(1): 19−27.

[13] BERNER T O, MURPHY M M, SLESINSKI R. Determining the safety of chromium tripicolinate for addition to foods as a nutrient supplement [J]. Food and Chemical Toxicology, 2004, 42(6): 1029−1042.

[14] ZAYED A, LYTLE C M, QIAN J H, TERRY N. Chromium accumulation, translocation and chemical speciation in vegetable crops [J]. Planta, 1998, 206(2): 293−299.

[15] ZHANG M, CHEN Z, CHEN Q, ZOU H, LOU J, HE J. Investigating DNA damage in tannery workers occupationally exposed to trivalent chromium using comet assay [J]. Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 2008, 654(1): 45−51.

[16] PERALTA V J R, LOPEZ M L, NARAYAN M, SAUPE G, GARDEA T J. The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain [J]. International Journal of Biochemistry & Cell Biology, 2009, 41(8−9): 1665−1677.

[17] 7467−87. Ministry of Environment. Water and wastewater monitoring and analysis methods [S]. (in Chinese)

[18] ZENG G, LIANG J, GUO S, SHI L, XIANG L, LI X, DU C. Spatial analysis of human health risk associated with ingesting manganese in Huangxing Town, Middle China [J]. Chemosphere, 2009, 77(3): 368−375.

[19] WANG X, SATO T, XING B, TAO S. Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish [J]. Science of the Total Environment, 2005, 350(1−3): 28−37.

[20] MORGADO P, PEREIRA V, PINTO M S. Chromium in Portuguese soils surrounding electroplating facilities [J]. Environmental Geochemistry and Health, 2001, 23(3): 225−228.

[21] BHATTACHARYA P. Metal contamination at a wood preservation site: characterization and experimental studies on remediation[J]. Science of the Total Environment, 2002, 290(1−3): 165−180.

[22] GARNIER J. Solid speciation and availability of chromium in ultramafic soils from Niquelandia, Brazil[J]. Journal of Geochemical Exploration, 2006, 88(1−3): 206−209.

[23] LEBOW S, FOSTER D, EVANS J. Long-term soil accumulation of chromium, copper, and arsenic adjacent to preservative-treated wood[J]. Bulletin of Environmental Contamination and Toxicology, 2004, 72(2): 225−232.

[24] HANSEL C M, WIELINGA B W, FENDORF S. Structural and compositional evolution of Cr/Fe solids after indirect chromate reduction by dissimilatory iron-reducing bacteria [J]. Geochimica et Cosmochimica Acta, 2003, 67(3): 401−412.

[25] GRIFFIN R A, AU A K, FROST R R. Effect of pH [hydrogen-ion concentration] on adsorption of chromium from landfill-leachate by clay minerals [J]. Journal of Environmental Sciences. Health. Part A, 1977, 12(6): 431−449.

[26] ZAYED A M, TERRY N. Chromium in the environment: factors affecting biological remediation [J]. Plant and Soil, 2003, 249(1): 139−156.

[27] KUMAR P, DUSHENKOV V, MOTTO H, RASKIN I. Phytoextraction: the use of plants to remove heavy metals from soils [J]. Environmental Science & Technology, 1995, 29(3): 1232−1238.

[28] CUI Y J, ZHU Y G, ZHAI R H, CHEN D Y, HUANG Y Z, QIU Y, LIANG J Z. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China [J]. Environment International, 2004, 30(6): 785−791.

[29] DRIS (Food and Nutrition Board). Dietary reference intakes. Recommended intakes for individuals [R]. Washington DC: Institute of Medicine, National Academy of Sciences, 2004.

[30] BIEGO G H, JOYEUX M, HARTEMANN P, DEBRY G. Daily intake of essential minerals and metallic micropollutants from foods in France [J]. Science of the Total Environment. 1998, 217(1−2): 27−36.

铬在铁合金厂周边土壤–蔬菜系统中的迁移转化及健康风险

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摘　要：分析湖南省某铁合金厂附近重金属铬在土壤中的分布及迁移特征，在土壤−植物系统中的迁移转化规律，以及铬污染蔬菜对人体的健康风险。结果表明：铁合金厂外排污口、污灌区和对照区土壤的铬含量平均值分别为 2 239.5，995.33 和 104.9 mg/kg。总铬在排污口附近土壤中主要富集在地表下 200−400 mm；在污灌区，主要富集于地表下 0−200 mm；而在对照区，铬浓度从上至下逐渐降低且各层之间富集浓度相差不大。结果也表明芹菜、莴苣和白菜均能够把土壤中吸收的致毒性较强的六价铬转化成低毒的三价铬，且蔬菜中的铬含量平均值为 11.95 mg/kg。铬在土壤–蔬菜中的生物富集因子大小依次为：白菜>莴苣>芹菜。居民每天摄入的铬含量严重超过食物中最大铬允许摄入量，表明铬污染对当地居民存在一定的健康风险。

关键词：重金属；铬；迁移；生物富集因子；健康风险；土壤；蔬菜

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