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Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China

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Abstract: A field survey was conducted to investigate the metal and arsenic contamination in soils and vegetables on four villages (Shuichuan (SCH), Beiwan (BWA), Dongwan (DWA) and Wufe (WFE)) located along, Baiyin, China, and to evaluate the possible health risks to local population through foodchain. Results show that the most significantly contaminated soils occurred upstream at SCH where Cd, Cu and As concentrations exceeded maximum allowable concentrations for Chinese agricultural soil. Further downstream the degree of contamination semi-systematically decreased in concentrations of metal. Generally, the leafy vegetables were more heavily contaminated than non-leafy vegetables. Chinese cabbage is the most severely contaminated, the concentrations of Cd exceeded the maximum permit levels (0.05 mg/kg) by 4.5 times. Bio-accumulate factor also shows that an entry of Cd to food chain plants is the greatest potential. Furthermore, the estimated daily intake amounts of the considered toxic elements (Cd, Pb and Cu) from the vegetables grown at SCH and BWA and DWA have exceeded the recommended dietary allowance levels. Thus, the vegetables grown in three villages above, which affected by Baiyin mining and smelting have a health hazard for human consumption.

Keywords: vegetable species; heavy metals; mining and smelting; pollution

Introduction

Mining and smelting activities are the major source of metals entering into the environment and can lead to ecological damages (Lee and Stuebing, 1990). In the process of mining, ore concentrating, mine tailing, wastewaters, and dust maybe produced. If these are not carefully managed, the surrounding environment can be polluted. River contamination near the mining and smelting area has drawn public attention, because of the improper wastes treatments (Lewin *et al.*, 1977; 1989, 1992; Macklin *et al.*, 1994; Swennen *et al.*, 1994; Miller, 1997; Hudson-Edwards *et al.*, 2003). The amount of hazardous wastes released from base-metal mining and smelting operations and transported into rivers can be enormous (e.g., 1010 kg in the United States in 1985 alone; USEPA, 1985; Maron, 1989; Moore and Luoma, 1990; Jambor and Blowes, 1994; Swanson, 2002). In 2000 alone, there were a total of five reported major mining and smelting accidents around the world resulting in significant soil and river pollution (in China, Romania, Sweden, and USA; Macklin *et al.*, 2003).

In China, the accumulation of heavy metals and metalloids in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems (Hu *et al.*, 2004; Sun *et al.*, 2005; Zhang, 2005; Zhu *et al.*, 2005; Li *et al.*, 2006), particularly in vegetable plantation within suburban areas of industrial cities. Such as Hangzhou, Tianjin, Xi'an, Nanchang and

Chongqing cities, China, are polluted by various heavy metals (Tianjin Environmental Protection Bureau, 1991, 1996; Li *et al.*, 2003; Ma *et al.*, 2003; Li *et al.*, 2004; Zhu *et al.*, 2005), but information on the health risks of these metals is quite limited.

Health risk due to soil contamination with single heavy metal has been widely studied. It also poses potential barriers for international trading of foodstuffs. Regulatory frameworks and guidelines for heavy metals in the environment and foodstuffs have been developed (McLaughlin *et al.*, 2000). Several studies have indicated that crops and vegetables grown in heavy metals contaminated soils have higher concentrations of heavy metals than those grown in uncontaminated soil (Guttormsen *et al.*, 1995; Dowdy and Larson, 1995). As a result, an increased metal uptake by crops and vegetables grown for human consumption is often observed. Excess consumption of non-essential trace elements such as As and Cd can result in various skin lesions, bone and cardiovascular diseases, renal dysfunction, and various cancers, even at relatively low levels (Calderon, 2000). Türkdogan *et al.* (2002) found that the high concentrations of metals (Co, Cd, Pb, Mn, Ni and Cu) in fruit and vegetables in Van region of Eastern Turkey are related to the high prevalence of upper gastrointestinal (GI) cancer rates. Lacatusu *et al.* (1996) reported that the soil and vegetables polluted with Pb and Cd in Copsa Mica and Baia Mare, Romania, significantly contributed to decreased human life expectancy within the affected areas, reducing average age at death by 9–10 years.

Metals are ubiquitous in the environment either naturally or anthropogenically. Both industry and agriculture has contributed considerably to the elevated concentrations of heavy metals through waste disposal, smelter stacks, atmospheric deposition, fertilizer and pesticide use and the application of sewage sludge in arable land. In riverside, the primary pathways of metal accumulation in humans are through the ingestion of contaminated drinking water, crops, fruits, fish and soil. A major pathway of soil contamination is through atmospheric deposition of heavy metals from point sources such as: metaliferous mining, smelting and industrial activities. Other non-point sources of contamination affecting predominantly agricultural soils include inputs such as fertilisers, pesticides, sewage sludge, organic manures and composts (Singh, 2001; Li *et al.*, 2006). Additionally, foliar uptake of atmospheric heavy metals emissions has also been identified as an important pathway of heavy metal contamination in vegetable crops (Bassuk, 1986; Salim *et al.*, 1992).

Soil-to-plant transfer of heavy metals is the major pathway of human exposure to soil contamination. Generally, soil to plant transfer factor of metals is computed based on total metal contents of soils (Hooda *et al.*, 1997). However, total metal content in soils does not take into account the other soil factors that modify the bioavailability of metals. Hence, computation of soil to plant transfer factor of metals should be based on available soil metal pools.

In the Baiyin non-ferrous metals mining and smelting area, previous investigations have shown that soil was severely polluted by heavy metals (Nan and Zhao, 2000). It is therefore anticipated that crops grown in the downstream area cannot be free from metals pollution. Under this scheme, the Yellow River water irrigation has been provided to the farmers' fields for more than four decades. Various vegetables and cereal crops, especially great amounts vegetables, have successfully been grown thereon. Thus far, information on the health risks of these metals is quite limited. The objectives of this paper were: (1) to quantify the content of metal in agricultural soil and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China; (2) to investigate the degree of pollution and the daily intake amount of toxic elements through vegetables; (3) to identify the interactions between soil and vegetable metal concentrations.

1 Materials and methods

1.1 Study area

Baiyin City is located at the Loess Plateau of northwest, China (Fig.1), which is one base of non-ferrous metals mining and smelting in China. The total yield of non-ferrous metals are 3.0×10^5 t in 1962

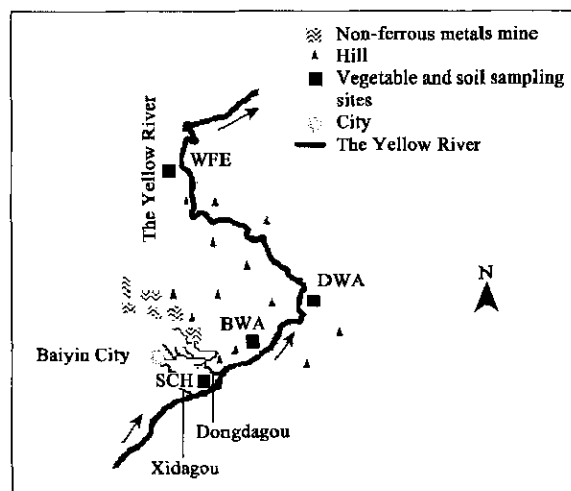


Fig.1 Schematic view of the four vegetables and soils sampling sites in Baiyin region (Gansu Province, China): Shuichuan (SCH), Beiwang (BWA), Dongwan (DWA) and Wufe (WFE) sites

and 3.15×10^6 t in 2004, and one of copper was 1.45×10^6 t. More than 38000 workers were engaged in the mining, smelting, and transport services associated with the mining activities, which continue at full speed today.

All the non-ferrous metal mining and smelting plants and several other factories are located along the upper reaches of Dongdagou stream, and one copper processing plant and several other factories are located along the upper reaches of Xidagou stream (Fig.1), both of which accept domestic wastewater and different industrial sewage. Study by Nan and Zhao (2000) demonstrates that there are several sources of metals to the headwaters of Dongdagou and Xidagou stream basins. The most significant sources are the mills and non-ferrous metals smelting that release flotation effluent and tailings materials directly into the Yellow River through two basins: Dongdagou and Xidagou stream basins.

The Yellow River runs through this area, and the farmlands are irrigated with the water from the river. The water exhibits a yellow color characteristic of the obtained high concentrations clay soil and sand particles and contaminated milling effluent. Mining and metals smelting of the Baiyin has led to the severe contamination of the Yellow River water and sediments for at least 200 km downstream of the mines (Wang *et al.*, 2003), and metal mixtures is receiving increasing attention from the public as well as governmental agencies. The soil here is gray calcareous soil. The main agricultural activities include application of irrigation, pesticides and fertilization (farmyard manure or/and chemical fertilizers), and the irrigation with river water has had a long history in the Yellow River valley because of the semi-arid geographical location.

Four sampling sites were selected along the

Yellow River (Fig.1). Shuichuan (SCH, 15 and 14 km from Baiyin City and mine area, respectively, was affected by atmospheric deposition, mining activities, metal smelting and polluted water. Vegetables, maize and some other cereals are grown on aereally extensive terraces, largely for domestic consumption.

Beiwan (BWA) is located approximately 32 and 17 km from Baiyin City and mine, historic terraces are preserved, both the fans and the alluvial terraces are utilized for agriculture. This area was affected by mining activities and polluted water. Dongwan (DWA) is located approximately 70 km downstream from Baiyin City on the right (east) bank of the Yellow River and approximately 6 km upstream from the main highway connecting Jingyuan County. Irrigation water is used intensively to grow a range of vegetables for sale in Gansu, Ningxia, Inner Mongolia and Qinghai and via wholesalers elsewhere in north-west China. This area was possible affected by polluted water.

Wufe (WFE), approximately 160 km downstream of Baiyin City has a small area of irrigated valley-bottom land farmed intensively for vegetables that are sold in Jingtai County and throughout highland Baiyin region. Wheat and maize are the principal crop although cabbage, capsicum, pumpkin and tree fruit are produced in small quantities.

1.2 Sampling

Eight vegetable species were selected for this study: cucumber (*Cucumis sativus* L.), pumpkin (*Lagenaria siceraria* (Molina) Stardl.), capsicum (*Capsicum annuum* L.), eggplant (*Solanum melongena* L.), cabbage (*Brassica oleracea* var. *capitata* L.), brassica napus (*Brassica campestris* var. *oleifera* DC.), spinach (*Spinacia oleracea* L.) and Chinese cabbage (*Brassica pekinensis* (Lour.) Rupr.), which represented the major vegetable species growing in riverside in the sampling season of March–June 2003.

At each sampling site, 3–5 of replicate samples (vegetables and soil, soil was cored at 0–20 cm in depth) was random collected. Sometimes, more than one vegetable grew on the same plot; we sampled them individually. Samples of soil and vegetables were stored in polyethylene bags in the field, and were transferred to the laboratory within 4 h for sample processing.

1.3 Analytical procedures

In the laboratory, edible parts of the each vegetable crop were weighed after washing with deionized water and blotting dry with tissue paper. The samples were then cut into slices by a pair of plastic scissors, and oven-dried to constant weights, so as to obtain finely divided specimens for analysis. The dried samples were grinded in porcelain mortar and passed through 200 mech sieve, then stored in fridge

at 4°C prior to analysis.

The soil samples, after air-drying at room temperature, were sieved with nylon mesh (0.149 mm). The < 0.149 mm fraction was grinded in an agate mortar for analysis.

1.4 Analytical procedures

1.4.1 Soil pH

The pH values were determined using the classical method described by Allen *et al.* (1974). About 4.0 g of the soils (< 2 mm) were mixed with 10.0 ml of deionized water in centrifuge tubes. The mixtures were shaken for 30 min on a mechanical shaker and then centrifuged at 3000 r/min for 10 min. pH of the supernatants were measured using a pre-calibrated pH meter.

1.4.2 Metal analysis

Metal concentrations were analyzed by an Agilent 7500i inductively coupled plasma mass spectrometer (ICP-MS) at the Instrument Analysis Research Center, Lanzhou University. Complete dissolution of samples was performed by an acid digestion method based on the procedure described by Hernandez *et al.* (2003) with minor modification.

1.4.3 Quality control

For the quality control, standard reference materials GBW 08505 (tea leaves, China National Center for Standard Materials) and NIST 1572 (Citrus Leaves for As analysis in vegetables only, from National Institute of Standards and Technology, USA) for vegetable samples, and GSS-2 (China National Center for Standard Materials) for soil samples were used. Results were well agreed with certified concentrations (Table 1).

1.5 Data analysis

1.5.1 Bio-accumulate factor (BAF)

The bio-accumulate factors (BAF) of metal and As from soils to vegetables were calculated as follows:

$$BAF = E_v / E_s$$

Where: E_v is the element concentration in vegetable; E_s is the element concentration in corresponding soil.

1.5.2 Daily intake estimate of metals through food

The daily intake amount of metals (DIM) depends on both the element concentration (M) and the amount of the vegetable consumed (W) (Liu *et al.*, 2005). We choose the average quantity of vegetable consumed by a person (70 kg in body weight) as 200 g/(person·d), which is recommended amount from nutritional point of view (Hassan and Ahmed, 2000). Then, the total daily intake quantity of Cu, Zn, As, Cd and Pb by a person is calculated as:

$$DIM = M \times W$$

2 Results

Table 1 Summary of measured and certified reference (*) element concentrations in GBW 07402, GBW08505 and SRM 1572							
Soil GBW 07402 (n=3)				Tea leaves GBW 08505 (n=3)			
	Certified value±SD	Observed value±SD	Recovery ^a , %		Certified value±SD	Observed value±SD	Recovery ^a , %
Cu	16.3±0.4	16.0±0.7	98	Cu	16.2±1.9	15.6±2.1	96
Zn	42.3±1.2	44.4±1.5	105	Zn	38.7±3.9	37.5±4.2	97
As	13.7±0.6	12.6±0.8	92	As	3.1±0.3 ^b	3.0±0.4 ^b	98 ^b
Cd	0.071±0.0009	0.108±0.002	152	Cd	0.032±0.005	0.031±0.002	97
Pb	20.2±1.0	20.6±1.2	102	Pb	1.06±0.1	1.31±0.06	124
Cr	47±2	47±1.5	100	Cr	0.8	—	—

Notes: * Values quoted on a dry weight basis; ^a recovery (%)=(mean measured value/mean certified value)×100%; ^b citrus leaves NIST SRM 1572

2.1 Metals and arsenic concentration in soils

Preliminary geomorphic data suggest that the mean total concentrations of the considered metals and arsenic in soil adjacent to the upper reaches sample sites have significant elevated trend, although individual difference is different in the elevated concentrations and the ranges of metals (Table 2). In the lowest downstream, at the WFE village, the mean concentrations of Cd, Pb, Cu, Cr and As are quite low. At other three sites, the mean concentrations of Pb and

As decrease in the order: $C_{SCH} > C_{BWA} > C_{DWA}$, while the mean concentrations of Cr show the order: $C_{BWA} > C_{SCH} > C_{DWA}$. However, the mean concentrations of Cr and Zn in the soils from BWA are the highest. No significant variations of the mean concentration of Zn is found among the four sites ($p = 0.059$). Among the individual soil samples within each site, strong variability is observed in the concentrations of Cd, Cu, Pb and As at four sites.

Table 2 Mean total concentrations of metals in the agricultural soils along the Yellow River (< 2 mm, mg/kg dw)												
Element	SCH			BWA			DWA			WFE		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Cd	7.43	0.25	19.75	0.86	0.13	2.82	1.05	0.86	1.69	0.49	0.08	1.07
Cu	132.82	36.13	329.60	67.05	25.92	160.90	18.05	13.33	30.84	25.38	0.65	53.33
Pb	223.22	55.70	700.90	33.59	22.94	52.51	17.65	16.40	18.80	11.38	6.82	16.40
Zn	224.86	63.88	558.80	266.07	160.13	421.51	133.87	54.68	417.70	203.91	162.88	251.02
Cr	47.07	44.52	49.22	50.45	29.61	68.73	27.13	13.61	33.82	9.63	4.64	15.43
As	446.64	325.13	522.18	214.17	151.08	261.57	44.57	28.46	68.16	9.87	8.08	12.22

Compared with the available mean concentrations in WFE soils at the lowest downstream, Cu, Cd, Pb and As are predominantly elevated in all the soil samples of the other three sites. The highest total concentrations of Pb (223 mg/kg), Cd (7 mg/kg) and As (447 mg/kg) are found in the soils of SCH at upstream, which are 20.3, 15.2 and 45.3 times over those of WFE.

2.2 Metal concentrations in vegetables

Mean contents of metals in the dry matter of various vegetables grown on mine and smelter effluent soils are summarized in Table 3. In general, leaf vegetables (cabbage, *Brassica napus*, spinach and Chinese cabbage) accumulated much higher amount of Cd, Pb, Cu, Zn and As compared to non-leaf vegetables (cucumber, pumpkin, eggplant and capsicum) grown on river water irrigated soils at the same sites. At SCH (Table 3a), Cd, Pb, Zn and As concentrations in Chinese cabbage, Cu in brassica napus, and Zn in spinach are very high. The highest concentrations of Pb, Cd and As are found to be 17.4, 1.3 and 1.8 mg/kg, respectively, in Chinese cabbage. The highest concentration of Zn is found to be 106.2

mg/kg in spinach leaves. *Brassica napus* has a significantly high concentration of Cu in the edible parts (48.8 mg/kg). However, the metal concentrations in cucumber, pumpkin, eggplant and capsicum are generally low, except Cu and Zn in pumpkin (21.6 and 67.9 mg/kg, respectively).

At BWA and DWA (Tables 3b and 3c), like at SCH, the concentrations of all the considered elements (Cu, Zn, As, Cd and Pb) are predominantly high in the leaf vegetables (cabbage, *Brassica napus*, spinach, Chinese cabbage), except of Cu and Zn in cabbage at BWA, and Cu in cabbage and spinach, and Zn in cabbage at DWA. Chinese cabbage is strongly associated with high concentrations of Cd, Pb and As (1.17, 15.15 and 2.02 mg/kg, respectively, at BWA, and 0.86, 11.69 and 1.50 mg/kg respectively, at DWA). The concentrations of the considered metals in the non-leafy vegetables are generally lower, but pumpkin contains extremely high Cu and Zn concentration (20.3 and 63.2 mg/kg, respectively, at BWA, and 22.8 and 65.4 mg/kg, respectively, at DWA) in the edible parts.

At WFE, only four species of capsicum, eggplant

Table 3 Elemental concentrations in vegetables grown along the Yellow River (Baiyin, China, mg/kg dw)

Elements	Cucumber	Pumpkin	Capsicum	Eggplant	Cabbage	<i>Brassica napus</i>	Spinach	Chinese cabbage
a SCH								
Cd	0.66±0.22	0.46 ±0.08	0.41 ±0.14	0.40±0.16	0.71±0.15	1.29±0.42	1.06±0.46	1.31±0.58
Pb	10.30±2.01	10.56 ±1.96	8.15 ±2.61	4.96±3.28	10.97±3.99	11.19±0.59	15.64±3.41	17.36± 4.54
Cu	21.26±5.33	21.58±6.40	14.15±3.81	15.67±3.22	13.41±2.11	48.81±10.83	31.95±16.50	36.98±14.96
Zn	60.53±15.00	67.92±20.14	44.78±22.74	26.04±13.31	55.97±20.30	69.81±23.35	109.44±34.84	91.84±60.32
As	0.49±0.17	0.50±0.22	0.75±0.27	0.45±0.13	1.21±0.57	1.48±0.75	1.37±0.83	1.85±0.76
b BWA								
Cd	0.57±0.21	0.40±0.06	0.39±0.13	0.37±0.16	0.65±0.11	1.14±0.26	0.97±0.43	1.17±0.66
Pb	9.31±1.94	9.21±1.49	7.18±1.98	4.28±2.70	9.64±3.39	10.65±2.13	13.84±2.90	15.15±4.93
Cu	20.23±5.23	20.31±6.80	12.69±4.04	12.59±3.68	11.41±2.96	43.53±9.18	27.75±15.07	33.73±13.12
Zn	58.00±14.77	63.17±19.89	40.97±20.40	23.64±14.20	52.90±19.97	66.82±22.67	91.47±16.02	84.85±58.99
As	0.61±0.28	0.56±0.23	0.91±0.42	0.45±0.06	1.05±0.54	1.61±0.69	1.47±0.78	2.02±0.71
c DWA								
Cd	0.40±0.16	0.46±0.15	0.35±0.08	0.20±0.08	0.55±0.28	0.48±0.21	0.67±0.23	0.86±0.38
Pb	7.35±1.01	8.20±1.19	5.54±0.82	4.87±2.40	9.50±3.29	12.11±0.20	10.27±3.27	11.69±2.95
Cu	18.16±3.12	22.78±7.11	12.89±4.41	15.43±5.29	12.06±4.21	29.39±8.65	14.99±4.41	26.77±13.57
Zn	47.59±3.83	65.41±30.19	38.81±9.19	31.20±6.72	56.93±34.31	72.70±36.99	106.18±48.02	84.55±41.34
As	0.41±0.08	0.37±0.14	0.91±0.04	0.39±0.29	1.18±0.70	1.51±0.87	1.37±0.93	1.50±0.56
d WFE								
Cd	0.24±0.06	0.28±0.05	0.19±0.04	-	0.30±0.11	-	-	-
Pb	5.27±0.54	4.49±0.44	5.32±2.91	-	4.86±1.44	-	-	-
Cu	12.06±3.03	12.27±1.65	7.73±2.30	-	11.08±2.99	-	-	-
Zn	28.02±3.77	35.93±6.36	30.03±3.26	-	31.33±5.16	-	-	-
As	0.26±0.08	0.45±0.27	0.41±0.14	-	0.81±0.47	-	-	-

and Chinese cabbage are available. The mean concentrations of Cd, Pb, Cu, Zn and As are 0.25, 5.0, 10.8, 31.3, and 0.48 mg/kg, respectively, which is lower than those in the other sites.

2.3 Daily intake estimate of metals through vegetables

Daily intake of heavy metals was calculated according to the average metal concentrations in vegetables and the average amount of vegetables that local residents consume. According to the mean observed element concentrations in vegetables at each village (Table 4), the estimated daily intake amounts are listed in Table 5. Results show higher intake values that local residents consume the same amount vegetables in SCH was probably due to its shorter distance from the mine and smelter (Fig.1). Adults from SCH had the highest intake of Cd, Pb, Zn and Cu through vegetables, and those from WFE had the lowest intake of Cd, Pb, Cu, Zn and As. Zn and As intakes via vegetables were similar between BWA and DWA; consuming vegetables grown at WFE, adults will intake a lesser amount of metal.

2.4 Bio-accumulate factor (BAF) from soils to vegetables

To appraise the bio-accumulation effects of crops

Table 4 Mean concentrations of metal in vegetables from the four areas SCH, BWA, DWA and WFE (mg/kg dw)

	Number of vegetable species	Cd	Pb	Cu	Zn	As
SCH	8	0.79	11.14	25.48	65.79	1.01
BWA	8	0.71	9.91	22.78	60.23	1.08
DWA	8	0.52	8.94	19.68	65.15	1.01
WFE	4	0.25	4.97	10.73	31.47	0.49

Table 5 Estimated daily intake amounts of metals through vegetables for adults (mg/d)

	Vegetable intake, g/d	Cd	Pb	Cu	Zn	As
SCH	200	0.16	2.23	5.10	13.16	0.20
BWA	200	0.14	1.98	4.56	12.05	0.22
DWA	200	0.10	1.79	3.94	13.03	0.20
WFE	200	0.05	0.99	2.15	6.29	0.10

that uptake toxic elements from the contaminated soils, BAF (bio-accumulate factor, a ratio of element concentration in crop to that in the corresponding soil) is calculated for each crop at each site separately. The results show that BAF values of considered toxic elements for various vegetables varied greatly between vegetable species and sites (Fig.2). Mean BAFs of

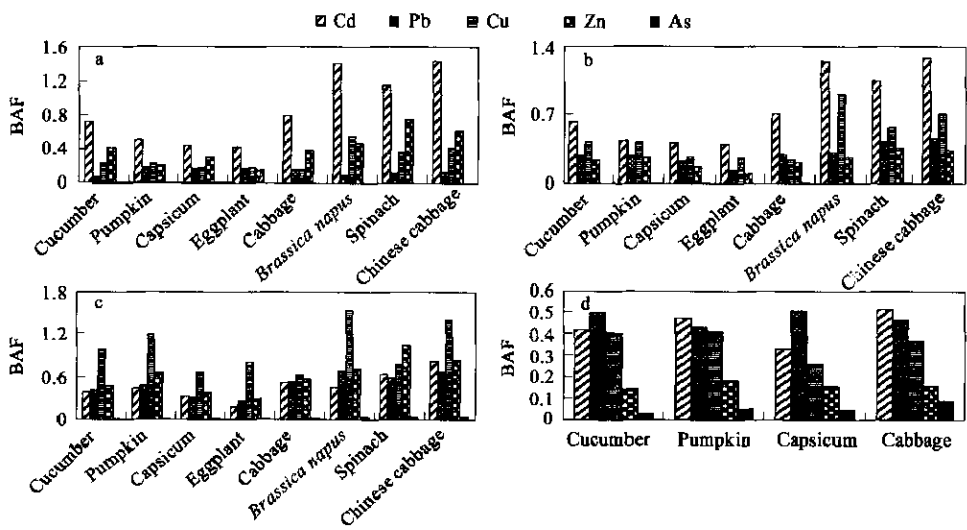


Fig.2 BAF (bio-accumulation factor), a ratio of element concentration in vegetable to that in the corresponding soil at four sites
a. SCH; b. BWA; c. DWA; d. WFE

eight vegetables for these considered elements are in the order: Cd>Zn>Cu>Pb>As in SCH and Cd>Cu>Pb>Zn>As in BWA and Cu>Zn>Pb>Cd>As in DWA. Moreover, the BAF values for Cd, Zn, Pb, Cu and As for various vegetables varied greatly between vegetable species and sites. The BAF values for Cd varied from 0.433 (eggplant) to 1.438 (Chinese cabbage) and 0.190 to 0.822 in SCH and DWA; values for As were much lower than those for Cd, varying from 0.001 (cucumber and eggplant) to 0.006 (Chinese cabbage) and 0.003 (eggplant) to 0.013 (Chinese cabbage) in SCH and BWA. The BAF values for Cu were generally slightly lower than those for Cd (except Cu in vegetables at DWA), but higher than Pb and As (except Cu in cabbage in SCH, and Cu in cucumber, pumpkin, capsicum and cabbage in WFE). The BAF values for Pb and Zn were within the similar range of variation as those for Cu.

3 Discussion

3.1 Soil contamination

In SCH, BWA and DWA, there were substantial build-up of elevated Cd, Pb, Zn, Cu, Cr and As in agricultural soils over its in gray calcareous soils in China, excepted Cu in soils in DWA (Tables 2 and 6). Whereas, Cu content in soils of DWA was only declined by 0.8%, as a result of mining and smelting effect. In WFE, on an average, mining and smelting resulted in 444%, 270% and 39% increase Cd, Zn and Cu, respectively. However, Pb, Cr and As contents in agricultural soils were declined in different degree.

To assess the impact of mining and smelting on agricultural soils, a ratio of metal concentrations in soil to the corresponding maximum allowable concentration (MAC; National Environmental Protection Agency of China, GB15618, 1995) values was computed separately for four villages (Fig.3).

Results show that of the considered elements in agricultural soils along the Yellow River (Baiyin region, China), arsenic contamination is the heaviest, especially in SCH. The usual arsenic content in uncontaminated soils in the world ranges from 1 to 40 mg/kg, and in Chinese agricultural soil is 11.2 mg/kg (Liu *et al.*, 2005). But in the WFE soil, As concentration is quite low (9.9 mg/kg). Even so, mean As concentrations of soils from BWA and DWA are still over that of threshold of As in gray calcareous soils in China by 18.6 and 3.9 times, respectively, and exceed the MAC level (30 mg/kg) by 7.1 and 1.5 times, respectively. The second most contaminated element is cadmium, with 12.4, 1.4 and 1.8 times, respectively, exceeding the MAC level in SCH, BWA and DWA. Comparing Cd concentration in soils of SCH, BWA and DWA with that of threshold of Cd in gray calcareous soils in China, we can find that Cd concentrations are still much higher. The following are Cu, with concentrations exceeding the corresponding MAC levels by 1.3 times in the soils of BWA, indicating a slight contamination in the site. At WFE, the ratio is less than 1 for these elements,

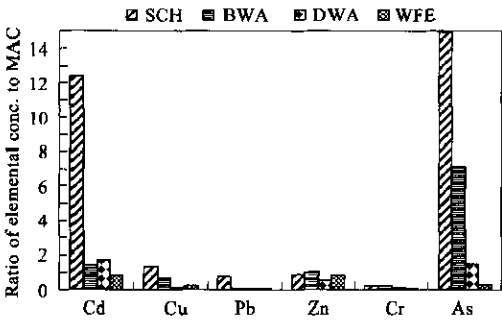


Fig.3 The ratios of metal concentrations in soil to the corresponding maximum allowable concentration (MAC) values

A ratio > 1 indicates that this element concentration exceeded the corresponding MAC level, thus contamination occurred in the soil

indicating no contamination here.

Moreover, the ratios of mean concentrations of Cr to the corresponding MAC levels are in the range of 0.05–0.2, indicating no Cr contamination in agricultural soils along the Yellow River.

3.2 Downstream variations in metal concentrations within the agricultural soils

The agricultural soil data show that in general, there is a downstream decrease in the magnitude of contamination of the agricultural fields from the mines and Baiyin City (non-ferrous metals smelting) along the Yellow River (Fig.4), similar to that found in other metal mining contaminated river systems (Hudson-Edwards *et al.*, 2003; Miller *et al.*, 2004). Inspection of Table 2 illustrates that the fields at SCH and BWA are contaminated with Cd, Cu, Pb, As and Zn compared to background levels in gray calcareous soils in China (Table 6). At DWA, mean concentrations of As and Cd exceed Chinese recommended Maximum allowable concentrations (MAC) for agricultural soil (Fig.3). Further downstream at WFE,

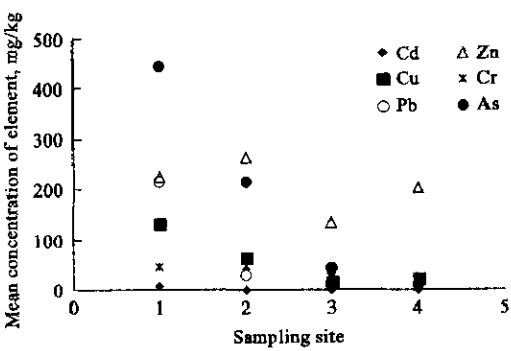


Fig.4 Mean concentrations of metal and As in soils from four sampling sites
1. SCH; 2. BWA; 3. DWA; 4. WFE

Zn, Cd and Cu concentrations in this soil still exceed the corresponding background levels in Chinese gray calcareous soils, but only indicating a slight elevation in these sample sites. However, a significant number of the samples are clearly contaminated as demonstrated by comparison to background data in grey calcareous soil at SCH and BWA (Table 6).

Table 6 Maximum allowable concentration (MAC) and threshold levels of metals in contaminated and natural soils and vegetables (mg/kg dw) and recommended dietary allowance (RDA) or provisional tolerable daily intake for adult (PTDI)

Element	MAC of elements in agricultural soils in China ^a	Threshold of elements in gray calcareous soils in China ^a	World range of elements in non-polluted soils ^b	Maximum permit limit of elements in vegetables, mg/kg fresh weight ^c	RDA or PTDI for adult (mg/d) set by WHO/FAO ^d
Cd	0.6	0.09	0.07–1.10	0.05	0.072
Pb	300	18.2	10–70	0.2	0.429
Cu	100	20.3	6–60	10.0	1.5–3.0
Zn	250	55.1	17–125	20.0	15
As	30	11.5	1–40	0.5	0.58 ^e
Cr	200	90	5–121	—	—

Notes: ^a National Environmental Protection Agency of China, GB15618, 1995; ^b Kabata-Pendias and Pendias, 1992; ^c Quote in food hygienic standard for vegetable security of China, GB4810-1994, GB2762-1994, GB15201-1994, GB14935-1994, GB14961-1994 and GB15199-1994; ^d Iyengar and Nair, 2000; ^e Liu *et al.*, 2005

The least contaminated site downstream of WFE (Table 2 and Fig.4). It is located further than 160 km downstream from Baiyin non-ferrous metals mine, and therefore, appears to represent an exception to the expected downstream trends in contaminant levels. In contrast to the immediately near Baiyin non-ferrous metals mining and smelting area of SCH and BWA, however, its fields are also irrigated using the Yellow River water. The difference in contaminant magnitudes suggest that at least some of the metals observed within the soils are derived from irrigation practices. In fact, as mentioned above, most of the contamination along the Yellow River must be derived from irrigation with river water and thus, the continued use of contaminated irrigation waters could lead to a further buildup of metals within the agricultural fields (Xiong *et al.*, 2003; He *et al.*, 2003, 2004; Zhang, 2005; Feng *et al.*, 2005; Yang, 2005).

While irrigation waters appear to be an important

source of contaminants within the soils, decreases in metal concentrations with increasing distance from Baiyin non-ferrous metals mining and smelting (China), indicates that the metals are primarily derive from polluted alluvial sediments, also receive contaminants by irrigation depositional processes (Zeng, 1995; Yang, 2005).

In conclusion, the extent of soil contamination among these four affected sites is in the order of $C_{SCH} > C_{BWA} > C_{DWA} > C_{WFE}$ (Fig.4 excepted of Zn levels in BWA and WFE). Arsenic and Cd are the most contaminated elements in the upstream sample sites, and Cu concentrations in SCH and Zn concentrations BWA soil still exceed the corresponding MAC levels, respectively.

3.3 Metal concentrations in vegetables

Since maximum permit limit (MPL) is the most commonly used vegetable test for assessing the extent of contamination of metals in vegetables grown on

contaminated soils (Türkdogan *et al.*, 2002; Warren *et al.*, 2003; Liu *et al.*, 2005), ratios were worked out between vegetable metal concentrations (fresh weight; a factor of 0.085 was used to convert the dry to fresh weight of these green vegetables (Rattan *et al.*, 2005))

and MPL (Table 6). A ratio>1 indicates a certain extent of contamination. Results indicate that the ratios of considered toxic elements for various vegetables varied greatly between vegetable species and sites (Fig.5).

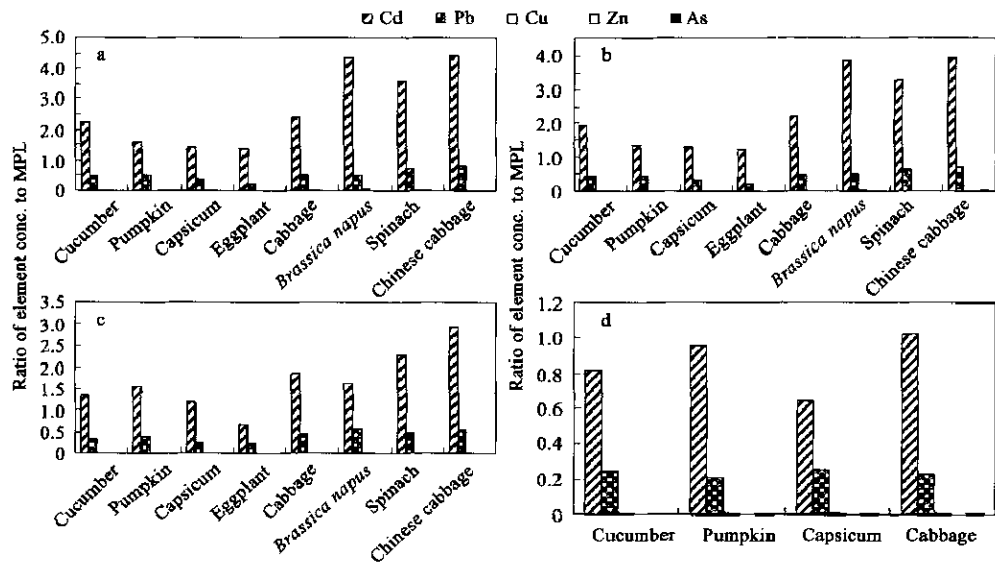


Fig.5 Ratios of element concentrations (fresh weight) in the vegetables from the sample sites (Baiyin, China) to the maximum permit limits (MPL) a. SCH; b. BWA; c. DWA; d. WFE

Among eight vegetables analyzed, Chinese cabbage, a common leafy vegetable consumed by local inhabitants, is the most contaminated species. Chinese cabbage can accumulate high concentrations of Cd, which are 4.5 times higher than the MPL value at SCH and 4.0 times at BWA, respectively. It is important to note that the ratios of Cd at SCH, BWA and DWA range from 1.2 to 3.9 in other leafy vegetables, exception is Cd in eggplant in DWA, respectively, and also exceed MPL values (Figs.5a, b and c). This indicates that vegetables, particularly leafy vegetables have the ability of preferential Cd uptake from soil. Stalikas *et al.* (1997) have found that spinach and lettuce could accumulate high Cd concentration in the edible parts, probably because Cd is found in an active form in soils (Hernandez *et al.*, 2003). In addition, leafy vegetables also can accumulate high concentrations of Pb in the SCH, BWA and DWA, although not exceed MPL values (Fig.5). Miller *et al.* (2004) and Lacatusu *et al.* (1996) found that Pb concentrations in lettuce is higher than onions and carrots, suggesting that the accumulation effect strongly depends on the crop physiological properties, or on the mobility of metal in soils, not on the total element concentrations in the soils.

Brassica napus can accumulate high concentrations of Cu in the SCH, BWA and DWA. Spinach has a high Zn ratio in SCH and DWA. However, the ratio for the As elements is very low in four sample sites (Fig.5a, b, c and d). Liu *et al.* (2005) found that

Cd has high bio-availability, whereas As has the lowest bio-availability. They give a good explanation for the low contamination of arsenic in crops, despite the high arsenic concentration in the soils, and high contamination extent of Cd in crops, even if its concentrations are quite lower in the soil in comparison with As.

At WFE, where the distance is farther from mine area, the ratios of the considered elements in vegetables are general low (<1), exception is Cd in cabbage (=1.0).

These data suggest that the consumption of vegetables from the non-ferrous metals mining and smelting sites, Baiyin, China, is generally a significant exposure pathway. It is possible, however, that the accumulation is related to the Baiyin mining and smelting activities.

3.4 Human exposure to metal contamination

Consuming vegetables grown in the influencing area by non-ferrous metals mining and smelting in Baiyin, China, human beings are exposed to metal contamination. By comparing the data from Wang *et al.* (2004) for vegetables grown in Tianjin, China, which are average Pb concentrations of 0.018 mg/kg and average Cd concentrations of 0.025 mg/kg in vegetables, we can find that Cd and Pb concentrations in the vegetables grown around non-ferrous metals mining and smelting sites are much higher.

The daily intake amounts of Cd, Pb, and Cu from the vegetables grown are much higher than the

recommended levels (Table 6) by 2.2, 5.2, and 1.7 times, respectively, at SCH, by 1.9, 4.6 and 1.5 times, respectively, at BWA, and by 1.4, 4.2 and 1.3 times, respectively, at DWA. The daily dietary intake amount of arsenic from the vegetables grown at three sample sites is lower than the provisional tolerable daily intake (PTDI) value (0.58 mg/kg).

High concentration of Zn in food and good nutrient state can help human stand metal toxicity (King and Keen, 1994). Türkdogan *et al.* (2002) suggested that the high prevalence of upper gastrointestinal cancer rates in Van region (Turkey) is related to the high concentrations of Co, Cd, Pb, Mn, Ni and Cu, and extremely low concentration of Zn in the soil and crops grown in the area. Roychowdhury *et al.* (2003) found that nutritional level of the food that people consumed is an important factor to arsenic toxicity. Humans receiving nutritious food can tolerate arsenic toxicity up to a certain range. Vegetables grown in non-ferrous metals mining and smelting waste affected areas (Baiyin, China), although the major contribution to daily intake of metals is from vegetables, people also intake metals from cereal, air, water and everything in the environment as well. As a consequence, a large daily intake of these vegetables is likely to cause a detrimental health hazard to the consumer, particularly these metals of Cd. Previously investigation also found that the concentrations of cadmium in hair or excreta (urine) was several times over those obtained from unpolluted regions (Gansu Environment Monitoring Station, 1984). However, in spite of these highly contaminated vegetables having been consumed by the local inhabitants for many years, no prevalent disease is reported in this area. The reasons may be the good nutrition status and high Zn concentration in the foods.

3.5 Metal translocation between soil and vegetables

Soil-to-plant transfer is one of the key components of human exposure to metals through foodchain. In order to assess the health risk associated with soil contamination with metals, it is necessary to establish mathematical models to predict the transfer of metals from soil to plant tissues (edible parts) (Hough *et al.*, 2003). For better prediction of the models, it requires large datasets on soil to plant bio-accumulate factor (BAF) for different soil types and different plant species. In this study, the soil-to-plant BAF for various metals and for most common vegetables consumed by local residents were calculated (Fig.2). The result indicates that uptake of metals by vegetables does not increase linearly with increasing concentrations of metals in soils. This is in concurrence with the findings of Hooda *et al.* (1997). The apparent advantage of this phenomenon is that although long-term polluted water irrigation, mining

and smelting wastes and other agrochemicals resulted into elevated concentration of metal in soil, the same would not be proportionately transferred to food chain. Taking all the vegetables together, relative orders of transfer of metals from soil to plants grown on four sample site soils are Cd > Cu > Zn > Pb > As. These results show that as far as entry of these metals to food chain plants is concerned, Cd has the greatest potential, followed by Cu, Zn and Pb, whereas As has the lowest bio-availability. Based on the BAFs, relative efficiency of eight vegetables to absorb metals from heavily contaminated soil (in SCH) could be arranged in the following order:

Cd: Chinese cabbage > *Brassica napus* > spinach > cabbage cucumber > pumpkin > capsicum > eggplant.

Cu: *Brassica napus* > Chinese cabbage > spinach > cucumber > pumpkin > capsicum > eggplant > cabbage.

Zn: spinach > Chinese cabbage > *Brassica napus* > cucumber > cabbage > capsicum > pumpkin > eggplant.

Pb: pumpkin > capsicum > eggplant > cabbage > Chinese cabbage > spinach > *Brassica napus* > cucumber.

As: Chinese cabbage > *Brassica napus* > spinach > cabbage > capsicum > pumpkin > cucumber > eggplant.

This information will be very useful in selecting the suitable vegetables to be grown on metal-contaminated soils.

Our results also show that BAFs values differed significantly ($p < 0.001$) between locations and plant species. The difference in BAFs between locations may be related to the vegetable crop physiological properties, soil nutrient management and soil properties. In our study, the soils from WFE are generally lower in organic matter and clay content and soil pH high (data not shown). The high soil pH can stabilize soil toxic elements, resulting in decreased leaching effects of the soils toxic elements. In the meantime, because the toxic elements are stabilized due to the high soil pH value, the element concentrations in the soil solution will be quite low, this will restrain the absorbability of the elements from the soil solution and the translocation into the crop tissues. Liu *et al.* (2005) found that BAF values for Cd or Zn are negatively correlated to the soil pH value and a positive relationship between the element concentrations and the corresponding soil pH values (pH values range from 4.7 to 8.2); Baroni (2004) and Liu *et al.* (2005) found that there no linear relationship is found between the BAFs with the soil properties (OM, OC, N, C/N, CEC, and total concentration of element in soil). This supports the assessment that the

accumulation effect strongly depends on the soils chemical and biological properties and crop physiological properties, and the other factor, such as soil nutrient management, in this study, we do not attempt to investigate in different sites. These data clearly show that, by selecting particular vegetables, it is possible to reduce the risk of human exposure to soil metal contaminations. According to the BAFs calculated in this study, we may draw the conclusion that leafy vegetables (cabbage, *Brassica napur*, Chinese cabbage and spinach) are high Cd-accumulator in study area. Therefore, we strongly suggest that in Baiyin non-ferrous metals mining and smelting contaminated area (along the Yellow River) one should avoid eating the vegetables listed above in order to reduce health risks.

4 Conclusions

The heavy metal content of agricultural soils was examined in four villages located between approximately 14 and 160 km from the mines and metal smelters at Baiyin region. The most significantly contaminated soils occurred upstream at SCH where Cd, Cu and As concentrations exceeded maximum allowable concentrations for agricultural use. Further downstream the degree of contamination semi-systematically decreased, and the ratios of metal concentrations to maximum allowable concentrations are very low. Contamination of the soils results from the mining and smelting activities, the agricultural management (such as the input of agrochemicals), or a combination of these two processes.

Among the eight species of vegetables analyzed, non-leafy vegetables are generally less contaminated than those leafy vegetables cultivated in same area. Chinese cabbage is the most severely contaminated, the concentrations of Cd exceed the maximum permit levels at SCH, BWA and DWA.

The estimated daily intake amounts of the considered toxic elements (Pb in four sample sites; Cd and Cu in SCH, BWA and DWA) from the vegetables grown have exceeded the RDA levels. Therefore, the vegetables grown in Baiyin non-ferrous metals mining and smelting affected area have a hazard effect on human's health. This area needs effective measures to cure the Cd, Pb and Cu contamination.

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