Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China)

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Abstract

In 1985, the collapse of the tailing dam in Chenzhou lead/zinc mine (Hunan, southern China) led to the spread of mining waste spills on the farmland along the Dong River. After the accident, an urgent soil cleaning up was carried out in some places. Seventeen years later, cereal (rice, maize, and sorghum), pulses (soybean, Adzuki bean, mung bean and peanut), vegetables (ipomoea, capsicum, taro and string bean) and the rooted soils were sampled at four sites: (1) the mining area (SZY), (2) the area still covered with the mining tailing spills (GYB), (3) the cleaned area from mining tailing spills (JTC), and (4) a background site (REF). Metal concentrations in the crops and soils were analyzed to evaluate the long-term effects of the spilled waste on the soil and the potential human exposure through food chains. The results showed that the physical–chemical properties of the soils obviously changed due to the different farming styles used by each individual farmer. Leaching effects and plant extraction of metals from some soils were quite weak. Certain soils were still heavily polluted with As, Cd, Zn, Pb and Cu. The contamination levels were in the order of GYB>NZS>YJTC showing that the clean-up treatment was effective. The maximum allowable concentration (MAC) levels for Chinese agricultural soils were still highly exceeded, particularly for As and Cd (followed by Zn, Pb and Cu), with mean concentrations of 709 and 7.6 mg kg\textsuperscript{-1}, respectively. These concentrations exceed the MAC levels by 24 times for As and 13 times for Cd at GYB. Generally, the edible leaves or stems of crops were more heavily contaminated than seeds or fruits. Ipomoea was the most severely contaminated crop. The concentrations of Cd and Pb were 3.30 and 76.9 mg kg\textsuperscript{-1} in ipomoea leaves at GYB, which exceeded the maximum permit levels (0.5 mg kg\textsuperscript{-1} for Cd and 9 mg kg\textsuperscript{-1} for Pb) by 6.6 and 8.5 times, respectively. Taro (+skin) could accumulate high concentrations of Zn and Cd in the edible stem, and rice and capsicum had high Cd concentration in the edible parts. However, the toxic element concentrations in maize, sorghum, Adzuki bean, soybean and mung bean remained lower than the threshold levels. The bio-accumulation factors (BAFs) of crops were in the order: Cd>Zn>Cu>Pb>As. BAF was typically lower in the edible seeds or fruits than in stems and leaves. The accumulation effect strongly depends on the crop’s physiological properties, the mobility of the metals, and the availability of metals in soils but not entirely on the total element concentrations in the soils.
Even so, the estimated daily intake amount of Cu, Zn, Cd, and Pb from the crops grown in the affected three sites and arsenic at SZY and GYB exceeded the RDA (Recommended dietary allowance) levels. Subsequently, the crops grown in Chenzhou Pb/Zn mine waste affected area might have a hazardous effect on the consumer’s health. This area still needs effective measures to cure the As, Cd, Pb, Zn and Cu contamination.

Keywords: Heavy metals; Arsenic; Soil; Crop; Contamination; Lead/zinc mine; China

1. Introduction

Mining activity is a chief source of metals entering into the environment. In the process of mining exploitation and ore concentrating, mine tailing and wastewaters are created, and dust is emitted. This results in the surrounding environment being severely polluted. The most serious problem is that of spilled mine tailing. Since 1970, there have been 35 reported major mine tailing dam failures around the world resulting in significant soil and river pollution and the loss of more than 500 lives (Macklin et al., 2003). In 2000 alone, there were a total of five reported accidents (in China, Romania, Sweden, and USA; Macklin et al., 2003).

In China, on August 25th, 1985, the mine tailing dam of Chenzhou lead/zinc mine (Hunan, southern China) collapsed because of heavy rain. In that disaster, a strip of farmland about 400 m in width on both sides of the Dong River channel was covered with an about 15-cm-thick layer of black sludge. After the collapse of the dam, an emergency soil clean-up procedure was quickly carried out in some places. The toxic sludge and a major portion of the contaminated soil surface were mechanically removed. Nevertheless, most of the contaminated farmlands are still covered with spills and a part of these contaminated farmlands are cultivated at present.

Crops can uptake toxic elements through their roots from contaminated soils, and even leaves can absorb toxic elements deposited on the leaf surface. Queirolo et al. (2000) found that corn and potatoes (+skin), growing in a volcano-influenced location of Talabre (Northern Chile), contain very high arsenic concentration in the edible parts (1.85 and 0.86 mg kg\(^{-1}\) fresh weight, respectively), exceeding the National Standard of Chile for arsenic (0.5 mg kg\(^{-1}\)) by approximately 400% and 180%, respectively.

Chronic lower level intakes of toxic elements have damaging effects on human beings and other animals (Ikeda et al., 2000), since there is no efficient mechanism for their elimination, and the detrimental impact becomes apparent only after several years of exposure (Bahemuka and Mubofu, 1999). Consuming food contaminated by Pb, Hg, As, Cd and other metals can seriously deplete body stores of Fe, vitamin C and other essential nutrients, leading to decreased immunological defenses, intrauterine growth retardation, impaired psycho-social faculties and disabilities associated with malnutrition (Iyengar and Nair, 2000). Türkdogan et al. (2003) 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.

In Chenzhou Pb/Zn mine area (Fig. 1), previous investigations have shown that soil and waters were severely polluted by heavy metals (Zeng et al., 1995, 1997). It is therefore anticipated that crops grown in this area cannot be free from metals pollution. Thus far, there still has been very little published information on the uptake of toxic elements by cereal, vegetables and pulses in the Chenzhou Pb/Zn mine affected area after the mine tailing dam collapse. The objective of this paper is; (1) to quantify the content of metal in soil and crops; (2) to investigate the degree of pollution and the daily intake amount of toxic
elements through foods; (3) to identify the relationship between accumulation of toxic elements by plants and the extent of soil contamination; (4) to assess the long-term effects on the environment surround.

2. Materials and methods

2.1. Description of the sampling sites

Chenzhou lead/zinc mine is located about 10 km east of Chenzhou city, Hunan Province, southern China (Fig. 1). In 1988, the annual production capacity was 4,855 tons of lead, 4,869 tons of zinc, 300 tons of tungsten, 87 tons of bismuth, 200 tons of molybdenum, 2.33 tons of sulfur and 15.42 tons of silver. More than 3,800 workers were engaged in the mining, smelting, and transport services associated with the mining activities, which continue at full speed today.

The Dong River runs through this area, and the farmlands are irrigated with the water from the river. The soil here is yellow red soil (by Chinese system). Four sampling sites were selected along Dong River (Fig. 1). SZY (near Shizuyuan, Chenzhou Pb/Zn mine, at 25°47’26”N, 113°07’34”E) was affected by atmospheric deposition, mining activities and polluted water. GYB (close to Guanyin Bridge, at 25°49’39”N, 113°08’32”E) was located approximately 8 km from the mine down Dong River. The soil was covered with mine tailing spills after the tailing dam collapsed in August 1985; this mine tailing has not been removed. JTC (near Jintianchun, at 25°50’57”N, 113°08’40”E) was located approximately 9.5 km from the mine. This area was affected by the spills, but the sludge was removed immediately after the tailing dam collapsed. An REF (reference background sample site) was chosen on a hill about 10 km from the mine upper Dong River.

2.2. Crops and soils sampling

Eleven crop species were selected for this study: cereal (rice, maize, sorghum), pulses (soybean, Adzuki bean, mung bean and peanut) and vegetables (ipomoea, String bean, taro and capsicum), which
represented the major crop species growing in this area in the sampling season of August 2002.

At each sampling site, samples were collected in the field by means of a random sampling method. Crops and their rooted soil samples (at 0–15 cm in depth) were collected.

2.3. Sample pre-treatment

In the laboratory, the crop samples were carefully cleaned with de-ion water. The root, stem, leaf and fruit were cut into pieces by a pair of plastic scissors; skin and flesh parts of rice grains, sorghum grains and bean were separated by hand. Afterward, all the crop samples were oven-dried to constant weights. So as to obtain finely divided specimens for analysis, the crop samples were ground by a stainless grinder (IKA analysis grinder A10). To check for the possibility of contamination by the stainless grinder during the sample grinding, a quantity of samples were ground in an agate mortar.

The soil samples, after air-drying at room temperature, were sieved with nylon mesh (2 mm). The <2-mm fraction was grinded in an agate mortar for analysis.

2.4. Analytical work

2.4.1. Physical–chemical parameters of soils

The physical–chemical parameters of soils (pH, organic matter, organic carbon and nitrogen contents, C/N, CEC (cation exchangeable capacity) and exchangeable cations) were analyzed at the INRA Laboratory of Soil Science-Arras (France), following the classical methods (Ponette et al., 1997).

2.4.2. Metal analysis

Metal concentrations were analyzed by a Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS) at the Laboratoire des Mécanismes et Transferts en Géologie (Toulouse, France). Complete dissolution of samples was performed by an acid digestion method based on the procedure described by Hernandez et al. (2003) with minor modification.

2.4.3. Quality control

For the quality control, standard reference materials SRM1515 (apple leaves, from National Institute of Standards and Technology, USA) for crop samples, and CRM142R (light sandy soil, from Commission of the European Communities) for soil samples were used. When compared to the results generally obtained in the literature, the results obtained were in excellent agreement with the certified concentrations (Table 1).

2.5. Daily intake estimate of metals through food

The daily intake amount (DI) of metals depends on both the element concentration ([M]) and the amount of the respective food consumed (W). We choose the

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified value ± S.D.</th>
<th>Measured mean value ± S.D.</th>
<th>Recovery (%)</th>
<th>Certified value ± S.D.</th>
<th>Measured mean value ± S.D.</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>0.03 ± 0.002</td>
<td>0.024 ± 0.007</td>
<td>80</td>
<td>Sc</td>
<td>–</td>
<td>9.477 ± 0.580</td>
</tr>
<tr>
<td>Co</td>
<td>0.11 ± 0.007</td>
<td>0.111 ± 0.007</td>
<td>124</td>
<td>Co</td>
<td>12.322 ± 0.66</td>
<td>11.633 ± 0.275</td>
</tr>
<tr>
<td>Ni</td>
<td>0.15 ± 0.007</td>
<td>0.945 ± 0.066</td>
<td>104</td>
<td>Ni</td>
<td>64.480 ± 2.46</td>
<td>62.648 ± 0.887</td>
</tr>
<tr>
<td>Cu</td>
<td>12.5 ± 0.3</td>
<td>12.687 ± 0.743</td>
<td>101</td>
<td>Cu</td>
<td>69.690 ± 1.24</td>
<td>66.364 ± 1.249</td>
</tr>
<tr>
<td>Zn</td>
<td>0.038 ± 0.007</td>
<td>0.035 ± 0.012</td>
<td>92</td>
<td>Zn</td>
<td>–</td>
<td>97.144 ± 6.357</td>
</tr>
<tr>
<td>As</td>
<td>0.181 ± 0.027</td>
<td>–</td>
<td>–</td>
<td>As</td>
<td>–</td>
<td>17.800 ± 1.285</td>
</tr>
<tr>
<td>Cd</td>
<td>0.17 ± 0.002</td>
<td>0.202 ± 0.011</td>
<td>154</td>
<td>Cd</td>
<td>0.336 ± 0.036</td>
<td>0.331 ± 0.025</td>
</tr>
<tr>
<td>Pb</td>
<td>0.470 ± 0.024</td>
<td>0.479 ± 0.014</td>
<td>102</td>
<td>Pb</td>
<td>40.19 ± 1.85</td>
<td>40.168 ± 4.923</td>
</tr>
</tbody>
</table>

Recovery (%) = (Mean measured value / Mean certified value) × 100%; –: value not certified.
average quantity of food consumed by a person (70 kg
in body weight) as 445, 55 and 105 g day\(^{-1}\) for cereal,
pulses and vegetables respectively (Tripathi et al., 1997). Then, the total daily intake quantity of Cu, Zn,
As, Cd and Pb by a person is calculated as:
\[ DI = [M] \times W. \]

2.6. Provisional tolerable daily intake (PTDI) of arsenic calculation

The daily intake of arsenic includes both organic and inorganic types. Inorganic arsenic is more toxic to biota than organic arsenic. The provisional tolerable daily intake for an adult (PTDI) of inorganic arsenic (established by WHO in 1989) is 2.14 µg inorganic arsenic per kg body weight per day. Being that there is no standard value for total arsenic intake for an adult, we have calculated the total As intake by averaging the percentages of As found in rice, vegetables, and fruits (35%, 5%, 10%, respectively) obtaining 25% (WHO, Environmental Health Criteria 224, 2001). Based on an average body weight of 68 kg in adults (established by WHO), the PTDI of total arsenic should be 0.58 mg day\(^{-1}\) for adult.

3. Results

3.1. Physical–chemical characteristics of soil samples

Descriptive statistics of physical–chemical characteristics of the soils are presented in Table 2. The REF soil is acidic (pH 4.7). Soils at SZY are weakly acidic, with about 80 % of the soils having pH values lower than 5.6. Most soils at GYB are alkaline, about 70 % of the soil pH values are higher than 7.0. Although a large variability is observed among the individual samples soils from JTC, the mean pH value is nearly neutral.

Mean organic matter and organic carbon contents of the soils decrease in the order:SZY>GYB>JTC, REF (Table 2), while mean nitrogen content shows the order: SZY>GYB>JTC, REF.

Cation exchange capacities (CEC) in the soils from GYB and JTC are higher than that from SZY. The REF soil is the lowest. Ca\(^{2+}\) is the dominated element of CEC, followed by Al\(^{3+}\) and Mg\(^{2+}\).

3.2. Metals concentrations in soils

Table 3 shows the mean total concentrations and the ranges of the considered metals in the soil samples
of the four sites. In general, at REF site, concentrations of Cu, Zn, As and Pb are quite low. At the other three sites, the mean concentrations of Zn, As, Cd and Pb decrease in the order: GYB > SZY > JTC, while the mean concentrations of Cu and Sn show the order: SZY > GYB > JTC. However, the mean concentrations of Cr, Ni and Zr in the soils from JTC are the highest. No significant variations of the mean concentrations of Sc and Co are found among the three sites. Among the individual soil samples within each site, strong variability is observed in the concentrations of Zn, As, Cd, Sn and Pb at SZY and GYB.

Compared with the available mean concentrations in REF soils, Cu, Zn, As, Cd and Pb are predominantly high in all the soil samples of the other three sites. The highest total concentrations of Pb (1444 mg kg\(^{-1}\)), Zn (1252 mg kg\(^{-1}\)) and As (1226 mg kg\(^{-1}\)) are found in the soils of GYB, which are 23.9, 8.9, and 12.6 times over those of REF.

### 3.3. Metal concentrations in crops

Metal concentrations in the measured crops are listed in Table 4.

At SZY (Table 4a), Cu, Zn, As, Cd and Pb concentrations in ipomoea leaves and stems and Zr in ipomoea leaves are very high. The highest concentrations of Cu, Zn and Cd are found to be 74.2, 442.8 and 12.8 mg kg\(^{-1}\), respectively, in ipomoea leaves. Taro (+skin) has a significantly high concentration of Zn and Cd in the edible stem (528.7 mg Zn kg\(^{-1}\) and 3.64 mg Cd kg\(^{-1}\)). However, the metal concentrations in maize, capsicum and string bean fruits are generally low except Cd in capsicum (1.37 mg kg\(^{-1}\)) and string bean fruits (0.67 mg kg\(^{-1}\)).

At GYB (Table 4b), like at SZY, the concentrations of all the considered elements (Co, Cu, Zn, As, Cd and Pb) are predominantly high in the ipomoea leaves and stems. Taro (+skin) is strongly associated with high concentrations of Zn, As and Pb (243.9, 16.6 and 15.2 mg kg\(^{-1}\), respectively). The concentrations of the considered metals in the seeds or fruit foods are generally much lower, but rice grain contains extremely high Cd concentration (6.99 mg kg\(^{-1}\)), sorghum and capsicum are high in Pb (4.25 mg kg\(^{-1}\) in sorghum and 23.8 mg kg\(^{-1}\) in capsicum), and string bean are high in Pb (13.3 mg kg\(^{-1}\)) and As (7.87 mg kg\(^{-1}\)) in the edible parts.

At JTC (Table 4c), the element concentrations are generally low, except for Zn, Cd and Pb in taro stem (+skin), Cd, Pb in capsicum fruits, and Cu, Zn, Pb and As in string bean pods.

At REF site, only one crop species of string bean is available. The mean concentrations of Cu, Zn, As, Cd and Pb are 2.8, 46.9, 0.54, 0.21 and 0.84 mg kg\(^{-1}\), respectively, which is lower than those in the other sites.

Finally, the total concentrations of Sc, Co, Zr and Sn are generally low in all these edible parts of the analyzed crop samples except ipomoea.

### Table 3
Mean total concentrations of metals in the soils of SZY, GYB, JTC and REF soil (<2 mm, mg kg\(^{-1}\) dry matter)

<table>
<thead>
<tr>
<th>Elements</th>
<th>SZY ((n=5))</th>
<th>GYB ((n=6))</th>
<th>JTC ((n=4))</th>
<th>REF ((n=4))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min</td>
<td>Max</td>
<td>Mean</td>
</tr>
<tr>
<td>Sc</td>
<td>8.56</td>
<td>2.81</td>
<td>24.35</td>
<td>6.44</td>
</tr>
<tr>
<td>Cr</td>
<td>48.52</td>
<td>46.79</td>
<td>49.34</td>
<td>51.28</td>
</tr>
<tr>
<td>Co</td>
<td>11.94</td>
<td>9.09</td>
<td>13.73</td>
<td>9.88</td>
</tr>
<tr>
<td>Ni</td>
<td>23.16</td>
<td>20.92</td>
<td>24.85</td>
<td>22.17</td>
</tr>
<tr>
<td>Cu</td>
<td>174.03</td>
<td>111.58</td>
<td>221.4</td>
<td>135.83</td>
</tr>
<tr>
<td>Zn</td>
<td>855.44</td>
<td>612.95</td>
<td>1064.21</td>
<td>1000.71</td>
</tr>
<tr>
<td>As</td>
<td>459.02</td>
<td>346.77</td>
<td>533.49</td>
<td>709.29</td>
</tr>
<tr>
<td>Zr</td>
<td>114.11</td>
<td>106.09</td>
<td>132.39</td>
<td>100.35</td>
</tr>
<tr>
<td>Cd</td>
<td>6.77</td>
<td>4.11</td>
<td>9.05</td>
<td>7.57</td>
</tr>
<tr>
<td>Sn</td>
<td>255.43</td>
<td>166.27</td>
<td>326.73</td>
<td>93.18</td>
</tr>
<tr>
<td>Pb</td>
<td>751.98</td>
<td>305.28</td>
<td>1061.54</td>
<td>1088.30</td>
</tr>
</tbody>
</table>

nd: not determined.
3.4. Metals distribution in different parts of grain

Usually, only the flesh part of grains is consumed by human beings, but the husk part is consumed sometimes by animals. Thus, it is interesting to compare metal distribution in the husks with that in the flesh parts. Rice and sorghum were chosen as examples. Table 5 shows that metal concentrations in the husks are generally higher than those in the flesh, especially for Pb, As and Zn. At GYB, the concentrations of Pb, As, and Zn in the husks are higher than those in the flesh by 28, 8.5 and 2.1 times respectively for rice, and by 5.9, 5.2 and 1.7 times respectively for sorghum, which indicates that...
a major part of the metal is blocked in the husk. The exception is Cu in rice, which is higher in the flesh than that in the husk by 1.9 times at JTC, and by 1.4 times at GYB.

3.5. Daily intake estimate of metals through foods

Table 6 shows the mean observed element concentrations in cereal (including: rice, sorghum, maize); Pulses (including: soybean, Adzuki bean, mung bean and peanut) and vegetables (including: taro, ipomoea (stems and leaves), capsicum and string bean (usually the tender pods of string bean are consumed as green vegetable)) at each site. The daily estimated intake amounts are listed in Table 7. The trends of mean concentrations of Cu, Zn, As, Cd and Pb in different crop types are in the order of vegetables > pulses > cereal. By consuming foods grown at GYB, an adult will intake 6.92 g Cu, 38.66 g Zn, 4.94 g As, 1.23 g Cd, and 7.0 g Pb a day. Consuming foods grown at JTC, adults will intake a lesser amount of metal.
4. Discussion

4.1. Long-term effect on soil physical–chemical characteristics and metal concentrations

Comparing the pH values of soils from the four sites and those history data in the literature (pH values range from 5.12 to 5.89, Zeng et al., 1997), the pH values of soils from GYB and one soil sample from JTC (see Table 2) are evidently raised (pH>6.0), and a wide range of variation is found between these samples. This situation may be the result of the addition of lime to the soil to stabilize toxic metal mobility. The large variations on the other parameters (OM, OC, N, CEC, etc.) may be due to the different farming styles practiced by individual farmers.

Comparing metal concentrations measured on 1997, which were 452–1279 mg kg\(^{-1}\) Pb, 559–1165 mg kg\(^{-1}\) Zn, 3.98–12.19 mg kg\(^{-1}\) Cd, 200.8–1351.9 mg kg\(^{-1}\) As, and 54.7–104.7 mg kg\(^{-1}\) Cu in the soils of GYB (Zeng et al., 1997), with our present data, no obvious decrease of metal concentrations is observed, indicating that the leaching effects and plant extraction functions are quite weak when compared to the extremely high concentration of metals in the soils. The high pH value in the soils can also help weaken these effects.

Fig. 2. Comparisons between element total concentrations [Element] in the soils of SZY, GYB and JTC and the maximum allowable concentrations [MAC]. —: threshold line.

4.2. Soil contamination extent

The extent of soil contamination was appraised by comparing the total concentrations of the metals in the soils from Chenzhou Pb/Zn mine area (southern China) with the maximum allowable concentrations (MAC) of metals in agricultural soil of China (National Environmental Protection Agency of China, GB15618, 1995), which are presented in Table 8. The ratios of metal concentrations in soil to the corresponding MAC values are illustrated in Fig. 2. A ratio>1 indicates that this element concentration exceeded the corresponding MAC level, thus contamination occurred in the soil.

Table 8

<table>
<thead>
<tr>
<th>Element</th>
<th>MAC of elements in agricultural soils in China*</th>
<th>Threshold of elements in natural background soil in China*</th>
<th>World range of elements in non-polluted soilsb</th>
<th>Maximum permit limit of elements in vegetables and fruitsc</th>
<th>RDA or PTDI for adult (mg day(^{-1})) set by WHO/FAOd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>200</td>
<td>90</td>
<td>5–120</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Co</td>
<td>–</td>
<td>–</td>
<td>0.1–20</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>Ni</td>
<td>50</td>
<td>40</td>
<td>1–200</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>35</td>
<td>6–60</td>
<td>20</td>
<td>1.5–3.0</td>
</tr>
<tr>
<td>As</td>
<td>30</td>
<td>15</td>
<td>1–15</td>
<td>20f</td>
<td>0.58f</td>
</tr>
<tr>
<td>Zn</td>
<td>250</td>
<td>100</td>
<td>17–125</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>Cd</td>
<td>0.6</td>
<td>0.2</td>
<td>0.07–1.10</td>
<td>&lt;0.5</td>
<td>0.072</td>
</tr>
<tr>
<td>Pb</td>
<td>300</td>
<td>35</td>
<td>10–70</td>
<td>9</td>
<td>0.429</td>
</tr>
</tbody>
</table>

a National Environmental Protection Agency of China, GB15618, 1995.
b Kabata-Pendas and Pendas, 1992.
c Türkdogan et al., 2003.
d Iyengar and Nair, 2000.
e Warren et al., 2003.
f The PTDI for total arsenic is calculated by: the PTDI for inorganic arsenic is 2.14 µg kg\(^{-1}\) body weight day\(^{-1}\) with an average body weight of 68 kg in adults, established by the World Health Organization (WHO) in 1989. Also, on the basis of approximately 25% of the daily intake of dietary arsenic is inorganic, which is established by US EPA, 1988 (WHO, Environmental Health Criteria 224, 2001).
Fig. 2 shows that of the considered elements in Chenzhou Pb/Zn mine area (Hunan, southern China), arsenic contamination is the heaviest. The usual arsenic content in uncontaminated soils in the world ranges from 1 to 40 mg kg\(^{-1}\), and in Chinese agricultural soil is 11.2 mg kg\(^{-1}\) (Mandal and Suzuki, 2002). But in the REF soil, As concentration is quite high (96.9 mg kg\(^{-1}\)). Even so, mean As concentrations of soils from GYB, SZY and JTC are still over that of REF by 7.3, 4.7 and 2.0 times, respectively, and exceed the MAC level (30 mg kg\(^{-1}\)) by 24, 15 and 6 times, respectively. The second most contaminated element is Cadmium, with 13, 11 and 4.5 times, respectively, exceeding the MAC level in the same order as arsenic in the three sites. Comparing Cd concentration in soils of GYB, SZY and JTC with that of REF soil, we can find that Cd concentrations are still much higher. The following are Zn and Pb, with concentrations exceeding the corresponding MAC levels by ranges of 1.7–4.0 times for Zn and 1.1–3.6 times for Pb in the soils of the three sites. The mean concentration of Cu is 1.7 times at SZY and 1.4 times at GYB, indicating a slight contamination in these two sites. At JTC, the ratio is less than 1 for these elements, indicating no contamination here.

Moreover, the ratios of mean concentrations of Cr and Ni to the corresponding MAC levels are in the range of 0.2–0.6, indicating no Cr or Ni contamination in this area.

In conclusion, the extent of soil contamination among these three affected sites is in the order of GYB>SZY>JTC (Fig. 2). Arsenic and Cd are the most contaminated elements, and Zn, Pb and Cu concentrations in the soil still exceed the corresponding MAC levels.

4.3. Crop contamination extent

To appraise the extent of contamination of the crops grown in Chenzhou Pb/Zn mine area, the observed concentrations in the crop samples (see Table 4) were compared with the corresponding maximum permit limit (MPL) of metals for vegetables and fruits (Türkdogan et al., 2003; Warren et al., 2003) (see Table 8). The results are shown in Fig. 3. A ratio\(\geq 1\) indicates a certain extent of contamination.

Among all the crops analyzed, ipomoea, a common leafy vegetable consumed by local inhabitants, is the most contaminated species. Ipomoea can accumulate high concentrations of Cd and Pb in the leaves and stems, which are 11 and 26 times higher than the MPL value at SZY and 6, 4 times at GYB for Cd in the leaves and stems, respectively, and 4.4, 3.3 times at SZY and 19.7, 7.3 times at GYB for Pb in the leaves and stems, respectively. The ratios of Co, Cu, Zn and As at GYB and Cu, Zn at SZY range from 1.5 to 5.0 times (Fig. 3a and b), exception is for Co and As in ipomoea leaves and stems at SZY (<1.0) (Fig. 3a).

Taro can accumulate high concentrations of Zn and Cd in the stem in the three sites. Capsicum fruits have a high Cd ratio in SZY and Pb in GYB.

Rice is Asia’s most important food. Most Asian governments have established critical maximum levels of heavy metals in rice to protect the health of their citizens (Chen, 2000). The Cd concentration in rice fresh grown at GYB is 17.5-fold higher than the critical maximum level (0.4 mg kg\(^{-1}\)) set by the Chinese government (Chen, 2000), and 14-fold higher than MPL (4.5 mg kg\(^{-1}\)) quoted from Türkdogan et al. (2003). However, the ratios of the other elements are very low (0.01–0.43 times) at GYB. At JTC, where the mining waste spills were cleaned, Cd ratio is still the highest among all the considered elements. However, the ratio for the other elements is lower than 1. This indicates that rice has the ability of preferential Cd uptake from soil. Not only rice, but also spinach and lettuce could accumulate high Cd concentration in the edible parts, too (Stalikas et al., 1997), probably because Cd is found in an active form in soils (Hernandez et al., 2003).

However, the other seed or fruit foods usually have low ratios of the considered contaminants, even if the ratios of Cu and Cd are slightly higher than 1 in string bean.

Considering of phyto-remediation of metals contaminated soil, ipomoea may be considered, with the advantages of fast growing, high adaptation, and easy harvesting, even if it is not a hyper-accumulation species, which is defined by Bake and Brooks to contain \(>1\,000\) mg kg\(^{-1}\) dry weight of Co, Cu, Cr, Pb, Ni, or \(>10,000\) mg kg\(^{-1}\) dry weight of Mn and Zn in their tissues (Simon et al., 2000).

In general, cereal contains 2.2–10.1 mg kg\(^{-1}\) Cu, 7.6–88.8 mg kg\(^{-1}\) Zn, 0.03–7.0 mg kg\(^{-1}\) Cd, 0.10–4.3 mg kg\(^{-1}\) Pb and 0.1–2.2 mg kg\(^{-1}\) As in Chenzhou Pb/Zn mine affected area. Comparing
with the metal concentrations in cereal grains grown around a lead smelter in the Upper Silesia Region (Poland) (Gzyl, 1995), which were 30.3–111.7 mg kg\(^{-1}\) for Zn, 0.10–2.16 mg kg\(^{-1}\) for Cd and 0.03–1.6 mg kg\(^{-1}\) for Pb, cadmium and lead concentrations in cereal grains in Chenzhou Pb/Zn mine area are much higher than that in the Upper Silesia Region, the exception is Zn.

4.4. Metal translocation and distribution between soil and plant tissues

It is worth noticing that the soils in Chenzhou Pb/Zn mine area (Southern China) contain extremely high concentrations of arsenic contamination, with the exception of ipomoea at GYB, having 101 and 63.5 mg kg\(^{-1}\) in the leaves and stems, respectively, severely exceeding the MPL (20 mg kg\(^{-1}\)) for human consumer and the maximum level (50 mg kg\(^{-1}\), Baroni et al., 2004) tolerated by cattle, sheep and swine, almost all the other crops grown in this area do not uptake and store high As concentration in the edible parts. To appraise the bio-accumulation effects of crops that uptake toxic elements from the 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 (Fig. 4) show that BAFs of crops for these considered elements are in the order: Cd\(>|\)Zn\(>|\)Cu\(>|\)Pb\(>|\)As (see Fig. 4), these results strongly agree with the literature data (McBride, 2003). The highest BAF value is 2.0 in Cd of Capsicum leaf tissue at

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Fig. 3. Ratios of element concentrations in the edible parts of the crop species from Chenzhou Pb/Zn mine area (Hunan, southern China; a: SZY, b: GYB and c: JTC) to the maximum permit limits.
SZY, the second one is 1.8 in Cd of Maize at the same site. BAF values of As are the lowest. The typical BAFs for As range from 0.01 to 0.1 (Warren et al., 2003). In our studies, BAFs for arsenic vary between 0.0004 (in ipomoea leaf tissue at GYB) to 0.216 (in maize seeds at JTC). These results indicate 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 (exception for ipomoea at GYB), 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.

BAFs of the edible seeds or fruits are typically lower than that of leaves, but that of rice is an exception. BAF value of Cd in rice flesh is 0.83 at GYB and 0.17 at JTC, which is higher than that in the leaf tissue. To search for the reasons why such large differences exist in BAF values of Cd in rice between different sampling sites, all of the corresponding factors (Cd concentration in the soils, soil pH, OM, CEC, etc.) are checked, the reasons may primarily rely on the difference between their physiology properties, indicating that their varying genetics make a great difference.

Comparing the relationship of BAFs with soil physical–chemical properties, we found that BAF values for Cd or Zn are negatively correlated to the soil pH value. In the meantime, a positive relationship can be found between the element concentrations and the corresponding soil pH values (pH values range from 4.7 to 8.2). The high soil pH can stabilize soil toxic elements, resulting in decreased leaching effects of the soils toxic elements. Thus, the element concentrations in the soil remain relatively high. Moreover, 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.

Fig. 4. BAF (bio-accumulation factor) of leaves or fruits of some crops from Chenzhou Pb/Zn mine (Hunan, southern China).
For the other factors of soil properties (OM, OC, N, C/N, CEC, and total concentration of element in soil), no linear relationship is found between the BAFs with these factors, which is similar to the results of Baroni et al. (2004) for arsenic bio-availability. This supports the assessment that the accumulation effect strongly depends on the crop physiological properties, and on the mobility of metal in soils, not on the total element concentrations in the soils.

However, solubility and bio-availability of toxic elements are subject to control by climatic factors, and the soils chemical and biological properties, the high concentrations of toxic elements in the contaminated soils are always a potential hazard to human health and eco-environment.

4.5. Human exposure to metal contamination

Consuming foods grown in Chenzhou Pb/Zn mine area, human beings are exposed to metal contamination. By comparing the data from Zhang et al. (1998) for cereals and pulses grown in north-eastern China, which are average Pb concentrations of $31.3 \times 10^{-3}$ mg kg$^{-1}$ in cereals and $25.7 \times 10^{-3}$ mg kg$^{-1}$ in pulses, and average Cd concentrations of $9.2 \times 10^{-3}$ mg kg$^{-1}$ in cereals and $55.7 \times 10^{-3}$ mg kg$^{-1}$ in pulses, we can find that Pb and Cd concentrations in the cereals and pulses grown at Chenzhou Pb/Zn mine area are much higher.

The daily intake amounts of Cu, Zn, Cd and Pb from the cereal and vegetables grown are much higher than the recommended levels (see Table 7) by 2.6, 4.6, 9.9 and 6.3 times, respectively, at SZY, by 2.3, 2.6, 17.1 and 16.3 times, respectively, at GYB, and by 1.2, 1.9, 2.7 and 1.2 times, respectively, at JTC. The daily dietary intake amount of arsenic from the crops grown at JTC is lower than the PTDI value ($0.58$ mg kg$^{-1}$), but 8.5 times over the standard PTDI level is found at GYB, and is slightly exceed at SZY.

High concentration of Zn in food and good nutrient state can help human stand metal toxicity. Türkdoğan et al. (2003) 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. In Chenzhou Pb/Zn mine area (Hunan, southern China), although the major contribution to daily intake of metals is from cereal, pulses and vegetables, people also intake metals from 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. However, in spite of these highly contaminated crops 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.

5. Conclusion

This field study indicates that the physical–chemical properties of soils obviously change due to the different farming styles implemented by individual farmers. The effects of leaching extraction and plant extraction of metals from soils are quite weak. Soils and crops are still severely contaminated with As, Cd, Zn, Pb and Cu in the mine spills contaminated area of Chenzhou Pb/Zn mine (Hunan province, southern China). The extent of contamination was in the order: GYB$>$SZY$>$JTC. Arsenic and cadmium were the most severely contaminated elements in the soils, followed by Zn, Pb and Cu.

The mine waste cleanup activity is effective, but the mean concentrations of As, Cd and Zn in the soils still slightly exceed the corresponding MAC levels for agricultural soils in China.

Among the edible parts of crops analyzed, seeds or fruits are generally less contaminated than leaves or stems. Ipomoea leaves and stems are the most severely contaminated, the concentrations of all the considered toxic elements exceed the maximum permit levels, especially Cd and Pb. Taro (+skin) can accumulate high concentrations of Zn and Cd, rice and capsicum have high Cd concentration in the edible parts. The toxic element concentrations in maize, sorghum, Adzuki bean, soybean and mung bean are lower than the threshold levels. The BAF values of crops for these considered elements are in the order: Cd$>$Zn$>$Cu$>$Pb$>$As.

The estimated daily intake amounts of the considered toxic elements (Cu, Zn, Cd, and Pb) from the
crops grown at the contaminated sites and arsenic from crops grown at GYB and SZY have exceeded the RDA levels. Therefore, the crops grown in Chenzhou Pb/Zn mine waste affected area have a hazard effect on human’s health. This area needs effective measures to cure the As, Cd, Pb, Zn and Cu contamination.

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