Soil As contamination and its risk assessment in areas near the industrial districts of Chenzhou City, Southern China

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Abstract

In order to assess soil As contamination and potential risk for human, soil, paddy rice, vegetable and human hair samples from the areas near the industrial districts in Chenzhou, southern China were sampled and analyzed. The results showed that the anthropogenic industrial activities have caused in local agricultural soils to be contaminated with As in a range of 11.0–1217 mg/kg. The GIS-based map shows that soil contamination with As occurred on a large scale, which probably accounted for up to 30% of the total area investigated. Soil As concentration abruptly decreased with an increase in the distance from the polluting source. High As concentrations were found in the rice grain that ranged from 0.5 to 7.5 mg/kg, most of which exceed the maximal permissible limit of 1.0 mg/kg dry matter. Arsenic accumulated in significantly different levels between leafy vegetables and non-leafy vegetables. Non-leafy vegetables should be recommended in As-contaminated soils, as their edible parts were found in relatively low As level. Arsenic concentrations in 95% of the total human hair samples in the contaminated districts were above the critical value, 1.0 mg/kg, set by the World Health Organization. Arsenic could be enriched in human hair to very high levels without being affected by As containing water. The results revealed that the soils and plants grown on them are major contributors to elevate hair As in the industrial population. Therefore, the potential impact on human health of ingestion/inhalation of soil As around the industrial districts seems to be rather serious. Hence proper treatments for As contaminated soils are urgently needed to reduce the contamination.

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1. Introduction

Arsenic (As) naturally occurs in the form of sulfides in association with sulfides of ores of silver, lead, copper, nickel, etc. (Matschullat, 2000). The element is biologically toxic and a threat to human health, in contrast to many positive industrial, agricultural, and medicinal applications. Arsenicals are extensively used as a wood preservative, in alloys, in glass manufacturers, semiconductor material, feed additives, herbicides, insecticides, hematosis additives, and veterinary chemicals (Kumaresan and Riyazuddin, 2001). Arsenic may be ultimately enriched in soils due to human activities such as mining, waste discharges, coal burning, and arsenical pesticide application (Fergusson, 1989). Nriagu and Pacyna (1988) reported 52,000–112,000 tons of As were released annually to soil from anthropogenic sources. Soil As was reported in high quantities through atmosphere deposition and As containing water around some industrial areas due to mining and smelting activity (Gidhagen et al., 2002; Pandey et al., 2002). Total As concentration in the soil in the vicinity of point emission sources, Pb/Zn smelter, increased up to 49 mg/kg (Lynch et al., 1980). In Central and Northern Chile, soil As concentration was up to 291 mg/kg caused by copper and gold smelting (Gidhagen et al., 2002). Soil deterioration by As contamination due to past and present human industrial activity may result in high exposure because the As from the enriched soils would eventually enter the human body through soil ingestion and the food chain. Mandal and Suzuki (2002) expatiated on 19
great arsenic poisoning episodes, which were related to industrial activity and reported all over the world. Diaz-Barriga et al. (1993) concluded that soil As could contribute from 30% to 88% of the total amount of As ingested by humans. An estimation of the potential hazard of contaminated areas is necessary, since soil contamination may affect human health directly and indirectly (Deckers et al., 2000).

In recent years, several serious As poisoning cases, caused by toxic discharges anthropogenic industrial activities have been reported in Chenzhou, one of the largest cities for metal exploitation in southern China. Chenzhou is a city with more than 4.5 million of people and is a multimeetal productive city. Arsenic is present at high level in soils from mining and smelting of various metals (Cai et al., 2004; Liao et al., 2004a); however, there is little information available on either soil As contamination or the environmental impact in this area. This paper reports the results of a survey and a regular study on soil and vegetable As concentrations and the impact on human health by contaminated soils in the city.

2. Materials and methods

2.1. Research area

Chenzhou City lies between 24°53’ and 26°50’ N latitudes and between 112°13’ and 114°14’ E longitudes. The total area of the city is 19,400 km², out of which 241,560 ha are paddy areas and 59,420 ha are vegetable areas. The climate is subtropical and the average rainfall is about 1500 mm. In the city, about 10,000 people are engaged in mining.

The research area was restricted to around four industrial districts including Bo Lin (BL), Bao Shan (BS), Shi Zhu Yuan (SZY), Deng Jia Tang (DJT), and a control area in Chenzhou. The district of BL is known as the “The golden town” where Au, Ag and As have been smelted by private factories for years. The BS mine is a strip mine for Cu, Pb, Zn and Ag, and the mining area has 324 ha. SZY mine is one of the biggest industrial districts in Chenzhou including mining and smelting of Pb, Zn, W and Mo. An As-product factory was located at DJT in 1992, but it has been out of production since 1999. The control area was far from any industrial districts and seldom influenced by industrial activity.

2.2. Sampling

2.2.1. Soil and plant

Soil samples were collected from agricultural lands every 0.5–2 km in the four industrial districts and every 3–5 km around these districts, on which samples of vegetable or paddy were also correspondingly collected. The surface soil layer to a depth of 15 cm was sampled. Ninety-five percent of agricultural production in these areas investigated is for self-consumption. The number of samples collected was decided according to the specific agricultural and industrial areas. The soils were air-dried and ground to pass through a 100 mesh screen. The plants were washed with tap water to remove adhering soil, rinsed with deionized water, dried at 60°C for 48 h in an oven and ground to a fine powder.

2.2.2. Human hair

Hair samples were collected from the residents of the above mentioned 4 industrial districts and control area. Hair was cut by using a stainless steel cutter and immediately stored in individual sealable polyethylene sample bags to avoid contamination. All samples were washed with shampoo to remove any surface contamination, rinsed in deionized water, and dried in an air oven at 50°C. Shampoo was determined as sample and no detectable As was found in it.

2.2.3. Sample analysis

The soils were digested by using HNO₃–H₂O₂ (Chen et al., 2002). The plants and hairs were digested by using HNO₃–HClO₄ (Liao et al., 2004b). Arsenic was quantified with a hydrogen generation-atomic fluorescence spectrometer (HG-AFS) (AFS-2202, Haiguang Instrumental Co., China). Standard reference materials for soil (GBW-07401), plant (GBW-07603) and hair (GSH1) were obtained from the China National Center for Standard Reference Materials and digested along with the unknown samples and used for the QA/QC program. The obtained As concentration of standard reference materials was in good agreement with the reference/certified values (GBW-07401: obtained 33±3 mg/kg (n = 3), reference 34±5 mg/kg; GBW-07603: obtained 1.25±0.04 mg/kg (n = 3), reference 1.25±0.10 mg/kg; GSH1: obtained 0.31±0.02 mg/kg (n = 3), reference 0.28±0.04 mg/kg).

2.2.4. Calculation and statistic analysis

The concentration factor (CF) of a plant was calculated using the following equation:

\[
CF = \frac{\text{As conc. in plants grown on contaminated soil} / \text{As conc. in contaminated soil}}{\text{As conc. in plants grown on control soil} / \text{As conc. in control soil}}.
\]

The enrichment factor (EF) of a vegetable was calculated using the following equation:

\[
EF = \frac{\text{As conc. in edible part grown on contaminated soil}}{\text{As conc. in edible part grown on control soil}}.
\]
All statistical analyses were performed using the Microsoft Excel 2000 and SPSS V10.0. Analysis of variance (ANOVA) was used to examine statistical significant differences in the mean As concentration among groups of soil, vegetable, or hair. A probability level of \( p < 0.05 \) was considered significant.

### 2.2.5. Construction of the map of As concentration distribution

The map was generated by using the ArcGIS V8.0 (ESRI Corporation). The values of As concentration were grouped into seven categories by using manual break criterion of the Arcmap, one of the ArcGIS programs, and the values in different groups were presented by using circle symbols with different diameters.

### 3. Results and discussion

#### 3.1. Arsenic concentrations in agricultural soils

Arsenic concentrations in agricultural soils investigated in this study are shown in Table 1. A wide range of As concentrations, 11.0–1217 mg/kg, was found in the soil samples collected from various industrial districts in Chenzhou City (Table 1). Compared with As concentrations in control soils (9.7–34.6 mg/kg, mean 18.9 mg/kg), all As concentrations in the four districts were greatly elevated by anthropogenic industrial activity. The highest concentration of As in soils was found at SZY where the mean concentration was 379.9 mg/kg. The mean As concentrations of DJT and BS were about 10 and 5 times the concentration of the control district, respectively. Arsenic concentrations in most samples collected from the BL district, which were associated with smelting of Au, Ag and As in a smaller scale and shorter period, were lower than those from other industrial districts. There was no significant difference between soil As concentrations at the BL and the control districts.

The normal range for As in soils of various countries was 0.1 to 40 mg/kg (mean of 6 mg/kg) (Chatterjee et al., 1993). It was indicated by a conservative risk analysis that As concentration in soil could reach 40 mg/kg without becoming a hazard to exposed organisms (Dudka and Miller, 1999). Desesso et al. (1998) concluded that As was likely to pose a risk to pregnant women and their offspring when soil As concentration was more than 100 mg/kg. The As concentration in the soil quality criterion set by USEPA for total arsenic is 20 mg/kg (Helgesen and Larsen, 1998). The SZY district was the most affected area but the contamination was not limited to it.

Fig. 1 presents more detailed information about As-contaminated conditions by using GIS-based mapping and analysis. Arsenic concentrations in most of the soils investigated were above the concentration criterion proposed by USEPA. The map also reveals soils contaminated by As appearing at a large scale. The contaminated soils probably accounted for up to 50% of total areas investigated and the total As-contaminated area is estimated to be more than 1000 km\(^2\). Mining and smelting have caused the problem of soil As contamination from tailing dam, abandoned mine, wastewater and exhaust gas to become increasingly prominent in recent years. More than 27 km\(^2\) of soil were considered to be contaminated around smelts in Butte and Anaconda, US, where As concentrations in the soil were more than 90 mg/kg (Wong et al., 1992). Mitchell and Barr (1995) found more than 110 mg/kg of As in soil occurred on 722 km\(^2\) of Cornwall and West Devon, Canada. Regionally contaminated soils around the Mole River mine in northern New South Wales, Australia, had a mean As concentration of 55 mg/kg and the contaminated area was estimated to be 60 km\(^2\) (Ashley and Lottermoser, 1999). There is also a likelihood that if more agricultural soils nearby mining and smelting activities were more extensively investigated, an even more serious situation might emerge in China.

In this investigation, all soils were collected from agricultural lands including paddy and vegetable soils. Fig. 2 shows soil As concentrations at some affected sites where paddy and vegetable soils distributed in very close proximity (<20 m). The vegetable and paddy soils of two districts were arranged in order of the increasing distance from the polluting source. The soil arsenic concentrations of BS and SZY persistently descended and could be fitted by power models. It is calculated by the models that the distance of the soils influenced by BS mine was 36 km and that by SZY mine was 24 km. A more abrupt decrease in soil As concentrations was observed in SZY than BS. Around the BS area, the As concentrations in vegetable soils ranged from 9.74 to 395.5 mg/kg and the As concentrations in paddy soils ranged from 17.7 to 305.0 mg/kg. Around the SZY district, the As concentrations in vegetable soils were from 11.0 to 1217 mg/kg and those in the paddy soils were from 15.3 to 865.8 mg/kg. Both the highest and lowest As concentrations were found in the vegetable soils around BS and SZY districts. Taking one with the other, soil As concentrations abruptly decreased with increasing distance from pollutant source. A much lower level of As existed in paddy soils than vegetable soils in and near the industrial districts. However, As concentrations in the paddy soils far from the sources were higher than vegetable soils. The results indicate that As deposition from smelting smoke and ore dust may be a main reason for soil contamination near the polluting source, while water could be a major carrier of As that leads to regional soil contamination in the

### Table 1

<table>
<thead>
<tr>
<th>Area</th>
<th>Mean</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Median</th>
<th>Standard deviation</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL ((n = 12))</td>
<td>22.8</td>
<td>11.0</td>
<td>72.0</td>
<td>18.9</td>
<td>16.3</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>BS ((n = 9))</td>
<td>98.0</td>
<td>29.1</td>
<td>395.5</td>
<td>68.5</td>
<td>114.2</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>DJT ((n = 13))</td>
<td>175.7</td>
<td>30.0</td>
<td>869.0</td>
<td>80.0</td>
<td>225.6</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>SZY ((n = 29))</td>
<td>379.9</td>
<td>82.9</td>
<td>1217.2</td>
<td>210.4</td>
<td>341.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Control ((n = 14))</td>
<td>18.9</td>
<td>9.7</td>
<td>34.6</td>
<td>17.9</td>
<td>6.7</td>
<td>&gt;0.05</td>
</tr>
</tbody>
</table>

\(P\) value, probability level, was calculated by ANOVA and >0.05 was considered to be not significant.
These findings are in agreement with those reported by Pandey et al. (2002) and Roychowdhury et al. (2002) who suggested that soil As concentrations decrease with increasing distance from the polluting source and that water could be a major carrier of As over long distances.

3.2. Arsenic concentrations in rice plants

Since rice could be the major dietary source of As to residents in the areas investigated, the consequences for elevated As in paddy soils must be considered. In the DJT district in 1999, two serious As-toxicity cases were reported due to soil and water contamination with; therefore, the farmers were reluctant to plant paddy rice (Liao et al., 2003). In the other areas near industrial districts investigated, As was found in remarkably high concentrations in the samples of rice. The grain of rice grown in BL contained 2.1–3.4 mg/kg of As with a mean of As concentration at 2.8 ± 0.5 mg/kg (Fig. 4A). Arsenic concentrations in grain in BS ranged from 0.5 to 1.8 mg/kg. In SZY, rice As concentrations ranged from 0.5 to 7.5 mg/kg, with a mean of 1.7 mg/kg, and had the largest variation. Most of the values exceeded the maximal permissible limit of food As standard 1.0 mg/kg dry weight (NFA, 1993). Previous studies showed that As levels in rice grown on As-contaminated soils ranged from 0.03 to 1.83 mg/kg (Meharg and

Fig. 1. The distribution of As concentrations in soils near the industrial districts of Chenzhou City, Southern China.
Rahman, 2003), with a mean of 0.70 mg/kg. It can be concluded that the As-contaminated rice may have posed a serious risk to humans, because rice is consumed in tens of kilograms per year per person by millions of the residents in Chenzhou.

The data on rice As concentrations clearly shows that regardless of soil As concentration (including the control), roots contained higher concentrations of As than any other parts of the plant (Fig. 3). Marin et al. (1993) and Xie and Huang (1998) also observed that more As accumulated in rice root than the other parts. Rice had an ability to store a certain mount of As in its root system; however, As was readily translocated to the shoot, when this storage ability of the root was exceeded (Abedin et al., 2002). Arsenic concentrations in all rice shoots greatly exceeded the maximal permissible limit of food hygiene standard (NFA, 1993) and the maximum concentration reached 67.0 mg/kg in BL. In Southern China, rice is a staple food, and rice shoot (leaf and stalk) is traditionally used as cattle feed, or combusted in the field for remediating soil fertility. Therefore, the high As concentrations in the shoot may pose a potential risk for increasing As exposure to humans via the plant–animal–human or the plant–air–human pathways.

### 3.3. Arsenic concentrations in vegetables

Paddy rice supplemented with vegetables serves as the main food in the diets of people in Southern China. Samples of various kinds of vegetables grown in these areas were also collected and analyzed for As. All the vegetables grown in the industrial districts had high As concentration that would be a health hazard for human consumption (Table 2). It is surprising that the As concentration of vegetables was higher in BL even though the soil As of this area was lower than any other industrial district. The arsenic concentrations in shoots of all vegetables were higher than those in the roots. A possible explanation is that vegetables were influenced mainly through atmospheric As deposition in this area. An obvious difference in As concentrations was found among edible parts of 7 plants. The data shows that leafy vegetables such as pumpkin, 25.8 mg/kg, and swamp cabbage, 20.1 mg/kg, contained higher mean As concentrations than non-leafy vegetables when grown in these As-contaminated soils. In both normal and contaminated soils, As concentration of the fruits of non-leafy vegetable had the same trend in the individual districts: shallot > eggplant > legume > capsicum.

Fig. 4 illustrates the concentration factor (CF) in the four districts and the enrichment factor (EF) of vegetables found in Chenzhou. The CF value was significantly higher (20.9) for edible parts of vegetable in BL than that in BS (1.3), DJT (0.9) and SZY (0.8). Compared with vegetables in the industrial areas of India (Sekhar et al., 2003), the CF values are approximately 4–20 times higher in the four industrial districts. The EF values of As in pumpkin, swamp cabbage, eggplant, capsicum, legume, and shallot were 51.5, 20.1, 6.3, 12.3, 5.8 and 7.2, respectively. The EF values of As in different plants grown on the contaminated soils were found in the order: pumpkin >> swamp cabbage > capsicum > shallot > eggplant > legume. The results show that As accumulated in greatly different levels by individual vegetables in the...
contaminated districts. The EF values of non-leafy vegetables were lower than those of leafy vegetables.

Vegetables tend to be short-term crops that are grown as part of a multiple cropping system. Therefore, more attention should be paid to minimizing As contamination in the farming and the non-leafy vegetables should be recommended to be cultivated in these contaminated soils for the sake of human health.

3.4. Arsenic concentrations in human hairs

To assess the risk due to As toxicity, hair samples were collected from residents of different occupational groups both male and female. The As concentrations in hairs of the residents of these districts ranged from 0.5 to 62.8 mg/kg, with the highest value of mean (60.8 mg/kg) in BS, while those in the control area only ranged from 0 to 0.80 mg/kg. The mean concentrations of As in hairs in BL, BS, DJT and SZY districts were very high; 13.2 ± 8.5, 60.8 ± 8.6, 3.9 ± 3.8 and 3.2 ± 4.0 mg/kg, respectively. Arsenic concentrations in 95% of the total hair samples in the contaminated districts surpassed the critical value of 1 mg/kg set by the World Health Organization (WHO, 1983; Hindmarsh, 2000).

Although it was suggested that As should be an essential trace element for a healthy life (Jager and Ostosky-Wegman, 1997), excess exposure to As was poisonous and the lethal dose for human is 125 mg (Bates et al., 1994). In human body, As was transported to different organs mainly through blood, and the major potion was slowly excreted through urine. However, a small portion of the As was deposited in hairs, nails, and shin. Hairs and nails had similar affinities for As, but hairs were more convenient to be sampled and analyzed than nails (Saad and Hassanien, 2001). Thus, hair As has been used as an index to monitor human exposure to As. Normal As concentrations in hair of unexposed humans were reported to range from 0.02 to 1.0 mg As/kg (Hindmarsh et al., 1999). Arsenic was also known to be deposited in hairs from external contamination such as As-containing dusts or washing with water contaminated with As (Hindmarsh and McCurdy, 1986). Although it was observed that the soil As concentrations of BS were not the highest levels, the hair As concentrations of BS were found to be

Table 3
Arsenic concentrations in human hairs collected from the industrial districts in Chenzhou City, Southern China

<table>
<thead>
<tr>
<th>Area</th>
<th>As concentration (mg/kg)</th>
<th>Above critical valuea</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
<td></td>
</tr>
<tr>
<td>BL (n=9)</td>
<td>13.2</td>
<td>5.1–32.4</td>
<td>100%</td>
</tr>
<tr>
<td>BS (n=3)</td>
<td>60.8</td>
<td>52.6–62.8</td>
<td>100%</td>
</tr>
<tr>
<td>DJT (n=26)</td>
<td>3.9</td>
<td>0.5–9.9</td>
<td>89%</td>
</tr>
<tr>
<td>SZY (n=27)</td>
<td>3.2</td>
<td>0.6–20.6</td>
<td>89%</td>
</tr>
<tr>
<td>Control (n=8)</td>
<td>0.4</td>
<td>0–0.8</td>
<td>0%</td>
</tr>
</tbody>
</table>

a Critical value: 1.0 mg/kg.
quiet high. This could be attributed to very high As concentrations (114–11,300 mg/kg, data not shown) in fallow land near the residential area of BS. The As concentrations in samples of drinking water collected from these areas were less than 0.005 mg/L, except for those from BL where the mean As concentration of well water was 0.15 mg/L. From the data given in Table 3, it is clear that people residing in BL suffered from higher As exposure than those in DJT and SZY. Arsenic polluting source in DJT had been eliminated since 1999, the As concentrations, 0.5–9.9 mg/kg, of human hairs were mainly contributed by dusts and foods. It is likely that exposure routes by soils, rice, and vegetables are principal causes of As accumulation in these populations studied.

People residing in the industrial districts were affected the worst by soil As contamination which is difficult to be remediated. It is fortunate that the As-hyperaccumulator, Chinese brake (Pteris vittata L.) newly discovered in Southern China, has been demonstrated to phytoremediate successfully about 1 ha of As-contaminated soils in DJT in a pilot field study by our group since 2001 (Chen et al., 2002; Liao et al., 2004b).

4. Conclusions

Arsenic contamination of agricultural soils from industrial districts and dietary exposure to As in Chenzhou City were assessed in this paper. It is observed that soils surrounding the industrial districts were extremely contaminated with As on a relatively large scale. Soil As concentrations abruptly decreased with increasing the distance from the pollutant source. The results also imply that atmospheric As deposition may be a main contributor to elevate soil As levels near the pollutant source. Compared with those in the control area, As concentrations of rice and vegetables in the industrial districts were found to be remarkably high. Arsenic concentrations in the edible parts of leafy vegetables were much higher than those of non-leafy vegetables, so non-leafy vegetables were recommended to be cultivated in the As-contaminated soils. It is concluded that the major contributors to elevate the hair As levels of residents in the industrial districts were the consumption of local foods produced from the As-contaminated soils and the ingestion/inhalation of As-contaminated soils. Therefore, great attention should be paid to the potential health risk by means of consumption of the local foods with high As concentrations and ingestion/inhalation of As-contaminated soils around the industrial districts.

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