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Assessment of selenium pollution in agricultural soils in the Xuzhou District, Northwest Jiangsu, China

HUANG Shunsheng[1,*], HUA Ming[1], FENG Jinshun[1], ZHONG Xinyong[2], JIN Yang[1], ZHU Baiwan[1], LU Hua[1]

1. Geological Survey of Jiangsu Province, Nanjing 210018, China. E-mail: geohuangss@163.com
2. Department of Land Environment & Resources of Hainan Province, Haikou 570203, China

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Abstract

Xuzhou City is an important base for coal production and coal-fired power. To evaluate selenium contamination in this area, we sampled agricultural soil, soil profile, irrigation water, bedrock, coal, fly ash, paddy rice, and vegetables from the north of Xuzhou City, and determined their selenium contents. The background level of selenium in the soil profile was 0.08 mg/kg. The selenium concentrations in agricultural soils and irrigation water were in the range of 0.21–4.08 mg/kg and 0.002–0.29 mg/L, respectively. Soils with high selenium content were located closely to coalmines and power plants. The average selenium concentrations in coal and coal fly ash were 5.46 and 2.81 mg/kg, respectively. In contrast, the concentrations of selenium in bedrock and in the soil profile were very low. These results imply that the high selenium level in agricultural soils is mainly caused by anthropogenic activities, rather than by parent material. The arithmetic mean of selenium concentration in paddy rice was 0.116 mg/kg, and in cabbage was 0.05 mg/kg. The selenium concentration in rice was positively correlated with total selenium concentration in soil, suggesting that selenium in soil is readily transferred into the crops. Furthermore, the estimated dietary intake (88.8 μg) of selenium from paddy rice and cabbage exceeds the recommended dietary allowance (55 μg). Therefore, there is a potential health risk from consumption of local staple food in the study area.

Key words: selenium; agricultural soils; paddy rice; Xuzhou District

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Introduction

Selenium is an essential trace element for both animal and human. It is an important component of antioxidant enzymes, which protect cells against the effects of free radicals produced during normal oxygen metabolism (Rotruer and Poue, 1993; Maleki *et al*., 2005). However, at high concentration, selenium is toxic to animal and human, as found in the Kesterson Reservoir (Ohlendorf, 1989). Selenium in soil is taken up by plants. Such contaminated plants are the main source of selenium in human food or animal fodder. The amount of selenium in plants is related to the selenium content of the soil. Selenium in livestock, therefore, results from intake of selenium-contaminated plants (Burk, 1994). Generally, selenium concentrations in soils in China are very low unless the underlying geology contains high level of selenium (Fordyce *et al*., 2000; Appleton *et al*., 2006). However, selenium may be enriched in agricultural soils due to human activities such as mining, waste irrigation, coal burning, and selenium-fertilizer application (Xu *et al*., 2005; Senesi *et al*., 1999; Diaz *et al*., 1996; Blagojevic *et al*., 1998). For instance, disposal of fossil fuel wastes and agricultural irrigation of arid, seleniferous soils at several locations in the United States have poisoned fish and wildlife, and threatened public health (Lemly, 1997). Previous studies found that the distribution of selenium in Yutangba, China was also affected by human activities (Zhu *et al*., 2008; Fang and Wu, 2004). The distribution was related to the pathways of selenium transport, including stone coal transport by local villagers, stone coal mining, and fertilizer application to improve soil. These activities caused various additions of selenium to the soil and consequently a large amount of bioavailable selenium could be released, resulting in the further accumulation of selenium in food chains to some extent. Many crops with extremely high concentrations of selenium were found at croplands nearby discarded coal spoils (Zhu *et al*., 2008; Fang and Wu, 2004). Both coal and its ash seem to be the main geochemical source of selenium in soils and plants, which might contaminate local agricultural ecosystem (Fang *et al*., 2003).

Xuzhou, the most developing industrial city in Jiangsu Province of China, has established many different industries, such as mining, metallurgy, electric power, and engineering. Nearly 90% of energy that sustains these

* Corresponding author. E-mail: geohuangss@163.com

industries comes from coal combustion, and this situation will last for another 50 years. Xuzhou City has exploited coal mines for over 124 years, and still has various scales of coalfields with total deposits of 3.9 billion tons. In 2006, its coal production was 259.7 million tons, and the generated electric power amounted to 7.2×10^9 kWh. The solid waste from coal-fired power plants is enriched in potentially toxic trace elements such as arsenic, mercury, selenium, and antimony. Unfortunately, the power plants in this area have only limited equipments to process such wastes. For example, the coal fly ash is simply piled in reservoirs in the open air, and effluents flow directly or indirectly into rivers. The gaseous and aerosol pollutants in the flue gases from coal combustion and the leachable constituents in coal ash also cause serious environmental pollution. Some coals have undergone diagenetic development causing the extraordinary enrichment of selenium (He *et al.*, 2002). The agricultural soil close to areas of waste production and disposal become contaminated with selenium, potentially impacting on biota (Stoewsand *et al.*, 1990; Besser *et al.*, 1996). Very little information is available on selenium accumulation in agricultural soils and crops in Xuzhou District, and the impact of selenium contamination on the ecosystem has not been fully discussed. In this study, we systemically measured selenium concentrations in power plant waste, soil, rice grains and vegetables in croplands in the Xuzhou District for the first time. The objectives of this paper is: (1) to study the spatial distribution of selenium levels in these different types of samples, (2) to identify the causes of selenium contamination, and (3) to assess the potential health risk of selenium contamination to the local residents.

1 Materials and methods

1.1 Study area

Xuzhou City lies between 33°43′N and 34°58′N latitudes and between 116°22′E and 118°40′E longitudes. It is a part of Huanghuai Plateau with altitudes varying from 20 to 50 m above sea level. The total area of the city is 11258 km^2; 47.9% of the area is under paddy rice cultivation, and 26.8% is under vegetable cultivation. Its climate is a typical warm humid monsoon with an average annual temperature of 14°C and rainfall of 900 mm. The bedrock in the study area is mainly carboniferous grey limestone, and the microlandform is mainly composed of wide diluvia plains and sporadic uplands. The main soil is a typical fluvo-aquic soil formed on the alluvium.

Three coal-fired power plants, Chacheng, Huarun, and Maocun, are located in the study area. The Maocun Power Plant has generated coal-fired power since 1930s. The Chacheng Power Plant, the largest power plant in Xuzhou City, had a capacity of 4.2×10^9 kWh in 2006. These power plants lie along the valley, and the most of surrounding lands is cropland.

1.2 Sampling and preparation

The sampling was carried out in October, 2006. Agricultural soils (70 samples) were collected from North Xuzhou City (Fig. 1). One soil sample was collected every 4 km^2. The region was divided into 2 km × 2 km plots. Within each plot, a composite of two sub-samples was taken from the upper 20 cm, which represents the ploughed layer. These sub-samples were then mixed to obtain a bulk sample that provided a representative measurement of concentrations at the site. To obtain the

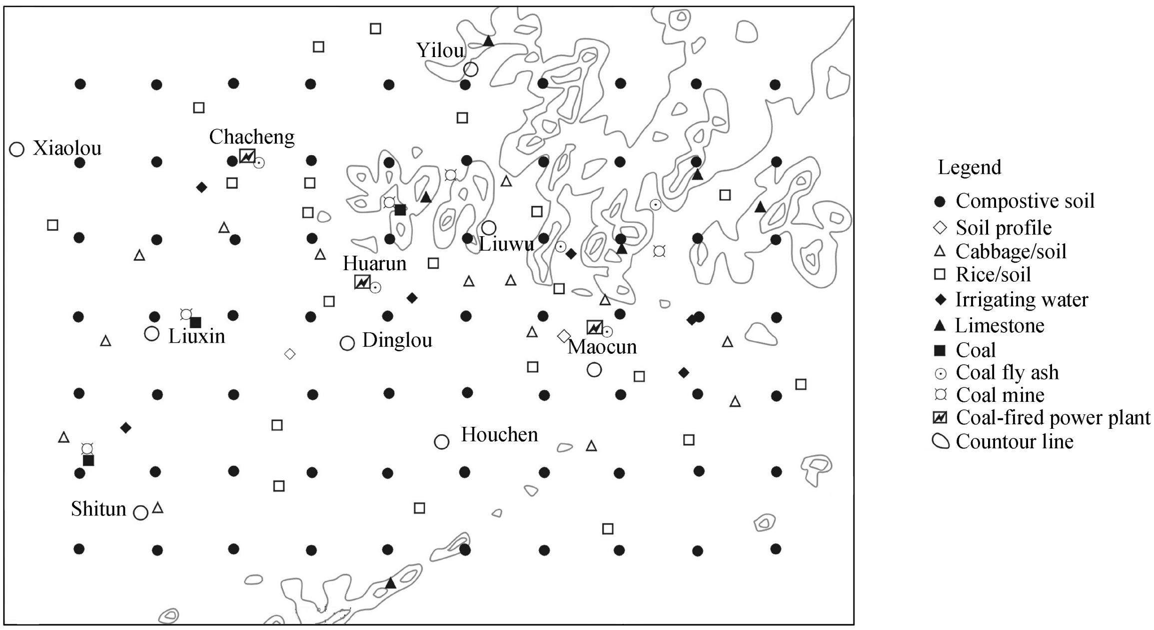

Fig. 1 Sampling locations of soils located North Xuzhou District.

selenium background value, a continuous 2.0-m profile was taken from cropland located distantly from the source of pollutants. A soil profile beside the Maocun Power Plant was used to exhibit vertical soil selenium distribution. These profiles were taken at approximately 20-cm interval using a stainless steel manual corer. Three coal samples from mines and five coal fly ash samples from power plants (or reservoirs) were collected. Six limestone samples were collected from the bedrock area. Furthermore, we collected six samples of irrigation water from creeks in the area. These samples (each 350 mL of 0.45 μm filtered water) were acidified by an addition of 0.3 mL analytic grade HNO_3 and HCl. We also collected 23 samples of paddy rice grain and 14 samples of Chinese cabbage from the cropland. Moreover, 37 samples of rhizosphere soils were collected from the corresponding plants at their sampling sites to determine the correlation between soil and plant selenium contents. These rhizosphere soils were separated from root tissue by gently shaking. To avoid effects of uptake of selenium by the plant, the tiny root hairs in rhizosphere soil were removed. All samples were stored in polyethylene bags in the field, and were transferred to the laboratory for preparation.

After removal of plant residues, the soils were air-dried, crushed, sieved through a 2-mm screen, then pulverized and passed through a 150-mesh sieve. The bedrock and coal samples were prepared by grinding and screening through a 150-mesh sieve. The coal fly ash samples were directly sieved through a 150-mesh sieve. The homogenized sample was dried in an oven at 50°C for 48 h. The rice grain and Chinese cabbage samples were washed with tap water, then with deionized water to remove soil particles or dust, and dried with tissue paper. The rice grains were dehulled and flecked cabbage leaves were eliminated. All the plant samples were then oven-dried at 45°C for 72 h to constant weight. Prior to chemical analysis, the dry plant samples were ground into a fine power (< 0.074 mm) using a stainless steel mill.

1.3 Chemical analysis

Total selenium concentrations in soil, coal, fly ash, and bedrock samples were determined by hydride generation atomic fluorescence spectrometry (AFS-820, Beijing Jitian Factory, China) following a HF-HNO_3-$HClO_4$ digestion (Johnson *et al*., 2000). The concentrations of total selenium in rice grains and cabbage were determined by AFS after digestion with concentrated HNO_3-$HClO_4$ (Tamari *et al*., 1992). Following initial acidification, irrigation water samples underwent no further treatment prior to AFS analysis for selenium. Quality control measures for each batch, including calibration with reference samples, blanks, and replicate analysis, were followed throughout the analysis. Standard reference materials for soil (GBW-07402) and plants (GBW-07604) were obtained from the China National Center for Standard Reference Materials, digested along with the unknown samples, and used for quality assurance and quality control procedures. The obtained selenium concentration of standard reference materials agreed well with the certified values (GBW-07402: obtained 0.15 ± 0.04 mg/kg (n = 4), certified 0.16 ± 0.03 mg/kg; GBW-07604: obtained 0.14 ± 0.04 mg/kg (n = 3), certified 0.14 ± 0.02 mg/kg). Reproducibility was tested by reanalyzing 5% of the samples and the recovery was good (94%–102%).

1.4 Soil selenium pollution assessment

The geoaccumulation index (I_{geo}) is a widely used indicator of heavy metal pollution in sediments in Europe (Müller, 1969). At present, it is also generally applied to assess the metal contamination in soil. The I_{geo} can be utilized to define whether the metals originating from human activities or from natural processes, and to assess the degree of anthropogenic influence. The degree of selenium pollution in agricultural soils was determined by I_{geo} (Müller, 1969; Netkim *et al*., 1993) using Eq. (1):

$$I_{geo} = \log_2(C_n/(1.5B_n)) \tag{1}$$

where, C_n is the measured total concentration in soils, B_n is the background value and the factor 1.5 compensates for possible variations of the background data due to lithological variations.

I_{geo} is classified into seven grades: 0 (class 0) indicates uncontaminated material; 0–1 (class 1) is uncontaminated to moderately contaminated; 1–2 (class 2) is moderately contaminated, 2–3 (class 3) is moderately to strongly contaminated; 3–4 (class 4) is strongly contaminated; 4–5 (class 5) is strongly to extremely contaminated; and 5–10 (class 6) is extremely contaminated.

1.5 Statistical analysis

All statistical analyses were performed using SPSS V10.0 for Windows. The correlation between selenium concentrations in the soils and in the crops was determined using the Pearson correlation procedure. MapGis software was used for vectorization of selenium content.

2 Results and discussion

2.1 Selenium concentrations in soil profiles

Comparison of the vertical distribution of selenium concentration in soil profiles between cropland site and the site beside power plant is shown in Fig. 2. Selenium concentrations were higher in the top 20 cm of soil profiles for both sites. However, the selenium content decreased sharply with increasing depth from 20 to 100 cm of the profile in the cropland, and reached the background level at 100 cm (Fig. 2a). The maximum concentration for selenium found in the surface layer (⩽ 20 cm) of the profile implies that selenium flux has increased over time (Ruiz-Fernández *et al*., 2003). Selenium concentration in the profile for the site beside power plant was highly elevated in the depth from 20 to 100 cm compared to the profile in cropland (Fig. 2b). The selenium concentration in the surface layer was 2.37 mg/kg and was much higher than that in the profile in cropland. Thus, the selenium level in the local soil compartment might be affected by the power plant.

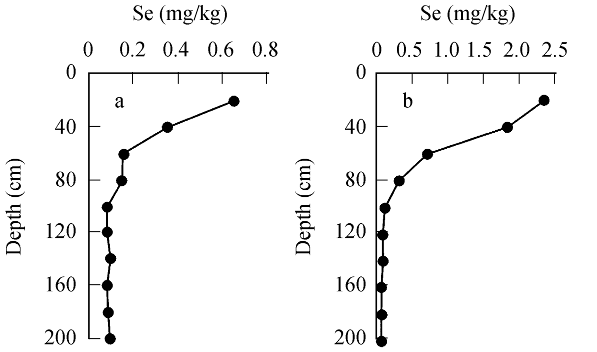

Fig. 2 Variation in Se concentrations with soil profiles in cropland (a) and a site beside a power plant (b).

A precise knowledge of the background values is essential to evaluate the extent of selenium contamination in Xuzhou District. However, the information about selenium values during the pristine era (pre-industrial) in the Xuzhou District is lack (Wang and Qin, 2005, 2006). Thus, we have to derive background concentrations from the results for the soil profile sites. The relatively constant concentrations of selenium at 100–200 cm suggest that this layer was not affected by human activities. In addition, average selenium concentration in this layer (0.08 mg/kg) is quite close to the background level in the earth's crust (0.05–0.09 mg/kg) (Adriano, 2001) and hereafter is assumed as the background level for agricultural soil in the study area.

2.2 Spatial distribution and pollution assessment of soil selenium

Total selenium in the agricultural soils ranged widely (0.21–4.08 mg/kg) with a geometric mean of 0.45 mg/kg (arithmetic mean of 0.57 mg/kg). The mean selenium concentration is almost six times the background level of 0.08 mg/kg. Furthermore, the mean selenium concentration is distinctly elevated compared with the levels in natural soils in Jiangsu Province and the soils in other parts of China (CNEMC, 1990). It is well known that Jiangsu is a selenium-deficient province in China (Cao *et al*., 2001; Tan *et al*., 2002). Therefore, the marked selenium enrichment in the topsoil may reflect the impact of contaminant inputs from anthropogenic activities. To assess the effects of the surroundings on variations in selenium concentrations in agricultural soils, we used a GIS spatial analysis to produce the spatial distribution map for selenium concentration and geoaccummulation index in agricultural soils (Fig. 3). High levels of selenium corresponded to local proximity of coal mines and power plants; a decreasing trend was observed with distance from these centers (Fig. 3a). Enhanced selenium concentrations (0.6–1.0 mg/kg) were found in the northwest direction. Selenium is usually used as a marker or tracer of coal and its associated industries (Finkelman *et al*., 1999; Yan *et al*., 2004). A "hot spot" for selenium pollution was noted at the sampling site near the Maocun Power Plant (4.08 mg/kg), which was surrounded by many sampling sites with high selenium concentration level (> 1.0 mg/kg). Moreover, high concentrations of selenium were found towards the southern margin of the sampling area, which is closer to Xuzhou City.

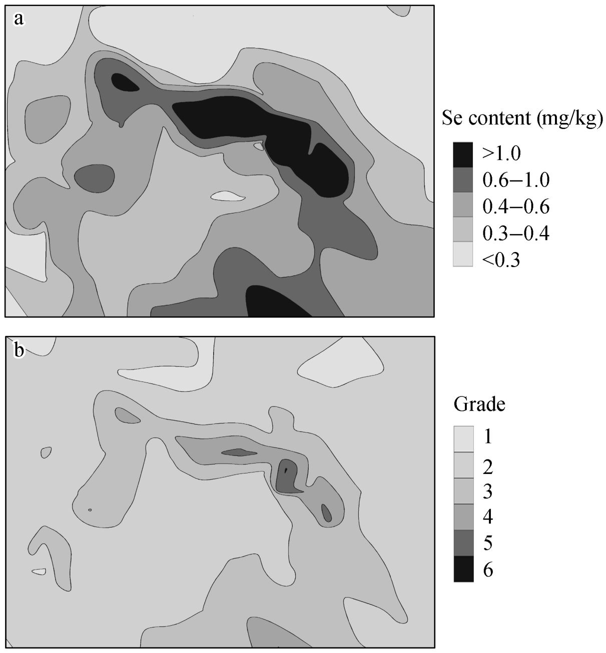

Fig. 3 Spatial distribution of Se content (a) and contamination (b) in agricultural soils by geostatistical interpolation using MapGis.

The geoaccumulation values ranged from 0.8 to 5.1, suggesting that agricultural soils were contaminated by selenium at different levels. The sampling site with maximum selenium was extremely contaminated (I_{geo} = 5.1). The distribution of soil selenium I_{geo} index was similar to that of selenium concentration. Sampling sites with strong to extreme grades of selenium contamination were consistent with the distribution of coalmines and power plants (Fig. 3b).

2.3 Selenium concentrations from different sources

To investigate possible factors influencing selenium distribution in agricultural soils, we collected various types of samples, including bedrock, irrigation water, coal, and fly ash. The selenium in the grey limestone ranged from 0.038 to 0.21 mg/kg with geometric mean value of 0.11 mg/kg (Table 1). This mean concentration is very close to the value reported previously (0.099 mg/kg) by Li *et al*. (2005). The concentrations in limestone are very low, similar to the background level in the earth's crust (0.05–0.09 mg/kg) (Adriano, 2001). Xia and Tan (1990) reported that bedrock in China had very low selenium content. Therefore, grey limestone does not affect the selenium status of the agricultural soils in the study area.

The selenium concentrations in three coal samples from coal mines ranged from 3.75 to 7.60 mg/kg (Table 1). This agrees with the results reported previously (8.6 and

Table 1 Selenium in different samples from Xuzhou District

Sample type	Min.	Max.	Geometric mean	Number
Limestone (mg/kg)	0.038	0.21	0.11	6
Coal (mg/kg)	3.75	7.60	5.46	3
Coal fly ash (mg/kg)	2.65	3.14	2.81	5
Irrigation water (mg/L)	0.002	0.29	0.05	6

4.1 mg/kg) by Chen and Tang (2002), who investigated selenium concentrations in coal in the Xuzhou District. These results also support the findings of He *et al*. (2002), who reported that selenium concentrations in southeast China are much higher than those in other areas. Xuzhou City is an important production base for coal, with many coal mines. During coal mining, selenium is released from the pyrite and carbonaceous shale and contaminates nearby agricultural soils and waters. Mao *et al*. (1999) found that the agricultural soils were seriously contaminated by selenium from nearby coal mines. Therefore, coal in this area might contribute significantly to the selenium content of the soil.

The selenium concentrations in five coal fly ash samples from power plants and ash reservoir ranged from 2.65 to 3.14 mg/kg, with an arithmetic mean value of 2.81 mg/kg (Table 1). During coal combustion, up to approximately 80% of the original mineral matter is released into the fly ash (He *et al*., 2002). Therefore, the selenium concentration in fly ash is still quite high. In most power plants, fly ash is conveyed through the system, and the most of them is discharged by pipelines to reservoirs. However, in power plants in Xuzhou District, the fly ash is transported by trucks to reservoirs. These trucks are not air-proof, which can lead to diffusion of fly ash during the transport process, and entry of contaminants into the surrounding agricultural system. Furthermore, the fly ash is also conveyed directly from coal-fired power plants to ambient cropland via atmospheric deposits. Together, these processes contribute to overall soil selenium concentration.

Total selenium in six irrigation water samples analyzed ranged from 0.002 to 0.29 mg/L with a geometric mean value of 0.05 mg/L (arithmetic mean of 0.079 mg/L) (Table 1). This value exceeds greatly the China irrigation water maximum recommended concentration of 0.02 mg/L (SEPAC, 1992). In comparison, total selenium concentration in Chinese river water ranges from 0.04 to 5 μg/L (Wang *et al*., 1991). This result suggests that the river water is contaminated by effluents from power plants. The highest value (0.29 mg/L) is for irrigation water sample collected from the lower reach of fly ash reservoir, which might imply that selenium is released from disposal of fly ash into the aquatic environment, or in such a way that aqueous ash leachate enters and contaminates the aquatic environments. Therefore, the river water in this area is not suitable for directly irrigating croplands.

Generally, soil selenium is inherited from bedrock and is enhanced by anthropogenic activities. The selenium in grey limestone and parent material from soil profile is too low to enrich soil to any great extent. Thus, parent rocks in the region did not contribute to distribution of selenium. Soils surrounding the coalmines and power plants were highly contaminated with selenium. Moreover, the local farmers in the area do not use selenium fertilizers. This further confirms that the enrichment of selenium in agricultural soils is mainly contributed by anthropogenic activities, especially mining and coal-fired power generation, rather than by parent material.

2.4 Selenium concentrations in crops

The arithmetic mean selenium concentration in paddy rice was 0.116 mg/kg (range of 0.035–0.36 mg/kg). Only two paddy rice grain samples exceed the food hygiene concentration limit of 0.3 mg/kg, and their corresponding rhizosphere soils were strongly contaminated with selenium (2.67 and 2.62 mg/kg). There was a significant positive correlation (r = 0.915, p < 0.001) between total soil selenium content and rice grain selenium content (Fig. 4a). This relationship between soil and plant selenium content has been also reported elsewhere (Severson *et al*., 1991; Peng *et al*., 1995). The regression equation indicates that a higher selenium concentration in rice is associated with a higher concentration in soil. Therefore, the soil selenium concentrations had influence on its concentration in rice in the study area.

Chinese cabbage is a staple green stuff in the Xuzhou, and is available almost year-round. We collected 14 Chinese cabbage samples from the cropland. The mean selenium concentration in cabbage was 0.05 ± 0.05 mg/kg (range 0.004–0.2 mg/kg) (Fig. 4b). Two cabbage samples exceeded the food hygiene concentration limit of 0.1 mg/kg fresh weight, which is consistent with a previous investigation in southeast Jiangsu Province (Wang *et al*., 2003). He *et al*. (2004) reported that the concentration of selenium in Chinese cabbage was just 0.02 mg/kg. The results from previous studies suggest that the selenium in Chinese cabbage is very low, and it is relatively deficient in selenium compared to paddy rice. Generally, vegetables contain less selenium than cereals. Selenium range from < 0.1 to 0.3 mg/kg in vegetables and from 0.02 to 0.8 mg/kg in cereals in China (Wang and Gao, 2001). No significant relationships between selenium content in cabbage samples and in contaminated soils could be detected in this study (Fig. 4b). The mechanisms of absorption and transformation of selenium differ among plants. In addition, the variation of selenium content in different plants and plant tissues might be genetically controlled by the genotype of plants (Cao *et al*., 2001; Li and Cao, 2006).

On the basis of previous investigations into human selenium imbalances carried out in China, threshold concentrations in various sample types indicative of low and toxic selenium diseases have been defined. Soils containing more than 0.175 mg/kg selenium and crops containing more than 0.04 mg/kg are considered in deficient for animal and human (Tan, 1989). Compared to these threshold concentrations, most samples of agricultural soils and rice grains in the study area were moderate-high in total

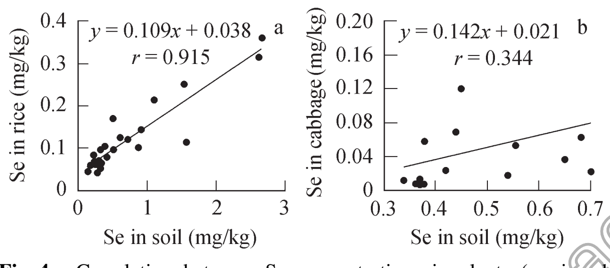

Fig. 4 Correlation between Se concentrations in plants (a: rice; b: cabbage) and soil.

selenium.

The main food of the local inhabitants is rice and cabbage, and hence, these foods contribute the major part of selenium in the total daily intake. Local adults have an average dietary intake of 550 g dehulled rice and 500 g cabbage, both of which are grown on local lands. Accordingly, the intake of selenium from these sources is 88.8 μg (0.116 mg/kg × 0.55 kg + 0.05 mg/kg × 0.5 kg). Selenium daily intakes for adults are up to 1.6 times higher than the recommended dietary allowance of 55 μg (Kech and Finley, 2006). Although no obvious health problems have been found in the study area, long-term exposure to selenium through regular consumption of rice, vegetables and incidental oral ingestion of soil around coal mines and power plants might pose a potential health risk.

3 Conclusions

In this study, we measured contents in agricultural soils, soil profile, bedrock, coal, fly ash, irrigation water, rice grains, and vegetables. Soils around the coal mines and power plants were heavily contaminated with selenium. The high level of selenium in agricultural soils corresponded well with the locations of coal mines and power plants. The irrigation water was also highly contaminated. In contrast, the selenium concentrations were very low in bedrock and parent material from the soil profiles. The results imply that high selenium levels in agricultural soils result from anthropogenic activities (coal mining and fired power) rather than from parent material. The selenium concentration in rice was significantly positively correlated with total selenium concentration in soil, suggesting that selenium in soil was readily transferred into rice. Relatively high levels of selenium were found in rice grains and vegetables, and selenium content partially exceeded the national guidelines for foodstuffs. Daily intake of selenium from rice and vegetables for the local residents is much higher than the recommended dietary allowance for adults. Therefore, the consumption of local staple foods poses a potential health risk. It is important to conduct long-term survey of selenium content in main foods in the local district, especially surrounding coal mines and power plants.

Acknowledgments

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