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Potential health risk in areas with high naturally-occurring cadmium background in southwestern China

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ABSTRACT

In various parts of the world, high cadmium (Cd) concentrations in environment are not related to anthropogenic contamination but have natural origins. Less is known about health risks that arise under these conditions. This study aimed to discuss the pollution of Cd with natural sources, and to investigate the concentration of Cd in food crops and the urine of inhabitants in an area of southwestern China. The results showed that the arable soils are moderately contaminated by Cd ($I_{geo}=1.51$) relative to the local background, with a high ecological risk ($E_r=218$). The chemical fractions of Cd in soils with natural sources are probably controlled by parent materials and mostly in residual phase. The average Cd concentrations were 0.68 mg kg^{-1} (fresh weight) in local vegetables, 0.04 mg kg^{-1} in rice, and 0.14 μg L^{-1} in water. Leafy vegetable tends to accumulate more Cd than the other crops. The calculated Target Hazard Quotient (THQ) had a much higher value (4.33) for Cd, suggesting that Cd represents a significant potential risk to the local population. The urinary Cd concentrations (mean at 3.92 μg L^{-1} for male and 4.85 μg L^{-1} for female) of inhabitants in the study area were significantly higher ($p<0.05$) than those from the control area (mean at 0.8 μg L^{-1} for male and 0.42 μg L^{-1} for female). Male and female test subjects had similar urinary Cd levels ($p>0.05$), but age seemed to lead to an increase in Cd in the urine. These findings show that naturally-occurring Cd in local soils is taken up appreciably by local food crops, and that dietary exposure of Cd through vegetable ingestion is a major exposure pathway for local populations, and a potential risk to public health in the study area.

1. Introduction

Cadmium (Cd) is a non-essential trace metal that is toxic to human beings, animals and plants. Cadmium generally occurs at concentrations of about 0.2 mg kg^{-1} in the lithosphere, 0.53 mg kg^{-1} in surface soils, and less than 0.66 mg kg^{-1} (dry weight) in the plant foodstuffs (Kabata-Pendias and Pendias, 2001). However, enrichment of Cd in the environment, from natural or anthropogenic sources, or both, is a major environmental concern. The anthropogenic origins are usually from sewage irrigation, fertilizer application, mining, smelting, and fuel combustion (Nriagu and Pacyna, 1988; Baveye et al., 1999; Luo et al., 2009), whereas the natural sources of Cd in soil are mainly volcanic activity and geological weathering of the parent rocks (Nriagu, 1989; Quezada-Hinojosa et al., 2009; Liu et al., 2013).

Human exposure to Cd may cause cancer, kidney and bone damage, and hematuria (Järup and Åkesson, 2009; Satarug et al., 2010; Han et al., 2013). Since the appearance of the Itai-Itai disease in Japan in 1912, the environmental impact of Cd has been the object of significant societal concern. Numerous studies have reported Cd contamination of soils, food crops, water and sediments worldwide, leading to serious potential health risks to humans (e.g., Robson et al., 2014; Zhang et al., 2014). Cadmium in soils may transfer to crops with a high soil-to-plant transfer factor, as a result of the influence of soil characteristics (pH, SOM, etc.), and physiological plant features (size of leaf, evaporation rate, etc.). The result is that crop consumption has been regarded as the primary exposure pathway for non-smoking and non-occupationally exposed populations (Järup and Åkesson, 2009; Satarug et al., 2010).

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Whereas researchers have intensively demonstrated Cd contamination of soils and crops, with subsequent health risks in areas with anthropogenic Cd pollution, little information is available about areas where Cd occurs naturally in soils, leading to elevated Cd concentrations crops (Khan et al., 2010; Liu et al., 2013). Such areas are found in various parts of the world. For example, in the Three Gorges Region of southwestern China, the weathering of Cd-rich sedimentary rocks over many centuries has produced soils that are naturally rich in Cd (Liu et al., 2013). The main health hazard in this rural area has traditionally been associated with endemic fluorosis due to the combustion of F-rich coal (Zheng et al., 1999), but the natural enrichment of Cd in the local environment has been considered to be a hidden, yet also very problematic, concern for the local populations (Tang et al., 2009; Liu et al., 2013).

Previous studies (Tang et al., 2009; Liu et al., 2013) have demonstrated the high Cd background values and distinguished the major sources of Cd in the study area. On the basis of these results, the objectives of our research were to assess the pollution level and ecological risk of Cd in the arable soils. By combining Cd concentrations in local food crops and waters, with the statistical data of local governments and other published results, the daily intake of Cd by the residents was estimated, the exposure pathways and potential health risk were assessed. In addition, urine samples were collected in the study area to identify the Cd burden of local residents. Throughout our research, efforts have been made to describe in enough detail the methodologies adopted, so that they can be implemented in other parts of the world where high geogenic background concentrations of Cd could similarly cause health risks to local populations.

2. Materials and methods

2.1. Study area

The study area is located at Jianping (109 °55′ – 109 °58'E, 31 °01′ – 31 °03′N), a rural area in Wushan County, the Three Gorges region of southwestern China (Fig. 1). The region's subtropical continental monsoon climate is warm and humid, with an annual average precipitation of 1052 mm and a mean temperature of 18 °C. The study area is part of an extensive area of karst terrain. Severe soil erosion has occurred in the region, caused by sparse vegetation cover and sloping topography. Rock outcroppings in the study area include lithologies from the Silurian to the Permian periods, mainly composed of carbonate stones, carbonaceous mudstones, siltstones, coal seams, and a few occurrences of siliceous mudstones, siliceous limestones and sandstones (Tang et al., 2009; Liu et al., 2013). There are no industrial activities or highways in the study area. Geological weathering of the parent rocks and historical rocky coal mining and combustion were demonstrated as the major sources of Cd in local soils (Liu et al., 2013). The daily consumed food crops were locally produced, except for the staple food, rice, which was purchased from markets, since no

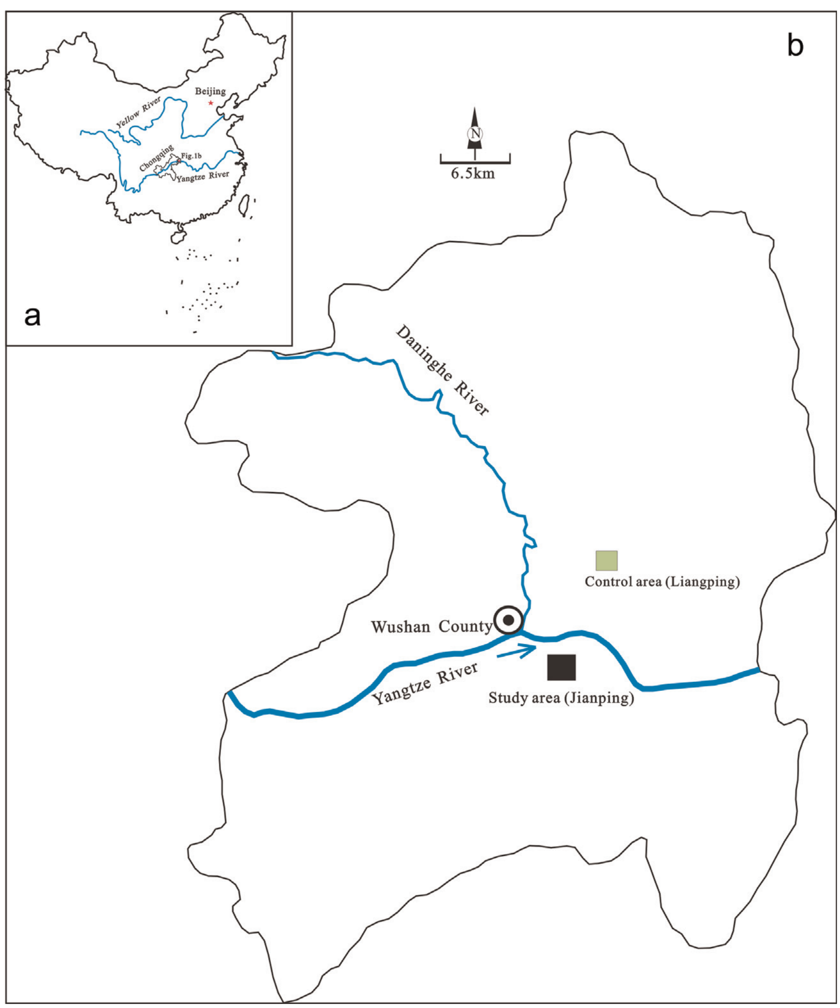

Fig. 1. Map showing the study area

paddy were planted in the study area, due to limited irrigating water supplies.

The control area is located in the Liangping township (109 °56′ – 109 °57′E, 31 °06′ – 31 °07′N) in Wushan County, approximately 7 km north-northeast of the study area (Fig. 1). The outcropping rocks in this control area have origins in the Triassic period, and are mainly composed of carbonate rocks, sand stones and mudstones (Chongqing Bureau of Geology and Minerals Exploration, 2002). The climate and living habitats were similar to the study area.

2.2. Sample collection and preparation

Thirty-three arable soils were collected in study area in 2010, as described by Liu et al. (2013). At the same time, samples of thirty-five of the edible parts of main local crops were collected, including leaves of Chinese cabbage (Brassica *pekinensis* L.) and green cabbage (Brassica *oleracea* L.), chili peppers (*Capsicum annuum* L.), maize (*Zea mays* L.), beans (*Glycine max* L.), potato (*Solanum tuberosum* L.), pachyrhizus (*Ipomoea batatas* L.) and radish (*Raphanus sativus* L.). All the crops were sampled *in situ*. In addition, four maize samples were collected from local households after harvest. Fourteen polished rice (*Oryza sativa* L.) samples were collected from local families, which were purchased from the local markets of Wushan County, since no paddy soils were planted with rice in the study area. These polished rice samples were mainly imported from the major grain producing areas in China, such as northeast and central China. Fifteen water samples were collected from local wells, springs, brooks, and rainfall. The water samples were filtered *in situ* with a 0.45 µm filter and then preserved in cooler at 4 °C. The soil and crop samples were placed in plastic bags at site, and were then transferred to the laboratory as soon as possible.

With the support of local Wushan Bureau of Health, forty-six urine samples were collected from residents of the study area, and ten urine samples were collected from the control area. During field sampling, a questionnaire was used to collect data on the age, sex, dietary and behavioral habits of each participant. The volunteers were also adequately informed of the aims, methods and anticipated benefits of the study. Informed consent was obtained from all study participants prior to the collection of urine samples. However, the urine samples from young people (age around 20 to 30 yr) were limited, as most work in cities as peasant-workers in the vast majority time of year. The urine samples were obtained in the pre-cleaned tubes, and then kept in a cooler at 4 °C until they were transported to the laboratory for analysis.

The crop samples were washed first with tap water and then with Milli-Q water. They were then dried at 60 °C in an electric oven until their weights were stable, after which the water content was calculated. The samples were ground in a mortar and pestle to a grain size small enough to pass through a 2-mm sieve, and then further ground to powders able to pass through 100-mesh (< 149 µm). Cadmium concentrations of foodstuff samples were based on the fresh weight, which were calculated from the dry weight and water content.

2.3. Analytical methods

Solid samples (50 mg) were digested with a mixture of HNO_3 and HF in Teflon tubes, and the water samples (10 mL) were directly subjected to analysis, using standard procedures described elsewhere (Qi and Gregoire, 2000; Liu et al., 2013). Urine samples were analyzed directly after a 1/5 (v/v) dilution with 1% HNO_3 (Heitland and Köster, 2004). Trace metals were measured by ICP-MS (PerkinElmer, ELAN DRC-e) at the Institute of Geochemistry, Chinese Academy of Sciences.

Quality control of trace element analyzes was assessed with standard reference samples (GSS-5, GSV-2, GSB-5), internal standards (rhodium (Rh) at 500 µg L^{-1}), blank and duplicate samples. For the urine and water samples, standard solution addition method (Cd at 20 µg L^{-1}) was applied to assess the quality control. The measured Cd concentrations in standard materials GSV-2 and GSB-5 were 0.36 ± 0.03 mg kg^{-1} ($n=5$) and 0.039 ± 0.004 mg kg^{-1} ($n=4$), respectively, which were consistent with the certified values at 0.38 mg kg^{-1} and 0.035 ± 0.006 mg kg^{-1}, respectively. The recovery of the standard addition ranged from 89% to 107%.

2.4. Statistical analysis

The data resulting from the various analyzes were treated statistically with the SPSS software (version 18.0 for Windows). Statistical significance was computed using the Independent Sample T-test, with a significance level of $\alpha=0.05$.

2.5. Geo-accumulation index

The Geo-accumulation index (I_{geo}), adapted from Müller (1969), was used to assess the Cd contamination level of arable soils, it was calculated according to the following equation:

$$I_{geo} = log_2(C_i/1.5B_i) \tag{1}$$

where C_i is the measured concentration of Cd in soils, B_i is the geochemical background concentration of Cd in soils, the constant, 1.5, is a correction coefficient that helps analyze the natural fluctuations and anthropogenic influences (Wei and Yang, 2010). In this study, three different background concentrations were used to calculate the I_{geo}, including the geochemical background value of study area (0.97 mg kg^{-1}; Liu et al., 2013), the value of Three Gorges region (0.134 mg kg^{-1}; Tang et al., 2008) and Chinese soils (0.09 mg kg^{-1}; Yan et al., 1997). According to Müller (1969), the I_{geo} was classified as: Uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < I_{geo} \leq 3$); heavily contaminated ($3 < I_{geo} \leq 4$); heavily to extremely contaminated ($4 < I_{geo} \leq 5$); extremely contaminated ($I_{geo} \geq 5$).

2.6. Ecological risk

The ecological risk factor (E_r) was calculated according to Håkanson (1980), which was first applied to assess the ecological risk of metals for water-sediment systems, and later applied to soils (Sun et al., 2010). Following equation was used to calculate E_r:

$$E_r = \frac{C_i}{B_i} T_i \tag{2}$$

where C_i is the measured concentration of Cd in soils, B_i is the geochemical background concentration of Cd in soils (including the value of study area, Three Gorges region and Chinese soils, as mentioned above), and T_i is the toxic factor, which was assumed at 30 for Cd (Håkanson, 1980). As described by Håkanson (1980), the E_r was classified as: low potential ecological risk (E_r40); moderate potential ecological risk ($40 \leq E_r < 80$); considerable potential ecological risk ($80 \leq E_r < 160$); high potential ecological risk ($160 \leq E_r$320) and very high potential ecological risk ($E_r \geq 320$).

2.7. Estimated daily intake

The estimated daily intake of Cd (*EDI*) through dietary exposure and other environmental exposure was calculated with the following equation:

$$EDI = \frac{C_i \times D_{\text{in take rate}}}{B_{\text{average weight}}} \quad (3)$$

where C_i represents the Cd concentration in food crops and other media. $D_{\text{intake rate}}$ represents the daily intake of foodstuffs. The parameter $B_{\text{average weight}}$ represents the average body weight, which was assumed to be 60 kg for Chinese adults (Wang et al., 2005). The reference dose (RD) of daily intake of Cd is 60 μg d^{-1} for a 60 kg adult according to USEPA (2002). To systematically evaluate the dietary exposure and health risk of Cd, published scientific results and government statistical data were used. The foodstuff daily intake rates for rural population were assessed at 511 g of rice, 346 g of vegetables, 97.5 g of meat, 19.5 g of fresh egg, 4.74 g of fresh milk, and 9.48 g of fish (BCS, 2012). Intake rates of air were assumed at 15 m^3 d^{-1} (Meng et al., 2007), and water consumption was at 2 L d^{-1} (NSC, 1998). Cadmium concentrations in rice (0.04 mg kg^{-1}), vegetables (0.68 mg kg^{-1}) and water (0.14 μg L^{-1}) were measured in this study, and the values of other foodstuffs (0.022 mg kg^{-1} for meat, 0.008 mg kg^{-1} for egg, 0.003 mg kg^{-1} for milk, 0.067 mg kg^{-1} for fish) were cited from a previous publication (Wang et al., 2002). Cadmium levels in the air were estimated at 0.007 μg m^{-3} (Tan and Duan, 2013). However, fruits and food additives were neglected in this research, because they are usually purchased from markets and have low amount of consumption.

2.8. Non- carcinogenic risk of Cd

According to the USEPA method (USEPA, 2000), the risk of non-carcinogenic effects is expressed as Target Hazard Quotient (THQ), which is the ratio of the dose resulting from exposure to site media compared to the highest dose without risk of adverse effects. The THQ through dietary exposure could be assessed based on the oral reference dose (RfD) for Cd and determined by the following equation:

$$THQ = \frac{EDI}{RfD} \quad (4)$$

where EDI represents the estimated daily intake of Cd, the RfD is the reference oral dose, 0.001 mg kg^{-1} d^{-1} for Cd (USEPA, 2002).

3. Results

3.1. Cadmium in soil

The total concentration of Cd ranged from 0.42–42 mg kg^{-1} (mean at 7.1 mg kg^{-1}) in the arable soils of the study area (Liu et al., 2013), which is nearly 80 times the background value of Chinese soils (0.09 mg kg^{-1}) and 24 times the safety threshold value (0.3 mg kg^{-1}) of the Chinese EPA (NSC, 1995; Yan et al., 1997). When compared to other high Cd background areas (Table 1), the soil Cd concentration in the study area is higher than that found in most of areas where Cd originated from geogenic sources, lower than for soils influenced by Cd-rich phosphorites in Jamaica. The calculated I_{geo} and E_r of Cd are listed in Table S1 (Supplementary Materials). Here, the I_{geo} relative to the Cd background value of the study area, ranged from −1.78 to 4.84 (mean at 1.39, moderate contamination). By comparison, it ranged from 1.08–7.71 (mean at 4.26, heavily to extremely contaminated) relative to background value of the Three Gorges region, and ranged from 1.60 to 8.22 (mean at 4.77, heavily to extremely contaminated) relative to that of Chinese soil. When Cd baseline of study area was considered, the E_r value of Cd was 13.1–1293 (mean at 218), which corresponded to a high ecological risk, while background values of Three Gorges region and China were adopted, ecological risk reach to very high level.

Table 2
Cadmium concentration in food crops (mg kg^{-1}, fresh weight) and water (μg L^{-1}) in study area

Crops	Min	Max	Mean	SD [a]	N [b]
Chinese cabbage	1.97	5.49	3.57	1.78	3
Pachyrhizus	0.01	0.23	0.08	0.07	8
Green cabbage	0.48	1.9	1.12	0.72	3
Chili	0.08	0.77	0.37	0.25	7
Radish	0.1	2.93	0.89	1.36	4
Bean	0.18	1.2	0.62	0.5	4
Potato	0.12	0.21	0.16	0.07	2
Maize	0.01	0.04	0.02	0.01	4
Total vegetables	0.01	5.49	0.68	1.16	35
Rice	0.01	0.13	0.04	0.05	14
Water	0.05	0.36	0.14	0.08	15
China Safety limits					
Leaf vegetables [c]			0.2 mg kg^{-1}		
Root vegetables [c]			0.1 mg kg^{-1}		
Other vegetables [c]			0.05 mg kg^{-1}		
Rice [c]			0.2 mg kg^{-1}		
Drinking water [d]			5μg L^{-1}		

[a] Standard deviation.
[b] number of sample.
[c] NSC (2005).
[d] NSC (2006).

3.2. Cadmium in local crops and water

The measured total concentrations of Cd in the food crops and waters (Table 2) suggest that most of the crops had high Cd concentration, while water samples contained low Cd concentrations. Average Cd concentrations in local food crops decreased in the following order: Chinese cabbage (3.57 mg kg^{-1}) > green cabbage (1.12 mg kg^{-1}) > radish (0.89 mg kg^{-1}) > beans (0.62 mg kg^{-1}) > chili (0.37 mg kg^{-1}) > potato (0.16 mg kg^{-1}) > pachyrhizus (0.08 mg kg^{-1}) > maize (0.04 mg kg^{-1}). Compared with the national standards of China (NSC, 2005), its concentrations in all the edible parts of the crops exceeded the safety limits, except in the pachyrhizus (0.08 mg kg^{-1}) and maize (0.02 mg kg^{-1}). Cadmium

Table 1
The comparison of Cd concentration (mg kg^{-1}) in soils with geogenic sources from different sites

Location	Cd concentration	Parent rocks	References
Study area	0.42–42	Black rock sereis	Liu et al. (2013
Switzerland	0.33–2.0	Carbonate rocks	Quezada-Hinojosa et al. (2009)
Gilgit, Pakistan	0.3–2.3	Vocanic&meta-sedimentary rocks	Khan et al. (2010)
USA	0.01–1.5	Shale	Jacob et al. (2013)
Okchon, Korea	0.2–20.1	Black shale	Lee et al. (1998)
Providence, Jamaican	142–771	Limestone + phosphorites	Garrett et al. (2008)
Portugal	0.1 (median)	Sulfide–gold mineralization area	Reis et al. (2012)

concentrations in the leaf vegetables (Chinese cabbage and Green cabbage) were higher than the others (Table 2). Cadmium concentrations in the polished rice samples ranged from 0.007 to 0.13 mg kg^{-1} (mean at 0.04 mg kg^{-1}), which was lower than the safety limits for rice (0.2 mg kg^{-1}). Cadmium in local water samples varied from 0.05 to 0.36 μg L^{-1}, with an average of 0.14 μg L^{-1}, all the samples were in the allowable range for drinking water (5 μg L^{-1}).

3.3. Estimated daily intake of Cd and target hazard quotient

Estimates of adults' daily intake (EDI) and health risk index of Cd in the rice, vegetables and other environmental sources in the study area (Table S2, Supplementary Materials) show that the EDI for Cd decreases in the order of vegetables (3.92E-03) > rice (3.41E-04) > meat (3.58E-05) > air (1.75E-05) > fish (1.06E-05) > water (4.67E-06) > egg (2.60E-06) > milk (2.37E-07). The total daily intake of Cd from local food crops for local inhabitants was estimated at 260 μg d^{-1}. Among the crops, the vegetables were the major source that contributed 90.5% of daily Cd intake to local residents, and then the rice contributed 7.9% (Table S2). The THQ value (4.33) for adults via the potential exposure paths in the study area was higher than 1, implying a non-carcinogenic risk of Cd for the local population.

3.4. Cadmium in human urines

Urinary Cd (UCd) is a biomarker of cumulative Cd exposure, associated with the level of body burden and proportional to the concentrations in kidneys (Järup and Åkesson, 2009; Wang et al., 2011). In order to investigate the influence of Cd on local populations, the urine samples of residents from the study area and control area were collected. The results of Cd concentrations (Table 3) showed that the urinary Cd concentrations of inhabitants in the study area were significantly higher than those of the control area ($p < 0.05$). In the study area, urinary Cd concentrations ranged from 0.43 to 27.60 μg L^{-1}, with the maximum and minimum values both found in males. Sixty seven percent of the urinary Cd concentrations were above 2 μg L^{-1}, whereas the Cd concentration in the urine of normal Chinese people was lower than 2 μg L^{-1} (Meng, 2000). Male (mean 3.92 μg L^{-1}) and female (4.85 μg L^{-1}) Cd concentrations were not significantly different ($p > 0.05$). In the control area, Cd concentrations in all the urine samples were below 2 μg L^{-1}. For the study area, the concentrations of Cd in the urine samples significantly correlated with age ($r^2 = 0.498$).

Due to the large variances of urinary Cd levels in the collected samples, log transformation (log(UCd)) was performed on the urine Cd concentrations (Table 3). The results showed that log(UCd)s of local residents (mean at 0.45) were significantly higher than those of the control area (−0.32) ($p < 0.05$), but not significantly different for males (0.36) and females (0.57) in the study area ($p > 0.05$).

4. Discussion

4.1. Soil contamination of Cd

The observations made earlier (Tang et al., 2009; Liu et al., 2013) demonstrated that the study area is characterized by high geochemical baselines of Cd, caused by geogenic sources, as well as, in part, by a history of mining of coal deposits rich in Cd. Cadmium in arable soils (7.1 mg kg^{-1}) of the study area exhibit significant enrichment; the enrichment factors relative to the average value of Chinese soils (0.09 mg kg^{-1}) are 79, and total Cd concentration in arable soils was 24 times the threshold value (0.3 mg kg^{-1}) for soils in China. The collected data listed in Table 1 showed that Cd concentrations in local arable soils were much higher than the concentrations reported in other soils with geogenic sources. Furthermore, the Cd concentration in the study area were even higher than some soils contaminated by anthropogenic sources, for instance 4.4 mg kg^{-1} Cd in garden soils have been recorded from a polymetallic sulfide mining area in southern China (Zhuang et al., 2009), and 0.84 mg kg^{-1} Cd have been recorded in soils impacted by wastewater irrigation in northern China (Khan et al., 2008). Carbonate rocks and black shales (or black series) are likely to be important geogenic sources of Cd in worldwide (Table 1). According to earlier results (Liu et al., 2013), the black rock series (0.37–21 mg Cd kg^{-1}) and the carbonate rocks (0.22–3.6 mg Cd kg^{-1}) of the study area were rich in Cd. These results indicate that more attention should be paid to the environmental problems induced by Cd originating from the natural weathering processes of Cd-rich sedimentary rocks.

In this research, three different soil background values of Cd were used to calculate the Geo-accumulation index and ecological risk of Cd in arable soils. The value of two indexes listed in Table S1 (Supplementary Materials) showed significant differences in pollution level and ecological risk. Results calculated from the baseline in the study area displayed moderate Cd contamination levels and high ecological risk in arable soils. While heavy to extremely heavy contamination levels and very high ecological risk levels were obtained when the background values of soils of the Three Gorges region and China were used. As mentioned before, the study area possesses a high geochemical background of Cd due to the weathering of Cd-rich parent rocks. Therefore the I_{geo} and E_r calculated from soil baseline from the Three Gorges region and China were likely to overestimate the pollution status of Cd in these arable soils, consequently unreasonable conclusion may be obtained. Therefore, in the areas with geogenic sources of Cd,

Table 3
Concentrations of Cd in the urine samples of residents (μg L^{-1})

	Study area				Control area			
	Range		Mean ± SD [a]		Range		Mean ± SD	
	UCd	log (UCd)	UCd	log(UCd)	UCd	log(UCd)	UCd	log(UCd)
Male [b]	0.43–27.60	−0.37–1.44	3.92 ± 5.69	0.36 ± 0.41	0.17–1.52	−0.78–0.18	0.80 ± 0.56	−0.21 ± 0.39
Female [c]	1.48–15.78	0.17–1.20	4.85 ± 4.17	0.57 ± 0.31	0.21–0.62	−0.69–0.21	0.42 ± 0.20	−0.43 ± 0.24
Total	0.43–27.60	−0.37–1.44	4.3 ± 5.09	0.45 ± 0.38	0.17–1.52	−0.78–0.18	0.61 ± 0.44	−0.32 ± 0.33

[a] Standard Deviation.
[b] 27 males in the study area, and 5 in the control area.
[c] 17 females in the study area, and 5 in the control area.

suitable background values should be adopted when these indexes are calculated.

The total Cd contents in soils does not give enough information on risk, therefore the distribution of chemical fractions of Cd in soils from different naturally-induced Cd area are discussed. In the study area, residual (27–66%, mean at 41%), reducible (8.2–36%, mean at 21%) and exchangeable (3.7–37%, meat at 21%) fractions were the dominant phases in soils, and the potentially bioavailable fractions (soluble, exchangeable, and carbonate together) ranged from 15% to 47% (mean at 31%) of the total Cd in the soils (Liu et al., 2013). For the soils from weathered carbonate rocks in Switerland, cadmium mostly existed in the carbonate fraction (49.3%), Fe-oxides (31.7%) and organic (12.7%) fractions. No exchangeable and little residual fraction (2.4%) were detected (Quezada-Hinojosa et al., 2009). For the soils where Cd originated from black shale (Korea), four fractions were analyzed, with the exchangeable fraction accounting for 18.4% in soils from the Bo-Eun area, and 22.5% for soils from the Chu-Bu area; the other two dominant factions were residual and oxidizable fractions (Lee et al., 1998). In the soils of a sulfide–gold mineralization area in Portugal, 29.4–67.9% (mean at 49%) of total Cd existed in the residual fraction (aqua-regia), 12% in the exchangeable, water and weak acid-soluble fractions, and 19% in the easily reducible fraction (Reis et al., 2012). However, in smelter-contaminated arable soils in France, the dominant phase containing Cd in soil was exchangeable, the water and acid soluble fraction (44.1%), and the reducible fraction (42.7%) (Pelfrêne et al., 2011). Similar results also demonstrated in other anthropogenically-polluted soils, which are characterized by a high portion of exchangeable fraction and low residual fraction (Chlopecka, 1996; Li and Thornton, 2001). Globally, residual, reducible and exchangeable fractions are the dominant chemical forms of Cd in soils, however, in the naturally-occurring Cd soils, low exchangeable and high residual fractions are found, indicating that the parent materials have significant influence on the chemical portioning of Cd, as in soils of Switzerland, where the carbonate fraction accounts for nearly half of total Cd. But in the anthropogenically-influenced soils, most of the Cd is found in the exchangeable fraction.

4.2. Food crops contamination of Cd

Heavy metals that are either naturally-occurring in soils or result from human activities may accumulate in food crops and lead to public health problems, (Kabata-Pendias and Pendias, 2001). In the study area, Cd accumulation in most of the local vegetables is much higher than the safety limits (Table 2). Leaf vegetable contained higher Cd concentrations than other vegetables, a result that was also observed in areas irrigated with wastewater (Khan et al., 2008, 2013) and at mining sites (Zhuang et al., 2009). This may be correlated with the high transpiration rate of some leafy plants (Tani and Barrington, 2005), and the expanded leaf of these vegetables may also make them more sensitive to dry and wet deposition (dust and rainwater) (Luo et al., 2011; Khan et al., 2013). Cadmium concentrations in vegetables of study area varied from 0.02 mg kg^{-1} in maize to 3.57 mg kg^{-1} in Chinese cabbage. The obvious differences of Cd among these kinds of food crops may be due to the morphological and physiological changes (Itanna, 2002), and to changes in the characteristics of the arable soils. While Cd in soils is the major source of Cd in crops, atmosphere deposition could be potential source of Cd in plant (Kabata-Pendias and Pendias, 2001). The heterogeneity of soil composition and elements, as well as the variance of Cd in soils (Liu et al., 2013) and the physiological differences of plants culminate in the variance of Cd accumulation in crops. Furthermore, soils from the study area also with relative high potential bioavailability (31% of potential bioavailable fractions) and most of soils displayed weak acidity, further inducing the uptake of Cd by plants. Since the rainwater analyzed in this study displayed low Cd concentrations (0.06–0.11 μg L^{-1}), it is reasonable to assume that the high Cd concentration in the soil and relatively high bioavailability are key factors determining the accumulation of Cd in local crops. Moreover, leafy vegetables such as Chinese cabbage and green cabbage are not recommended for cultivation in this area.

No rice paddy soils are available in the study area, due to the slopy nature of the terrain and the relative scarcity of surface water. Therefore the polished rice samples analyzed in the present study were obtained from both local markets and households. Cadmium concentration in the rice samples was found to be in the safe range, with a mean of 0.04 mg kg^{-1}, which similar to the Cd concentration (0.05 mg kg^{-1}) in Chinese market milled rice (Qian et al., 2010). Comparison with available international statistics suggest that Cd content in locally-consumed rice is lower than that in rice samples from Bangladesh (0.099 mg kg^{-1}), India (0.078 mg kg^{-1}), Japan (0.059 mg kg^{-1}), Nepal (0.050 mg kg^{-1}), Sri Lanka (0.081 mg kg^{-1}), and Vietnam (0.076 mg kg^{-1}), but higher than that in rice produced in the USA (0.018 mg kg^{-1}) and Spain (0.024 mg kg^{-1}), and equivalent to those in Italy (0.038 mg kg^{-1}) (Minh et al., 2012; Meharg et al., 2013). These results imply that the Cd in consumed rice in the study area is within safe limits.

4.3. Pathways of Cd exposure to residents

The study area is located in a mountainous region, far away from urban zones, and the arable soils are thin due to a bare topography and severe soil erosion. Although the local arable soils have high Cd concentrations, the local residents traditionally rely on them for planting multifarious food crops, except rice, in such a way that local residents may have long-term exposure to Cd through conventional consumption of Cd-rich food crops.

Generally, ingestion of food crops in a regular diet is the most important pathway of Cd exposure (Järup and Åkesson, 2009). Various studies have reported that metal contaminations of food crops are mainly due to anthropogenic contributions, e.g., wastewater irrigation and mining activities (Wilson and Pyatt, 2007; Khan et al., 2008; Khan et al., 2013; Zhuang et al., 2009). In the study area, high Cd concentrations (range of 0.01-5.49 mg kg^{-1}, mean at 0.68 mg kg^{-1}, fresh weight) are found in the locally-produced food crops. The majority of local food crops show elevated Cd concentrations that are above the Chinese safety limits for food stuffs (Table 2). Daily intake of Cd by dietary exposure listed in Table S2 (Supplementary Materials) show that intake of locally produced vegetables accounts for 90.5% (235 μg d^{-1}) of the studied total daily intake (Fig. 2), due to the high Cd concentration and high intake rate of vegetables. Notably, leaf vegetable has higher Cd concentration than other crops, and they are important daily food stuffs for local population in the Three Gorges region. For instance, daily intake of cabbage was 100 g d^{-1} (Yang et al., 2011). When only cabbage in the diet is considered, the average daily intake of Cd via cabbage is estimated at 234 μg d^{-1}, which means that intake of leaf vegetable is the most important exposure path.

Rice is the staple food of Chinese, especially in the south of China. Its intake rate is estimated at 511 g d^{-1} (BCS, 2012). This means that the daily Cd intake would be 20.4 μg d^{-1}, which only accounts for 7.9% of the total (Table S2), due to the low Cd concentration (mean at 0.04 mg kg^{-1}) in rice purchased from markets. Meat and other food stuffs contribute very little of total daily intake due to the low consumption rates and low Cd concentrations in them. Therefore, the dietary ingestion of Cd, mainly from consumption of local Cd-rich vegetables, is the major pathway of Cd exposure in the study area.

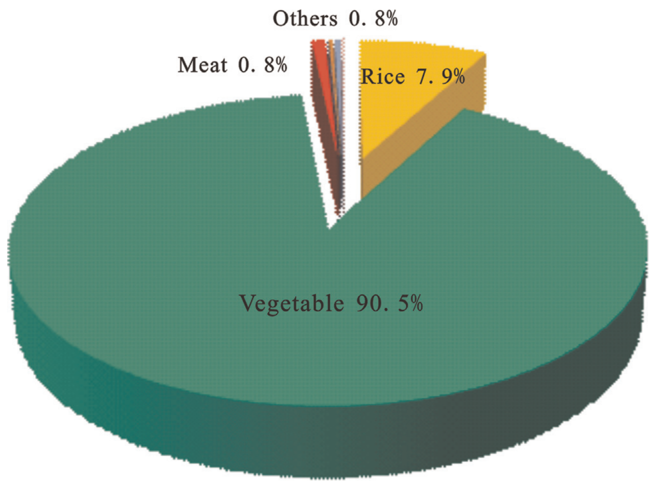

Fig. 2. Contribution of sources to daily Cd intake for residents in study area.

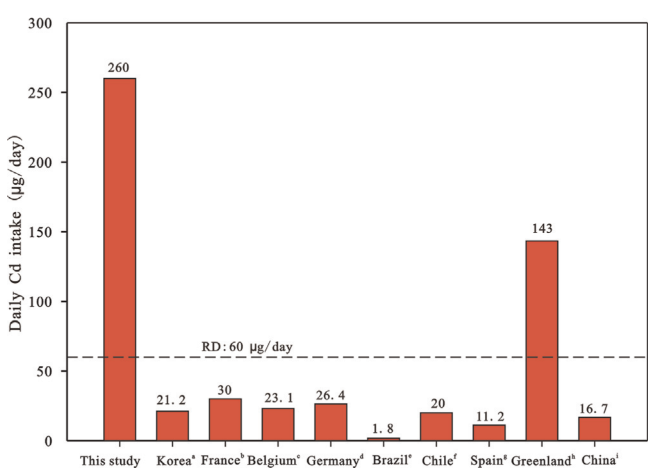

Fig. 3. Daily Cd intake for population in different areas ([a] Moon et al., 1995; [b] Biego et al., 1998; [c] Van Cauwenbergh et al., 2000; [d] Wilhelm et al., 2002; [e] Santos et al., 2004; [f]Muñoz et al., 2005; [g] Rubio et al., 2006; [h] Johansen et al. 2000; [i] He et al., 2013)

When compared to other locations of the world (Fig. 3), the daily Cd intake of the inhabitants of the study area (260 μg d^{-1}) is significantly higher than other locations, and 4 times the reference dose (RD, 60 μg d^{-1}). Other areas show lower daily Cd intakes than the reference dose, with the exception of Greenland (143 μ g d^{-1}) with 2 times the RD, in which the major source of Cd come from seal liver (Johansen et al., 2000). In these areas, diets may be responsible. For example, the major source of daily Cd intake in Chile and Spain is seafood (fish and shellfish) (Muñoz et al., 2005; Rubio et al., 2006); in Korea and China it is rice and vegetables (Moon et al., 1995; He et al., 2013); in France it is meat-poultry-eggs, milk-dairy-products and fish-crustaceans (Biego et al., 1998); in Belgium it is vegetables, potatoes and cereals (Van Cauwenbergh et al., 2000); in Germany it is vegetables and cereals (Wilhelm et al., 2002); and in Brazil it is rice and wheat flour (Santos et al., 2004). These comparisons indicate that cereal and vegetables may be the main contributors of daily Cd intake in most locations. While in some areas located beside ocean, seafood could be the major source of Cd in diet. Therefore, eating habits and geographical position are likely to be important factors controlling daily Cd intake.

Exposures via drinking water and inhalation of air were also estimated in this study. Cadmium concentrations in local waters ranged from 0.05 to 0.36 μg L^{-1} (mean at 0.14 μg L^{-1}), much lower than the Chinese national standard limit of 5 μg L^{-1} for drinking water (NSC, 2006). Thus the exposure to Cd from drinking water constitutes a relatively small contribution (0.28 μg d^{-1}) in the targeted area. Inhalation was estimated at 1.05 μg d^{-1}. These two sources are negligible when compared with other sources.

The local residents used to combust locally-mined coal, with high concentrations of fluorine and Cd for household heating and cooking, but the practice was stopped in 1983. Instead, they now use low-F coals imported from outside the area to prevent endemic fluorosis (Zheng et al., 1999; Tang et al., 2009). This substitution has improved the picture for fluorine, but not as dramatically for Cd. Compared to the locally-produced coals, characterized by very high Cd concentration (0.52–102 mg kg^{-1}, mean at 25 mg kg^{-1}; Liu et al., 2013), the currently-used coal, imported from outside the study area, also contains high Cd concentrations, ranging from 1.0 to 8.3 mg kg^{-1}, with a mean at 2.4 mg kg^{-1} (Tang et al., 2009). This is still significantly above the national average of 0.46 mg kg^{-1} for Chinese coal (Ren et al., 1999). Furthermore, the local residents mix coals with local clays, which are also rich in Cd, to make coal balls for easy domestic combustion, and this practice further contributes to the elevated Cd content of the coals. Indoor combustion of such coal balls produces fly ash, which may deposit onto the food crops stored there or may be directly inhaled by residents. Finally, the local custom of baking food crops such as chili and corn on a coal-burning stove indoors, because of the generally wet weather after harvest, is likely to elevate the Cd contents of stove-dried crops even more (Tang et al., 2009). Therefore, domestic coal combustion indoor may increase the Cd exposure of inhabitants via inhalation and diet in the study area.

The hand-to-mouth ingestion of Cd-rich soils may also lead to Cd exposure for local residents. Under normal living conditions, amounts of soil ingested by children are estimated to be of the order of 0–90 mg d^{-1} (Van Wijen et al., 1990), however it is far easier for children living in the countryside come into contact with soils. Adults who do farm work may also ingest and inhale more soil dust than most other people. Therefore, the hand-to-mouth behavior of soil ingestion may be a potential pathway of Cd exposure for local residents. Although the bioaccessibility of Cd in soils depends on soil characteristics, such as the pH or partitioning of Cd in soils (Tang et al., 2006), this exposure pathway should not be ignored.

As the research was carried out, it was observed that nearly all of the male adult residents smoked during the questionnaire survey. Various studies have demonstrated that smoking is an important source of Cd exposure due to enrichment of Cd in tobacco leaves (Olsson et al., 2002; Lugon-Moulin et al., 2006), and 10% of the Cd present in a cigarette is inhaled during smoking (WHO, 1992). The survey results show that a typical adult smoker in the study area consumes 20 cigarettes per day. Since the Cd content is 1–2 μg per cigarette (WHO, 1992), cadmium intake from smoking is therefore in the range of 2–4 μg d^{-1}. Although smoking represents a negligible Cd exposure to the local population compared with Cd intake from food crops, this exposure way may also have influence on the male inhabitants.

In summary, consumption of locally produced Cd-rich vegetables is the most important Cd exposure pathway for local inhabitants, but indoor coal combustion and smoking may also contribute to Cd exposure. These findings are in contrast with earlier observations, in other parts of the world, that consumption of rice and seafood is the major human Cd exposure pathway (Munõz et al., 2005; Minh et al., 2012).

4.4. Health risk of Cd

The health risk associated with Cd contamination in soils and food crops impacted by anthropogenic sources has given rise to widespread concern, whereas the potential health risk of Cd in areas without significant anthropogenic sources has been largely ignored. In the study area, action has been taken by local officials to combat endemic fluorosis, caused by the combustion of F-rich coal, but comparatively far less attention has been devoted to the health risk of Cd, in spite of the fact that it has been documented to lead to such as teeth and bone damage, with symptoms similar to those of fluorosis (Tang et al., 2009).

Urinary Cd (UCd) is a biomarker of cumulative Cd exposure (Järup and Åkesson, 2009; Tang et al., 2009; Wang et al., 2011). As discussed above, Cd has elevated THQ (4.33), thus elevated Cd concentrations may be observed in local residents′ urine samples. Indeed, elevated mean UCd level (4.3 μg L^{-1}) was observed in the study area, much higher than that found in the control area (0.61 μg L^{-1}). It was also higher than the mean UCd level (1.43 μg L^{-1}) of non-occupational dismantling people living in an electronic waste site in eastern China (Wang et al., 2011), and the urinary Cd of adults (1.88 μg L^{-1}) who lived in Shanghai, China (He et al., 2013). The local UCd levels are significantly higher than those of the general population of the USA, reported by Riederer et al. (2013). However, the age distribution in this study may have been skewed by the low numbers of young people (age around 20–30 yr), as most of these people work in cities as peasant-worker in the majority time of year. This social phenomena elevated the average age of study group (39.4 yr, $n=46$) higher than the average age of the control area (26.7 yr, $n=10$), which seem to elevate the urinary Cd concentrations of residents in the study area, although the dietary exposure mainly contribute to body Cd burden of residents. Both urinary Cd and log(UCd) were used for discussing the influence of large variance of Cd concentrations in urine samples, and showed significant differences in urinary Cd between the study area and the control area. For 16 local inhabitants aged under 18 yr, the observed urinary Cd contents ranged from 0.43 to 2.98 μg L^{-1} (mean at 1.64 μg L^{-1}), which was significantly higher than the average value for adolescents (0.65 μg L^{-1}) from the industrialized area of Ria of Huelva, Spain (Aguilera et al., 2010). When the residents of the study area over 20 years of age ($n=30$) were separated as a group, the average value of urinary Cd was 5.72 μg L^{-1} (ranging from 1.30 to 27.6 μg L^{-1}), which was significantly higher than for the group under 18 yr. The Pearson correlation coefficient analysis shows that UCd has significantly positive correlation with age ($r^2=0.498$, $p<0.01$), an observation that is consistent with results obtained by other researchers (Olsson et al., 2002; Cui et al., 2005), this may be related to the accumulation of Cd in the body. The local residents used to suffer from endemic fluorosis due to indoor combustion of F-rich coal that was also rich in Cd, therefore, they may also have long-term Cd exposure in the past. Such long term exposure of Cd may cause the older residents to have higher Cd burden than the younger group. In addition, there are no significant differences between male and female groups in the study area, but the female group has a higher mean UCd (4.85 μg L^{-1}) than the male group (UCd 3.92 μg L^{-1}), which may be explained by the higher absorption of Cd by the female body due to its lower iron status (Olsson et al., 2002).

In summary, the high Cd concentrations in local soils have resulted in significantly elevated Cd levels in locally-produced food crops, and the combustions of Cd-rich coal or coal balls elevates the Cd contents of both the air and food crops dried indoors. All the above processes may result in potentially high Cd exposure to the local population. This, in turn may have contributed to the elevated Cd levels observed in local residents′ urine samples, which were even higher than those from typical industrially-contaminated areas. In spite of this evidence, in the past several decades, the health risks resulting from Cd exposure through food chain and coal combustion have been entirely overlooked. As a matter of fact, there should be a drastically increased focus on the health risk of Cd in the study area, in addition to the current concern about endemic fluorosis.

5. Conclusions

This study points out the potential health risk of Cd in areas with high background of Cd. The local arable soils are significantly contaminated by naturally-occurring Cd, the chemical partitioning of Cd in naturally-occurring areas is influenced by parent rocks, which differs from the anthropogenic sources. The locally-produced food crops, in particular leaf vegetable, are rich in Cd, most of them exceed the safety limits for food. The daily Cd intake through ingestion of food stuffs and exposure to environmental sources is estimated at 260 μg d^{-1}, much higher than the reference dose and the dose received at other locations. The intake of vegetables is the most important exposure pathway, followed by rice and meat; indoor coal combustion could also be a potential exposure pathway. High daily intake of Cd induced a high THQ of 4.33, indicating that Cd is a health risk to local inhabitants. As a result of this exposure the concentration of Cd in the urine of local inhabitants is higher than that found in inhabitants from the control area. No significant differences between males and females were observed, but urinary Cd levels increased with age. These findings indicate that Cd in areas without significant anthropogenic contamination, but with a high natural Cd background concentration, may pose a sizeable health risk to local residents. This risk should be taken seriously, and measures should be devised to protect local populations against it.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2014.10.022.

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