High cadmium concentration in soil in the Three Gorges region: Geogenic source and potential bioavailability

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ARTICLE INFO

ABSTRACT

This study investigated the distribution and sources of Cd in soils from a Cd-rich area in the Three Gorges region, China. The results showed that in the study area arable soils contain 0.42–42 mg kg^{-1} Cd with 0.12–8.5 mg kg^{-1} in the natural soils, corresponding to high amounts of Cd (0.22–42 mg kg^{-1}) in outcropping sedimentary rocks in the area. Both lognormal distribution and enrichment factor (EF) plots were applied in an attempt to distinguish between geogenic and anthropogenic origins of Cd in the local soils. The lognormal distribution plots illustrated that geogenic sources dominated in soils with low and moderate Cd concentrations (<8.5 mg kg^{-1}), whereas anthropogenic sources (agricultural activities, coal mining) significantly elevated Cd contents in some arable soils (>8.5 mg kg^{-1}). The enrichment factor plots illustrated that the majority of the soil samples had EF values of <5, pointing to a geogenic origin of Cd in the soils, whereas some arable soils had EF values >5, pointing to an additional anthropogenic input of Cd to the soils. Sequential extraction results showed that Cd soluble in water and weak acid (water-soluble, exchangeable and carbonate fraction of the soil) accounts for an average of 31% of the total soil Cd, which indicates high potential for Cd mobility and bioavailability. The findings point to a potential health risk from Cd in areas with high geogenic background concentrations of this metal.

1. Introduction

Cadmium is a non-essential and toxic trace metal to human beings, animals and plants. Cadmium generally occurs at concentrations of 0.2 mg kg^{-1} in the lithosphere, 0.3 mg kg^{-1} in sedimentary rocks and 0.53 mg kg^{-1} in soil (Greenwood and Earnshaw, 1997; Kabata-Pendias and Pendias, 2001), but the enrichment of Cd in soil, from natural or anthropogenic sources, or both, is a major environmental concern. The natural sources of Cd in soil are mainly geological weathering (Garrett et al., 2008; Quezada-Hinojosa et al., 2009; Khan et al., 2010; Rambeau et al., 2010; Reis et al., 2012), whereas anthropogenic origins are usually from sewage irrigation, fertilizer application, mining, metal ore processing and smelting (Liu et al., 2005; Bi et al., 2006; Cloquet et al., 2006; Acosta et al., 2011; Li et al., 2011). With regard to Cd enrichment in soil, the source identification and potential bioavailability of this element have been the main considerations.

In the framework of systematic soil-surveying (scale 1:250,000), studies were carried out in the Yangtze River catchment during the early 2000s and anomalously high Cd concentrations were detected in the alluvial soils. Geological weathering, coupled with human activities, was regarded as the origin of the Cd enrichment (Cheng et al., 2005). Hitherto, only very limited studies have provided evidence on where and how the potential geogenic sources of Cd in contribute to its enrichment in soils. In a previous study, elevated Cd (1.01–59.7 mg kg^{-1}) was identified in soils from a rural area in the Three Gorges region, upper reach of the Yangtze River, which posed a potential health risk to the local population (Tang et al., 2009). The rural area in question is far removed from urban and industrial activity. The contributions of anthropogenic Cd from aerial deposition and application of sewage sludge, manure, and phosphate fertilizers are not sufficient to explain the anomalous Cd concentrations in soil, consequently, natural sources of Cd were hypothesized to be a potential source of the observed Cd enrichment in these soils (Tang et al., 2009). We also observed that the local coals are rich in Cd (Tang et al., 2009), however, local coal mining and past domestic use, which could be an important potential source of Cd in the soils, were not discussed for the purpose of source recognition by Tang et al. (2009).

To better understanding the distribution, source and potential bioavailability of the elevated Cd in the local soils, a follow-up

study was performed. This paper presents the results of the follow-up investigation on the occurrence of Cd in soils in the Cd-rich rural area within the Three Gorges region, and documents the sources and potential bioavailability of Cd in the soils.

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 of the Three Gorges region. The region's subtropical continental monsoon climate is warm and humid, with 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 that attains an elevation of 100–1200 m above sea level. Severe soil erosion has occurred in the region owing to the sparse vegetation cover and intensive agricultural activities (Tang et al., 2009). Rock outcrops in the study area include lithologies from the Silurian to the Permian (Fig. 1), and are mainly composed of carbonate rocks, carbonaceous mudstone, siltstone and coal seams (Tang et al., 2009).

There are no industrial activities in the study area, except for small-scale coal mines that have been abandoned for decades. Past mining and use of coal resulted in some endemic fluorosis in the local population. The residents formerly used the local F-rich coals for cooking and heating, but stopped this practice and used low-F coals brought in from outside the study area in 1983 (Zheng et al., 1999). However, the enrichment of Cd in the local coals and soils may act a hidden health hazard in addition to the risk of F (Tang et al., 2009). Past coal mining resulted in the exposure of Cd-rich gangue to weathering. A considerable amount of coal waste was directly disposed of on arable soils or was used to cover muddy country roads. In addition, ash from domestic utilization of coal may contribute to Cd in soil.

2.2. Sampling and analysis

Thirty-three rock and coal samples were collected from outcrops and abandoned mine sites, and 62 soil samples were collected from 49 sites in the Jianping area (Fig. 2). Rock samples consisted of carbonaceous mudstone, carbonaceous siltstone, carbonate rocks, coal and coal cinders. Soil samples consisted of arable soil, subsoil, and natural soil (including forest soil, slope wash materials, and in situ weathering soil). The arable and natural soil samples were collected using a stainless steel shovel. At least 3 subsamples (0–20 cm depth) were collected over an area of 5 m^2 to form a representative sample at each sampling site. Subsoil was collected from depths >20 cm in selected sites associated with arable soil, and represented soil which was less disturbed by anthropogenic activities. All the samples were placed in cloth bags at the field site and air-dried in the laboratory pending final processing. The soil and rock samples were processed for geochemical analysis by disaggregation to pass through a 2-mm sieve, and subsequent grinding to 200-mesh (<74 μm).

For trace metal determination, the rock and soil sample powders were digested with HNO_3 + HF in Teflon bombs in a method similar to that described by Qi and Gregoire (2000). One mL each of ultrapure HF (38% v/v) and ultrapure HNO_3 (68% v/v) were added to approximately 50 mg of sample. The bombs were placed in an electric oven (180 °C) for 24–30 h and then on a hot plate to remove F. Next, 1 mL of a 500 μg L^{-1} Rh solution was added as an internal standard and 2 mL of Milli-Q water and 2 mL HNO_3 (68% v/v) were added. The sealed bombs were then placed in an electric oven and heated to 140 °C for 4–5 h. After cooling, the final solution was made up to 100 mL by the addition of Milli-Q water. The reagent blanks were treated in the same way as the samples.

A modified sequential extraction method based on Zemberyova et al. (2006) was applied to investigate the geochemical partitioning of Cd in soil; the detailed procedures are summarized in Table 1. One g of soil sample (<74 μm) was weighed into a 100-mL glass
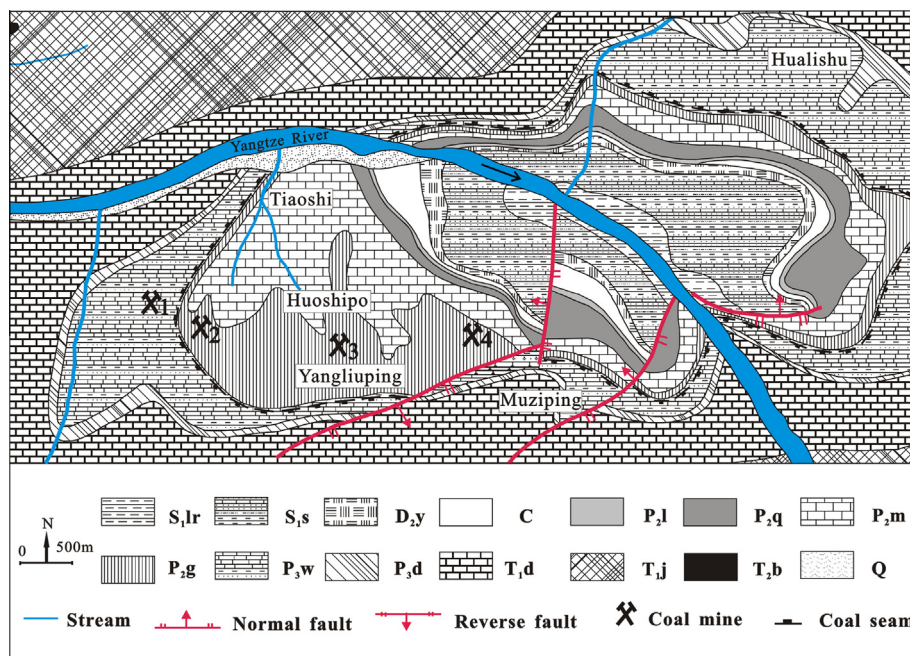

Fig. 1. Geological sketch map of the study area. S$_1$lr (Luoreping Fm.): Silurian siltstone and mudstone; S$_1$s (Shamao Fm.): Silurian silty mudstone and quartz sandstone; D$_2$y (Yuntaiguan Fm.): Devonian siltstone and sandstone; C: Carboniferous limestone, dolomite and sandstone; P$_2$l (Liangshan Fm.): Permian sandstone, carbonaceous mudstone and coal seam; P$_2$q (Qixia Fm.): Permian limestone; P$_2$m (Maokou Fm.): Permian limestone and dolomite; P$_2$g (Gufeng Fm.): Permian mudstone; P$_3$w (Wujiaping Fm.): Permian limestone, mudstone and coal seam; P$_3$d (Dalong Fm.): Permian mudstone and limestone; T$_1$d (Daye Fm.): Triassic limestone and mudstone; T$_1$j (Jialingjiang Fm.): Triassic limestone and dolomite; T$_2$b (Badong Fm.): Triassic limestone, mudstone, dolomite and sandstone; Q: Quaternary alluvium.
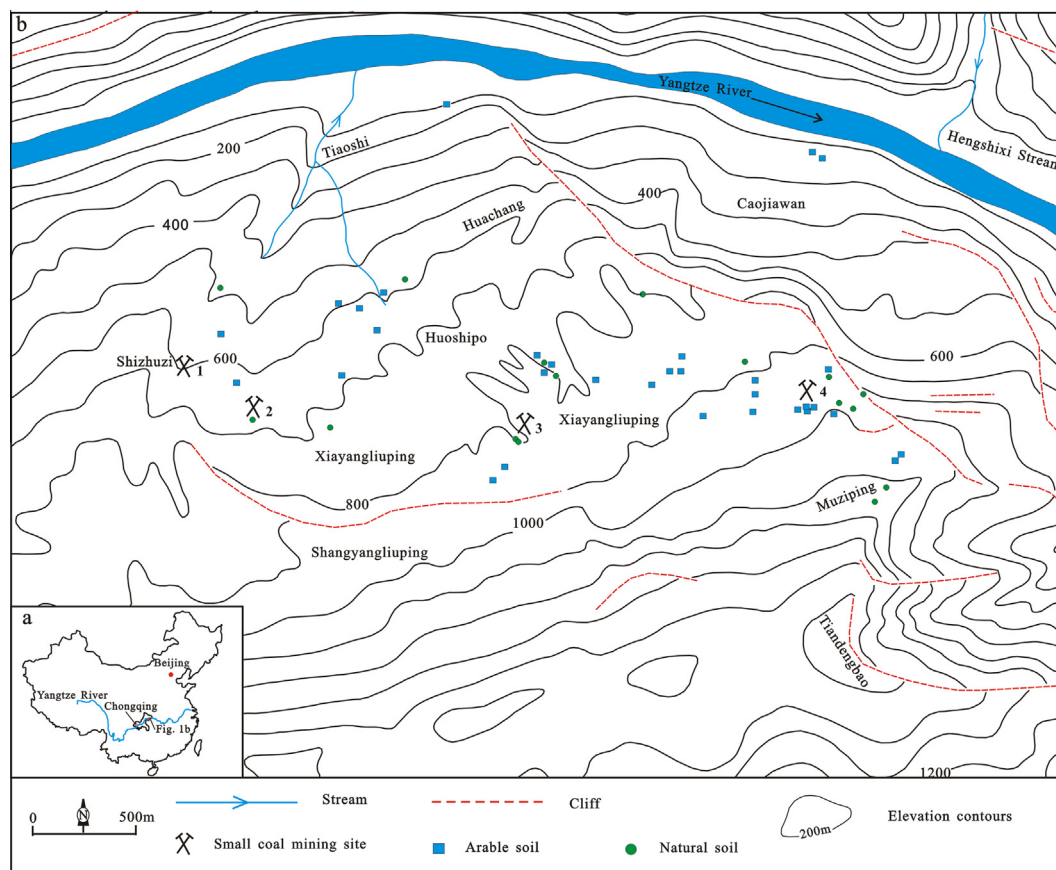
Fig. 2. Map showing the soil sampling sites.

Table 1
The sequential extraction procedure.

Fractions	Reagents
Water soluble	30 mL Milli-Q water
Exchangeable	8 mL MgCl$_2$ (1 mol L^{-1}, pH = 7)
Carbonate	8 mL NaAc (1 mol L^{-1}, pH = 5)
Reducible	40 mL NH$_2$OH·HCl (0.50 mol L^{-1}, pH = 1.5)
Oxidizable	10 mL H$_2$O$_2$ 8.8 mol L^{-1}
	10 mL H$_2$O$_2$ 8.8 mol L^{-1}
	50 mL NH$_4$Ac (1 mol L^{-1}, pH = 2)
Residual	HNO$_3$ + HF

centrifuge tube, and the procedures in Table 1 were followed to obtain water soluble, exchangeable, carbonate, reducible, oxidizable and residual fractions. Each 10-mL sample of the extracted fraction was mixed with 0.2 mL of the 500 µg L^{-1} Rh internal standard solution prior to analysis.

Soil pH was measured with a pH meter (AISI pHB9901, Taiwan, China) in a 1:2.5 soil-to-water solution after 10 min shaking and 5 min centrifugation. Soil organic matter (SOM, wt.%) was determined by the K$_2$Cr$_2$O$_7$–H$_2$SO$_4$ oxidation method.

The concentrations of trace metals were measured using inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, ELAN DRC-e) at the Institute of Geochemistry, Chinese Academy of Sciences. The analytical precision was better than ±10%, determined based on the standard quality control procedures of the laboratory using international certified reference materials (OU-6, AMH-1, GBPG-1, GSS-5, and TILL-1), internal standards (Rh at 500 µg L^{-1}), duplicates and reagent blanks. The major elements in selected soil samples were determined by X-ray Fluorescence (XRF, Axios PW4400). The mineral compositions of selected soil samples were determined by X-ray diffraction (XRD, D/Max-2200).

Statistical analysis was performed using SPSS software (version 18.0 for Windows).

3. Results and discussion

3.1. Physical–chemical characteristics of soil

The results of major elements determinations in the selected 25 soil samples are listed in Table 2. More than 85 wt.% of the major components are accounted for by SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$. Based on comparison to the upper crust (Taylor and McLennan, 1985) and Chinese soil (Yan et al., 1997), these soils are relatively richer in SiO$_2$ and Fe$_2$O$_3$ but have lower MgO, CaO and Na$_2$O contents. The high SiO$_2$ contents are probably due to the presence of siltstone, siliceous mudstone and sandstone in the study area (Fig. 1). High Fe$_2$O$_3$ contents (mean at 5.13 wt.%) have also been reported in the Three Gorges region (Tang et al., 2005). Low CaO contents (0.07–1.6 wt.% in the undisturbed natural soils) in the karst terrain of southwestern China have been reported (Xiao et al., 2004). All the soil types showed similar amounts of Al$_2$O$_3$, MgO and CaO, but the subsoil displayed high contents of Fe$_2$O$_3$. The XRD results for selected soil samples also showed similar mineralogical compositions, characterized by the clay mineralogy of the parent materials. The mineralogy was mainly composed of quartz, montmoduonite, illite and goethite.

The pH values range from 3.9 to 7.7 (Table 3), indicating the acidic and circumneutral soil. The SOM values range from 0.33% to 6.2%, with an average of 1.8%. This is likely due to the local

Table 2
Major composition of the selected soils (wt.%).

Sample		SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O
Arable soil (n = 16)[a]	Range	64–85	7.4–17	3.0–7.3	0.44–1.5	0.17–2.9	0.31–0.78	1.2–3.0
	Mean[b]	76	12	5.0	0.93	0.94	0.43	2.0
	SD[c]	7.3	3.2	1.4	0.39	0.82	0.12	0.59
Subsoil (n = 3)	Range	61–85	8.1–12	3.5–18	0.50–1.2	0.32–1.9	0.09–0.43	1.4–2.5
	Mean	74	11	8.9	0.86	0.92	0.31	1.8
	SD	12	2.5	8.1	0.35	0.82	0.19	0.58
Natural soil (n = 6)	Range	72–83	7.8–14	2.7–5.7	0.47–0.87	0.18–0.77	0.13–0.78	1.1–2.2
	Mean	79	11	4.3	0.73	0.37	0.50	1.7
	SD	3.8	2.5	1.2	0.14	0.21	0.25	0.41
Upper crust	Mean[d]	66	15.2	–	2.2	4.2	3.9	3.4
Chinese soil	Mean[e]	65	12.6	3.4	1.8	3.2	1.6	2.5

[a] n – Number of samples.
[b] Arithmetic mean.
[c] Standard deviation.
[d] Taylor and McLennan (1985).
[e] Yan et al. (1997).

Table 3
Summary statistics for concentrations of selected metals (mg kg^{-1}), pH and SOM (wt.%) in soil.

Samples		Cd	V	Cr	Ni	Cu	Zn	Pb	Zr	pH	SOM
Arable soil (n = 33)[a]	Range	0.42–42	100–1549	73–884	28–252	23–96	82–644	23–53	151–373	3.9–7.7	0.95–6.2
	Mean	7.1	401	301	95	50	230	36	260	6.1	2.3
	SD	9.4	308	230	54	19	124	8.7	9.9	1.1	1.1
Subsoil (n = 13)	Range	0.29–7.4	101–944	84–1181	31–217	20–347	75–352	22–42	115–408	4.8–7.5	0.41–2.1
	Mean	2.6	290	282	89	61	156	28	270	6.2	1.1
	SD	2.4	234	290	54	87	79	6	23	0.94	0.43
Natural soil (n = 16)	Range	0.12–8.5	80–545	69–1022	23–179	18–74	61–374	20–36	144–336	4.5–7.5	0.33–4.9
	Mean	2	197	194	59	34	158	28	251	6.1	1.5
	SD	2.4	124	236	40	15	91	5.4	15	1	1.1
Chinese soil	Mean[b]	0.09	82	65	26	24	68	23	250	–	–
	Safety limit[c]	0.3	–	200	50	200	250	300	–	–	–

[a] n – Number of samples.
[b] Yan et al. (1997).
[c] CNS (1995).

Table 4
Concentrations (mg kg^{-1}) of selected elements in rocks and coal.

Samples		Cd	V	Cr	Ni	Cu	Zn	Pb
Mudstone and siltstone (n = 15)[a]	Range	0.37–21	19–5960	43–1944	16–454	1.1–271	29–310	3.5–32
	Mean	4.6	978	426	112	65	132	15
	SD	6.7	1834	570	124	69	80	9.6
Carbonate rock (n = 5)	Range	0.22–3.6	5.9–1717	7.1–863	8.3–80	1.3–211	58–173	9.9–17
	Mean	1.7	410	207	34	55	111	14
	SD	1.6	740	369	32	89	43	2.9
Coal locally produced (n = 7)	Range	0.52–102	23–748	14–835	12–227	4.9–247	86–230	6.7–31
	Mean	25	397	256	92	123	147	16
	SD	37	237	288	69	99	61	8.8
Coal waste (n = 6)	Range	0.27–2.1	23–420	16–172	7.5–67	7.9–200	33–187	3.3–25
	Mean	0.97	217	89	34	101	112	18
	SD	0.77	170	66	25	94	59	8.5
World shale	Mean[b]	0.3	130	90	68	45	95	20
World carbonate rock	Mean[b]	0.035	20	11	20	4	20	9

[a] n – Number of samples.
[b] Turekian and Wedepohl (1961).

sparse vegetation cover. The arable soil display large values of SOM (mean at 2.3%), but the subsoils show lower SOM contents (mean at 1.1%), and the influence of agricultural activities is likely one of the reasons for this observation (Table 3).

3.2. Geochemical distribution of Cd in rocks and soils

The analytical data for Cd and selected elements in rocks and coals were listed in Table 4. The results reveal anomalies

Table 5
Pearson correlation coefficients among metals, SOM and pH in soils.

	SOM	pH	Cd	V	Cr	Ni	Cu	Zn	Pb
SOM	1								
pH	−0.003	1							
Cd	0.44[**]	0.004	1						
V	0.30[*]	0.006	0.76[**]	1					
Cr	0.26[*]	−0.26[*]	0.61[**]	0.84[**]	1				
Ni	0.27[*]	−0.2	0.75[**]	0.77[**]	0.79[**]	1			
Cu	0.11	0.06	0.2	0.27[*]	0.27[*]	0.60[**]	1		
Zn	0.30[*]	−0.11	0.73[**]	0.65[**]	0.57[**]	0.77[**]	0.45[**]	1	
Pb	0.44[**]	0.17	0.53[**]	0.43[**]	0.26[*]	0.37[**]	0.14	0.55[**]	1

[**] Correlation is significant at $p < 0.01$ level.
[*] Correlation is significant at $p < 0.05$ level.

concentrations of Cd in the local rocks of from 0.37 to 21 mg kg^{-1} in carbonaceous mudstone and siltstones, and from 0.22 to 3.6 mg kg^{-1} in carbonate rocks (Table 4). These elevated levels of Cd in the local rocks imply a high geochemical background for Cd in the study area, which is far greater than the average Cd concentrations in the upper crust (0.098 mg kg^{-1}; Taylor and McLennan, 1985), world shale (0.3 mg kg^{-1}; Turekian and Wedepohl, 1961), and world coal (0.1–3.0 mg kg^{-1}; Swaine, 1990). Thus, Cd enrichment in the local bedrocks revealed a geologically concentrated Cd zone within the Three Gorges region. It is of note that Cd anomalies in both sediments and bank soil along the Yangtze River have been identified previously, these being attributed mainly to natural weathering (Cheng et al., 2005). The high Cd concentrations in the local sedimentary rocks and coal seams demonstrate the natural contribution to elevated Cd found in the Yangtze River catchment.

The high Cd concentrations in the local rocks and coal consequently have contributed to the enrichment of Cd in the local soil, as a result of long-term natural weathering and human disturbance (e.g., coal mining and agricultural activities). The Cd concentration ranges in the arable soil are 0.42–42 mg kg^{-1} and 0.12–8.5 mg kg^{-1} in the natural soil (Table 3). The subsoil displayed lower concentrations of Cd (0.29–7.4 mg kg^{-1}, mean at 2.6 mg kg^{-1}) than the arable soil, which may reflect the influence of agricultural activities (Borgegard and Rydin, 1989). Generally, the concentrations of Cd decreased in the order arable soil > subsoil > natural soil. The concentrations of Cd in the local soils were far above the median value of 0.35 mg kg^{-1} for world soil (Bowen, 1979), 0.09 mg kg^{-1} for Chinese soil (Yan et al., 1997), and greatly exceeded the Chinese soil safety limit of 0.3 mg kg^{-1} (CNS, 1995) for agricultural soil. There is a significant correlation between the Cd concentration and SOM values ($R = 0.50$, Table 5), indicating that the organic adsorption or chelation could be an important factor controlling Cd accumulation in the local soils.

The local rock and coal also contained relatively high concentrations of V, Cr and Ni (Table 4). However, these metals were less enriched than Cd, compared with their average concentrations in world shale. The concentrations of Cu, Zn and Pb in the local soils were also greater than those of Chinese soil (Table 3), but the majority of them were generally below the safety limits for Chinese soil.

3.3. Recognition of Cd source in soil

There are no industrial activities or highways in the study area, except four small coal mines that have been abandoned for decades. Thus, the elevated Cd in the local soils could result from two major sources: the weathering of parent rocks and/or the impact of Cd-rich coal mining and use. The lognormal distribution

and the enrichment factor plots were used in an attempt to identify the sources of Cd in soil.

The natural soil represents the original soil in the study area, and the concentrations of metals in these soils may provide information about the local geochemical background. This soil type from the study area was enriched in Cd, ranging from 0.12 to 8.5 mg kg^{-1}. Similar enrichments were also observed for V, Cr, Ni and Zn. The sources for the elevated metals in soil were likely linked to the weathering of the local Cd-rich sedimentary rocks.

The natural processes of physical and chemical weathering of the outcrops or near-surface bedrocks could release large amounts of Cd and other metals to the soil. The bare topography with a number of cliffs and the warm and humid climate in the study area could facilitate the weathering of the Cd-rich black rock series. The Cd content of soil showed significant correlations with V, Cr, Ni, Zn and Pb (Table 5), which implied that these metals have the same origin. Large amounts of Cd in soil, originating from the weathering of black rock series, has also been reported by several authors (Peng et al., 2004; Falk et al., 2006; Tang et al., 2009; Tuttle et al., 2009). Thus, the large outcrops of the black rock series (carbonaceous mudstone and siltstone) of Permian age in the Three Gorges region could be potential natural sources of the Cd anomalies existing in the Yangtze River basin.

Human activity is another factor that may contribute to the enrichment of trace metals in soil. Cadmium may be transferred to the soil due to the weathering of Cd-rich gangue from the past coal mining and the indiscriminate disposal of coal wastes, such as being disposed directly into the arable soils, or their use to cover the muddy country roads. In addition, coal ash from the domestic utilization of coal may also contribute to the addition of Cd to the soil. The local residents used to crush the coal and mix it with local clays rich in Cd (Table 3) to make coal balls for easy domestic storage and combustion. Locally produced coals in the past were enriched in Cd (with concentrations of 0.52–102 mg kg^{-1}, mean at 25 mg kg^{-1}), whereas the currently used coal imported from outside the study area has Cd concentrations of 1.0–8.3 mg kg^{-1} (Tang et al., 2009). Ash from the coal combustion was added to the local arable soils as a soil additive, as evidenced by the coal ash particles observed in the field investigation. Consequently, domestic coal utilization may also contribute to the elevated Cd content of the local soils.

A lognormal distribution plot, which could give information on the background value and metal contamination of soil (Kaminski and Landsberger, 2000; Wang and Qin, 2007), was used to attempt to identify the source of Cd in the local soils (Fig. 3). The plot identified two groups of soil samples. The group with low and moderate levels of Cd (Cd < 8.5 mg kg^{-1}, green[1] square symbols) showed

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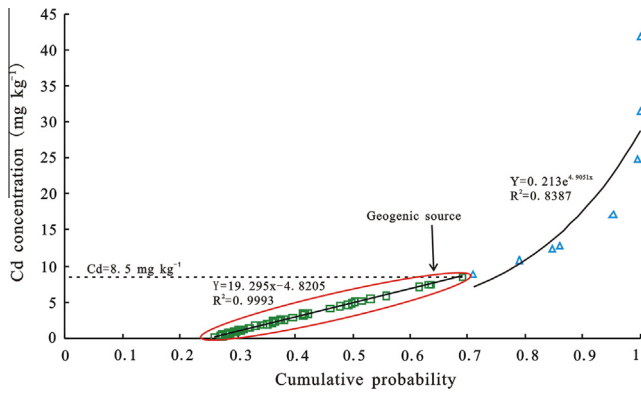[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

Fig. 3. Lognormal distribution plot of Cd in soils.

an almost smooth straight line, indicating that Cd in these soils (most of the arable soil and subsoil, and all of the natural soils) was likely to have a geogenic source deriving from weathering of the Cd-rich sedimentary rocks. However, the group with higher concentrations of Cd (Cd > 8.5 mg kg^{-1}, 8 arable soil samples, blue triangle symbols) showed an exponential curve, indicating that the elevated Cd in the soils was likely attributed to anthropogenic activities in addition to the geogenic contribution (Fig. 3). Of these 8 arable soil samples, three were located in the lower area of coal mine 4 with Cd contents of 12, 13 and 25 mg kg^{-1}, respectively, and two were sampled in the lower area of coal mine 3 with Cd contents of 11 and 17 mg kg^{-1}, respectively. These 5 arable soils were perhaps influenced by past coal mining activities. Two of the 8 arable soils were sampled in a local vegetable garden with Cd concentrations of 8.9 and 42 mg kg^{-1}, respectively; one bedrock sample in this garden had a high Cd content (3.0 mg kg^{-1}). In addition, during the field investigation, coal waste was noted to occur in the garden soils. One arable soil sampled in the field in the lower part of the study area, represented alluvium and contained 31 mg kg^{-1} Cd. Therefore, these 8 arable soils may have been affected by anthropogenic sources, in addition to the geogenic source (Fig. 3).

The enrichment factor (EF) has the potential to reveal anthropogenic influences on soil (Kaminski and Landsberger, 2000; Ferrand et al., 2012). In this study, Zr, which is generally an immobile element in the secondary environment, was chosen as the reference element because Zr in the local soils (115–408 mg kg^{-1}, mean of 260 mg kg^{-1}) was similar to the mean value for Chinese soil (250 mg kg^{-1}; Yan et al., 1997). The enrichment factor was calculated as:

$$EF = (Cd/Zr)_{sample}/(Cd/Zr)_{background}$$

The background values of Cd and Zr were calculated from the median of 16 natural soil samples to be 0.97 and 255 mg kg^{-1}, respectively. The distribution plot in Fig. 4 shows the results of EFs for Cd. Various classifications of EF values have been reported in previous publications: 1 (Yu et al., 2012), 2 (Loska et al., 2004), 3 and 5 (Halstead et al., 2000), and 10 or even 500 (Veysseyre et al., 2001). These classifications are intended to reflect the level of anthropogenic enhancement of the element of interest based on the group's preferred method for calculating the EF (Reimann and de Caritat, 2005). However, considering the high background value for Cd and the normal background value for Zr in this study area, EF = 5 was selected as the cut-off value in this paper. EF < 5 is considered to represent little or no anthropogenic input, and 5 < EF < 10 represents moderate anthropogenic contribution, and EF > 10 is considered to represent significant anthropogenic input.

The EF values in the natural soil ranged from 0.10 to 7.3 (mean at 2.0), and most of the EF values were <5, except for two soil samples with EF values close to 5 (i.e. 6.7 and 7.3), in which relatively high Cd concentrations were observed. These results indicated that the natural soils were less affected by anthropogenic activities. The EF values in the arable soil ranged from 0.47 to 45 (mean at 7.9); 61% of the soil samples showed EF values below 5 and four of the arable soil samples displayed EF values close to 5. However, 9 arable soil samples had EF values above 10, suggesting significant influence by anthropogenic activities. The EF values in the subsoils (0.26–17, mean at 3.3) were similar to those of the natural soil except for one sample with a high EF value of 17. Generally, most of the studied soil samples showed small EF values of below or close to 5, except for 10 soil samples having EF values significantly above 5 (10–45). These results suggest that Cd in the local soils primarily originated from weathering of the local sedimentary parent rocks, but that Cd in some arable soils and subsoils was likely influenced by additional anthropogenic inputs. This finding for the soils with high Cd contents (>8.5 mg kg^{-1}) and high EF values (>10) is consistent with the results of the lognormal distribution plot (Fig. 3). However, one arable soil and one subsoil with moderate Cd contents showed high EF values (>10); these two soils were sampled at the same site and showed moderate Cd and low Zr concentrations, resulting in larger EF values.

3.4. Partitioning and potential bioavailability of Cd in soil

The results for geochemical partitioning of Cd based on BCR sequential extraction for 7 selected soil samples (natural soil NS1 and NS2, arable soil AS1, AS2 and AS3, and subsoil SS1 and SS2)
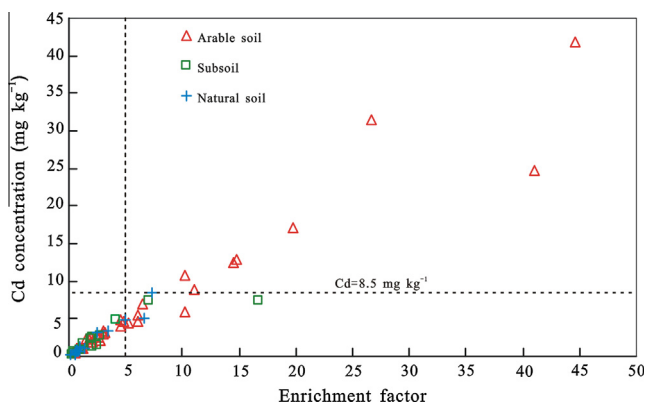

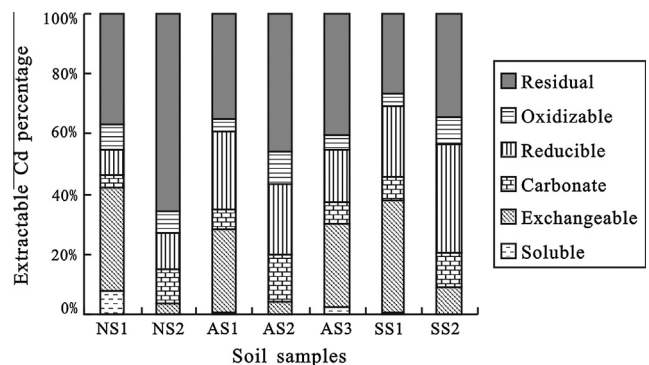**Fig. 4.** Plot of enrichment factor values for Cd in soils.

Fig. 5. Cadmium concentrations in various fractions of sequential extractions.

are shown in Fig. 5. The recovery for Cd was calculated as the sum of all BCR fractions (total) divided by the Cd contents (measured) from HNO_3 + HF digestion, and resulted in values ranging from 91% to 109%. In these soils, Cd was mainly observed in the residual (mean at 41%), reducible (mean at 21%), and exchangeable (mean at 21%) fractions. However, smaller portions of Cd were bound in the carbonate (mean at 9.2%), oxidizable (mean at 6.9%) and water soluble (mean at 1.7%) fractions. These results are consistent with the characteristics of the soil (Tables 2 and 3). For the natural soil NS1 (pH = 4.6, Cd = 1.1 mg kg^{-1}, EF = 1), the water soluble and exchangeable fractions accounted for 8.0% and 34%, respectively, which probably resulted from the weathering of the organic-rich carbonaceous mudstone (Yu et al., 2012). Sample NS2 (pH = 7.5, Cd = 0.36 mg kg^{-1}, EF = 0.6), collected from forested land without any anthropogenic disturbance, displayed a larger portion of residual phase (66%) and carbonate fraction (11%) than NS1. This is likely influenced by the outcropping carbonate rock (Fig. 1). The arable soil samples AS1 (pH = 5.3, Cd = 42 mg kg^{-1}, EF = 45) and AS3 (pH = 3.9, Cd = 8.9 mg kg^{-1}, EF = 11), collected in a local vegetable garden as mentioned above, showed relatively large exchangeable fractions (28% for both) that were likely related to the relatively lower pH, which may have resulted from the coal waste dumped in the soil. Sample AS2 (pH = 7.6, Cd = 12 mg kg^{-1}, EF = 15) had a relatively larger carbonate fraction (16%), corresponding to the relatively larger CaO content (2.9%). The subsoil SS1 (pH = 5.9, Cd = 2.6 mg kg^{-1}, EF = 2.1) showed a larger exchangeable fraction (37%), which may be influenced by the relatively lower pH, and SS2 (pH = 7.1, Cd = 0.88 mg kg^{-1}, EF = 1.0) showed a larger reducible fraction (36%) that was probably related to high contents of Fe (Table 2).

Based on the results of the sequential extraction, the fractionation and mobility of Cd is related to soil chemical composition and properties. The water soluble fraction (0.17–8%) is the most potentially bioavailable to the crop plants grown on the soils. Cadmium in the exchangeable fraction (3.7–37%) is also potentially bioavailable and could be adsorbed by either the clay minerals or humic acid in soil or both, but may tend to be released when the ionic strength changes. For instance, fertilization could influence the ionic strength of the soil and so influence the mobility of Cd in this fraction. The relatively minor portion of oxidizable Cd (4.3–16%) is combined with organic matter and sulfides in soil. The reducible fraction (8.2–36%) is combined with the Fe–Mn oxide/oxyhydroxide. Cadmium in both the oxidizable and reducible fractions is less labile; however, it could be released when the redox conditions change, for instance, in the conditions during cultivating activity. Cadmium in the residual fraction (27–66%) exists in the crystal lattices and is immobile compared with Cd in soil originating from anthropogenic sources (Chlopecka, 1996).

It was observed that the potentially bioavailable fraction (soluble, exchangeable, and carbonate together) averages 31% (range 15–47%) of the total Cd in the local soils, which may have significant environmental implications. The potentially bioavailable Cd in the local soils may easily transfer to and accumulate in the locally cultivated food crops and this may cause consequent health risk to the local residents. This process may be the source of the relatively high Cd (1.7–13.4 μg L^{-1}) in the urine samples of the local habitants (Tang et al., 2009).

4. Conclusions

The high Cd concentrations in soils from the identified Cd-enriched zone in the Three Gorges region mainly originate from a geogenic source. Both lognormal distribution plots and enrichment factor calculations indicate that Cd at low and moderate levels in the soils is derived mainly from geogenic origins, whereas high concentrations of soil Cd result from additional anthropogenic input of this element. The weathering of Permian sedimentary rocks is likely the natural source of Cd in the soils. However, mining and utilization of Cd-rich coal contributes additional Cd to the arable soils. Enrichment of Cd in these local soils increases the potential bioavailability of this element results in potential risk to public health.

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