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High cadmium concentrations in areas with endemic fluorosis: A serious hidden toxin?

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ABSTRACT

Environmental contamination with cadmium (Cd) and fluorine (F) and the associated health impacts on humans have raised significant concerns in the literature, but the additional health risks created by Cd have not been investigated in areas with endemic fluorine intoxication (fluorosis). Here, we report for the first time that naturally occurring Cd in areas where endemic fluorosis is related to coal combustion is a serious hidden toxin. The high Cd levels in rocks and soils of these areas may increase health risks to epidemiological level, irrespective of fluorine levels. We implemented a pilot study in a fluorosis-affected rural area within China's Three Gorges region, and revealed enrichment of Cd in local bedrock (4.48–187 mg kg^{-1}), coal (11.5–53.4 mg kg^{-1}), and arable soils (1.01–59.7 mg kg^{-1}). Cadmium was also observed to concentrate in local food crops (0.58–14.9 mg kg^{-1}) and in the urine of local residents (1.7–13.4 μg L^{-1}). A routine epidemiological investigation revealed that the two major Cd exposure pathways were through crop consumption and inhalation of emissions from coal combustion. Therefore, the naturally occurring Cd in areas with endemic fluorosis related to coal combustion represents a previously unrecognized toxin that must be addressed as part of efforts to control the endemic problem. The biogeochemical processes of Cd and the associated environmental effects will require additional in-depth study.

1. Introduction

Endemic fluorosis related to coal combustion is a disease that has affected around 35 million people in China, and represents a serious health concern because of the damage it causes to teeth and bones (Zheng et al., 1999; Finkelman et al., 2002). A number of previous studies have revealed that this endemic fluorosis was caused by the intake of elevated levels of fluoride emitted through domestic combustion of high-fluorine coal using conventional stoves without chimneys to vent the emissions to the outdoors (Zheng et al., 1999; Finkelman et al., 2002; Wu et al., 2004). Such fluorosis can be prevented using either low-F coal or chimneys that vent the emitted F outside the house (Li and Zhang, 2005). However, a recent epidemiological study revealed that endemic fluorosis related to coal combustion in the Three Gorges region of China was not significantly alleviated by efforts to improve domestic combustion of coal; on the contrary, the number of people exhibiting symptoms of fluorosis (i.e., teeth and bone problems) actually increased in some areas (Li and Zhang, 2005). Our recent investigation of this endemic disease in the Three Gorges region revealed surprisingly high concentrations of Cd in the local environment and in the urine of the local population, suggesting that Cd intoxication might be responsible for some of the observed illness (Xiao et al., 2007).

Toxicological studies of the effects of F and Cd on human health have demonstrated that patients who suffered from either F or Cd intoxication exhibited similar clinical symptoms in their teeth and bones. The victims' permanent teeth tended to be mottled with minute white flecks, with yellow or brown spots scattered irregularly over the tooth surface, and their gaits exhibited bilateral lameness and stiffness, although these symptoms occurred to different extents due to the wide range of exposures and nutritional conditions in the study population (ATSDR, 1999, 2003). Therefore, we hypothesized that Cd was a serious hidden toxin whose effects were concealed by those of fluorine, and that the locally endemic disease that has been ascribed to the combustion of F-rich coal in recent decades may have other causes. In the present paper, we report the results of our study of the geochemistry of Cd, with the goals of demonstrating the sources of Cd in the local environment and illuminating the pathways by which Cd affects people and the consequent health risks.

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2. Materials and methods

2.1. Study area

The study area is located near Jianping (109°55′–109°58′E, 31°01′–31°03′N), in Wushan County of the Three Gorges region of southwestern China. 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 400–800 m above sea level. Severe soil erosion has occurred owing to the low vegetation cover and intensive agriculture activity. The rock outcroppings in the study area include lithologies from the Silurian to the Permian periods, mainly composed of limestone, siltstone, shale, and coal seams.

The study area is an area of high health concerns due to the occurrence of endemic fluorosis related to coal combustion. The local residents formerly used the local F-rich coals for cooking and heating, but stopped this practice and began using low-F coals imported from outside areas since 1983 (Li and Zhang, 2005). However, an epidemiological investigation in 2003 showed that among the 2643 residents who were investigated, 77.7% still suffered from teeth damage and 19.6% from bone damage, including 148 persons with disabling bone-related symptoms (Li, H.J., personal communication). For comparative purposes, we chose an area with a low background F content and no occurrence of fluorosis near the Yangtze River, 30 km west of the study area, as a control area (109°46′–109°49′E, 31°01′–31°04′N).

2.2. Sampling and analysis

We collected local environmental samples (rock, coal, soil, crops, and water) and human urine during a routine epidemiological investigation. We also sampled the coals used for domestic combustion that are currently imported from outside the study area. We collected the water samples from shallow wells that are dug to provide the local drinking water supply, and filtered this water through a 0.45-μm membrane and acidified the filtrate to a pH of around 2 using ultra-pure HNO_3 for storage at site. The water samples were kept in a cooler at 4 °C until they were shipped to laboratory. During site urine sampling, a detailed questionnaire was employed to collect data on age, sex, dietary and behavioral habits of each participant. The urine samples were sealed in precleaned 60 mL Nalgene® bottles. The specimens were stored in coolers at −20 °C in both the field and the laboratory, and were analyzed within 2 weeks of collection.

The rock, coal, and soil samples were processed for Cd and other trace element analysis by disaggregation to pass through a 2-mm sieve. The sieved fractions were then ground in a Bico ceramic disc grinder and passed through a 200-mesh screen (<75 μm). The edible parts of several crops (corn, potatoes, chili, wheat, and beans) were sampled during the harvesting season. We did not include rice, as this crop is not grown in the study area, and is instead imported. The sampling sites for these crops generally corresponded to the locations of the collected soil samples. The crop samples were cleaned in the field using de-ionized water and cut into small pieces (1–2 cm long) in the laboratory, and were then placed in labeled paper bags and stored in an electric drying cabinet heated to 25 °C until they were completely dry. These dried samples were then crushed to fragments capable of passing through a 100-mesh screen (<150 μm) using a crushing machine (FZ102, China).

All the sample powders were digested in polytetrafluoroethylene bombs. To each sample (around 50 mg), 0.8 mL of ultra-pure HF (38% v/v) and 1 mL of ultra-pure HNO_3 (68% v/v) were added. The bombs were placed on a hot plate (190 °C) for 24–30 h, then 1 mL rhodium (Rh) at 50 $\mu g\,L^{-1}$ as an internal standard solution and 3 mL of Millipore water 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 a volume of 100 mL by the addition of Millipore water. The reagent blanks were treated following the same approach as the samples. Each 10-mL water sample was mixed with 0.2 mL of the Rh internal standard solution at 50 $\mu g\,L^{-1}$ prior to analysis. A 1-mL urine sample was diluted quantitatively (1:9 v/v) to 10 mL with Millipore water, and the 10-mL diluted solution was further spiked with 0.2 mL internal standard at 50 $\mu g\,L^{-1}$.

All the samples were analyzed for Cd and other trace metals using a Perkin–Elmer inductively coupled plasma–mass spectrometer (ICPMS) at the National Research Center of Geoanalysis, Beijing. The reference materials of OU-6 (rock), AMH-1 (rock), GBPG-1 (rock), GBW07401 (soil), and GBW07602 (plant) were analyzed every 20 determination for samples, and the determined results were within 10% error compared with the certified values. Both cadmium and thallium solutions (MTI standard regents at 20 $\mu g\,L^{-1}$) were also applied during the analysis, respectively, and a recovery rate of around 98% was both obtained. The analytical precision, determined by means of quality control using the duplicates, blanks, internal standards, and reference samples, was better than ±10%.

3. Results and discussion

3.1. Geochemical distribution of Cd in environmental substrates and source identification

The concentration analysis results of Cd and some selected metals in rocks, coals, soils, and water are listed in Table 1. The geochemical data revealed obvious geochemical anomalies of Cd, namely that Cd concentrations were much higher in both the rocks and soils of the study area than in those of the control area. In the study area, the high Cd contents in rocks originated from sedimentary rocks (black shale and siltstone, 4.48–187 $mg\,kg^{-1}$) and coals (11.5–53.4 $mg\,kg^{-1}$) from the Permian period, which is far above the global average Cd concentration of in the upper crust (0.098 $mg\,kg^{-1}$; Taylor and McLennan, 1985), in black shale (<0.3 $mg\,kg^{-1}$; Turekian and Wedepohl, 1961), and in coal (0.13.0 $mg\,kg^{-1}$; Swaine, 1990). In contrast, Cd was present at lower concentrations (ranging from 0.696 to 0.94 $mg\,kg^{-1}$) in sedimentary rocks of the control area (Table 1). The Cd enrichment in the bedrock of the study area reveals a geologically concentrated Cd zone within the Three Gorges region (Xiao et al., 2007). In addition, the currently used domestic coals imported from the coal mines within the Three Gorges region also contained higher Cd contents (from 1.0 to 8.3 $mg\,kg^{-1}$, with an average of 2.4 $mg\,kg^{-1}$) than in other Chinese coal (0.04–1.2 $mg\,kg^{-1}$; Ren et al., 1999). It is interesting to note that Cd anomalies in both sediments and bank soil along the Yangtze River were previously identified, which were attributed mainly to release by natural weathering from Cd-rich black shales from the Permian period (Cheng et al., 2005). The high Cd contents in the local shales and coals of the study area confirmed the previously reported Cd anomalies within the Yangtze River catchment.

The high Cd contents in the local rocks also contributed to Cd enrichment in the arable soils as a result of long-term natural weathering and human disturbance (e.g., agricultural activity). The concentrations of Cd in the arable soils of the study area ranged from 1.01 to 59.7 $mg\,kg^{-1}$, with an average of 6.6 $mg\,kg^{-1}$, which is far above the median values of 0.35 $mg\,kg^{-1}$ for world soils (Bowen, 1979) and the mean of 0.097 $mg\,kg^{-1}$ for Chinese soils (Yan et al., 1997), and greatly exceeded the Chinese soil safety

Table 1
Concentrations of Cd and other selected metals in rock, coal, soil, and water (unit in mg kg^{-1} except where indicated).

Samples		Cd	Ni	Zn	Mo	Sb	Pb
Study area							
Black shale and carbonaceous siltstone (n = 7)[a]	Range	4.48–187	76–383	117–412	11–67	5–55	6–21
	AM (GM)[b]	72 (77)	211 (198)	265 (229)	35 (32)	27 (25)	14 (16)
	STDEV[c]	92	113	121	21	22	6
Coal locally produced (n = 4)	Range	11.5–53.4	78–268	123–238	9–34	6.7–15	7.3–16.7
	AM (GM)	26 (13)	203 (263)	178 (173)	18 (12)	11 (11)	13 (14)
	STDEV	24	108	58	14	4	5
Coal currently used (n = 18)	Range	1.0–8.3	9–90	39–986	1.6–25	1.4–24	14.2–98
	AM (GM)	2.4 (2.2)	28 (27)	290 (289)	9 (8)	7 (5)	33 (25)
	STDEV	1.7	20	241	5.6	5.4	24
Soil (n = 74)	Range	1.01–59.7	20–388	78–962	0.6–99	1.7–32	10–65
	AM (GM)	6.6 (2.9)	67 (50)	188 (148)	11 (5.4)	5.5 (3.3)	30 (29)
	STDEV	10	59	143	18	5.6	9
Water[d] (n = 14)	Range	0.01–0.21	1.5–24	0.2–12.4	0.23–28	0.1–1.2	0.04–0.6
	AM (GM)	0.07 (0.05)	7.2 (3.8)	3.4 (2.1)	3.6 (1.1)	0.24 (0.12)	0.11 (0.05)
	STDEV	0.06	7.3	3.7	7.3	0.3	0.2
Control area							
Siltstone (n = 3)	Range	0.696–0.94	4.3–26	93–118	0.9–1.8	1.7–6.3	6.2–9.5
	AM (GM)	0.83 (0.85)	16 (17)	107 (110)	1.3 (1.1)	4.0 (4.1)	8.1 (8.7)
	STDEV	0.12	11	13	0.48	2.3	2
Soil (n = 7)	Range	0.59–0.76	20–39	67–108	0.5–1.1	1.96–3.4	15.7–32.1
	AM (GM)	0.67 (0.67)	27 (26)	84 (78)	0.9 (1.0)	2.4 (2.2)	26 (25)
	STDEV	0.1	7	15	0.2	0.5	6
World shale[e]	AM	0.30	68	95	2.6	1.5	20
World coal	Range[f]	0.1–3	0.5–50	5–300	0.1–10	0.05–10	2–80
	AM[g]	0.3[h]	15	50	5	3.0	25
Chinese coal[i]	Range	0.04–1.2	1.1–255	0.6–193	0.2–241	0.05–120	5.3–70
	AM (GM)	0.46 (0.32)	23 (15)	43 (29)	18 (4)	2.6 (0.6)	25 (20)
Chinese soil	AM[j]	0.097	26	68	0.8	0.8	23
	Safety limit[k]	0.3	50	250	–	–	300
Drinking-water[d]	Safety limit[l]	3	70	–	70	20	10

[a] n: Number of samples.
[b] AM: arithmetic mean, GM: geometric mean.
[c] Standard deviation.
[d] Unit is μg L^{-1}.
[e] Turekian and Wedepohl (1961).
[f] Swaine (1990).
[g] Valkovic (1983).
[h] Yudovich et al. (1985).
[i] Ren et al. (1999).
[j] Yan et al. (1997).
[k] CNS (1995).
[l] WHO (2006).

limit of 0.3 mg kg^{-1} (CNS, 1995) for agricultural soils (Table 1). In contrast with the study area, Cd concentrations in the soils of the control area ranged from 0.59 to 0.76 mg kg^{-1}, with an average of 0.67 mg kg^{-1} (Table 1).

The water collected from wells in the study area showed Cd concentrations ranging from 0.01 to 0.21 μg L^{-1}, with an average value of 0.07 μg L^{-1}, which is lower than the safety limit of 3 μg L^{-1} recommended by the World Health Organization (WHO, 2006). The sources of recharge water for the local drinking water are mainly from limestone caves or fissures located above the villages, and seem to pose no risk of Cd exposure for the population based on our results.

The local rocks and coals are also enriched in other metals of Ni, Mo, Zn, and Sb (Table 1). However, these metals are less concentrated than Cd, compared with their concentrations in world shale, world coal, Chinese coal, and in siltstone of the control area. The concentrations of Ni, Zn, and Pb in local soils are also higher than those in soil of the control area and Chinese soil (Table 1), but they are all under the safety limits of Chinese soils. In similar, all the metals present lower levels in local water, which are under the safety limits of drinking water (WHO, 2006). No significant correlations among these metals and Cd in rocks, coals and soils were identified by this study. Thus, the metals of Ni, Zn, Mo, Sb, and Pb seem to pose smaller risks than Cd in the local environment.

From the epidemiological perspective, the noticeably high concentrations of Cd in the local rocks, soils, and domestic coals pose a risk of high exposure to Cd for the local residents. Although Cd concentrations in the local drinking water currently appear to be safe, future drinking water wells should not be dug in or near black shale or carbonaceous siltstone.

3.2. Pathways of Cd exposure for humans

The study area is mountainous, and the local inhabitants mostly rely on the local Cd-rich arable soils for planting their staple food crops. The local population is thus suffering from long-term exposure to Cd through their consumption of food crops.

High concentrations of Cd in the major locally produced food crops, except for rice (which is not locally produced), were also identified (Table 2). The average Cd values in six crop groups in

Table 2
Concentrations of Cd in local crops (dry weight, mg kg^{-1}).

Samples		Cd	Ni	Zn	Mo	Sb	Pb
Study area							
Corn[a] ($n = 19$)	Range	0.58–6.57	1.1–4.5	53–244	0.2–1.8	0.06–0.44	1.7–12
	AM (GM)	1.81 (1.41)	2 (1.7)	105 (83)	0.8 (0.8)	0.21 (0.19)	5.7 (5.7)
	STDEV	1.4	0.8	51	0.4	0.1	2.9
Corn[b] ($n = 4$)	Range	15.2–76.5	1.9–15	111–236	0.4–1.6	0.31–0.77	4–10
	AM (GM)	39 (32.1)	5.3 (2.4)	176 (178)	1.0 (1.0)	0.45 (0.36)	7.9 (8.6)
	STDEV	26					
Chili ($n = 12$)	Range	1.74–7.63	1.8–13	43–99	0.6–4.6	0.06–0.37	1.5–8.5
	AM (GM)	3.81 (3.47)	6.7 (3.6)	64 (60)	1.8 (1.1)	0.17 (0.17)	4.5 (4.1)
	STDEV	1.9	3.1	16	1.4	0.08	2.2
Potato ($n = 13$)	Range	1.08–14.9	1.1–3.8	50–188	0.4–1.6	0.09–0.47	4–10
	AM (GM)	4.17 (2.48)	2.2 (2.1)	118 (124)	0.8 (0.7)	0.25 (0.22)	6.6 (5.6)
	STDEV	3.8	0.9	51	0.4	0.1	2.4
Wheat ($n = 3$)	Range	1.11–8.48	2.5–2.7	67–89	0.4–1.1	0.08–0.22	1.6–4.7
	AM (GM)	4.38(3.56)	2.6 (2.6)	75 (71)	0.9 (1.0)	0.14 (0.12)	3.2 (3.2)
	STDEV	3.8	0.12	12	0.37	0.07	1.5
Beans ($n = 4$)	Range	2.16–5.62	1.5–2.6	37–135	1.3–5.4	0.12–0.77	4.2–9
	AM (GM)	4.28 (4.66)	2.1 (2.1)	87 (88)	3.3 (3.2)	0.3 (0.2)	7 (7.3)
	STDEV	1.5	0.5	41	2.2	0.3	2.2
Control area							
Crops (corn, chili, potato) ($n = 8$)	Range	0.66–1.12	0.6–1.6	37–194	0.1–0.50	0.09–0.38	1.7–4.4
	AM (GM)	0.93 (0.93)	1.2 (1.1)	86 (56)	0.33 (0.37)	0.17 (0.13)	3.2 (3.4)
	STDEV	0.2	0.34	58	0.14	0.1	0.9
Edible plants worldwide[c]	Range	0.05–2.0	1.2–3.6	10–40	0.07–1.75	–	–

[a] Fresh corn collected from the field.
[b] Corn dried over an indoor coal-burning stove.
[c] Bowen (1979), and Kabata-Pendias and Pendias (1992).

the study area ranged from 1.81 to 4.38 mg kg^{-1}, which are far above the global values of 0.02–2.0 mg kg^{-1} for edible plants (Bowen, 1979; Kabata-Pendias and Pendias, 1992). The Cd enrichment in the local food crops strongly suggests the transfer of Cd from the soil into the food supply. In contrast, we found low Cd concentrations in the crops of the control area (0.66–1.12 mg kg^{-1}, with a mean of 0.93 mg kg^{-1}), corresponding to the low Cd levels in the arable soils of this area (Table 2).

In addition to food crops, other potential pathways for Cd entry into the human body include the drinking water, inhalation of emissions from cooking and heating, and inadvertent ingestion of soil. However, the low Cd concentrations in the local drinking water supply suggest that there is currently little health threat from water intake. Coals used in the study area represent an important concern, as they are rich in Cd and are often used for indoor cooking and heating without chimneys to vent the emissions to the outdoors. As noted previously, the incidence of fluorosis did not decrease after the replacement of local coal with coal imported from outside the study area, suggesting that F and Cd in the emissions from this combustion may also represent a respiratory hazard; although these emissions are less concentrated outdoors than they are inside the houses of residents, the cumulative effect may still be severe, particularly on days when gentle winds are not able to carry away or dilute these emissions. It is interesting to note that four corn samples that were dried indoors over a coal-burning stove showed elevated Cd concentrations (from 15.2 to 76.5 mg kg^{-1}); the average of 39 mg kg^{-1} for these samples is more than 20 times the mean (1.81 mg kg^{-1}) in the corn before drying. The elevated Cd in these dried corns indicate that Cd released from the coal into the indoor air was then absorbed by the corns. Unfortunately, the extent of Cd exposure from indoor air is not yet clear, and will require further study. Finally, the inadvertent ingestion of Cd-bearing soils should not be overlooked. The Cd-rich soil may be inadvertently ingested by so-called hand-to-mouth behavior, particularly for children, who tend to ingest more soil than adults. Manual farming activity is also likely to increase soil ingestion. For example, local villagers often do not wash their hands properly prior to meals. Although soil ingestion has also been shown to be a health concern (Lambert and Lane, 2004), we did not quantitatively assess the amount of inadvertent soil ingestion, which thus needs further study.

The metals of Ni, Zn, and Mo are slightly enriched in local crops, compared with their concentrations in crops of the control area and the world edible plants (Table 2). No significant correlations among Ni, Zn, Mo, and Cd in crops were identified. The metals of Ni, Zn, and Mo are less concentrated than Cd in the local crop plants, and suggest for less health risks than Cd through food chain to local population.

Our primary findings strongly suggest that high Cd concentrations in the study area, which result from natural Cd enrichment, are resulting in ready transfer of Cd into the human body mainly through the ingestion of local food crops and the inhalation of coal-burning emissions, and possibly from inadvertent soil ingestion, although further studies will be required to reveal Cd mobility and bioavailability in these individual pathways.

3.3. Health impacts of Cd

High concentrations of Cd in the urine of local volunteers were identified through routine epidemiological investigations. The concentrations of Cd in urine ranged from 1.7 to 13.4 μg L^{-1} and averaged at 5.4 μg L^{-1}, which are far above the values (<1.0 μg L^{-1}) from both the control area and from non-exposed populations around the world (Table 3). No significant differences were observed for Cd in urine as a function of the sex or age of the volunteers, indicating that Cd exposure is similar for all members of the local population. However, we did not attempt to measure Cd levels in fetuses, so it is possible that prenatal exposure to Cd may be

Table 3
Concentration of Cd and other metals in human urine (μg L^{-1}).

Samples		Cd	Ni	Zn	Mo	Sb	Pb
Study area							
All volunteers ($n = 26$)	Range	1.7–13.4	6.3–114	112–763	64–561	0.2–2.4	0.01–0.2
	AM (GM)	5.4 (4.6)	26 (16)	371 (300)	252 (250)	0.7 (0.5)	0.02 (0.01)
	STDEV	3.2	26	216	126	0.5	0.04
Male ($n = 10$)	Range	1.7–12.9	6.3–56	151–702	64–561	0.2–2.4	0.01–0.2
	AM (GM)	4.9 (4.3)	19 (14)	426 (404)	250 (224)	0.8 (0.5)	0.03 (0.01)
	STDEV	3.3	15	215	137	0.7	0.06
Female ($n = 16$)	Range	1.7–13.4	8.5–114	112–763	97–506	0.3–1	0.01–0.03
	AM (GM)	5.8 (5.3)	31 (20)	334 (243)	254 (250)	0.6 (0.6)	0.01 (0.01)
	STDEV	3.2	30	215	122	0.3	0.01
Adult ($n = 21$)	Range	1.7–13.4	6.3–481	112–763	41–561	0.2–1.5	0.01–0.2
	AM (GM)	6.0 (5.4)	47 (16)	370 (300)	252 (250)	0.6 (0.5)	0.02 (0.01)
	STDEV	3.3	102	214	134	0.3	0.04
Children ($n = 5$)	Range	1.7–4.1	9–35	151–702	97–377	0.2–2.4	0.01–0.02
	AM (GM)	3.0 (3.4)	16 (12)	256 (256)	212 (197)	0.8 (0.4)	0.01 (0.01)
	STDEV	1.1	11	228	116	0.9	0.005
Volunteers from control area ($n = 4$)	Range	0.4–0.9	3.9–5.8	149–370	19–37	0.1–0.4	0.01–0.02
	AM (GM)	0.6 (0.6)	5.3 (4.8)	259 (259)	30 (32)	0.3 (0.3)	0.01 (0.01)
	STDEV	0.2	1	124	8	0.2	0.005
Unexposed population	Range	0.59–0.77[a]	<3.0[b]	67[c]	69[d]	1.3[d]	2.9[d]

[a] Kowal et al. (1979).
[b] Wilhelm et al. (2004).
[c] Schuhmacher et al. (1994).
[d] Paschal et al. (1998).

an additional concern. The metals of Ni and Mo in urine also show higher levels than their concentrations in unexposed population (Table 3), but no correlations with Cd are observed. The enrichment of Ni and Mo in urine conforms to their concentrations in the local food crops, and their associated health impacts are suggested for further study.

We identified no industrial activity that contributed to Cd release into the local environment. The sources of Cd taken up by humans thus appear to be mainly limited to consumption of food crops and inhalation of emissions from coal combustion in the houses, with both pathways leading to ingestion of large amounts of Cd. This finding was supported by the lower Cd concentrations in urine of the volunteers from the control area, where low concentrations of Cd in the bedrock contributed to low Cd levels in the soil and crops, and consequently to lower Cd loads on the human body (Table 3).

The accumulation of Cd in human bodies tends to cause health problems, and particularly dental and skeletal damages. However,

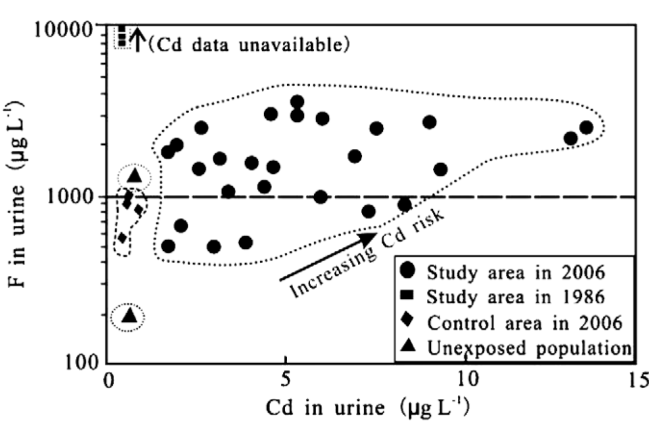

Fig. 1. Plot of Cd versus F concentrations in urine. Urinary F data for the study area in 2006 are from Xiao et al. (2007), and those (7.0–13.8 mg L^{-1}) in 1986 from Li and Yi (1990). Urinary F and Cd data for unexposed populations are from Wang et al. (2004) and Kowal et al. (1979), respectively.

the presence of these problems in the study area has conventionally been explained solely by fluorosis, and the contribution of Cd was not previously recognized. The non-locally produced coals currently used for domestic functions in the study area contained 129–735 mg F kg^{-1}, with an average of 377 mg kg^{-1}, and these values are markedly lower than those (1220–2170 mg F kg^{-1}) in the local coals, which can no longer be mined (Xiao et al., 2007). This suggests that the health risk to the local population from F in the currently used coals has been greatly reduced. However, the associated high levels of Cd in these coals brought about new health risks, particularly from indoor emissions. A graph of Cd versus F levels in the urine of volunteers (Fig. 1) suggested a reduced impact of F, but also revealed an increasing health threat of Cd in the study area. In the study area, half of the urine samples had F contents within the normal range for an unexposed population, but all samples revealed Cd levels higher than those in the control population and unexposed populations. Therefore, it will be critical to study the geochemical speciation and release processes for Cd in various pathways (e.g., from rock to soil to crops) and for Cd resulting from indoor coal combustion. In addition, similar regional contexts, with high primary Cd contents, can be found in other areas of China and the world, suggesting that a thorough geochemical study must be a primary step in any environmental or epidemiological monitoring in these areas to guide land-use management, whether for mining, agriculture, or habitation. Without proper knowledge of the background values in an area, the hidden health hazard of Cd may become worse if coupled with unsafe mining or agricultural activities. In addition, the damage caused by Cd may not be detected if investigators focus on more obvious problems such as fluorosis.

4. Conclusions

This pilot study revealed for the first time that naturally occurring Cd in areas with endemic fluorosis is acting as a critical but hidden health hazard that may underlie the risk of F, possibly even at epidemiological proportions. Studies of the impact of this toxin should be carefully considered based on proper knowledge of the background values of Cd and the biogeochemical processes responsible for Cd mobility in an area, otherwise the damage caused by Cd might become worse if coupled with domestic coal combustion or unsafe agricultural activities such as growing crops on soils with high Cd levels. Our ongoing in-depth investigation is currently using stable-isotope tracers ($^{114}Cd/^{110}Cd$) to further reveal the sources and geochemical mobility of Cd in various pathways.

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