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Geogenic cadmium pollution and potential health risks, with emphasis on black shale

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A B S T R A C T

Cadmium (Cd) is a non-essential trace element that is toxic to humans. Previous studies of Cd in the environment have primarily focused on pollution resulted from anthropogenic sources, but little is known on naturally occurring sources of Cd. This paper aims to review the geochemical distribution of geogenic Cd and associated environmental risk. The source, accumulation, mobility, transportation, and health risk of Cd are discussed in a geo-environmental perspective, with an emphasis on black shale soils. Cadmium generally occurs in sulfides in black shale, and is easily released when exposed to oxygen and water. Leaching of these rocks tends to elevate Cd concentrations in aquatic systems, and may pose the potential to produce acid rock drainage (ARD) as well. Weathering of Cd-rich rocks also elevates soil Cd concentrations, and influence the geochemical species of Cd. Crops grown in these soils tend to accumulate higher Cd and threaten the food safety. Local inhabitant exposed to high geogenic Cd via food chains may experience Cd-related health risk. High Cd concentrations are observed in urine, and renal damage is also detected in Cd naturally enriched area based on low molecular weight proteins in urine. Overall, the findings in literature have provided with insights for potential health risk of Cd in areas with high Cd geochemical background levels, particular for the black shale exposed areas, more attentions should be paid on the geogenic Cd pollution, and suitable strategies of remediation and geo-environmental management for geogenic Cd pollution need further research.

1. Introduction

Cadmium (Cd) is a non-essential trace metal that is toxic and carcinogenic, and that can occur as a food contaminant and global pollutant (Satarug et al., 2003; WHO, 2010). Long term occupational exposure to Cd may contribute to the developing of lung cancer, and high Cd exposure may induce kidney and bone damages (Järup and Åkesson, 2009; Satarug et al., 2010; WHO, 2010), and hematuria (Han et al., 2013). Since the appearance of Itai-Itai disease in Jinzu Valley of Japan, Cd in the environment has been an object of significant societal concern. Generally, Cd occurs at low concentrations in the environment, averaging 0.2 mg/kg in the lithosphere, 0.53 mg/kg in surface soils, and <0.66 mg/kg (dry weight) in the plant foodstuffs (Kabata-Pendias and Pendias, 2001). However, elevated Cd concentrations have been measured at many locations around the world due to both natural processes such as volcanic eruptions and geological weathering (Nriagu, 1989; Quezada-Hinojosa et al., 2009; Liu et al., 2013a), and to anthropogenic discharges from sewage irrigation, fertilizer application, mining, smelting, and fuel combustion (Nriagu and Pacyna, 1988; Baveye et al., 1999; Luo et al., 2009). Although anthropogenic discharges are the main sources of Cd in the environment, geogenic inputs may also result in elevated environmental Cd in regions with Cd-rich rocks (Quezada-Hinojosa et al., 2009; Khan et al., 2010; Park et al., 2010; Jacob et al., 2013; Liu et al., 2013a; Jyoti et al., 2015). For example, in China, the geochemical mapping in the Yangtze River catchment during the early 2000s detected anomalously high Cd concentrations in the alluvial soils, for which geological weathering was regarded as a critical contributing source (Cheng et al., 2005). In Switzerland, Cd-rich carbonate rocks of the Jura Mountains elevated Cd concentrations in local soils (Quezada-Hinojosa et al., 2009). In Korea, weathering of black shale has lead to Cd enrichment in soils up to 5.7 mg/kg (Park et al., 2010). In the Santa Monica Mountains area of California, USA, soils developed from shale parent materials present high Cd up to 22 mg/kg, with an average of 8 mg/kg, significantly higher than those in soils developed from basalt and sandstone (Burau, 1981; Lund et al., 1981).

Black shales are generally rich in organic materials and metals (e.g., As, Cd, Mo, Ni, Zn, etc.). Mining or drilling for extraction of natural resources such as nonferrous metals and shale gas or natural weathering of these rocks could be an important geogenic source of

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Cd to the environment (Perkins and Mason, 2015), and may even be linked to serious endemic diseases (Peng et al., 2004; Tang et al., 2009; Liu et al., 2015). Black shales are widely distributed in the world. For example, the South China black shale horizon, one of the largest black shale areas on earth, extends discontinuously for 1600 km in a west-east direction (Yu et al., 2012). In Sweden, the occurrence of black shale is estimated at nearly 18,300 km^2, of which 1900 km^2 are exposed to surface weathering (Lavergren et al., 2009a). And, in eastern and central USA, Devonian black shales such as the Antrim, Chattanooga, New Albany, and Ohio Shales underlie thousands of square kilometers (Tuttle et al., 2009). As showed in Fig. 1, black shales exposed to air and water can easily be weathered and metals such as Cd can be translocated into overlying soils, taken up by vegetation, or leached into local waters and sediments. Human activities like mining and road construction may accelerate the exposure and consequently facilitate the release of Cd and other metals, leading to environmental pollution and human health threats. In addition, weathering of sulfides (notably, pyrite) in black shale may generate acid rock drainage, which may lead to acidification of soils and water. Thus, natural weathering of black shales is of great geo-environmental significance, especially with continued development of shale gas exploration and oil shale mining.

This study reviewed a host of representative cases of geogenic Cd pollution worldwide, combining our recent work and existing literatures, in order to discuss the environmental contamination brought about by geogenic Cd, and the subsequent health risks to human. To evaluate and compare contaminant levels and the geo-environmental risks posed by geogenic Cd from different sites, we first calculated a geo-accumulation index I_{geo} (Müller, 1969; Liu et al., 2015): $I_{geo} = \log_2 (C_i/1.5B_i)$, where C_i is the measured concentration of Cd in soils, and B_i is a reference value that is 0.35 mg/kg referring to the average level in global non-polluted soil (Adriano, 2001). We then calculated a potential ecological risk factor, E_r, which was first applied to assess ecological risk of metals for aquatic systems, and later also applied to soils (Sun et al., 2010; Liu et al., 2015): $E_r = C_iT_i/B_i$, where T_i is the "toxic-response" factor, which was calculated to be 30 for Cd using the methods described by Håkanson (1980). Finally, the exposure pathways and health risk of Cd in selected areas were discussed to illustrate the potential threat of geogenic Cd sources, and soil remediation and environmental management methods that might minimize risks from geogenic Cd were discussed.

2. Cadmium occurrence in rocks

The geochemical behavior of Cd is similar to that of Zn. It is generally found in Cu—Pb—Zn ore minerals, particularly sphalerite. Though Cd is generally present only in low concentrations in various igneous rocks, (e.g., 0.03–0.05 mg/kg in ultramafic rocks, 0.13–0.22 mg/kg in mafic rocks, 0.13 mg/kg on average in intermediate rocks, 0.05–0.20 mg/kg in acid rocks; Kabata-Pendias and Pendias, 2001), it may concentrate in argillaceous sediments (average 0.30 mg/kg), shales (0.22–0.30 mg/kg), and phosphorites (average 18 mg/kg) (Nathan et al., 1996; Kabata-Pendias and Pendias, 2001). However, Cd enrichment in certain rocks results from specific geological conditions. For instance, elevated Cd in black shales and phosphorites (e.g., up to 345 mg/kg in the Phosphoria Formation; Perkins and Foster, 2004) is due to high marine primary production and biogenic enrichment, as evidenced by its nutrient-type seawater concentration profile in modern oceans, nearly completely depleted in the photic zone and elevated at depth and to sulfide precipitation under anoxic bottom water conditions (Piper and Calvert, 2009; Piper and Perkins, 2014). Extremely biologic enrichment of Cd (up to 6200 mg/kg) has been observed in phosphorites of guano origin in Jamaica (Garrett et al., 2008).

Although carbonate rocks generally contain low Cd concentrations (averaging 0.035 mg/kg; Kabata-Pendias and Pendias, 2001), they may be slightly to moderately enriched in Cd in certain geological

Fig. 1. Weathering and release of Cd from black shales.

zones. For example, elevated Cd (up to 21.4 mg/kg) is observed in carbonate rocks (mostly oolitic limestone) outcropped in the Jura Mountains of Europe (Rambeau, 2006), and in carbonate rocks (0.22–3.6 mg/kg) in the Three Gorges region of China (Liu et al., 2013a). Cadmium in calcareous rocks may also be initially concentrated in ocean sediments via accumulation of organic material; on oxidation of organics, the liberated Cd^{2+} is retained via formation of a solid solution with calcite (Andersson et al., 2014).

However, worldwide, elevated Cd concentrations are most commonly associated with black shales (Table 1), such as those from California, USA (up to 35 mg/kg, Burau, 1981), Korea (36 mg/kg; Kim and Thornton, 1993; Lee et al., 1998), Chongqing, China (21 mg/kg; Liu et al., 2013a), the Talvivaara deposits of Finland (15 mg/kg; Loukola-Ruskeeniemi et al., 1998), SE Sweden (15.9 mg/kg; Lavergren et al., 2009a), and the Appalachian Basin in the eastern United States (up to 130 mg/kg and averaging 24 mg/kg in the Sunbury Shale; Tuttle et al., 2009; Perkins and Mason, 2015). In addition to high organic matter contents, black shales commonly contain high concentrations of sulfides (Lavergren et al., 2009b; Perkins and Mason, 2015). Microanalyses and sequential extraction tests of fresh black shales have demonstrated that Cd in these rocks is primarily hosted by the sulfide fraction (52–64%: Perkins and Foster, 2004; 60% of total Cd: Lavergren et al., 2009b). Tuttle and coworkers document that the main carriers of Cd in New Albany Shale are pyrite and sphalerite, and that the median Cd concentration in framboidal pyrites is 1.7 mg/kg, higher than that in massive pyrite (median 0.43 mg/kg) (Tuttle et al., 2009). Similarly, Perkins and Mason (2015) observed with scanning electron microscopy (SEM) that Cd in the Sunbury Shales existed mainly in sphalerite grains, with a strong correlation between bulk rock Cd and Zn. They also found a moderate correlation between Cd and P, suggesting that a small fraction of Cd may exist in apatite, likely substituting for Ca. SEM analysis of weathered Cd-rich black shale from Three Gorges region of China also showed pyrite and metal enriched sulfosalt (Fig. 2; Liu, 2014). Overall, sulfide minerals in black shale are the primary reservoir of Cd and other metals, and their weathering products, sulfosalts, are readily soluble, releasing Cd to the surface environment (Perkins and Mason, 2015). For better understanding of Cd mobility in black shale, the approach to fractionate the geochemical portions of Cd is necessary.

3. Cadmium release from black shales

Exposed black shales are easily weathered and transported, aided by macro- and microbiological processes (Fig. 1). When exposed, sulfides in black shales, chiefly pyrite (Fig. 2) and sphalerite, are readily subject to oxidation in the surface environment, releasing Cd and other potentially toxic elements (Peng et al., 2004; Tang et al., 2009; Yu et al., 2012; Liu et al., 2013a; Perkins and Mason, 2015). The oxidation of sulfides, exemplified by pyrite, can be described in the following reactions (Tuttle et al., 2009):

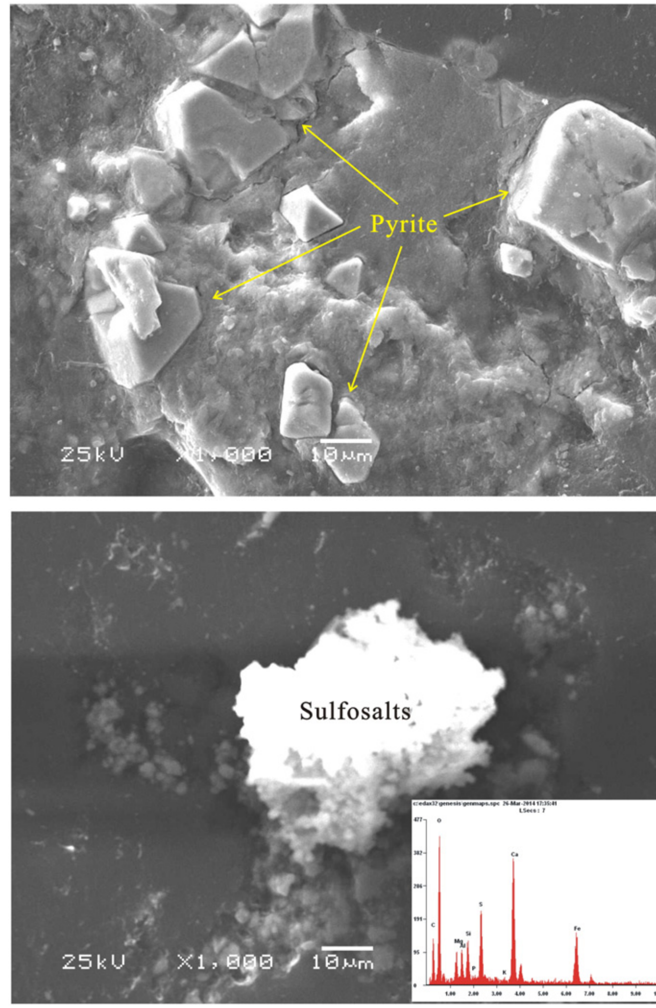

Fig. 2. SEM-EDS images of Cd-rich black shale from southwest China.

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-}(aq) + 16H^+_{(aq)} \quad (1)$$

$$Fe^{2+}_{(aq)} + 1/4O_{2(aq)} + H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1/2H_2O_{(l)} \quad (2)$$

Table 1
The Cd concentration (mg/kg) in soils and rocks of representative high Cd background sites.

Location	Cd in soil	pH	I_{geo}	E_r	Cd in rock	Parent rocks	References
Switzerland	0.33–2.0 (0.82)	7.2	0.64	70	0.03–4.91	Carbonate rocks	Quezada-Hinojosa et al. (2009)
Gilgit, Pakistan	0.3–2.3 (1.04)	6.60–7.77	0.99	89	–	Volcanic, meta-sedimentary rocks	Khan et al. (2010)
Providence, Jamaica	142–771 (638)	–	10.25	54,700	771–6200	Limestone, phosphorites	Garrett et al. (2008)
California, USA	0.59–22 (8)	–	3.93	686	0.85–33	Shale	Lund et al. (1981)
Northern Plains, USA	0.01–1.5 (0.38)	7.5	−0.47	33	–	Shale	Jacob et al. (2013)
North Dakota, USA	0.24	3.6–7.4	−1.13	21	–	Shale	Jyoti et al. (2015)
Wushan, China	0.42–42 (7.1)	3.9–7.7	3.76	609	0.37–21	Black shale	Liu et al. (2013a)
Chengkou, China	0.53–12.80 (4.94)	–	3.23	423	0.32–2.91	Black shale	Unpublished data
Hunan, China	0.08–1.46 (0.67)	–	0.35	57	0.45–11.09	Black shale	Peng et al. (2004)
Okchon, Korea	0.2–20.1 (0.93)	–	0.82	80	0.4–36	Black shale	Lee et al. (1998)
Deog-Pyoung, Korea	0.3–8.3 (1.2)	2.8–7.1	1.19	103	0.4–46 (6.3)	Black shale	Kim and Thornton (1993)
Korea	0.2–5.7 (0.8)	3.7–7.2	0.61	69	0.20–1.3	Black shale	Park et al. (2010)

Average Cd concentration in soils were listed in parentheses.

$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_{3(amorp)} + 3H^{+}_{(aq)}. \quad (3)$$

The above weathering processes result in acid and metal release. Leaching tests on un-weathered black shale samples showed that the pH in leachate dramatically decreases from 8 to 3, with a significant release of Cd (Falk et al., 2006). Similarly, water extraction tests of un-weathered black shale samples have resulted in acidic solutions (pH of 3.6 to 6.4) and aqueous Cd concentrations as high as 350 μg/L (Perkins and Mason, 2015). Both tests have illustrated the high mobility of Cd in black shale.

We leached weathered Permian black shale from the Three Gorges region, China, for three months with deionized water (50 mm × 500 mm column, 100 g weathered shale, 200 mL water per cycle. The sampling intervals were 1, 2, 5, 10, 20, 30 d. Leachates were collected at the 2nd, 3rd, 5th, 7th, 12th, 17th, 27th, 37th, 57th and 87th d, with intermittent periods of drying to mimic natural weathering cycles. High initial Cd concentrations were detected in the leachates, but the concentrations decreased with time. The initial flush may be attributed to the presence of Cd-bearing soluble sulfosalts (Fig. 2) resulting from the prior weathering of pyrites (Carmona et al., 2009). Cadmium concentrations in the leachates were positively correlated to SO_4^{2-}, and negatively correlated with pH (Fig. 3; Liu, 2014).

According to the estimates made by Tuttle et al. (2009), the aqueous flux of Cd in New Albany Shale (Cd in un-weathered shale is 0.13 to 3.0 mg/kg, with a median of 0.42 mg/kg) ranges from 0.03 g/ha/a to 0.09 g/ha/a; while the mechanical flux ranges from 0.01 g/ha/a to 0.04 g/ha/a. In another study, it was observed that 76% of the Cd in the 50-year weathered Sunbury Shale samples was lost during weathering process, compared to mean bulk concentration of 40 mg/kg Cd in fresh samples (Perkins and Mason, 2015).

The extent natural of rock weathering is constrained by local climatic conditions and topography, but the amount of Cd released is clearly influenced by Cd concentrations in parent rock. However, human activities such as road construction, mining or agricultural activities may accelerate the sulfide oxidation and Cd release to the environment (Peng et al., 2004; Liu et al., 2013a).

Cadmium, liberated from sulfides or organics oxidation in black shales, tends to be transported in dissolved form by surface or ground waters (Tuttle et al., 2009). However, Cd may also be retained in the surrounding soils and/or sediment through sorption onto organic and clay minerals, or Fe/Mn hydroxides, or by formation of secondary minerals such as $Cd_3(PO_4)_2$ and $CdCO_3$, or through substitution for Ca in calcite or apatite. These processes are subject to local environmental conditions (e.g., pH, Eh, and the availability of suitable ligands), and these may vary widely along transport pathways. In addition, mechanical transportation in mountainous areas with steep slopes may also contribute to the transport of Cd-bearing minerals in weathered black shale.

4. Cd contamination in soil

The weathering process of Cd-rich rocks such as black shales is prone to cause Cd accumulation in soils. Table 1 summarizes Cd concentrations in rock and soil, soil pH, and the calculated geo-accumulation index and ecological risk factors, from literature reports. Most soil samples have elevated Cd concentrations when compared to world non-polluted soil (0.35 mg/kg, Adriano, 2001). The highest values (142–771 mg/kg, $I_{geo} = 10.25$) are in soils associated with guano-type phosphorites in Jamaica, which are three orders of magnitude higher than the reference value, posing a high potential for ecological risk ($E_r > 54.000$). Cadmium in soils developed from California black shale, have a geo-accumulation index of 3.93, and an E_r of 686. The soils in Wushan and Chengkou, southwest China, are also rich in Cd due to black shale weathering ($I_{geo} = 3.76$ and 3.23; $E_r = 609$ and 423, respectively). The arable soils formed from black shale in the Jianping area of Wushan County are enriched in Cd at 0.42–42 mg/kg (mean of 7.1 mg/kg, $I_{geo} = 3.76$; Liu et al., 2013a), nearly 80 times the background value of Chinese soils (0.09 mg/kg) and 24 times the safety threshold value (0.3 mg/kg) of the Chinese EPA (NSC, 1995; Yan et al., 1997). The soil samples, collected from an undisturbed mountain top where Cd-rich black shale (0.32–2.91 mg/kg) outcrops in Chengkou County, China, contain Cd at 0.53–12.8 mg/kg (mean at 4.94 mg/kg, $I_{geo} = 3.23$; unpublished data).

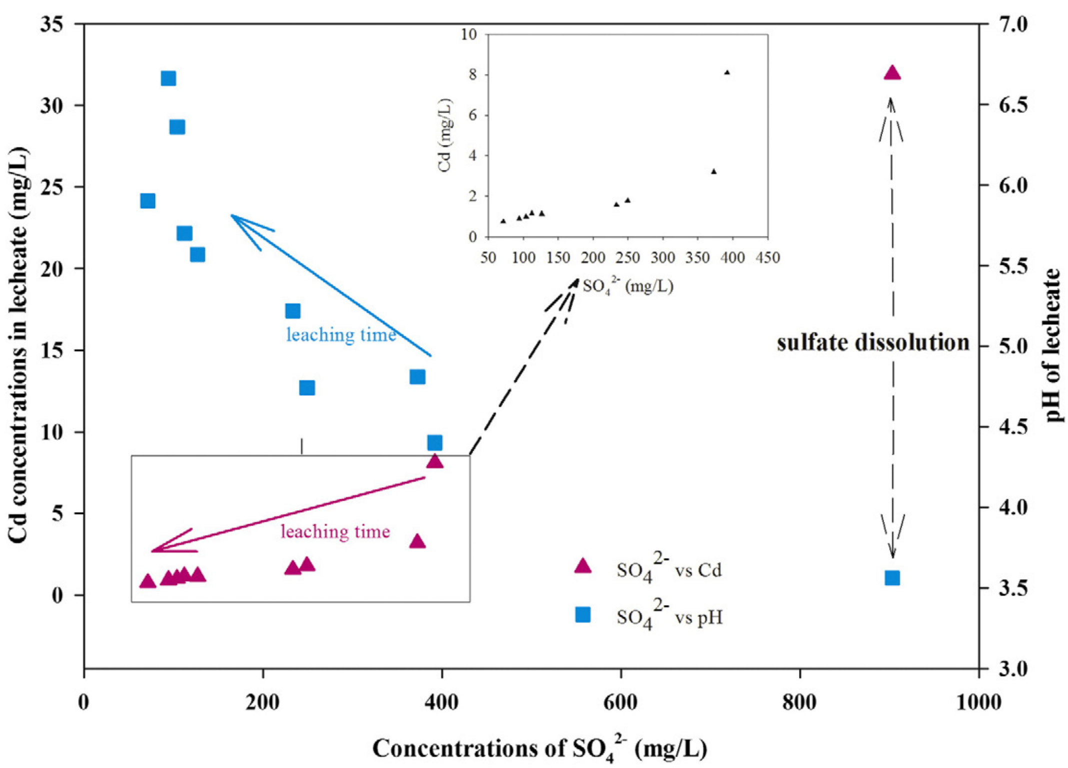

Fig. 3. Results of leaching test for Cd-rich black shale.

Elevated Cd concentrations in pristine soils are linked to Cd-rich parent rocks, such as soils associated with black shales and phosphorite. This is contrast to soils developed on other rock groups such as non-black shales, carbonates, and volcanic sedimentary rocks (Table 1). However, total Cd concentrations in soils alone are insufficient clue to environmental mobility. To better explore the potential mobility and bioavailability of Cd in soils, the sequential extraction is a good approach to determine various geochemical fractions of Cd. For instance, Cd in soils developed from black shales in Wushan County of China. is predominantly present in the residual (27–66%, mean of 41%), followed by the reducible (8.2–36%, mean of 21%) and exchangeable (3.8%–42%, mean of 22%) fractions, and small portion (4.3% to 16%, mean of 9.2%) is associated with the carbonate fraction (Fig. 4; Liu et al., 2013a). In contrast, Cd in soils developed from carbonate rocks in Switzerland, exist mainly in the carbonate fraction (45–53%, mean of 49.3%), Fe-oxides (23–37%, mean of 31.7%) and organic (6.1–17%, mean of 12.7%) fractions, with little associated with the residual fraction (one sample with 2.4%), and none in the exchangeable fraction (Fig. 4; Quezada-Hinojosa et al., 2009). Partial dissolution of carbonate particles of parent rocks may explain major Cd existing in the carbonate fraction (Quezada-Hinojosa et al., 2009). This clearly shows that the geochemical fractions of Cd in various pristine soils are significantly different, reflecting dependence on parent rock composition.

The geochemical fractions of Cd in soils vary with soil Cd source. The geogenic Cd in soils developed from Korean black shale, account for 18.4% of total Cd in the exchangeable fraction from the Bo-Eun area, and 22.5% from the Chu-Bu area; the dominant factions are composed of residual and oxidizable fractions (Lee et al., 1998). In the soils from a sulfide-gold mineralization area in Portugal, 29.4–67.9% (mean 49%) of total Cd existed in the residual fraction, 12% in the exchangeable, water and weak acid-soluble fractions, and 19% in the easily reducible fraction (Reis et al., 2012). However, in smelting impacted arable soils in France, Cd dominates in the exchangeable, water and acid soluble fraction (44.1%), against 42.7% in the reducible fraction (Pelfrêne et al., 2011). Cadmium fractionation in soils from a non-ferrous metal mine area in eastern China decreases in the order of exchangeable and carbonates (45.2%) > residual (35.2%) > reducible (16.7%) > oxidizable (2.9%) fraction (Liu et al., 2013b). Similar fractionations for Cd are also observed in anthropogenically-polluted soils in Poland and England, where higher percentages are found in the exchangeable fraction and lower load in the residual fraction (Chlopecka, 1996; Li and Thornton, 2001). Generally, Cd dominates in the residual and reducible fractions in pristine soils, which suggests it is associated with silicate minerals and Fe—Mn oxides. Only about 20% of the potential bioavailable fraction of Cd is found in soils with a geogenic origin, but about 40% with soils originating from anthropogenic sources.

In addition to elevated Cd in soils, the black shale weathering process may result in soil acidification due to the oxidization of organic materials and sulfides (generally pyrite). As summarized in Table 1, soil pH in black shale areas range from 2.8 to 7.7, with the majority of samples showing pH below 6.0. This is in contrast to the more neutral pH from samples taken in areas free of black shale. Soil pH plays an important role in Cd adsorption, by controlling pH-dependent sites in organic materials, clay minerals and oxyhydroxides. Lower pH increases Cd mobility, and accelerates its release from relatively stable fractions, but limits the formation of carbonates ($CdCO_3$) and oxyhydroxides (such as $Al(OH)_3$ and $Fe(OH)_3$). Increased mobility also increases bioavailability and uptake by plants, which can pose a risk to food safety and human health. We selected 15 Cd-rich soil samples to determine the water soluble Cd and pH, the results showed that water soluble Cd is significantly negatively correlated to soil pH, except for one outlier (pH = 5.3) with the highest water soluble Cd (0.25 mg/kg). The outlier could be attributed to the extremely high total Cd concentrations (41 mg/kg) (Fig. 5). The water soluble Cd fraction in soil is easily bioavailable to plants. So, low soil pH makes more bioavailable Cd, which is preferentially taken up by plants (McBride, 2002).

5. Cadmium pollution in aquatic environment

Geogenic Cd also contributes to elevated Cd in water and sediment. Elevated Cd (0.125–4.20 μg/L, mean 1.32 μg/L) has been observed in Swedish Degerhamn groundwater within a black shale deposit. The Cd in these groundwater samples was significantly higher than those found in reference sample (0.0379 μg/L) from an area with glacial till overlying Proterozoic granite (Lavergren et al., 2009a). In addition, higher Cd occurs in acidic water than neutral water, with some samples containing Cd concentrations >10 μg/L (Lavergren et al., 2009a), far above the WHO guideline (3 μg/L) for Cd in drinking water (WHO, 2006). The Cd flow to the groundwater in the region was up 0.87 kg/year, a quarter from black shale bedrock, compared to 270 kg/year to the water environment from the black shale of Sweden (Lavergren et al., 2009a). The aqueous flux of Cd from New Albany shale is estimated at 0.03 g/ha/a to 0.09 g/ha/a (Tuttle et al., 2009). Further, 4–6.9% of the Cd was released from un-

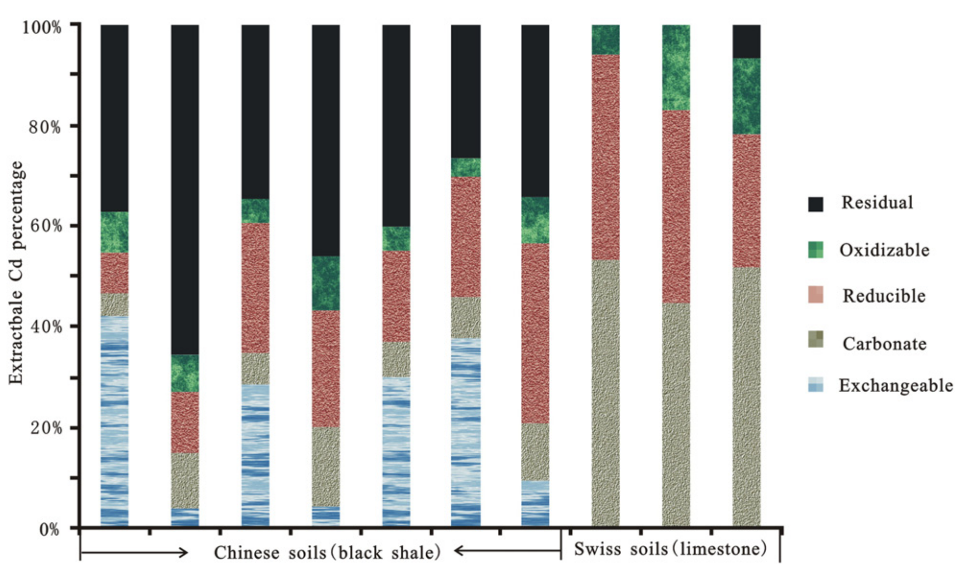

Fig. 4. Chemical fractions of Cd in soils from two high Cd background areas (Chinese soil: Liu et al., 2013a; Swiss soil: Quezada-Hinojosa et al., 2009).

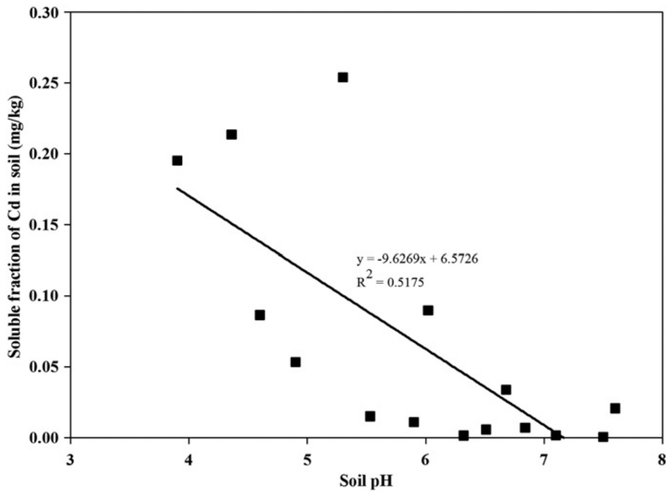

Fig. 5. The relationship between water soluble Cd and soil pH.

weathered black shales during a leaching process of 36 weeks (Falk et al., 2006). Our 3-month leaching test for weathered black shale samples (Cd: 101 mg/kg) from the Three Gorges region showed that Cd reached to 1000 μg/L in leachate. These results have revealed that considerable Cd tends to release from weathering of black shale, which is prone to risk the water environment.

Sediment is an important sink for Cd in aquatic systems. Soluble Cd may precipitate into sediments after hydrodynamic conditions have changed. Erosion processes also contribute to Cd loading to sediment. In the Cd-rich black shale (15 mg/kg) outcropped Talvivaara area of Finland, Cd in the local stream sediment ranges from 0.21 to 4.45 mg/kg (mean of 1.62 mg/kg), and 0.4–11.7 mg/kg (mean of 4.0 mg/kg) in local lake sediments. These concentrations are significantly higher than those Cd concentrations found in area with gneiss granite or quartzite (mean of 0.66 mg/kg for stream sediment, and 1.1 mg/kg for lake sediment; Loukola-Ruskeeniemi et al., 2003). Here, the authors found that there is a clear correlation between Cd in organic lake sediment and lake water, and a significant variance from black shale area and gneiss granite area (Loukola-Ruskeeniemi et al., 1998), documented the influences of Cd release from black shales.

The acid rock drainage originating from the weathering of black shale is also of environmental concern. The ARD in stream water running through black shale formations in the Yukon Territory of Canada contains high Cd concentrations, ranging from 9 to 130 μg/L (mean 51 μg/L) (Kwong et al., 2009). The water acidification impacted by ARD has been intensively documented by either lab leaching test (Falk et al., 2006; Yu et al., 2014; Perkins and Mason, 2015) or in situ measurements (Loukola-Ruskeeniemi et al., 1998; Woo et al., 2002; Kwong et al., 2009). For example, lab tests on effluents from Swedish black shale showed that leachate pH (2.4) remained low for extended periods of time (Yu et al., 2014). And pH at 4.8 in groundwater was detected in area with black shales in Korea (Woo et al., 2002), pH at 3.0 to 3.8 in stream water samples from Yukon Territory of Canada (Kwong et al., 2009). Low pH (3.8) has also been observed in Finnish sediment cores, which suggested that the lake acidified >9000 years ago, induced by intense weathering of black shales (Loukola-Ruskeeniemi et al., 1998). Anthropogenic activities such as mining and road construction may promote the outcrop and crush of black shale, further accelerate the generation of ARD. The potential for acid generation from rocks is conventionally determined in laboratory using acid-base account. However, this method may not be suitable for the evaluation of acid generation potential for specific areas. To remedy this, a new protocol based on the analysis of regional sediment samples was suggested by Ahn et al. (2015).

6. Potential health risk

As discussed in the above sections, black shale weathering processes tend to elevate Cd concentrations in the surface environment, and may result in human health risk. It is therefore prudent, that the exposure pathways and potential health risk of geogenic Cd from black shale should be considered.

High Cd concentrations occurring in arable soils, from geogenic or anthropogenic sources, may accumulate in food crops and result in public health risks (Kabata-Pendias and Pendias, 2001). Generally, ingestion of foodstuffs in a regular diet is regarded as primary exposure pathway for the non-smoking and non-occupationally exposed populations (Järup and Åkesson, 2009; Satarug et al., 2010). In areas with elevated naturally-occurring Cd in soils, Cd accumulations in plants have been widely detected. For instance, elevated Cd, up to 7.6 mg/kg, has been observed in native vegetation (*Avena*, *Brassica*) sampled from geogenic Cd-rich soils of California (Lund et al., 1981). The same study also found that various vegetables grown in black shale soils (Cd at 22 mg/kg) in the greenhouse also took up high amounts of Cd (dry weigh, DW), 52 mg/kg in pepper leaves, 4.7 mg/kg in fruit, and 82 mg/kg in Swiss chard (Lund et al., 1981). Elevated Cd concentrations in six plant species, growing in Swiss Jura Mountain pastures with Cd-rich carbonate rocks, were also detected, 2–6 mg/kg (DW), with a maximum at 13.4 mg/kg in *Alchemilla xanthochlora*, far above the safety limits (1 mg/kg) for vegetation and animal feedstuffs (Quezada-Hinojosa et al., 2015). Cadmium has also been shown to be presented at 0.31–2.30 mg/kg (DW) in vegetables grown in a black shale exposed area in Korea (Lee et al., 1998), 2.3 mg/kg in lettuce and 1.9 mg/kg in red peppers from Deog-Pyoung area of Korea (Kim and Thornton, 1993). In Three Gorges region of China, vegetables grown in soil derived from black shales contained Cd of 0.01 to 5.49 mg/kg (mean of 0.68 mg/kg, fresh weight; Liu et al., 2015). Among crop plants, leaf vegetables (such as cabbages) seem to have a high potential for Cd uptake (Khan et al., 2010; Liu et al., 2015). Such high Cd contents in vegetables may pose a potential health risk through the food chain to livestock and humans.

Rice, the world's main staple food, is also prone to enrich for Cd. Studies have demonstrated that Cd contamination in rice, may be impacted from anthropogenic activities, such as mining discharges and waste water irrigation (Simmons et al., 2005; Yang et al., 2006). Elevated Cd has been also observed in rice from areas with a geogenic Cd contribution. Rice containing Cd at 0.17 to 0.61 mg/kg has been reported from the black shale exposed Okchon area in Korea (Lee et al., 1998), and 0.1–3.5 mg/kg from Deog-Pyoung area also in Korea (Kim and Thornton, 1993), much higher than the normal range of 0.01–0.1 mg/kg (Meharg et al., 2013).

High Cd levels in food crops may lead to an elevated daily human population intake rate of Cd (Khan et al., 2010; Liu et al., 2015). It has been reported that a daily intake of Cd through Cd-rich vegetables is at 234 μg per adult in the Three Gorges region, China, significantly higher than the reference dose (60 μg for a 60 kg adult) (Liu et al., 2015). As a result, the urinary Cd levels of local inhabitants range from 0.43 to 27.6 μg/L (mean of 4.3 μg/L), were significantly higher than those from the control area (0.17–1.52 μg/L, mean of 0.61 μg/L) (Liu et al., 2015). In Jamaica, elevated Cd concentrations (male: 0.3–22.3 μg/g creatinine, with median of 2.46 μg/g creatinine; female: 0.01–35.9 μg/g creatinine, with median of 3.42 μg/g creatinine) and β2-MG concentrations (male: median of 78 μg/g creatinine; female: median of 74 μg/g creatinine) were also detected in urine samples of people living in the naturally occurring high Cd areas (Wright et al., 2010). High β2-MG (>200 μg/g creatinine) levels in urine correlate to high U—Cd concentrations (>2.5 μg/L), suggesting an impairment in the reabsorption capacity of the renal tubules. Autopsy examination subjects also show elevated Cd concentrations to some long-term residents, double those found in the general population (Wright et al., 2010). The above findings have demonstrated that geogenic Cd, especially from the weathering of black shales and other Cd-rich rocks, could enhance Cd exposure to local population, with a concomitant human health risk. In-depth investigations should be carried out in such Cd-rich areas, not only targeting the soil, but also the food crops and biological samples, to evaluate the potential health risk of geogenic Cd.

7. Remediation and management of geogenic Cd contamination

Remediation approaches have been carried out in many areas contaminated by anthropogenic Cd, but little has been done to control geogenic Cd risk. As discussed above, the excavation activity (such as mining and road construction) may accelerate the Cd-rich rock weathering. The environmental assessment of Cd risk should be carried out whenever excavation is planned in areas underlain by black shales or other rocks known to be enriched in Cd and other potentially toxic trace elements. Appropriate land management is also encouraged in areas with high geogenic Cd, such as, land use for forest rather than arable cultivation, and no cultivation for leaf vegetables and rice preferably uptaking for Cd. With respect to geogenic Cd-contaminated soil remediation, better understanding for Cd fractionations is necessary, from which proper remediation approaches may be designed. In all, geo-environmental management for geogenic Cd risks in areas with black shale should not be overlooked.

8. Conclusions

Geogenic Cd in the environment is an important source of health risk to humans. Exposed black shale anywhere on the planet is a major source of geogenic Cd. Cadmium is found in sulfides minerals, and the weathering process causes significant Cd release to surface environment, producing Cd contamination to soil, water and food crops. High Cd concentrations and potential bioavailability of Cd in soils facilitate Cd uptake by crop plants, resulting in Cd contamination in the food chain. Cadmium expose via food chain to humans induce a health risk, biomarked with high urinary Cd levels. Further in-depth research into the biogeochemical cycling of geogenic Cd is necessary for better geo-environmental management of the Cd risk to human health.

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