



ELSEVIER

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Barium concentration, phytoavailability, and risk assessment in soil-rice systems from an active barium mining region

Qinhui Lu^{a,b}, Xiaohang Xu^{a,b}, Longchao Liang^c, Zhidong Xu^{a,b}, Lihai Shang^a, Jianyang Guo^a, Dean Xiao^{d,**}, Guangle Qiu^{a,*}

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China

^b University of Chinese Academy of Sciences, Beijing, 100049, China

^c College of Resource and Environmental Engineering, Guizhou University, Guiyang, 550025, China

^d College of Resource and Environmental Engineering, Guizhou Institute of Technology, Guiyang, 550003, China



ARTICLE INFO

Editorial handling by Dr Q Gong

Keywords:

Barium
Phytoavailability
Paddy soils
Rice
Risk assessment

ABSTRACT

Barium (Ba) is a non-essential and toxic element. In China, intensive Ba mining and Ba salt manufacturing have led to sharp increases in Ba in the environment, but little information is available regarding Ba concentrations in paddy soil and rice. The total concentrations and phytoavailability of Ba in paddy soils and paired rice samples collected from the world's largest Ba mine in Dahebian, Tianzhu, Guizhou Province, southwestern China, were investigated. Risk assessments of Ba exposure via rice consumption were also evaluated. The results indicated that extremely high Ba concentrations existed in paddy soils, ranging between 518 mg/kg and 65,760 mg/kg, which demonstrated severe Ba contamination, as expected. The concentrations of rice Ba varied from 0.10 to 3.5 mg/kg, and a significantly positive correlation ($r = 0.51$, $p < 0.05$) between rice Ba and water-extractable Ba was observed, suggesting that water, rather than weak acid (0.43 M CH₃COOH), chelating agents (DTPA) or neutral salts (0.1 M NaNO₃, 0.01 M CaCl₂ or 1 M NH₄OAc), is a suitable extractant for predicting the phytoavailable Ba in the studied soils. Risk assessments showed that residents experienced low Ba exposure via rice consumption when considered in isolation of other sources in this study area.

1. Introduction

Barium (Ba) is a dense alkaline earth metal that is located in Group IIA of the periodic table and displays similar behavior to calcium (Ca) and magnesium (Mg) (Choudhury and Cary, 2001). Barium is considered to be a non-essential element for organisms and is harmful to animals and plants (Lamb et al., 2013). Barium exposure may cause multiple deleterious effects in animals, including damage to the cardiovascular, renal, respiratory, hematological, nervous, and endocrine systems (Çanlı, 2018; Ohgami et al., 2012; Perry et al., 1989), eventually resulting in cardiovascular and kidney diseases, metabolic, neurological, and mental disorders, and even death (Kravchenko et al., 2014). Thang et al. (2011, 2015) observed cancer-promoting effects on human precancerous keratinocytes and the constitutive malignancy of HaCaT keratinocytes upon exposure to 687 µg/L Ba²⁺ solution. Yajima et al. (2012) reported that Ba might promote arsenic's carcinogenic effects by modulating the balance between arsenic-mediated promotive and suppressive apoptotic pathways and thus inhibiting arsenic-

mediated cancer apoptosis. Pa Ping disease, which broke out in the region of Kiating, Sichuan Province, China, during the 1930s, was a fatal Ba poisoning accident that occurred because residents consumed salt contaminated with BaCl₂ (Bowen et al., 2010; Xu, 2008).

Barium compounds in the environment include BaSO₄, BaCO₃, BaHCO₃, BaNO₃, BaCl₂, BaCl⁺, BaOH⁺, BaF⁻, BaB(OH)⁴⁺, Ba²⁺, and Ba(CH₃COO)₂ (McGrath et al., 1989). The toxicity of a Ba compound is significantly related to its solubility, and the more soluble the compound is, the more toxic it is. Barium chloride is more toxic than barium carbonate owing to its high water solubility (Kravchenko et al., 2014; Kresse et al., 2007). Although barite has low solubility, it can still release amounts of Ba²⁺ in negatively charged soil colloids, posing a potential toxicity risk to plants and invertebrates (Lamb et al., 2013). Recently, Abbasi et al. (2016) found that barite-contaminated soils can release Ba in gastric solution and eventually pose health risks to biota.

Barium ore mining and refining, as well as Ba salt manufacturing, are the major anthropogenic sources of Ba (Choudhury and Cary, 2001). During the last 40 years, Ba compounds have been widely used

* Corresponding author.

** Corresponding author.

E-mail addresses: xiaodean@git.edu.cn (D. Xiao), qiuguangle@vip.skleg.cn (G. Qiu).

<https://doi.org/10.1016/j.apgeochem.2019.05.010>

Received 14 February 2019; Received in revised form 15 May 2019; Accepted 16 May 2019

Available online 17 May 2019

0883-2927/ © 2019 Elsevier Ltd. All rights reserved.

in industrial and medicinal fields, including applications in the petroleum industry, the steel industry, and as an agent for gastrointestinal (GI) tract radiography (Kravchenko et al., 2014). Significant quantities of Ba have been introduced into the environment, which is associated with an increasing public awareness of the risk of Ba exposure (ATSDR, 2007). Given the widespread use of Ba and rapid urbanization, Ba pollution has become a potential environmental issue. The USEPA (2002) reported that more than 150,000 people in the USA are exposed to Ba at levels higher than the limit of 2000 µg/L in drinking water.

Chemical extraction is a commonly applied method for estimating bioavailable or phytoavailable pollutants in soils; such availability is the major concern related to the uptake and accumulation of pollutants by plants and biota (Chavez et al., 2015). The commonly used extractants for the bioavailable forms of heavy metals are usually operationally defined by various laboratory extraction procedures and include water, weak acid (CH₃COOH), neutral salts (CaCl₂, NaNO₃ and NH₄OAc), and chelating agents (Ethylene Diamine Tetraacetic Acid and Diethylene Triamine Pentaacetic Acid) (Quevauviller, 1998; Rauret, 1998; Séguin et al., 2004; Menzies et al., 2007; Zhang and Young, 2010; Zhang et al., 2010; Kowalska et al., 2012; Beckers and Rinklebe, 2017). These extractants can supposedly quantify the so-called bioavailable or phytoavailable fraction in soils and have mainly been applied to the study of cadmium, mercury, arsenic, zinc, and copper. Generally, the soil total Ba content provides a poor prediction of phytoavailability (McBride et al., 2014); however, abnormally high concentrations of Ba have been reported in vegetation growing in Ba mining areas (Reddy, 2010). Hence, under certain conditions of elevated total Ba in soils from Ba-mining areas, the evaluation of the phytoavailable fraction of Ba is of great concern.

China produces the most Ba in the world, and its output of Ba between 1990 and 2016 occupied approximately 50% of the global total (USGS, 2017). The major Ba mines, Dahebian, Gongxi, and Banbi, are located in Guizhou, Hunan and Guangxi provinces, respectively, among which the Dahebian Ba mine is the largest and is located in Tianzhu County, Guizhou Province, southwest China. Guizhou Province is also the producing center of Ba-related chemical compounds, namely, Ba salts. Intensive Ba mining and Ba salt manufacturing have released large amounts of Ba into the surrounding environment, resulting in elevated concentrations of Ba in the water (Lu et al., 2017). The anoxic conditions in flooded soils favor the activity of sulfate-reducing bacteria (SRB), which are able to obtain sulfate from barite, which causes Ba²⁺ release (McCready, 1980; Phillips et al., 2001). Since rice is a staple food for residents and rice farming and Ba mining coexist in the region, flooded cultivation generates a favorable environment for the activities of SRB, which in turn cause elevated Ba²⁺ in soils, which might result in the accumulation of Ba in rice. However, few studies have focused on the characteristics of Ba in rice that is grown in heavily Ba-contaminated soils.

To understand Ba concentrations and phytoavailability in the soil-rice system and the health risk of Ba exposure through rice consumption, we selected paired paddy soils and rice in the district of the world's largest Ba mine in Dahebian for investigation. The goals of this study were to 1) elucidate Ba accumulation and distribution in soil-rice systems, 2) evaluate commonly used extractants for predicting the phytoavailable Ba in soils used to grow rice, and 3) assess the potential health risk to the local population of rice Ba exposure. This is the first investigation on Ba concentrations, bioavailability, and risk assessments in soil-rice ecosystems impacted by Ba mining and manufacturing activities.

2. Materials and methods

2.1. Description of study area

Tianzhu (N: 26°41′–27°09′; E: 108°54′–109°36′) is located in eastern Guizhou Province, southwest China, covering an area of 2201 km².

Tianzhu has a subtropical humid monsoon climate. The annual average precipitation is 1280 mm, and the average annual temperature is 16 °C (www.tianzhu.gov.cn). The major river flowing through the Ba mining area is the Jianjiang River, with the Mibei, Langjiang, and Fuluo rivers as tributaries. The aquatic system belongs to the Yuanjiang River, which is a tributary of the Yangtze River. In this region, rice is the main cereal crop, and its planting area was 22,175 ha in 2016. Irrigation water is obtained from local aquatic systems.

Tianzhu is the largest Ba mining and Ba salt manufacturing area in China. Ba mining activities began in the 1950s. The Ba deposit type is sedimentary (Li, 2004), and the primary ore is barite combined with minor dolomite and calcite. The gangue minerals are mostly quartz, illite, potash feldspar, and pyrite (Hou et al., 2014). The largest Ba mine in Tianzhu, known as the Dahebian Ba mine, lies in the village of Dahebian, which is approximately 15.5 km north of Tianzhu Town. The Dahebian mine is located upstream of the Fuluo River, which receives the mine drainage introduced by the intensive Ba mining activities.

Tianzhu is also the center of Ba salt manufacturing in China. Four large Ba salt plants, the Liuhe Chemical Plant (LH), Jiuji Chemical Plant (JJ), Xingfa Chemical Plant (XF) and Haohua Chemical Plant (HH), are located in this region. Among these plants, LH, JJ and XF are distributed in the village of Bangdong, which is approximately 8.0 km north of Tianzhu Town. HH is located approximately 3.6 km east of Tianzhu Town. LH, JJ and XF are located downstream of the Fuluo River, and their wastewater discharges into the river. The HH Ba salt plant is located downstream of the Jianjiang River, and its smelting wastewater discharges directly into the Jianjiang River.

2.2. Sample collection and preparation

A total of 82 rice grain samples and their paired paddy soils, taken from the roots, were collected from the study area during the harvest seasons in 2016 and 2017 (Fig. 1). Rice grain samples were individually sealed in clean polyethylene bags in situ. Soil samples were placed into clean polyethylene bags to avoid cross-contamination. All collected samples were labeled and transported to the laboratory for processing.

For rice, whole grain samples were freeze-dried (EYELA model FDU-1100; Japan) and then separated into hull, bran, and polished parts (white rice). The white rice was ground to 150 mesh (IKA-A11; IKA, Germany) for Ba measurements.

The soil samples were freeze-dried, ground with a mortar and pestle, and then filtered with a 200-mesh sieve. Gravels and plant residues were removed before grinding. The ground samples were kept in sealed clean polyethylene bags. Among all of the soil samples, twenty one soil samples collected from three zone types, MZ, FZ, and RZ (Fig. 1), were selected for the extraction of Ba by different extractants. MZ was impacted by intensive Ba mining, and FZ was impacted by Ba salt chemical plants. RZ, which is approximately 20 km south of the Dahebian Ba mine, was selected as a control site.

2.3. Sample analysis

2.3.1. Soil

2.3.1.1. Pseudo-total Ba. Soil samples (0.05 g) were acid-digested in a Teflon crucible with a mixture of concentrated subboiling ultrapure HNO₃ (3 mL, Sinopharm Chemical Reagent Company, China) and HF (1 mL, Guaranteed reagent, Sinopharm Chemical Reagent Company, China) in an oven at 160 °C for 48 h. Then, HNO₃ (1 mL) was added to the Teflon crucible and heated until complete evaporation of the solution occurred. Then, deionized water (2 mL) and HNO₃ (3 mL) were added to dissolve any residues. The digestion solution was transferred to a 15 mL centrifuge tube. Approximately 10 mL of diluted digestion solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES; Wasst-mpx, USA) to determine the Ba concentration.

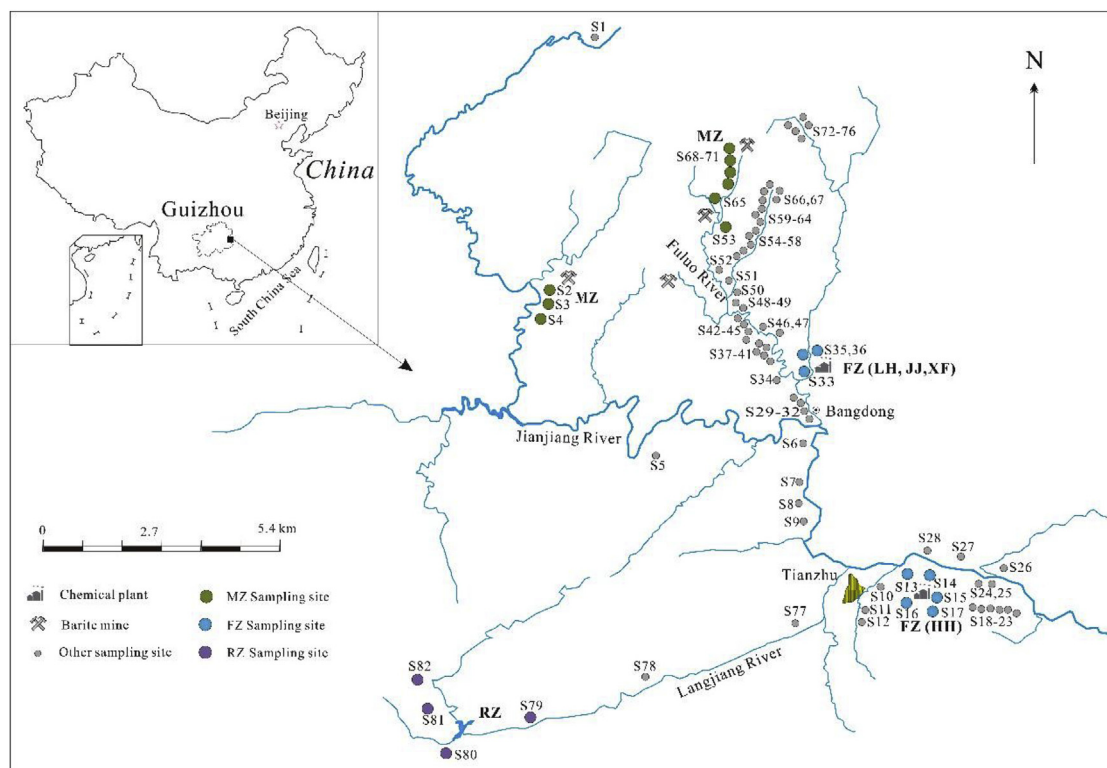


Fig. 1. Map of sampling sites.

2.3.1.2. Phytoavailable Ba. A total of six different extractants (DTPA, 0.43 M CH_3COOH , 0.1 M NaNO_3 , 0.01 M CaCl_2 , 1 M NH_4OAc and H_2O) were applied to extract Ba in soils for evaluation of the phytoavailable fraction. The detailed extraction procedures are described in Table S1. The suspensions were shaken in a reciprocal shaker. The solution and the solid phase were separated by centrifugation at $3400 \times g$ for 20 min. The supernatant was removed and preserved in borosilicate glass for Ba analysis. Approximately 10 mL was collected from each extract to measure the Ba concentration by ICP-OES using a process similar to that used for pseudo-total Ba.

2.3.1.3. X-ray diffractometry. The minerals in the soils were identified via X-ray diffractometry (XRD) analysis. The XRD data were collected on a Panalytical multifunction X-ray diffractometer (Model: Empyrean, Malvern Panalytical Ltd., United Kingdom) equipped with an Anton Paar high-temperature accessory (APHTK-16N) and a 3D PIXcel detector. The XRD measurements were performed in a 2θ range of 4.1° – 60° in continuous scanning mode with a 0.026° step size and a counting time of 35 s per step. The working voltage and current were 40 kV and 40 mA, respectively.

2.3.1.4. Soil pH and organic matter. Soil pH was measured by transferring a 5 g soil sample into 12.5 mL of deionized water (The Ministry of Agriculture of the People's Republic of China, 2007) and then analyzing the pH by a pH meter (Leici ZD-2; Shanghai, China). The potassium dichromate oxidation spectrophotometric method was used to measure the organic matter (OM) content of the soil (Ministry of Environment Protection of the People's Republic of China, 2011).

2.3.2. Rice Ba analysis

White rice (0.2 g) was placed into a Teflon crucible with 3 mL of HNO_3 . Then, the crucible was sealed in a stainless-steel container and heated in an oven at 150°C for 6 h. After the digestion solution cooled, 2 mL of H_2O_2 (Guaranteed reagent, Sinopharm Chemical Reagent Company, China) was added, and the solution was heated until

complete evaporation occurred. Deionized water (3 mL) and HNO_3 (2 mL) were added into the Teflon crucible for another 5 h of digestion. The digestion solution was transferred to a 15 mL centrifuge tube. Approximately 10 mL of diluted digestion solution was measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent HPLC 1290–7700x, USA).

2.4. Quality assurance/Quality control

Duplicates, method blanks, matrix spikes and certified reference materials (GSS-5, yellow red soil, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences; GBW10020, citrus leaf, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) were employed for quality assurance and quality control of the Ba analysis. The relative difference in Ba between duplicate soil samples was less than 7.5%. For the analyzed soil reference material (GSS-5), the recovery ranged from 89% to 102%. For rice samples, the relative percentage difference was less than 10%. The Ba concentration in the certified reference material (GBW 10020) was measured, with a recovery ranging from 98% to 103%. The recovery of the matrix spikes ranged from 80% to 115%. During the analysis process, a diluted standard stock solution (ICP-MS-04N-0.1X-1, AccuStandard) was measured for every 20 samples, and the recovery ranged from 99% to 100%.

2.5. Health risk assessment

The daily intake of Ba via rice consumption and its potential health risk to residents were calculated using the estimated daily intake (EDI) and hazard index (HI). In this study, an average daily rice intake of 0.6 kg/day and an average bodyweight of 60 kg were adopted, according to the Guizhou Statistical Yearbook (BGS, 2007). The oral reference dose (RfD) value of 0.2 mg/kg BW/day was that recommended by the USEPA (2013). The EDI and HI were calculated as follows:

$$EDI = (C \times DI)/BW \quad (1)$$

Table 1

Amount of Ba released during single extractions with H₂O, 0.43 M CH₃COOH, 0.1 M NaNO₃, 0.01 M CaCl₂, 1 M NH₄OAc, and DTPA in soil (mg/kg).

| Zone | ID | H ₂ O | CH ₃ COOH | NaNO ₃ | CaCl ₂ | NH ₄ OAc | DTPA | Sum of the six species | |
|------|-----|------------------|----------------------|-------------------|-------------------|---------------------|------|------------------------|-----|
| MZ | S2 | 2 | 79 | 2.1 | 11 | 63 | 0.77 | 158 | |
| | S3 | 4 | 111 | 15 | 37 | 87 | 0.4 | 254 | |
| | S4 | 3.4 | 54 | 12 | 9.5 | 28 | 0.41 | 107 | |
| | S53 | 7.8 | 48 | 16 | 12 | 28 | 0.36 | 112 | |
| | S65 | 9.6 | 22 | 4.9 | 4 | 8.8 | 0.17 | 49 | |
| | S68 | 3.7 | 83 | 50 | 49 | 58 | 1.7 | 245 | |
| | S69 | 4.2 | 50 | 2.4 | 8 | 12 | 0.25 | 77 | |
| | S70 | 2.2 | 81 | 9.8 | 32 | 71 | 0.89 | 197 | |
| | S71 | 4.1 | 85 | 22 | 21 | 68 | 0.41 | 200 | |
| | FZ | S13 | 5.6 | 81 | 24 | 20 | 41 | 0.58 | 172 |
| S14 | | 8.8 | 53 | 13 | 9.2 | 23 | 0.28 | 107 | |
| S15 | | 8.7 | 20 | 5.4 | 4.2 | 9.4 | 0.15 | 48 | |
| S16 | | 11 | 76 | 21 | 13 | 34 | 0.44 | 155 | |
| S17 | | 11 | 75 | 19 | 16 | 29 | 0.38 | 150 | |
| S33 | | 10 | 25 | 6.2 | 3.7 | 11 | 0.29 | 56 | |
| S35 | | 6.9 | 78 | 18 | 14 | 43 | 0.38 | 160 | |
| S36 | | 8.5 | 86 | 0.73 | 4.9 | 19 | 0.41 | 120 | |
| RZ | | S79 | 1 | 50 | 18 | 17 | 38 | 0.44 | 124 |
| | | S80 | 1.1 | 54 | 16 | 16 | 37 | 0.32 | 124 |
| | S81 | 0.56 | 40 | 10 | 13 | 35 | 0.36 | 99 | |
| | S82 | 1.1 | 43 | 12 | 11 | 37 | 0.26 | 104 | |

$$HI = EDI/RfD \quad (2)$$

where,

C Concentration of Ba in rice (mg/kg)

DI Daily intake of rice (kg/day)

BW Average body weight (kg)

EDI Estimated daily intake of Ba (mg/kg BW/day)

RfD Oral reference dose for Ba (mg/kg BW/day)

3. Results and discussion

3.1. Soil Ba

The pseudo-total Ba concentrations in paddy soils ranged from 518 to 65,760 mg/kg, with an average of 6855 mg/kg ($n = 82$, Table S2). Elevated pseudo-total concentrations were detected in soils adjacent to the Dahebian Ba mine owing to the intensive Ba mining activity. The highest value was recorded in sample S56, approximately 500 m downstream of the Dahebian Ba mine. A decreasing trend in soil Ba concentrations was observed with increasing distance from the Ba mining site. Samples S79, S80, S81 and S82, which are located approximately 20 km from the Dahebian Ba mining site, exhibited low Ba concentrations, ranging from 518 to 590 mg/kg. A relatively high Ba concentration of 9120 mg/kg was detected in sample S25, adjacent to the HH Ba salt plant. Often, the process of thermal decomposition of barites can generate fine Ba-containing particles that are transported to surrounding areas via deposition, resulting in high Ba concentrations. The high Ba levels in soils in the present study confirmed that Ba mining and Ba salt manufacturing were two significant sources.

The Ba concentrations measured in this study were approximately 1–2 orders of magnitude higher than the background value of 469 mg/kg Ba in soils in China (Wei et al., 1991). Compared with Ba concentrations of 15–3500 mg/kg in soils reported by ATSDR (2007) and concentrations of 30.9–1210 mg/kg in garden bed soils reported by McBride et al. (2014), the soils in the present study yielded even higher levels. The extraordinarily high Ba concentrations observed in paddy soils might cause a potential risk for biota and need to be assessed in the future.

The XRD results are displayed in Fig. S1. In the present study, barite was found in samples S56, S58, S61, S62 and S63, which were all near

the Dahebian Ba mine and had high Ba concentrations. This further confirmed that Ba ore mining is a dominant source of Ba in paddy soils. The lack of a BaSO₄ signal detected in other soil samples might be attributed to the detection limit (greater than 1%) of the XRD technique. Abundant quartz and muscovite contents were also found in samples, and the latter is attributed to chemical fertilizers used in paddy soils. Other minerals, such as orthoclase, calcite, anatase and albite, were also observed in the paddy soils.

3.2. Rice Ba

The concentrations of Ba in rice ranged from 0.10 to 3.5 mg/kg (Table S2), with an average of 0.76 mg/kg ($n = 82$). The highest rice Ba concentration was observed in sample S15, adjacent to the HH Ba salt plant. High Ba concentrations were also obtained in rice from site S53, adjacent to the Dahebian mining area. The results demonstrated that the rice was heavily contaminated with Ba released from Ba mining and manufacturing activities and indicated that both Ba mining and Ba manufacturing can release significant quantities of bioavailable Ba compounds. The highest recorded concentrations of Ba in rice, which were as high as 3.5 mg/kg, could pose a potential exposure health risk.

Compared to an average of 0.81 mg/kg with a range of 0.26–1.5 mg/kg and an average of 1.29 mg/kg with a range of 0.47–3.5 mg/kg in rice from Ba mining zones and Ba salt plant zones, respectively, in the present study, a comparable average of 0.43 mg/kg with a range of 0.06–1.2 mg/kg was reported by Ma et al. (2017) in rice from Guangdong Province, a developed region with no Ba-related industry in South China. Given the absence of Ba-related manufacturing and mining activities in Guangdong Province, the high levels of rice Ba relative to our results indicated that Ba contamination is not limited to mining and manufacturing regions and might be more widespread than initially understood in China.

3.3. Phytoavailability of Ba in soil

The results for phytoavailable Ba in soil extracted by six extractants are displayed in Table 1. Phytoavailable Ba varied from 0.56 to 11 mg/kg, 20–111 mg/kg, 0.73–50 mg/kg, 3.7–49 mg/kg, 8.8–87 mg/kg, and 0.15–1.7 mg/kg for H₂O, CH₃COOH, NaNO₃, CaCl₂, NH₄OAc, and DTPA, accounting for 0.068–0.98%, 0.16–9.2%, 0.015–5.3%, 0.028–5.2%, 0.062–6.1% and 0.0012–0.18% of pseudo-total, respectively (Fig. 2). The lowest extraction ratio occurred in the DTPA-extractable fraction, and the highest value appeared in the CH₃COOH-extractable fraction. The largest amounts of Ba were extracted by CH₃COOH among the six extractants, indicating that an increase in soil

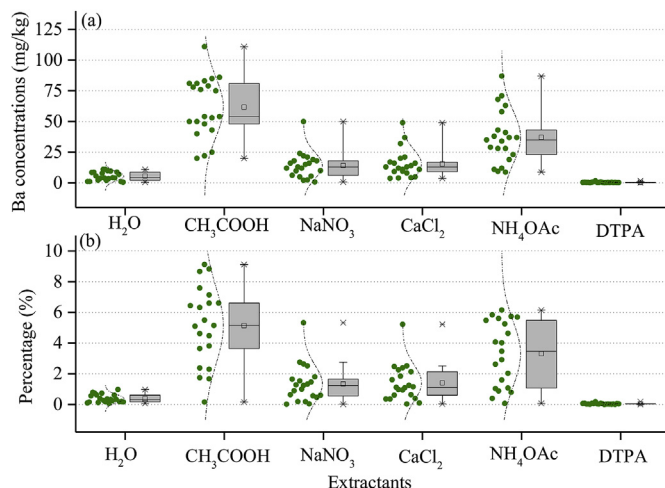


Fig. 2. Amount of Ba extracted from six extractants (a) and the percentage of each extracted Ba to pseudo-total Ba (b).

acidity leads to the release of Ba^{2+} (Frančišković-Bilinski, 2006; Sloot et al., 1996). The smallest amounts of Ba extracted by DTPA suggested a low ability to chelate organic matter, which agrees with the previous study by Bodek (1988), who found that Ba complexation by organic ligands occurs to a limited extent. The use of neutral salts for metal extraction from soils is based on desorption/ion exchange processes, but neutral salts are always considered weak extractants due to the strong metal binding to soil minerals (McLaughlin et al., 2000). Equally small amounts of Ba were obtained with $NaNO_3$, $CaCl_2$ and NH_4OAc in the study. Generally, Ba is immobile and geochemically associates with feldspars and biotites in soils (Pichtel et al., 2000), and free Ba^{2+} can be immobilized by precipitation, by adsorption onto oxides and hydroxides, or by fixation onto clays (Bodek, 1988; Kabata-Pendias, 2011); these processes are probably reasons for the low amounts of water-extractable Ba in the present study.

The plant uptake of Ba was affected by Ba species. Myrvang et al. (2016a) investigated the Ba uptake in white clover and tall fescue, which was mainly controlled by exchangeable Ba in the growth media. Uptake of Ba from soil by plants varies among species (Myrvang et al., 2016b). In the current study, water-extractable Ba was significantly correlated with rice Ba ($r = 0.51$, $p < 0.05$, Fig. 3a), suggesting that this fraction is easily absorbed by rice. Lamb et al. (2013) also found that pore water Ba is strongly related to lettuce shoot Ba and shoot biomass production. No obvious correlations between rice Ba and other extractable Ba in soils were obtained (Fig. 3b–f). The sum of six extractable Ba fractions had a poor relationship with rice Ba (Fig. 3g). And the correlation between soil pseudo-total Ba and rice Ba was also not significant (Fig. S2). This phenomenon suggests that the water-soluble fraction is readily bioavailable and can be the most absorbed form by rice. Hence, among all six extractants employed in the present study, water is the most suitable extractant for predicting the bioavailability of Ba in soils, can be regarded as a bioavailability indicator and merits further attention.

The soil pH and OM affect the availability of heavy metals in paddy soils (Zeng et al., 2011). The results for soil pH and OM are presented in Table S2. The pH values varied from 4.41 to 7.97 with an average of 5.76. Approximately 88% of the soil samples in the present study

exhibited values below 7, indicating acidic conditions. Soils adjacent to Ba salt plants are more acidic, which might be attributed to the dry and wet deposition of acidic gases (i.e., SO_2 , H_2S) that are emitted from the processing of barite ores during thermal decomposition (Zhang et al., 2012). A low soil pH enhances the release of Ba^{2+} from soil, while a high pH results in Ba^{2+} sorption to Al and Fe oxyhydroxide minerals, which are difficult for plants to take up (Abbasi et al., 2016; Reddy et al., 2010). In this study, we chose two separate areas to evaluate the effects of soil pH and soil OM for rice. The two areas included an area surrounding Ba mining activities and a Ba salt chemical plant. The results were displayed in Fig. 4. A significant correlation between soil pH and rice Ba was obtained (R-square = 0.22, $p = 0.000$, Fig. 4a; R-square = 0.21, $p = 0.000$, Fig. 4b). As decreased soil pH, rice Ba increased, demonstrating that low soil pH also promotes the release of Ba from soil, thereby increasing plant availability. However, no obvious correlation between soil OM and rice Ba was observed (Fig. 4c–d), indicating that soil OM was not a significant factor for the absorption of Ba by rice in the current study.

3.4. Risk assessment

According to equations (1) and (2), the *EDI* and *HI* values were calculated. The results showed that the *EDI* ranged from 0.001 to 0.035 mg/kg BW/day, with an average of 0.008 ± 0.006 mg/kg BW/day (Fig. 5a). The highest value occurred at S15, which is adjacent to the HH Ba salt plant; this result was attributed to the effect of Ba salt manufacturing. The average *EDI* values of the three zones are displayed in Fig. 5b. A relatively high *EDI* was found at site FZ, with averages of 0.013 ± 0.0096 mg/kg BW/day. The lowest *EDI* was obtained at site RZ, with an average of 0.0032 ± 0.0019 mg/kg BW/day. All *EDI* values in the present study were below the USEPA recommended *RfD* of 0.2 mg/kg BW/day, indicating low levels of Ba exposure via rice consumption to local populations.

The *HI* values ranged from 0.005 to 0.17, with an average of 0.04 ± 0.03 (Fig. 5a). The maximum *HI* occurred near the HH Ba salt plant. In the three zones, the order of *HI* was $FZ > MZ > RZ$ (Fig. 5b). High values were found at Ba salt plants. Compared to the water-

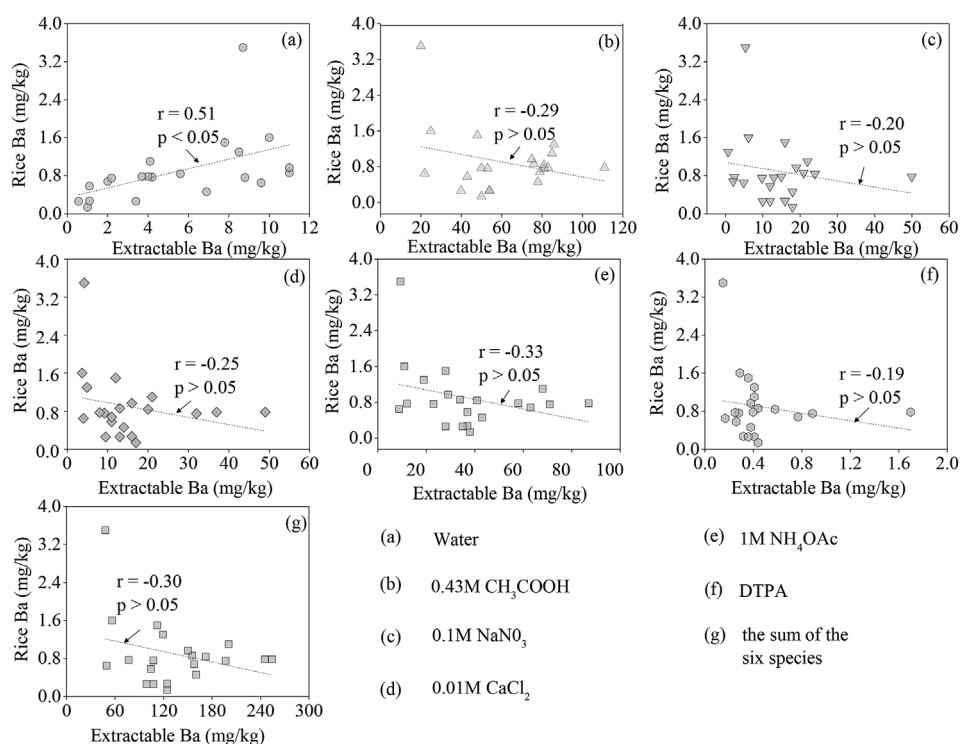


Fig. 3. Correlations between the amount of Ba released during single extractions and rice Ba concentrations (a–f) and the sum of six species and rice Ba (g).

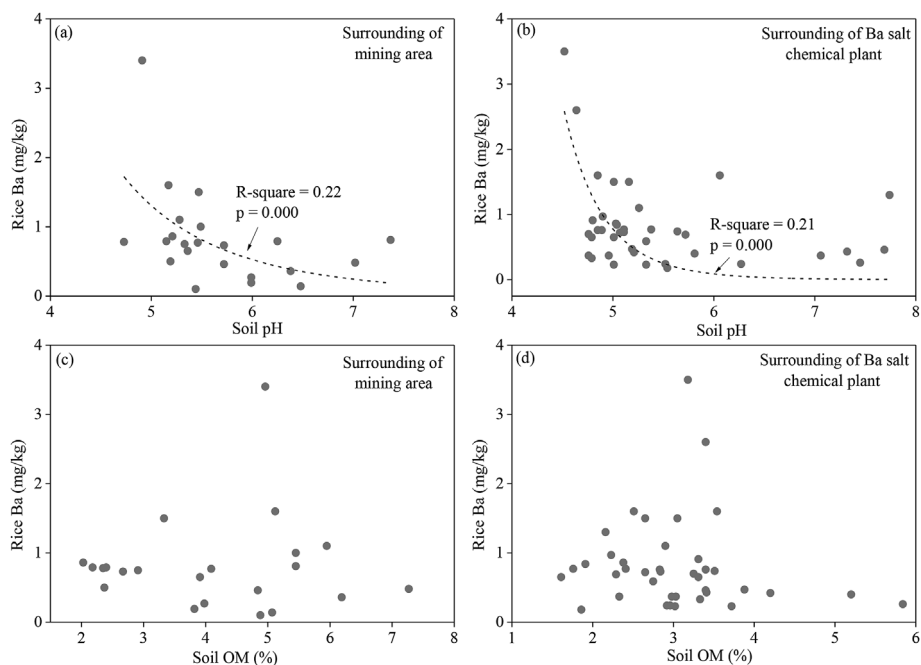


Fig. 4. Correlations between rice Ba and soil pH (a–b) and rice Ba and soil OM (c–d).

extractable Ba in soil from MZ and RZ, the highest concentration was observed at FZ (Fig. S3), indicating a greater amount of available Ba in the soil that can be taken up by rice, hence entering the human body and causing high exposure risks. All HI values were less than 1 and demonstrated that rice consumption may not pose an obvious adverse health risk to inhabitants (Yu et al., 2010). However, human exposure to Ba may also occur through breathing air, drinking water, and eating other foodstuffs containing Ba (ATSDR, 2007; Poddalgoda et al., 2017). Hence, future studies on Ba intake via breathing, drinking, and vegetation consumption are needed for accurate risk assessments.

4. Conclusions

The concentrations, bioavailability, and exposure risks of Ba in the soil-rice systems of active Ba mining areas were studied. The results showed that 1) extremely high Ba concentrations existed in paddy soils, especially near the Ba mining area as well as Ba salt plants. 2) rice can accumulate high Ba concentrations; values as high as 3.50 mg/kg Ba were observed in grain adjacent to the Ba salt plant. 3) water-extractable Ba can be used as an indicator of the phytoavailability of Ba in paddy soils. 4) inhabitants who dwell in areas adjacent to Ba salt plants

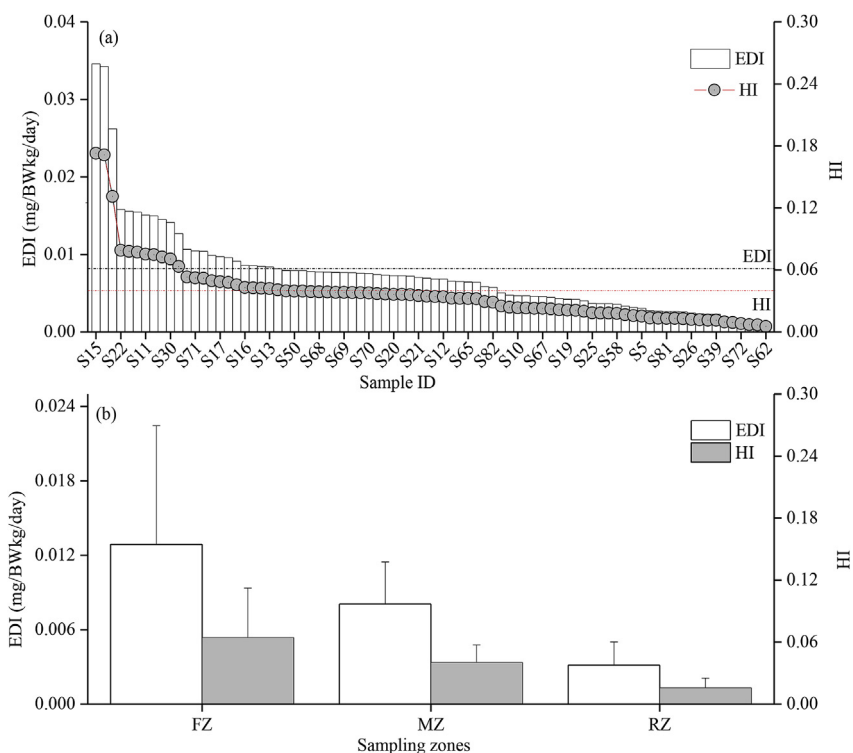


Fig. 5. The values of EDI and HI for each sample (a) and their distribution in samples collected from three sampling zones (b).

experienced the highest level of 0.035 mg/kg BW/day. Future studies on the exposure pathways of drinking, breathing, oral ingestion, and vegetation consumption are necessary to provide an overall view of health exposure and risk assessment in such highly Ba-polluted regions.

Acknowledgments

This study was supported by the Opening Fund of the State Key Laboratory of Environmental Geochemistry (SKLEG2019716). We would like to express our appreciation to Dr. Yong Meng for his help with the X-ray diffraction analysis in soils.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.05.010>.

References

- Abbasi, S., Lamb, D.T., Palanisami, T., Kader, M., Matanitobua, V., Megharaj, M., Naidu, R., 2016. Bioaccessibility of barium from barite contaminated soils based on gastric phase in vitro data and plant uptake. *Chemosphere* 144, 1421–1427.
- ATSDR (Agency for Toxic Substances and Disease Registry), 2007. Toxicological Profile for Barium and Compounds. Department of Public Health and Human Services, Public Health Service, Atlanta.
- Beckers, F., Rinklebe, J., 2017. Cycling of mercury in the environment: sources, fate, and human health implications: a review. *Crit. Rev. Environ. Sci. Technol.* 47 (9), 693–794.
- BGS (Bureau of Guizhou Statistics), 2007. Guizhou Statistical Yearbook 2006. Guiyang, China. China Statistics Press (in Chinese).
- Bodek, I., 1988. *Environment Inorganic Chemistry: Properties, Processes, and Estimation Methods*. Pergamon Press, New York, pp. 799–801.
- Bowen, L.N., Subramony, S.H., Cheng, J., Wu, S.S., Okun, M.S., 2010. Elementary, my dear Dr. Allen: the case of barium toxicity and Pa Ping. *Neurology* 74, 1546–1549.
- Çanlı, M., 2018. A new perspective to aberrations caused by barium and vanadium ions on *Lens culinaris* Medik. *EES (Ecotoxicol. Environ. Saf.)* 160, 19–23.
- Chavez, E., He, Z.L., Stoffella, P.J., Mylavarapu, R.S., Li, Y.C., Moyano, B., Baligar, V.C., 2015. Concentration of cadmium in cacao beans and its relationship with soil cadmium in southern Ecuador. *Sci. Total Environ.* 533 (9), 205–214.
- Choudhury, H., Cary, R., 2001. Concise international chemical assessment document 33. Barium and barium compounds 5–10 9241530332.
- Frančišković-Bilinski, S., 2006. Barium anomaly in Kupa River drainage basin. *J. Geochem. Explor.* 88 (1), 106–109.
- Hou, D., Wu, X., Zhu, Y., 2014. Organic geochemistry characteristic and significance of dahebian barite deposit in Tianzhu country, Guizhou province. *Chin. J. Nonferrous Metals* 24, 3095–3107 (in Chinese).
- Kabata-Pendias, A., 2011. *Trace Elements in Soils and Plants*, fourth ed. CRC Press, Boca Raton, pp. 135–146.
- Kowalska, J., Stryjewska, E., Bystrzejewska-Piotrowska, G., Lewandowski, K., Tobiasz, M., Pańdyna, J., Golimowski, J., 2012. Studies of plants useful in the Re-cultivation of heavy metals-contaminated wasteland—a new hyperaccumulator of barium? *Pol. J. Environ. Stud.* 21 (2), 401–405.
- Kravchenko, J., Darrach, T.H., Miller, R.K., Lyerly, H.K., Vengosh, A., 2014. A review of the health impacts of barium from natural and anthropogenic exposure. *Environ. Geochem. Health* 36 (4), 797–814.
- Kresse, R., Baudis, U., Jäger, P., Riechers, H.H., Wagner, H., Winkler, J., Wolf, H.U., 2007. *Barium and Barium Compounds*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 17.
- Lamb, D.T., Matanitobua, V.P., Palanisami, T., Megharaj, M., Naidu, R., 2013. Bioavailability of barium to plants and invertebrates in soils contaminated by barite. *Environ. Sci. Technol.* 47 (9), 4670–4676.
- Li, Z., 2004. Barite resource distribution and development prospect in China. *Chin. Non-Metallic Min. Ind. Her.* 5, 86–88 (in Chinese).
- Lu, Q., Xu, X., Xu, Z., Liang, L., Shang, L., Xiao, D., Zhang, S., Jiang, Y., Qiu, G., 2017. Barium concentrations and speciation in surface waters collected from an active barium mining area in Guizhou Province, southwestern China. *Environ. Sci. Pollut. Res.* 25 (7), 1–10.
- Ma, L., Wang, L., Tang, J., Yang, Z., 2017. Arsenic speciation and heavy metal distribution in polished rice grown in guangdong province, southern China. *Food Chem.* 233, 110–116.
- McBride, M.B., Shayler, H.A., Spliethoff, H.M., Mitchell, R.G., Marquezbravo, L.G., Ferenz, G.S., Russellanelli, J.M., Casey, L., Bachman, S., 2014. Concentrations of lead, cadmium and barium in urban garden-grown vegetables: the impact of soil variables. *Environ. Pollut.* 194 (7), 254–261.
- McCready, R.G.L., 1980. Preliminary studies on the chemical, physical, and biological stability of Ba/RaSO₄ precipitates. *Hydrometallurgy* 5 (2), 109–116.
- McGrath, M., Davison, W., Hamilton-Taylor, J., 1989. Biogeochemistry of barium and strontium in a softwater lake. *Sci. Total Environ.* 87 (1), 287–295.
- Mclaughlin, M.J., Zarcinas, B.A., Stevens, D.P., Cook, N., 2000. Soil testing for heavy metals. *Commun. Soil Sci. Plant Anal.* 31 (11–14), 1661–1700.
- Menzies, N.W., Donn, M.J., Kopittke, P.M., 2007. Evaluation of extractants for estimation of the phytoavailable trace metals in soils. *Environ. Pollut.* 145 (1), 121–130.
- Myrvang, M.B., Gjengedal, E., Heim, M., Krogstad, T., Almas, A.R., 2016a. Geochemistry of barium in soils supplied with carbonatite rock powder and barium uptake to plants. *Appl. Geochem.* 75, 1–8.
- Myrvang, M.B., Bleken, M.A., Krogstad, T., Heim, M., Gjengedal, E., 2016b. Can liming reduce barium uptake by agricultural plants grown on sandy soil? *J. Plant Nutr. Soil Sci.* 179 (4), 557–565.
- Ministry of Environment Protection of the People's Republic of China, 2011. Soil-determination of Organic Carbon-Potassium Dichromate Oxidation Spectrophotometric Method. HJ615-2011. (in Chinese).
- Ohgami, N., Hori, S., Ohgami, K., Tamura, H., Tsuzuki, T., Ohnuma, S., Kato, M., 2012. Exposure to low-dose barium by drinking water causes hearing loss in mice. *Neurotoxicology* 33 (5), 1276–1283.
- Perry, H.M., Kopp, S.J., Perry, E.F., Erlanger, M.W., 1989. Hypertension and associated cardiovascular abnormalities induced by chronic barium feeding. *J. Toxicol. Environ. Health* 28, 373–388.
- Phillips, E., Landa, E.R., Kraemer, T., Zielinski, R., 2001. Sulfate-reducing bacteria release barium and radium from naturally occurring radioactive material in oil-field barite. *Geomicrobiol. J.* 18, 167–182.
- Pichtel, J., Kuroiwa, K., Sawyerr, H.T., 2000. Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites. *Environ. Pollut.* 110 (1), 171–178.
- Poddalgoda, D., Macey, K., Assad, H., Krishnan, K., 2017. Development of biomonitoring equivalents for barium in urine and plasma for interpreting human biomonitoring data. *Regul. Toxicol. Pharmacol.* 86, 303–313.
- Quevaullier, P., 1998. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *Trends Anal. Chem.* 17 (5), 289–298.
- Rauret, G., 1998. Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta* 46 (3), 449–455.
- Reddy, K.R., Danda, S., Yukselenaksoy, Y., Alhamdan, A.Z., 2010. Sequestration of heavy metals in soils from two polluted industrial sites: implications for remediation. *Land Contam. Reclam.* 18 (1), 13–23.
- Séguin, V., Gagnon, C., Courchesne, F., 2004. Changes in water extractable metals, pH and organic carbon concentrations at the soil-root interface of forested soils. *Plant Soil* 260, 1–17.
- Sloot, H.A.V.D., Comans, R.N.J., Hjelmar, O., 1996. Similarities in the leaching behaviour of trace contaminants from waste, stabilized waste, construction materials and soils. *Sci. Total Environ.* 178 (1–3), 111–126.
- Thang, N.D., Yajima, I., Kumasaka, M.Y., Ohnuma, S., Yanagishita, T., Hayashi, R., Shekhar, H.U., Watanabe, D., Kato, M., 2011. Barium promotes anchorage-independent growth and invasion of human HaCaT keratinocytes via activation of c-SRC kinase. *PLoS One* 6 (10), e25636.
- Thang, N.D., Yajima, I., Ohnuma, S., Ohgami, N., Kumasaka, M.Y., Ichihara, G., Kato, M., 2015. Enhanced constitutive invasion activity in human nontumorigenic keratinocytes exposed to a low level of barium for a long time. *Environ. Toxicol.* 30 (2), 161–167.
- The Ministry of Agriculture of the People's Republic of China, 2007. Determination of pH in Soil. NY/T 1377-2007. (in Chinese).
- USEPA (U.S. Environmental Protection Agency), 2002. *National Primary Drinking Water Regulations. Office of Ground Water and Drinking Water*. U.S. Environmental Protection Agency, Washington, D.C. <http://www.epa.gov/safewater/consumer/pdf/mcl.pdf>.
- USEPA (U.S. Environmental Protection Agency), 2013. *Integrated risk information system*. Chem. Assess. Summ. 2.
- USGS (U.S. Geological Survey), 2017. *U.S. Geological Survey, Mineral Commodity Summaries 1991-2017*.
- Wei, F., Chen, J., Wu, Y., Zheng, C., 1991. Study on the background contents on 61 elements of soils in China. *Chin. J. Environ. Sci. (Beijing)* 12 (4), 12–19 (in Chinese).
- Xu, Z., 2008. Barium in sichuan salt. *Res. Salt Ind. Hist.* 2, 60–64 (in Chinese).
- Yajima, I., Uemura, N., Nizam, S., Khalequzzaman, M., Thang, N.D., Kumasaka, M.Y., Akhand, A.A., Shekhar, H.U., Nakajima, T., Kato, M., 2012. Barium inhibits arsenic-mediated apoptotic cell death in human squamous cell carcinoma cells. *Arch. Toxicol.* 86 (6), 961.
- Yu, B.M., Xiao, L.S., Yin, G.Z., Lopez, B.N., Shan, S.C., Sheng, C.W., Cheung, K.C., Ming, H.W., 2010. Health risk assessment of abandoned agricultural soils based on heavy metal contents in Hong Kong, the world's most populated city. *Environ. Int.* 36 (6), 570–576.
- Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., Zhang, G., 2011. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ. Pollut.* 159 (1), 84–91.
- Zhang, H., Young, S.D., 2010. Characterizing the availability of metals in contaminated soils. II. *Soil Use Manag.* 21 (s2), 459–467.
- Zhang, J., Zhang, Q., Wang, Z., Zhang, W., Gan, G., Xing, J., An, Y., Xie, W., Gao, G., Hu, Y., Li, M., 2012. Distribution of barium and barium species in the soil around a barium salt factory. *Earth Environ.* 40 (4), 548–553 (in Chinese).
- Zhang, M.K., Liu, Z.Y., Huo, W., 2010. Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice. *Commun. Soil Sci. Plant Anal.* 41 (7), 820–831.