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Original Paper

Interspecific Differences in Barium Accumulation and Health Risk Assessment of Crops in a Barite Mining Area

Hairun Wang[1*]

[1] College of Eco-environment Engineering, Guizhou Minzu University, Guiyang, Guizhou, China

[*] Corresponding Author

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Abstract

Understanding barium (Ba) accumulation in crops from barite mining areas is crucial for assessing dietary health risks. This study investigated Ba concentrations, bioaccumulation factors (BCF), and translocation characteristics in various crops from a barite mining region in Guizhou, China. Results showed significant interspecific differences. Pakchoi (Brassicaceae) exhibited the highest Ba concentration (947.92-952.37 mg·kg^{-1}*) and BCF (0.028), while grains of Poaceae (rice and maize) had the lowest (1.50-7.14 mg·kg*$^{-1}$*). Ba distribution in Poaceae followed root>leaf>stem>grain, with very limited translocation to grains (TF stem→grain: 0.0135–0.0559), whereas pakchoi showed efficient translocation to leaves (TF: 0.4732). Health risk assessment revealed that pakchoi's estimated daily intake (EDI) was 17.5-18.4 times the USEPA reference dose (0.2 mg·kg*$^{-1}$*·day*$^{-1}$*), with hazard index (HI)>1, indicating a potential health risk. Solanaceae fruits and Poaceae grains had HI<1, posing negligible risk. Therefore, in high-Ba areas, priority should be given to planting Solanaceae or Poaceae crops rather than leafy vegetables.*

Keywords

Barium, Crops, Health risk assessment, Barite mining area

1. Introduction

Barite ($BaSO_4$) is an essential industrial raw material used in chemical, petroleum, pharmaceutical, building materials, and electronics industries. Since 2008, it has been listed as a critical mineral by the United States[1]. China is the world's largest producer of barite; between 2012 and 2018, its annual output accounted for approximately 42% of global production [2,3]. Barite resources in China are mainly distributed in Guizhou, Chongqing, Shandong, Hunan, Shaanxi, Fujian, and other provinces [4]. The Dahebian barite deposit in Tianzhu County, Guizhou Province, is one of the largest sedimentary barite deposits in China and even in the world.

During barite mining, transportation, and processing, large amounts of barium-bearing dust enter surrounding soils via atmospheric deposition, surface runoff, and tailings leaching, leading to significantly elevated soil barium (Ba) concentrations [5-8]. Studies have shown that Ba levels in mining-impacted soils can reach tens of thousands of mg·kg^{-1}, far exceeding the Chinese soil background value (469 mg·kg^{-1}) [9]. Although barite is extremely insoluble in water (Ksp ≈ 1×10^{-10}), under long-term weathering, leaching, and reducing conditions (e.g., flooded paddy fields), Ba is gradually released from barite into the soil solution [10-12], where it can be taken up by plants and enter the food chain.

Barium is a non-essential element for living organisms. Excessive intake of soluble Ba salts (e.g., $BaCl_2$, $BaCO_3$) is neurotoxic and cardiotoxic, causing hypokalemia, hypertension, cardiac arrhythmia, and even heart failure [13,14]. The U.S. Environmental Protection Agency (USEPA) has established an oral reference dose (RfD) of 0.2 mg·kg^{-1} BW·day^{-1} for Ba [15]. Dietary intake is the primary pathway for Ba exposure among residents in mining areas, and the Ba concentration in the edible parts of crops directly determines the daily intake. Therefore, assessing the accumulation characteristics and health risks of Ba in crops is crucial for ensuring food safety and guiding agricultural practices in these areas.

Different crop species show marked differences in their capacity to take up, accumulate, and translocate Ba. Leafy vegetables (e.g., pakchoi, lettuce) generally exhibit strong Ba accumulation, with edible-part Ba concentrations reaching hundreds to thousands of mg·kg^{-1} [16,17]. In contrast, Solanaceous fruits (tomato, hot pepper, eggplant) and Poaceae grains (rice, maize) tend to contain low Ba levels [18]. These differences may be attributed to root physiological traits, competitive cation absorption (e.g., Ca^{2+}, Mg^{2+}), and variations in xylem-phloem transport efficiency [19,20]. Moreover, soil pH, organic matter content, iron-manganese oxides, and redox conditions significantly influence the speciation and bioavailability of Ba [21,22]. However, systematic health risk assessments of multiple common crops in barite mining areas remain scarce, and the mechanisms governing Ba accumulation and translocation across different plant families are still poorly understood.

In this study, we selected a range of crops commonly grown by local residents in the Dahebian barite mining area of Tianzhu County, Guizhou Province, including Brassicaceae (pakchoi, white radish, red radish), Solanaceae (cherry tomato, hot pepper, eggplant), Convolvulaceae (sweet potato), Fabaceae (green bean), and Poaceae (rice, maize). Ba concentrations in the edible parts were measured, and the bioaccumulation factors (BCF), transfer coefficients (TF), and hazard indices (HI) were calculated to systematically assess the health risks of different crops. Key factors influencing Ba accumulation and translocation in plants are also discussed. The results provide a scientific basis for adjusting agricultural planting structures, screening low-accumulation crops, and ensuring safe land use in high-barium contaminated areas.

2. Materials and Methods

2.1 Field Site and Experiment Setup

The study was conducted in the Dahebian barite mining area, Tianzhu County, Guizhou Province, southwestern China (approximately 109°12′E, 26°58′N). This region hosts one of the largest sedimentary barite deposits in China, with proven barite reserves exceeding 178 million tons, accounting for more than 70% of the national total. The mining area is located in a hilly low-mountain terrain at elevations of 300-700 m. The climate is a subtropical humid monsoon climate, characterized by mild temperatures and abundant rainfall. The multi-year average annual temperature is 16.5 °C, and the average annual precipitation ranges from 1200 to 1400 mm, of which approximately 70% falls during the wet season from April to September. The dominant soil types in the region are yellow soils (Haplic Alisols) and paddy soils (Stagnic Anthrosols), both developed from the weathering of Cambrian black rock series (mainly carbonaceous shale, siliceous rock, and limestone). The background concentration of Ba in non-contaminated soils of Guizhou Province is about 469 $mg\cdot kg^{-1}$, whereas in the mining area it can exceed 30 000 $mg\cdot kg^{-1}$ due to long-term mining and transportation activities.

2.2 Sample Collection

Sample collection was carried out from August to October 2024 in the Dahebian barite mining area, Tianzhu County, Guizhou Province. Along the ore transportation route and at various distances from the mining site, the main crops consumed by local residents were collected, including pakchoi, white radish, red radish (Brassicaceae); cherry tomato, hot pepper, eggplant (Solanaceae); sweet potato (Convolvulaceae); green bean (Fabaceae); and rice and maize (Poaceae). For rice and maize, roots, stems, leaves, and grains (or ears) were separately collected. For pakchoi, the aboveground parts (leaves and tender stems) were taken; for radish and sweet potato, the fleshy roots were collected; for tomato, hot pepper, eggplant and green bean, ripe fruits were harvested. For each crop, 3–5 healthy plants without visible disease or pest damage were collected, and samples of the same crop from different plants were pooled into one composite sample. All samples were placed in clean polyethylene bags, transported on ice to the laboratory, and stored at 4 °C for further processing.

2.3 Sample Pretreatment

The collected plant samples were first rinsed with 18.2 MΩ·cm ultrapure water, then placed in a pre-cleaned oven and dried at low temperature. Finally, they were cut into small pieces using a ceramic knife and ceramic scissors for subsequent processing.

The detailed pretreatment steps are as follows:

(1) Drying: Plant samples were dried in an oven at 40°C for 3-4 days.

(2) Grinding: The dried plant samples were first cut into small pieces with ceramic scissors and then ground in an agate mortar. After grinding each sample, quartz sand was ground in the same mortar and rinsed with 18.2 MΩ·cm ultrapure water (Milli-Q Integral, Merck Millipore) to thoroughly clean any remaining sample residues and avoid cross-contamination.

(3) Weighing: Based on preliminary tests, approximately 20 mg of plant sample was weighed using an SQP electronic balance. For plant parts with low element content (e.g., rice grains, sweet potato), 50-100 mg was weighed.

2.4 Sample Digestion

All digestion and measurement procedures were carried out at the State Key Laboratory of Lithospheric and Environmental Evolution, University of Science and Technology of China (USTC). The acids (HCl, HNO_3, and HF) used in the experiments were purified by double sub-boiling distillation, and the water used for sample digestion and reagent dilution was 18.2 MΩ·cm ultrapure water (Milli-Q Integral, Merck Millipore). After filtration, 5 mL of water sample was transferred into a PFA beaker (Savillex®), digested with 2% HNO_3, and then evaporated to dryness. The residue was quantitatively redissolved with 2% HNO_3, and Rh standard solution was added to a final concentration of 10 ppb for drift correction. Ba and other relevant element concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, Optima 8000, PerkinElmer, Branford, CT, USA).

For plant samples, after drying and grinding, approximately 10 mg of soil sample powder was weighed into a Teflon® PFA vial (Savillex®). A mixture of 2.1 mL HNO_3 and 0.7 mL HF was added, and the vial was heated on a hot plate at 120 °C for 24 hours to remove silicates. After complete decomposition, the sample was evaporated to dryness at 120-130 °C on a hot plate. Then, 4 mL of aqua regia was added, allowed to stand for 8 hours, heated at 120 °C for 24 hours, and again evaporated to dryness at 120-130 °C. The residue was dissolved in 2% (m/m) HNO_3, and an aliquot was taken for Ba concentration measurement by ICP-MS (Elan DRC II; PerkinElmer, Waltham, MA, USA).

2.5 Health Risk Assessment

To evaluate the accumulation behavior and in vivo translocation characteristics of barium in crops, and to further assess their potential health risks, this study selected maize and rice as representative crops. The bioaccumulation factor (BCF) and translocation factor (TF) were calculated to quantitatively analyze the migration process of Ba in the "soil-plant system":

$$BCF=\frac{C_1}{C_2} \tag{1}$$

$$TF=\frac{C_3}{C_4} \tag{2}$$

Among them, BCF represents the plant's ability to absorb Ba from rhizosphere soil, and TF reflects the translocation efficiency of Ba from lower to upper organs within the plant. C_1 represents the Ba concentration in a given plant part (mg·kg^{-1}), C_2 represents the Ba concentration in the corresponding rhizosphere soil (mg·kg^{-1}), C_3 represents the Ba concentration in the lower part of the plant (mg·kg^{-1}), and C_4 represents the Ba concentration in the upper part of the plant (mg·kg^{-1}).

For risk assessment, the estimated daily intake (EDI) and hazard index (HI) were used to quantify the exposure levels of Ba in the edible parts of different plants and to evaluate the potential health risks to local residents. In addition, the average daily dose (ADD) (mg·kg^{-1} BW·day^{-1}) was used to support the calculation of exposure through inhalation, dermal contact, and crop consumption. The average body weight for adults was taken as 60 kg (according to the Guizhou Statistical Yearbook, 2022), and that for children (aged 2-6 years) was taken as 17.4 kg (according to the U.S. Environmental Protection Agency (EPA) standard values). The daily intake amounts of cereals and vegetables were set at 0.44 kg·day^{-1} and 0.2 kg·day^{-1}, respectively. The oral reference dose (RfD) for Ba was 0.2 mg·kg^{-1} BW·day^{-1}. The formulas for ADD, EDI, and HI are as follows:

$$ADD_{ing}=\frac{CS\times IR_{ing}\times EF\times ED}{BW\times AT}\times 10^{-6} \tag{3}$$

$$ADD_{inh}=\frac{CS\times IR_{inh}\times EF\times ED}{PEF\times BW\times AT} \tag{4}$$

$$ADD_{dermal}=\frac{CS\times SA\times SL\times ABS\times EF\times ED}{BW\times AT}\times 10^{-6} \tag{5}$$

$$ADD_{ingc}=\frac{C\times IR_{food/water}\times EF\times ED}{BW\times AT} \tag{6}$$

Among them, ADD_{ing}, ADD_{inh}, ADD_{dermal}, and ADD_{ingc} represent the average daily doses (mg·kg^{-1} BW·day^{-1}) via soil ingestion, inhalation, dermal contact, and crop consumption, respectively. CS is the Ba concentration in soil (mg·kg^{-1}); C is the Ba concentration in rice, vegetables, pork, fish, or water (mg·kg^{-1} or mg·L^{-1}). IR_{ing} is the ingestion rate; IR_{inh} is the inhalation rate; EF is the exposure frequency; ED is the exposure duration; BW is body weight; AT is the averaging time for non-carcinogens; SA is the surface area of the skin; SL is the skin adherence factor; and ABS is the dermal absorption factor.

$$EDI= (C\times DI)/BW \tag{7}$$

$$HI=\frac{EDI}{RfD}=\sum HQ_i=\sum\frac{ADD_i}{RfD_i} \tag{8}$$

$$HQ=ADD/RfD \tag{9}$$

Where C is the Ba concentration in different plant species (mg·kg^{-1}); DI is the daily intake (kg·day^{-1}); BW is the average body weight (kg); EDI is the estimated daily intake of Ba (mg·kg^{-1} BW·day^{-1}); RfD is the oral reference dose for Ba (mg·kg^{-1} BW·day^{-1}); HI represents the hazard index; HQ_i represents the non-carcinogenic risk posed by a single contaminant. When HI/HQ > 1, it indicates that the element may pose a potential non-carcinogenic health risk to humans.

3. Results

3.1 Ba content in Plant Samples from Different Species

Significant differences in Ba concentrations were observed among different plant species. In this study, various typical crop samples were collected along the transportation route of the barite mining area at increasing distances from the mining site, including Brassicaceae (pakchoi, white radish, and red radish), Solanaceae (cherry tomato, hot pepper, and eggplant), Cucurbitaceae (pumpkin), Convolvulaceae (sweet potato), Fabaceae (green bean), and Poaceae (rice and maize). The results showed that the accumulation capacity of Ba in different edible parts varied considerably.

Among them, pakchoi, with leaves as the edible part, exhibited the highest Ba concentration (947.92-952.37 mg·kg^{-1}), indicating a pronounced enrichment characteristic. Root vegetables (white radish: 32.90-34.29 mg·kg^{-1}; red radish: 54.47 mg·kg^{-1}; sweet potato: 40.94 mg·kg^{-1}) showed moderate Ba levels. Solanaceae crops generally had low Ba concentrations, with cherry tomato at 9.07-11.67 mg·kg^{-1}, eggplant at 5.86-27.01 mg·kg^{-1}, and hot pepper at 3.97-5.58 mg·kg^{-1}. Poaceae crops, whose edible parts are seeds, had the lowest Ba concentrations: rice 3.16-7.14 mg·kg^{-1} and maize 1.50-3.71 mg·kg^{-1}.

3.2 Enrichment, Migration, and Health Risks of Ba Across Different Species

Based on the organ distribution characteristics of Ba concentrations in various plant species, it is suggested that Ba in plants may be jointly controlled by a continuous process of "rhizosphere uptake, internal translocation, and organ fractionation".

Table 1. Enrichment Coefficient and Transport Coefficient of Different Crops

Plants	Groups	Enrichment coefficients						Transport coefficient			
		Whole Plant	Root	Stem	Leaf	Tassel	Seed	Root→ Stem	Stem→ Leaf	Stem→ Seed	Stem → Tassel
Corn	S13	1.0050	0.0534	0.0065	0.0111	0.0102	0.0003	0.1214	3.1400	0.0456	6.7595
	S15	0.0800	0.0517	0.0020	0.0064	0.0138	0.0001	0.0396	1.7049	0.0942	3.1079
Paddy	S13	1.0000	0.8476	0.0085	0.0438	/	0.0005	0.0100	5.1495	0.0559	/
	S15	0.6330	0.4548	0.0320	0.0458	/	0.0004	0.0705	1.4286	0.0135	/
Pak choi	S13	0.0281	/	/	/	/	/	0.4400 (Whole Plant)	/	/	/
		0.0282	/	/	/	/	/	0.5063 (Whole Plant)	/	/	/

From the perspective of plant accumulation, rice and maize exhibited consistent distribution patterns (Table 1). In rice, the bioaccumulation factor of Ba was highest in roots (0.4548-0.8476), followed by leaves (0.0438-0.0458) and stems (0.032-0.085), and lowest in grains (0.0004-0.0005), showing a decreasing trend of "root>leaf>stem>grain". Maize showed a similar pattern (root>leaf≈tassel>stem>seed). Thus, Ba preferentially accumulates in roots after entering the plant, while its translocation to grains is significantly limited.

Table 2. Different Plant Enrichment Coefficients

Plants	Groups	Enrichment coefficients
		Edible parts
Pak choi	S13	0.0281
		0.0282
Red radish		0.0016
French bean		0.0014
		0.0013
Sweet potato		0.0012
White radish	S15	0.0010
		0.0011
Cherry tomato		0.0003
Eggplant		0.0002
Hot pepper		0.0002
Eggplant		0.0011
Cherry tomato		0.0018
Hot pepper		0.0006
Corn		0.0001

In comparison, the bioaccumulation factors of edible parts among different species also showed marked differences (Table 2). The Brassicaceae leafy vegetable pakchoi exhibited the highest bioaccumulation factor, ranging from 0.0281 to 0.0282. The root vegetables, white radish and red radish, had similar bioaccumulation factors of approximately 0.0010–0.0016. Sweet potato (Convolvulaceae) displayed comparable levels to the root vegetables. In contrast, the bioaccumulation factors of Solanaceae fruit crops, such as cherry tomato, pepper, and eggplant, were significantly lower, ranging from only 0.0002 to 0.0018, while those of grain crops like rice and maize were even lower. Overall, pakchoi, as a leafy vegetable, exhibited a much higher Ba accumulation capacity than fruit and grain crops.

Table 3. Risk Index of Edible Parts of Crops

Plants	Groups	EDI	HI	HQ
Pak choi	S13	3.968	15.872	4.508

		3.950	15.356	4.487
Red radish		0.182	0.908	0.258
French bean		0.157	0.783	0.222
		0.150	0.749	0.213
Sweet potato		0.136	0.682	0.194
White radish		0.114	0.572	0.162
		0.110	0.548	0.156
Cherry tomato		0.030	0.151	0.043
Eggplant		0.020	0.098	0.028
Hot pepper		0.019	0.093	0.026
Eggplant		0.0219	0.4502	0.1278
Cherry tomato	S15	0.0389	0.1945	0.0552
Hot pepper		0.0132	0.0662	0.0188
Corn		0.0002	0.0012	0.0003

There were significant differences in the exposure risk of Ba through the edible parts of different plants (Table 3). Pakchoi showed the highest estimated daily intake (EDI) of Ba, reaching 3.50-3.68 mg·kg^{-1} BW·day^{-1}, much higher than that of Solanaceae crops: cherry tomato (0.030-0.0389 mg·kg^{-1} BW·day^{-1}), eggplant (0.020-0.0219 mg·kg^{-1} BW·day^{-1}), and pepper (0.0132-0.019 mg·kg^{-1} BW·day^{-1}). Poaceae crops (maize and rice) had the lowest EDI values.

The hazard index (HI) for edible parts was highest for pakchoi (15.356-15.872) and lowest for Solanaceae and Poaceae crops. Notably, the HI/HQ of pak choi exceeded 1, indicating a non-carcinogenic risk from Ba. Therefore, among the common crops in the study area, pakchoi is the crop type with the highest dietary Ba exposure risk and represents the greatest potential health threat to humans (Table 3).

The translocation factor results further revealed the migration characteristics of Ba within plants. In rice, the translocation factor of leaves was the highest, ranging from 1.4286 to 5.1495, which was significantly higher than those from root to stem (0.0100-0.0705) and from stem to grain (0.0135-0.0559), indicating that Ba is more readily translocated to leaves than to grains. In maize, the translocation factors from stem to leaf (1.7049-3.1400) and from stem to ear (3.1079-6.7595) were also markedly higher than that to seeds. The average translocation factor of pakchoi was 0.4732, suggesting a strong ability to transfer Ba to its edible parts. In summary, although Poaceae crops exhibit pronounced root accumulation, the translocation to grains is restricted; whereas leafy vegetables are more efficient at translocating and accumulating Ba in their edible parts.

4. Discussion

4.1 Ba Health Risk in Crop

The concentrations, bioaccumulation factors, and hazard indices (HI) of Ba in all plants followed the order: pakchoi >radish >green bean >sweet potato >cherry tomato >eggplant > pepper > maize, which is consistent with the findings of Lu et al. [5] Moreover, pakchoi exhibited the highest estimated daily intake (EDI) and HI values, with HI significantly greater than 1, indicating a clear health risk. In contrast, the HI values of Solanaceous and Poaceae crops were all below 1, indicating relatively low risk. This result is consistent with the conclusion of Xu et al. [17] that under the same contamination background, leafy vegetables tend to contribute more to dietary Ba exposure than grain and fruit crops. This indicates that plant type is a key factor controlling the risk of dietary Ba exposure. Therefore, local residents can avoid excessive Ba intake by consuming Solanaceous fruits (e.g., cherry tomato, pepper, eggplant) and Poaceae grains (e.g., rice, maize). However, because soil Ba concentrations in the mining area show strong spatial variability and residents' food sources are somewhat scattered, further risk assessment and management of actual exposure for residents near the mining area should be conducted in combination with local conditions.

4.2 Differences in Barium Accumulation in Crops

The uptake and accumulation of barium in plants are jointly regulated by ion channel selectivity, xylem-phloem transport efficiency, and competition among soil cations. Due to the similar ionic radius of Ba^{2+} and Ca^{2+}, barium primarily enters plants non-selectively through root calcium channels. White (2001) reported that the conductivity sequence of calcium channels for divalent cations is $Ba^{2+} > Sr^{2+} > Ca^{2+}$, indicating that Ba^{2+} passes through readily. [23] However, Ca^{2+} and Ba^{2+} compete with each other; Wallace and Romney (1971) demonstrated that high Ca suppresses Ba uptake and promotes its upward translocation. [24] Consequently, crops with higher calcium demand, such as legumes, passively absorb more barium, which is consistent with the moderate Ba level observed in green bean in this study.

Translocation of Ba to above-ground parts depends on xylem loading (a temperature-sensitive, active process), whereas transport to grains is restricted by selective exclusion in the phloem. Marschner (2012) pointed out that grain nutrients are mainly supplied via the phloem, and Ba mobility in the phloem is extremely low. [25] This explains why Ba concentrations in Poaceae grains are much lower than in leaves – leaves are supplied by xylem, which allows relatively easier entry of Ba. Brassicaceae plants, such as pakchoi, possess efficient xylem transport and leaf vacuolar sequestration capacities (Clemens et al., 2013; Sharma et al., 2016), leading to high Ba accumulation in leaves.[26,27]

Furthermore, soil Ca and Mg compete with Ba for adsorption sites on root surfaces, and increasing Ca availability can reduce Ba bioavailability (Myrvang et al., 2016).[28-30] In summary, leafy vegetables accumulate high Ba due to efficient xylem transport and vacuolar storage, thus posing a health risk; whereas Poaceae grains contain very low Ba because of the phloem barrier, making their risk negligible. In high-barium contaminated areas, priority should be given to planting Poaceae or Solanaceae crops, while reducing leafy vegetable cultivation.

5. Conclusions

In summary, significant differences in barium accumulation were observed among crop species. Pakchoi (Brassicaceae) exhibited the highest Ba concentration (947.92-952.37 $mg \cdot kg^{-1}$) with a bioaccumulation factor of 0.028, while Poaceae grains (rice and maize) showed the lowest Ba levels (1.50-7.14 $mg \cdot kg^{-1}$). The distribution of Ba in Poaceae followed a decreasing trend of root>leaf>stem>grain, with extremely low translocation factors to grains (0.0135-0.0559), whereas pakchoi showed a translocation factor of 0.4732 to leaves, indicating efficient Ba transport. Health risk assessment revealed that the estimated daily intake (EDI) of Ba via pakchoi consumption (3.50-3.68 $mg \cdot kg^{-1} \cdot day^{-1}$) was 17.5-18.4 times the USEPA reference dose (0.2 $mg \cdot kg^{-1} \cdot day^{-1}$), and its hazard index (HI) exceeded 1, indicating a potential non-carcinogenic risk. In contrast, Solanaceae fruits and Poaceae grains had HI values below 1, posing negligible risk. Therefore, in high-barium contaminated areas, priority should be given to planting Solanaceae or Poaceae crops instead of leafy vegetables to reduce dietary Ba exposure risk for local residents.

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