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ORIGINAL ARTICLE

Barium transport and isotopic fractionation in plants

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Abstract Excess barium (Ba) in soil can result in Ba over-enrichment in crops, which may adversely affect human health. However, the transport and isotopic fractionation of Ba in plants remain poorly understood. We analyzed the Ba content and isotopic composition of three crops (rice, pak choi, and maize) grown in Ba-contaminated soil. Results for rice and maize demonstrated significant fractionation and environmental sensitivity in the transport of Ba, and longer flooding durations were found to increase Ba accumulation in rice grains during the filling stage. In contrast, research on pak choi revealed limited fractionation and strong uptake and transport of Ba. The estimated daily intake of Ba in the edible portion of pak choi (stems and leaves) was 15–24 times the recommended daily intake of 0.2 mg/kg body weight per day. Therefore, pak choi was the least suitable crop for Ba-contaminated areas. This study provides new insights into how Ba isotopic fractionation can trace Ba transport in crops, offering practical applications for food safety and environmental monitoring.

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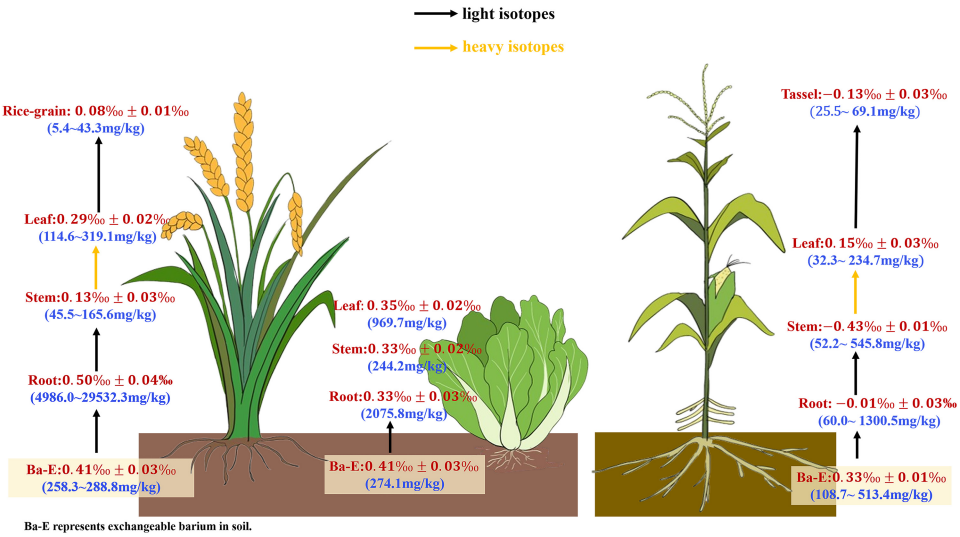
Graphical abstract



Keywords Barium pollution · Plant · Health risks · Barium isotopes · Fractionation

1 Introduction

Barium (Ba) is an alkaline earth metal element situated in group IIA of the sixth period, predominantly occurring in barite ($BaSO_4$) and witherite ($BaCO_3$) in its natural state. $BaSO_4$ is an important raw material in the chemical, metallurgical, pharmaceutical, oil exploitation, and building materials industries (Daungwilailuk et al. 2022; Morgano et al. 2010; Zielinski et al. 2001). $BaSO_4$ is released into water bodies and soils during $BaSO_4$ mining and Ba salt production processes (Gu et al. 2023). Because $BaSO_4$ is extremely stable in oxidizing environments, the environmental hazards of Ba do not pose a threat (Brusnitsyn et al. 2023). However, in reducing soil environments, in the presence of sulfate-reducing bacteria, barite can serve as a sulfate source for the respiration of anaerobic bacteria, which will lead to an increase in the bioavailable barium in the soil (Phillips et al. 2001). Ba in $BaSO_4$ is released in large quantities and taken up by plants, which creates environmental hazards (Chamberlain and Miller 1982). Excessive quantities of Ba are harmful to soil fauna and flora (Choudhary and Kumar 2024). A substantial increase in the Ba concentration in soil can result in earthworm mortality, and it can cause a significant reduction in the dry weight of lettuce (Lamb et al. 2013).

Excessive Ba intake can result in adverse health outcomes for humans. For example, the ingestion of soluble Ba salts is linked to the development of hypokalemic paralysis, which can potentially lead to respiratory and cardiac arrest (Krishna et al. 2020). Additionally, elevated Ba levels in pregnant women are associated with an increased risk of congenital heart disease in infants (Zhang et al. 2018).

Food intake represents a significant pathway for Ba absorption in individuals residing in areas with elevated Ba contamination (Kravchenko et al. 2014). A study of the Ba content in crops and soil around a Ba salt factory revealed concentrations of 1106.0 mg/kg and 2858.7 mg/kg in chili peppers and peanuts, respectively (Zhang et al. 2012), posing potential health risks to local residents. Furthermore, the Ba enrichment coefficients (the ratio of content of Ba in plants to that in the soil) of the two crops differed significantly, with 0.35 and 3.11 for chili peppers and peanuts, respectively (Zhang et al. 2012), which demonstrates the heterogeneous Ba uptake process in different plants. Studying the migration and enrichment mechanisms of Ba in plants can provide a scientific basis for prevention and control strategies to address environmental hazards.

Ba isotopes are potential indicators of Ba uptake and transport in plants. Ba has seven stable isotopes: ^{130}Ba (0.11%), ^{132}Ba (0.10%), ^{134}Ba (2.42%), ^{135}Ba (6.59%), ^{136}Ba (7.85%), ^{137}Ba (11.23%), and ^{138}Ba (71.70%) (Charbonnier et al. 2018). The application of Ba isotopes is not limited to tracing high-temperature geochemical processes (Horner et al. 2015; Wu et al. 2020; Zhao et al. 2021), but also extends to indicating Ba transport and transformation processes in ecosystems. Gong et al. (2019, 2020) demonstrated that Ba isotopes were fractionated during adsorption on clay minerals and when associated with Fe–Mn (oxy-hydr)oxides (Gong et al. 2020, 2019). Bullen and Chadwick (2016) observed that plants may prefer to take up lighter Ba isotopes from the soil. Furthermore, studies on cyanobacteria indicated that their vital activity may give rise to Ba

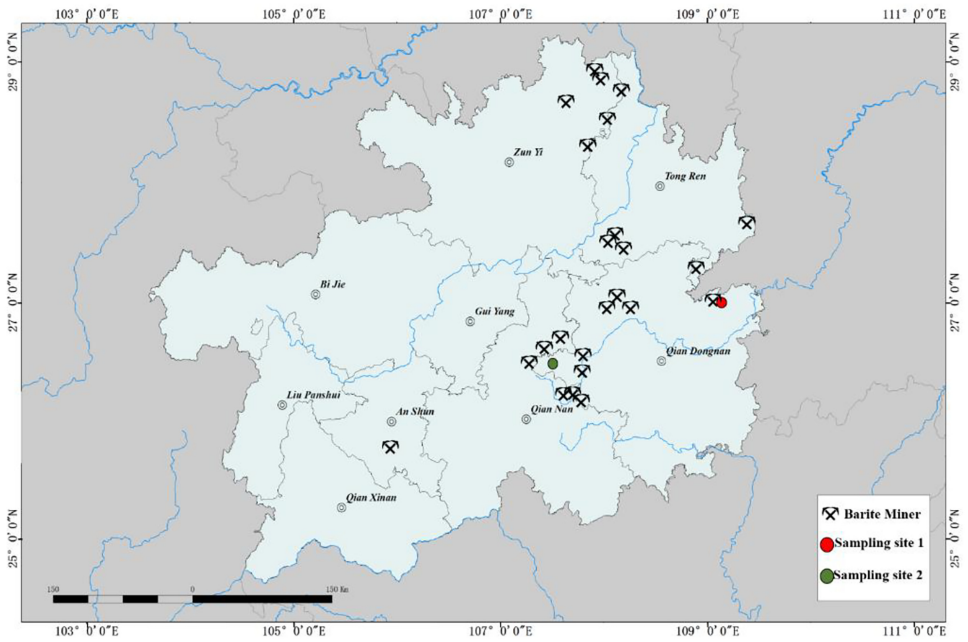


Fig. 1 Study area map, where the triangle area represents the size of the barite deposit

isotope fractionation (Bullen and Chadwick 2016; Mehta et al. 2023). However, Ba isotopic fractionation during plant uptake and transport remains poorly constrained, requiring further investigation.

Here, we used Ba-polluted soil (about 3.14 wt% of Ba) from the vicinity of a $BaSO_4$ mine to cultivate rice plants and pak choi. Maize grown in proximity to a $BaSO_4$ mine was collected. These crops were chosen due to their widespread cultivation in Ba-contaminated regions and differences in root morphology (the roots of rice and maize are usually thinner and form fibrous roots, while the roots of pak choi are straight; Petrova et al. 2023), which may influence Ba uptake. We then analyzed the Ba content and isotopic composition of the soil and crops to provide a scientific foundation for elucidating Ba transport and isotopic fractionation in plants.

2 Materials and methods

2.1 Field site and experiment setup

Guizhou, located in southwestern China, is endowed with a wealth of barite mineral resources, and barites are released into the soil during the intensive mining operations. Sampling site 1 is located near the Dahebian barite mine, which is the largest in the world. Rice is the principal staple crop among local residents, and following its harvest, they frequently cultivate pak choi.

Paddy soil was collected from the mining area (Fig. 1, Sampling site 1) for experiments conducted on rice and pak choi cultivation (to simulate the yearly crop growing habits of most local residents, rice was planted in May 2023 and pak choi was planted in October 2023).

Soil was dried, smashed, and sieved (0.5 cm) to remove gravel (Van De Voorde et al. 2012). The sieved contaminated soil was thoroughly mixed and divided into 12 equal portions. Each portion was placed in a plastic bucket (bottom diameter: 52 cm; top diameter: 64 cm; height: 46 cm) and filled to a soil depth of approximately 30 cm. The bottom of the bucket was complete and impermeable, preventing any water from leaking out.

After the tillering stage of rice, the experimental units were divided into four groups based on their cultivation methods to study the influence of the soil oxidation–reduction environment on Ba transport and isotopic fractionation in rice: the continuous flooding (SD-1), continuous drainage (SD-2), and two alternating flooding and drainage (SD-3 with drainage for 10 days and flooding for 10 days, SD-4 with drainage for 20 days and flooding for 20 days) cultivation groups. In flooded conditions, a water depth of approximately 10 cm was kept at the soil surface. Each group consisted of three experimental units. The pH and Eh values were directly measured. Once the crop reached maturity, the mature rice and soil were collected for analysis. To further investigate the Ba differences in rice under the four flooding conditions, we collected soil pore water from the end of tillering to maturity using a pre-buried Rhizon sampler. After the collection of rice, the pak choi was planted in these buckets. When the pak choi matured, the plants and soil were collected. Four groups were randomly selected (BC-1, BC-2, BC-3, and BC-4) for the analysis.

Maize samples were taken from the farmland near the barite mine site in September 2023, which is illustrated in

Fig. 1, Sampling site 2 (the highest value of Ba in the soil was recorded at 14,672.4 mg/kg, with an average value of 9280.5 mg/kg). In this maize field, the maize exhibited significant variability in its growth patterns. By harvest time (in September), some plants had reached normal maturity, with a height of approximately 320 cm, while others showed incomplete development, remaining at just 45 cm. Maize samples were collected during the harvesting period. Four distinct growth status categories of maize and their surrounding root soils were selected for analysis: MJ-S0 = plants with undeveloped cobs and kernels (plant height approximately 45 cm); MJ-S2 = severely stunted plants (plant height approximately 154.6 cm), MJ-Z = moderately stunted plants (plant height approximately 165 cm), MJ-3 and MJ-5 = normal, fully developed plants (plant height approximately 320 cm).

2.2 Sample digestion and chemical purification

Sample digestion, chemical purification, and measurements were conducted at the State Key Laboratory of Lithospheric and Environmental Coevolution, University of Science and Technology of China (USTC). The acids employed throughout the digestion and chemical purification process were HCI, HNO_3, and hydrofluoric acid (HF), which were purified by secondary sub-boiling distillation. Additionally, all the water utilized for sample preparation and reagent dilution was ultrapure water with resistivity of 18.2 MΩ·cm.

Sample digestion was conducted according to the methodology outlined by An et al. (2020). Soil and plant material were separated into distinct categories. Plant roots were rinsed repeatedly with ultrapure water in an ultrasonic cleaner, ensuring thorough removal of surface contaminants. All samples were dried in an oven. Subsequently, the samples were ground to a particle size of less than 200 mesh using a ball mill. Approximately 10 mg of soil sample powder or 20–50 mg of plant samples were weighed into Teflon® perfluoroalkoxy alkane (PFA) vials (Savillex®) and then a mixture of 3 mL of concentrated HF and 1 mL of HNO_3 was added for digestion. After evaporating to dryness, the samples were treated with aqua regia. In the case of plant samples, the addition of concentrated 0.1 mL HNO_3 and 1 mL H_2O_2 was required to completely decompose the organic matter. In addition, the exchangeable-Ba in soil was extracted by 1 M ammonium acetate (NH_4OAc) and maintained under continuous shaking for 24 h (Gong et al. 2020). All of the decomposed samples were measured for Ba content with a PerkinElmer ELAN DRC II inductively coupled plasma–mass spectrometer (ICP-MS). The relative standard deviations in the data were less than 10% (Hou et al. 2020).

Ba was purified from the matrix using cation-exchange columns with AG 50W-X12 resin (200–400 mesh, Bio-Rad, USA) (An et al. 2020; Nan et al. 2015, 2018). Ba was collected using 3 mol/L HNO_3 after the elution of the matrix elements with 3 mol/L HCl. The samples were purified twice, first using a column with 2 mL resin, followed by a second column with 0.5 mL resin. Purified samples were dried and diluted in 2% HNO_3 for instrumental measurements. The yield of the purification process was > 99%, while that of the column blank was < 5 ng.

2.3 Ba isotopic composition analyses

Ba isotopic composition was determined using a multi-collector inductively coupled plasma–mass spectrometer (MC-ICP-MS) (Thermo Fisher Scientific, Bremen, Germany). The Ba isotope ratios were determined using the double-spike method (^{135}Ba–^{136}Ba) (An et al. 2020; Nan et al. 2015, 2018). The Ba isotopic composition of the measurement results can be expressed as follows:

$$\delta^{138/134}\mathrm{Ba} = \left[\left(^{138}\mathrm{Ba}/^{134}\mathrm{Ba}\right)_{\mathrm{sample}}/\left(^{138}\mathrm{Ba}/^{134}\mathrm{Ba}\right)_{\mathrm{NIST3104a}} - 1\right] \times 1000\,(‰),$$

where NIST3104a represents the international standard for Ba isotope values and is a $Ba(NO_3)_2$ solution produced by the US National Institute of Standards and Technology (NIST) (Nan et al. 2015, 2018). The long-term external precision of the laboratory is better than 0.05‰ (2SD) (Deng et al. 2021). The Ba isotopic composition of the soil reference material (GBW07427) from the National Research Centre for Geoanalysis, China (http://igeo.cags.ac.cn) was independently tested three times (independent digestion of the sample powder, separate chemical purification, and measurement), and results were in good agreement with prior research reports (Table S1).

2.4 Indicators for the evaluation of Ba in crops

To evaluate the ability of the three crops to accumulate Ba from the soil and transfer it from the soil to the plant, the enrichment coefficients (EC) and the translocation coefficients (TC) of the plants and individual parts were calculated as follows (Dong et al. 2024):

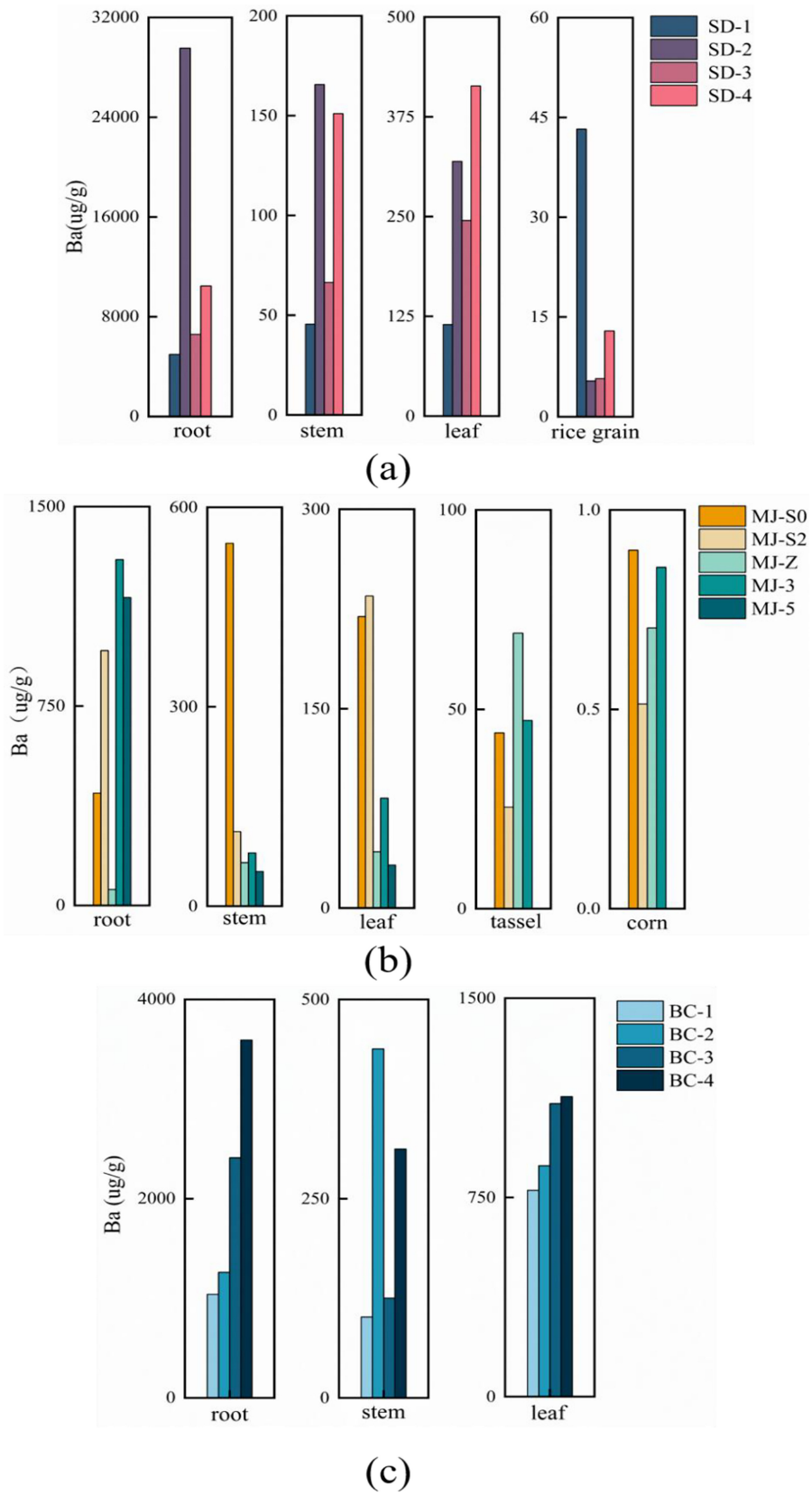


Fig. 2 **a** Ba concentration in various parts of rice; **b** Ba concentration in various parts of maize; **c** Ba concentration of various parts of pak choi

$$EC = C_{\text{plant}}/C_{\text{soil}}\,, \tag{1}$$

$$TC = C_i/C_j\,, \tag{2}$$

where C_{plant} represents the content of an element in plants (mg/kg), C_{soil} represents the content of that element in the soil (mg/kg), and C_i and C_j represent the content of Ba in different parts of plants (mg/kg), where Ba was transported from j to i.

Here, the estimated daily intake (EDI) and hazard index (HI) were employed to calculate the daily intake of Ba through the three crops and to assess the potential health risks for residents (Lu et al. 2019). Based on an average adult weight of 60 kg (Bureau of Guizhou Statistics 2022), the food and vegetable intake were set at 0.44 kg/day and 0.2 kg/day, respectively. The oral reference dose (RfD) value was established at 0.2 mg/kg BW/day (USEPA 2013). EDI and HI were calculated using the following formulas:

$$EDI = C \times \mathrm{DI}/\mathrm{BW}\,, \tag{3}$$

$$HI = \mathrm{EDI}/\mathrm{RfD}\,, \tag{4}$$

where C represents the content of Ba in the crop (mg/kg), DI denotes daily intake (kg/day), BW represents average body weight (kg), EDI is the estimated daily absorption of Ba (mg/kg BW/day), RfD is the reference measure for oral Ba (mg/kg BW/day), and HI stands for hazard index.

3 Results

3.1 Ba content in crops and risk evaluation

3.1.1 Ba content in crops

Obvious heterogeneity was observed in the Ba content of the different parts of the three crops (Table S2). The Ba content of each part in rice (Fig. 2a) was ranked as follows: roots (4986.0–29,532.3 mg/kg) > leaves (114.6–319.1 mg/kg) > stems (45.5–165.6 mg/kg) > rice grain (5.4–43.3 mg/kg); the rank of Ba content in parts of pak choi was roots (1040.4–3592.8 mg/kg) > leaves (777.0–1129.5 mg/kg) > stems (101.5–437.9 mg/kg); and the rank of Ba content

Table 2 EDI and HI of three plants

Edible parts of crops	Group	EDI	HI
Pak choi leaf + stem	BC-1	2.929	14.643
	BC-2	4.357	21.785
	BC-3	4.094	20.470
	BC-4	4.806	24.031
Maize seed	MJ-S0	–	–
	MJ-S2	0.006	0.030
	MJ-Z	0.003	0.017
	MJ-3	0.005	0.023
	MJ-5	0.006	0.029
Rice grain	SD-1	0.290	1.440
	SD-2	0.040	0.180
	SD-3	0.040	0.190
	SD-4	0.090	0.430

Dash (–) indicates the absence of part of the crop

Table 1 Ba enrichment coefficient and transport coefficient in different parts of three crops

		Enrichment coefficients						Transport coefficients			
Crop	Group	Whole plant	Root	Stem	Leaf	Tassel	Seed	Root → Stem	Stem → Leaf	Stem → Seed	Stem → Tassel
Rice	SD-1	0.2153	0.2100	0.0020	0.0050	–	0.0020	0.0100	2.5200	0.9500	–
	SD-2	1.6311	1.0600	0.0060	0.0110	–	0.0002	0.0100	1.9300	0.0300	–
	SD-3	0.3692	0.2700	0.0030	0.0100	–	0.0002	0.0100	3.7000	0.0900	–
	SD-4	0.5000	0.7700	0.0110	0.0300	–	0.0009	0.0100	2.7400	0.0900	–
Pak choi	BC-1	0.0400	0.0200	0.0020	0.0200	–	–	0.1000	7.6600	–	–
	BC-2	0.0650	0.0300	0.0100	0.0200	–	–	0.3500	1.9800	–	–
	BC-3	0.0880	0.0600	0.0030	0.0300	–	–	0.0500	8.8100	–	–
	BC-4	0.1580	0.1100	0.0100	0.0400	–	–	0.0900	3.6200	–	–
Maize	MJ-S0	0.2400	0.0850	0.1100	0.0440	–	–	1.2900	0.4000	–	–
	MJ-S2	0.0900	0.0650	0.0080	0.0160	0.0030	0.0010	0.1200	2.1000	0.0100	0.3500
	MJ-Z	0.0600	0.0180	0.0200	0.0130	0.0080	0.0090	1.0900	0.6500	0.0100	0.3900
	MJ-3	0.1000	0.0870	0.0050	0.0060	0.0050	0.0010	0.0600	1.0300	0.0100	0.8600
	MJ-5	0.1500	0.1370	0.0060	0.0040	0.0060	0.0010	0.0400	0.6200	0.0200	0.9000

Dash (–) indicates the absence of part of the crop

in various parts of maize (Fig. 2b) was roots (mean value 779.8 mg/kg) > stems (mean value 171.0 mg/kg) > leaves (122.2 mg/kg) > tassel (25.5–69.1 mg/kg) > maize seed (0.5–1.0 mg/kg). When comparing the Ba content in edible parts of the three crops, the Ba content in stems and leaves in pak choi (1213.9 mg/kg) was significantly higher than that in rice grains (16.8 mg/kg) and maize seeds (0.7 mg/kg).

Additionally, the Ba content in rice grains varied among experimental environments. The rank of Ba content in rice grain showed the following: continuous flooding group (SD-1, 43.3 mg/kg) > alternating wet and dry culture (drainage for 20 days and flooding for 20 days) (SD-4, 12.9 mg/kg) > alternating wet and dry culture (drainage for 10 days and flooding for 10 days) (SD-3, 5.7 mg/kg) > continuous drainage cultivation (SD-2, 5.4 mg/kg).

3.1.2 Crop enrichment and transport of Ba and corresponding health risk

The EC values for the three crops exhibited a similar pattern: in rice, the coefficients were the highest in roots (0.21–1.06), followed by those in leaves (0.005–0.03), then stems (0.002–0.01), and lowest in grains (0.0002–0.002). In pak choi, the order was roots > leaves > stems, and in maize, it was roots > stems ≈ leaves > tassel > seed. Comparing the Ba EC values of the edible parts of the three crops (Table 1), it can be seen that the mean value of the Ba EC in the stems and leaves of pak choi was 0.03, which was much higher than that of rice (0.0008) and maize seeds (0.003).

Relevant studies have demonstrated that when the TC value exceeds 1, the metal can be considered to possess a robust transport capacity in plants (Boechat et al. 2016). As shown in Table 1, the TC values of Ba in the rice leaves (mean value of 2.72) were higher than those in the edible portion of rice (mean value of 0.29) and stems (mean value of 0.01). In pak choi, leaves (mean value 5.52) had a higher TC than stems (mean value 0.15). In maize, leaves (mean value 1.10) had a higher TC than tassels (mean value 0.77), stems (mean value 0.33), and edible parts of the maize kernel (mean value 0.01). Therefore, the highest Ba transport coefficients in rice, maize, and pak choi were clearly observed during stem-to-leaf transfer. The highest value (7.66) was recorded for the stem-to-leaf transfer process in pak choi, indicating that this process demonstrated the strongest migration and enrichment of Ba.

Finally, in rice cultivation experiments, the TC from stem to leaf in the continuous drainage group (SD-2) (1.93) was found to be less than that in the continuous flooding (2.52) and the wet–dry alternating (2.47 and 3.70) groups. The TC of Ba from stem to rice grain under continuous flooding conditions (0.95) was markedly higher than that observed in other groups (0.03 in the long-term drainage group; 0.09 in both the alternating wet and dry drainage groups). Similarly, the EC of Ba in rice was significantly higher in the flooded group than that in the other groups.

The EDI of Ba in the stems and leaves of pak choi (2.93–4.81 mg/kg BW/day) was much higher than that of maize seeds (0.003–0.006 mg/kg BW/day) and rice grains (0.04–0.29 mg/kg BW/day), and the rank of the

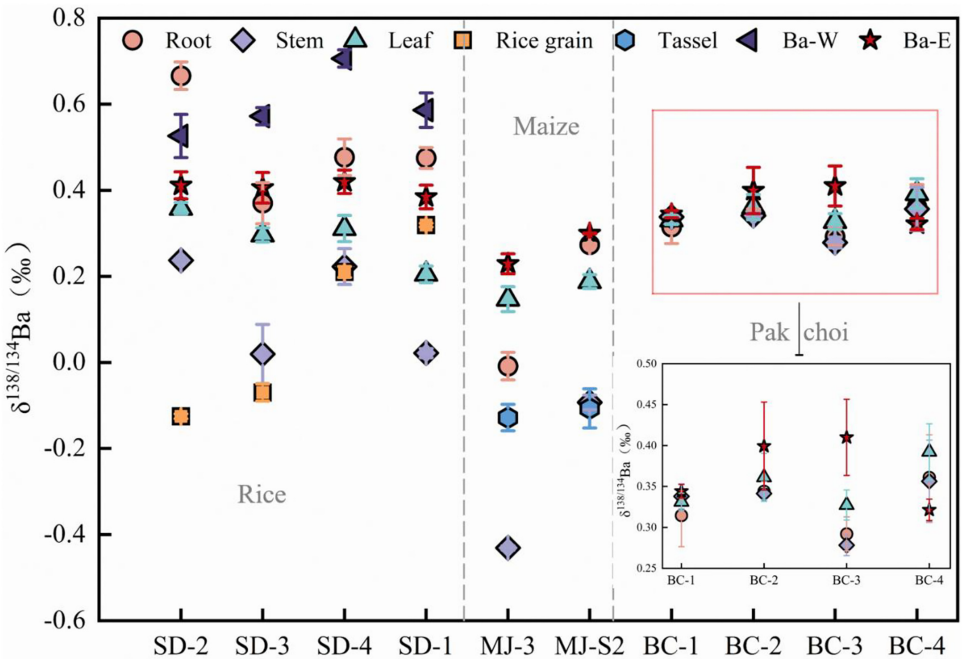


Fig. 3 The barium isotope composition diagram of three crops, where Ba-W represents the Ba isotope composition of soil pore water, and Ba-E represents the exchangeable barium isotope composition of soil

Table 3 Correlation of Ba, Ca, and Mg in different parts of three crops (Spearman's ρ)

Crop	Crop part	Ba-Ca	Ba-Mg
Rice	Root	0.200	1.000**
	Stem	−0.800	1.000**
	Leaf	0.400	0.800
	Rice grain	0.775	−0.400
Pak choi	Root	−1.000**	0.600
	Stem	−1.000**	−1.000**
	Leaf	0.400	0.800
Maize	Root	0.800	0.700
	Stem	0.300	0.300
	Leaf	−0.800	−0.400
	Tassel	0.800	0.400
	Maize seed	0.800	0.000

$N=4$. *Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed)

HI was pak choi (14.64–24.03) > maize (0.017–0.03) and rice (0.18–1.44). Among the three crops most commonly grown by the local residents, the edible part of pak choi demonstrated the highest EC for Ba and the greatest potential hazard to human health (Table 2).

3.2 Ba isotopic composition in the crops

The Ba isotopic composition of various parts of different crops also varied considerably (Table S3). In rice (as shown in Fig. 3), the mean value of Ba isotopic composition of the four groups of rice roots was $\delta^{138/134}Ba_{root} = 0.50‰ \pm 0.04‰$, which was heavier than that of leaves $\delta^{138/134}Ba_{leaf} = 0.29‰ \pm 0.02‰$, stems $\delta^{138/134}Ba_{stem} = 0.13‰ \pm 0.03‰$, and seed $\delta^{138/134}Ba_{rice\ grain} = -0.19‰ \pm 0.06‰$. Compared with that of the rice Ba isotopic composition $\delta^{138/134}Ba_{rice\ grain} = 0.32‰ \pm 0.0‰$ in the continuous flooding group (SD-1), the other groups had significantly lighter rice Ba isotope composition $\delta^{138/134}Ba_{rice\ grain} = -1.10‰ \pm 0.2‰$ to $0.21‰ \pm 0.01‰$. The Ba isotopic composition of the various parts of the maize plant varied considerably. The Ba isotopic composition of maize roots ($\delta^{138/134}Ba = 0.01‰ \pm 0.04‰$ to $0.27‰ \pm 0.0‰$) and leaves ($\delta^{138/134}Ba = 0.15‰ \pm 0.03‰$ to $0.19‰ \pm 0.02‰$) were both heavier than that of the stems ($\delta^{138/134}Ba = -0.43‰ \pm 0.01‰$ to $-0.09‰ \pm 0.02‰$). However, no significant Ba isotopic fractionation was observed in pak choi leaves ($\delta^{138/134}Ba = 0.33‰ \pm 0.02‰$ to $0.39‰ \pm 0.03‰$), roots ($\delta^{138/134}Ba = 0.29‰ \pm 0.01‰$ to $0.36‰ \pm 0.05‰$), or stems ($\delta^{138/134}Ba = 0.28‰ \pm 0.01‰$ to $0.36‰ \pm 0.05‰$) (Fig. 3).

4 Discussion

4.1 Ba health risk in crops

The concentration, EC, and HI of Ba in all crops were in the order of roots > stems > leaves > seeds, which is consistent with the results of Lu et al. (2019). Thus, the EDI and HI of the edible parts of pak choi were much higher than those of rice and maize seeds (paired-sample *t*-test results showed that the Ba content in the edible part of pak choi was significantly higher than that in the rice grain, $p = 0.002$). Additionally, the EDI of Ba in the edible portion of pak choi (stems and leaves) was 15–24 times the recommended daily intake of 0.2 mg/kg BW/day, as outlined by the US Environmental Protection Agency (USEPA 2013). The HI of Ba in pak choi was also considerably higher than 1. Consequently, the intake of Ba by local residents through the consumption of cereal crops, such as rice and maize, was relatively low. Therefore, pak choi was the least suitable crop for Ba-contaminated areas. We suggest that farmers in Ba-contaminated areas avoid planting crops with edible parts of roots, stems, and leaves, unless specific crops are proven to have low Ba EC values.

The significantly higher EC and TC in pak choi were in agreement with previous studies on other heavy metals, e.g., Cd and Pb, and they attributed the favored uptake of heavy metals to the high transpiration rates and rapid growth (Han et al. 2017). We suggest that future studies should explore soil amendments, microbial interactions, or plant breeding strategies to minimize Ba accumulation in edible plant parts.

4.2 Ba transport and isotopic fractionation in crops

Previous studies have suggested that Ba^{2+} may enter plants in a manner similar to that by the divalent cations of nutrients such as Ca^{2+} and Mg^{2+} (Kabata-Pendias and Pendias 2001; Sha et al. 2012). Our data showed that the correlation between Ba content and Ca and Mg in each part of the crops was more complex; for example, in stems, positive correlations between Ba and Mg and negative correlation between Ba and Ca were observed for rice and the negative

Table 4 Correlation between Ba content in maize parts and plant height and soil exchangeable-Ba

	Pant height (cm)	Soil exchangeable-Ba (μg/g)
Ba-Root (μg/g)	0.716	0.676
Ba-Stem (μg/g)	−0.777	−0.526
Ba-Leaf (μg/g)	−0.725	−0.546
Ba-Tassel (μg/g)	0.696	0.328
Ba-Maize seed (μg/g)	0.209	0.561

correlation among Ba, Mg, and Ca for pak choi; however, no correlation was observed for maize (Table 3). Therefore, the mechanisms underlying Ba absorption and transport in plants may be more complex than was previously understood. Further research should examine whether Ba competes with essential nutrients at the transporter level. A robust indicator is needed to reveal the transport processes of Ba in soil–plant systems.

4.2.1 Ba transport and isotopic fractionation in rice under various oxidation–reduction environment

Ba isotopes were used as fingerprints to show the behavior of Ba in biogeochemical systems. Except for the root of the continuous drainage group, Ba isotopes in all rice tissues were lighter than in pore water (Fig. 3). Given that long-term drought is highly stressful for rice, these results suggest that rice preferentially takes up light Ba isotopes under normal growth conditions (Bullen and Chadwick 2016), whereas Ba isotope fractionation becomes anomalous under unfavorable environmental stress.

A comparative analysis of the isotopic composition of the sites revealed that the roots had the heaviest Ba isotopes, indicating that lighter Ba isotopes were more readily transported. The Ba isotopes in the stems were lighter than those in leaves, suggesting that heavy Ba isotopes were more likely to enter the leaves.

The average Ba content of pore water in the long-term flooding group reached 204.32 μg/L, which was higher than that of the average Ba content in the other groups: 154.33, 152.87, and 133.42 μg/L in the continuous drainage group (SD-2), alternating wet and dry culture (drainage for 10 days and flooding for 10 days) (SD-3), and alternating wet and dry culture (drainage for 20 days and flooding for 20 days) (SD-4), respectively. The SD-1 Ba content in the rice roots, stems, and leaves was lower than that in the other groups (Fig. 2a). And in SD-4, the Ba content in the roots, stems, and leaves of rice was not as low as that in the pore water compared with that of the other groups. This might imply that the transport and fractionation of Ba in rice are affected by the growth environment, i.e., flooding conditions instead of the Ba content and the isotopic composition in pore water in this study may be because the content difference of Ba in pore water was not high enough to influence the uptake and transport of Ba by rice. It is important to determine whether flooding increases Ba availability due to root exudation or altered microbial activity.

It should be highlighted that for the highest Ba content (Fig. 2a) and $\delta^{138/134}$Ba (Fig. 3) in the rice grain of SD-1 and second-highest values in SD-4, which flooded from August 12th to September 1st, both values were much lighter and very close in SD-2 and SD-3. No consistent trend was observed in either Ba content (Fig. 2a) or $\delta^{138/134}$Ba in pore water (Fig. 3). Considering the filling stage of rice from about August 10th, it could be concluded that longer flooding durations during the filling stage resulted in an increase in Ba content and heavier isotopes in rice grains. $\delta^{138/134}$Ba values in rice grains of SD-2 and SD-3 were less than those in stems, leaves, and roots. The value was equal to that in stems for SD-4, and was greater than that in stems and leaves. The variation in $\delta^{138/134}$Ba in rice grains may imply that longer flooding conditions promote the transport of Ba from roots through stems.

4.2.2 Ba transport and isotope fractionation behavior in maize and pak choi

The study on maize showed that shorter plants were associated with lower exchangeable Ba content. This might imply that Ba pollution was not the principal cause to stunt maize. Correlations between maize height and Ba content in the root, stems, and leaves (Table 4) highlighted the relationship between the physiological process and the transport of Ba in maize.

The pattern of Ba isotope fractionation in maize was also consistent with that of rice; the stems of both crops had lighter Ba isotopic composition than that of roots and leaves. However, different correlations existed between Ba content and Ba isotopic composition in stems and leaves with rice, for example, for MJ-S2 with higher Ba content and lighter $\delta^{138/134}$Ba in stem and leaf. Given the growth abnormalities in maize, we infer that Ba translocation and isotopic fractionation might be disrupted.

In contrast to rice and maize, the Ba isotope data of pak choi showed that the differences in Ba isotopic composition among roots, stems, and leaves were essentially consistent with the long-term laboratory precision (0.05‰) (Fig. 3). Additionally, the transport coefficient of Ba from the stem to the leaf in pak choi (5.51) was much higher than that in other crops (2.56 and 0.96 for rice and maize, respectively). Therefore, the differences in Ba isotope fractionation among the roots, stems, and leaves of pak choi and other crops may be due to the higher Ba transport capacity of pak choi or its shorter stems. The specific mechanism requires further research.

In conclusion, although the transport mechanism of Ba in plants is still not fully understood, two Ba transport strategies are proposed: pak choi demonstrated strong uptake and transport capability with limited fractionation of Ba; in contrast, studies on maize and rice revealed significant fractionation and environmental sensitivity during transport of Ba. Therefore, Ba isotopes have considerable potential as indicators of Ba migration and enrichment mechanisms in plants.

5 Conclusions

The results of this study showed the following:

(1) The Ba content, TC, EC, EDI, and HI of the edible parts were significantly higher for pak choi than those for rice grains and maize seeds. Therefore, farmers in Ba-contaminated areas should grow cereal crops (e.g., rice, maize) and avoid planting barium-accumulating vegetables like pak choi.
(2) The flooding conditions are important for Ba transport and isotopic fractionation in rice. Longer flooding times increased Ba content in the rice grains during the filling stage.
(3) The mechanisms of Ba transport and isotopic fractionation in pak choi may differ from those in rice and maize.

These findings can inform strategies for reducing Ba accumulation in crops by adjusting flooding practices and selecting species with lower Ba translocation.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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