Dominant role of soil iron and organic matters in arsenic transfer from soil to plant in a mine area in Hunan Province, Central China

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Abstract

The transfer of arsenic (As) from soil to plant could be significantly influenced by soil parameters through regulating soil As bioavailability. To distinguish the bioavailable As provided by soil and the As uptaken by plants, herein two different soil bioavailable were defined, namely potential soil bioavailable As (evaluated through the bioavailable fraction of As) and actual soil bioavailable As (assessed through plant bioaccumulation factor, BF, and $BF_{available}$). To identify the dominant soil parameters for the two soil bioavailable As forms, soil and plant samples were collected from a former As mine site. The results showed that the potential bioavailable As only accounted for 1.77 to 11.43% in the sampled soils, while the BF and $BF_{available}$ in the sampled vegetables ranged from 0.00 to 1.01 and 0.01 to 17.87, respectively. Despite a similar proportion of As in the residual fraction, soil with higher pH and organic matter (OM) content and lower iron (Fe) content showed a higher potential soil bioavailable As. Correlation analysis indicated a relationship between the soil pH and potential soil bioavailable As ($r = 0.543$, $p < 0.01$) and between the soil Fe and actual soil bioavailable As ($r = -0.644$, $p < 0.05$, $r = -0.594$, $p < 0.05$). Stepwise multiple linear regression (SMLR) analysis was employed to identify the dominant soil parameters and showed that soil pH and phosphorus (P) content could be used to predict the potential soil bioavailable As ($R^2 = 0.69$, $p < 0.001$). On the other hand, soil Fe and OM could be used to predict the actual soil bioavailable As ($R^2 = 0.18$–0.86, $p < 0.001$–0.015, in different vegetables). These results suggest that different soil parameters affect potential and actual soil bioavailable As. Hence, soil Fe and OM are the most important parameters controlling As transfer from soil to plant in the investigated area.

Keywords Arsenic · Bioavailability · Soil parameter · Stepwise multiple linear regression

Introduction

Arsenic (As), a ubiquitous element in the Earth's crust, is carcinogenic and noxious to humans. The release of As into the environment by natural processes and anthropogenic activities would cause As pollution (Sun et al. 2014; Zhao et al. 2010). Notably, soil As contamination would lead to As entering into the food chain through daily diet, which poses a health risk to people (Tripathi et al. 2007). Therefore, limiting the transfer of As from soil to plant edible parts is essential to ensure food safety, especially in As-contaminated areas.

Previous studies have documented that the amount of As accumulated in plants from soil is more dependent on As bioavailability in soil rather than soil total As content (tAs) (Chen et al. 2020; Khan et al. 2010). A lot of research has been carried out to investigate the bioavailability of As by using sequential extraction procedure (SEP) (Shiowatana et al. 2001; Wan et al. 2017) and studying As accumulation in various plants (Bergqvist et al. 2014; Huang et al. 2006). Generally, As bioavailability in soil is affected by several soil parameters, such as pH, organic matter (OM), cation exchange capacity (CEC), iron (Fe), and phosphorus (P) content (Khan et al. 2021; Liu et al. 2015; Suriyagoda et al. 2018). Caporale et al. (2018) fertilized carrot plants (*Daucus carota* L.) with humic acid (HA, a kind of OM)

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in pot experiments and found that the application of HA could reduce the soil As bioavailability and minimize the As concentration in carrots by increasing the sorption sites for As. Yu et al. (2017) found that the application of Fe oxides could reduce rice grain As concentration by lowering the soil As bioavailability in pot experiments. These findings suggest that some parameters affect more than others the fraction of As in soil that can be practically utilized by plants. Notably, it had been recognized that not all the soil bioavailable As could be transferred into plants, and in fact, only part of the bioavailable As could be absorbed by plants (Niazi et al. 2011). However, no information clarified the relation between the As uptaken by plants and the soil bioavailable As. In order to distinguish between them, two different soil bioavailable As should be defined, one is the bioavailable As that soil could provide, which can be determined by SEP (Huang et al. 2006; Luo et al. 2008; Wan et al. 2017); another one is the bioavailable As that actually transfers from soils to plants, which can be assessed by plant bioaccumulation factor (BF), since BF has been employed to evaluate the transfer of As from soil to plant in several researches (Dai et al. 2019; Du et al. 2020; Yang et al. 2019; Zhang et al. 2020). Here, two questions arise: one is which soil parameters are dominant in significantly affecting these two soil bioavailable As forms; another is how to identify these dominant soil parameters. Since in recent studies various empirical models based on soil parameters have been successfully established to predict As concentration in plants using stepwise multiple linear regression (SMLR) analysis (Chen et al. 2020; Dai et al. 2016, 2019; Ding et al. 2015; Yang et al. 2019; Yao et al. 2021; Zhang et al. 2020), we reasonably supposed that these dominant soil parameters could be identified through SMLR analysis.

In this study, soil and plant samples were collected from a former As mining area. The bioavailable As in soil was defined as the potential soil bioavailable As and determined by SEP, and the As in plant was defined as the actual soil bioavailable As and quantified by determining the total As in plant biomass after sample digestion. The relationships between the two soil bioavailable As forms (potential and actual) and soil parameters (e.g. pH, OM, CEC, Fe, and P content) were discussed and SMLR equations were established aiming at identifying the dominant soil parameters. The findings of this study are useful to develop practices to regulate As accumulation in plants in arsenic-contaminated areas.

Materials and methods

Study area and sample collection

The study area is located in Shimen, Hunan Province, China. Shimen had a realgar mine with a history of more than 1500 years, and this mine was the largest realgar mine in Asia until it was closed in 2011 due to severe As contamination to the local environment (Yang et al. 2018). In this study, twenty-two sampling sites were established along the road at equal intervals in a village living region within 50.64 km² according to local topography features and population density (Fig. 1). Among these sites, S1 to S17 sites were around the mining area and tailings dam, and S18 to S22 sites were located in the downwind area of the mining area. S2, S5, S6, S8, and S14 sites were barren grassland; other sites were residential backyards or farmland. In order to collect as many vegetable samples as possible, we collected
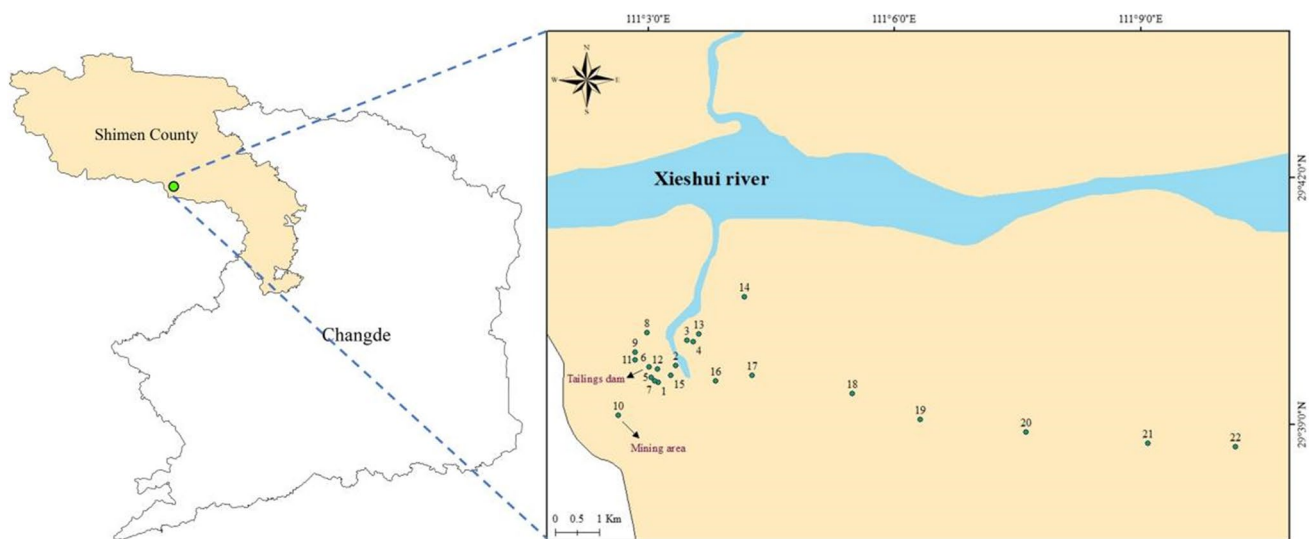

Fig. 1 Location of sampling sites and study area

vegetable samples based on the species of plants cultivated in residential backyards or farmland. The map used to describe the location of sampling sites and study area in Fig. 1 was downloaded from the National Catalogue Service for Geographic Information in China (www.webmap.cn).

Soil and plant samples (*Pteris vittata* L., *Brassica pekinensis* (Lour.) Rupr., *Capsicum annuum* L., *Lablab purpureus* (L.) Sweet, *Ipomoea aquatica*, *Ipomoea batatas* (L.) Lam., *Allium fistulosum* L., *Allium tuberosum* Rottler ex Spreng., *Daucus carota* L.var. *sativa* Hoffm., *Vigna unguiculata* (L.) Walp., *Fortunella margarita* (Lour.) Swingle) were collected in September 2018. For the soil samples, a composite soil sample consisting of three subsamples with a depth of 0–20 cm (topsoil layer) was taken by a spade. After air-drying at room temperature, the soil samples were separated from plant debris and stone by a 2-mm nylon sieve, then ground and sieved through a 0.149-mm nylon sieve. For the plant samples, only aboveground parts were taken, except for *Daucus carota Linn. var. sativa* of site S20 and *Brassica pekinensis*, which were seedlings, and the whole plants were taken. The plant samples were washed thoroughly with tap water and ultrapure water three times, respectively. Then, these samples were freeze-dried and ground into powders before digestion.

Soil parameters analysis

The pH was measured according to the Ministry of Agriculture of the People`s Republic of China method NY/T 1377–2007, which is applicable for various types of soil (Ministry of Agriculture of the People`s Republic of China 2007). The organic matter (OM) content was determined using the loss on ignition method (Heiri et al. 2001; Martínez et al. 2018). This method has the advantage of simple operation and is suitable for rapid determination of a large number of samples. However, the potential loss of bound water caused by this method might result in higher detection results. The cation exchange capacity (CEC) was determined by the hexamine cobalt trichloride solution–spectrophotometric method (Ministry of Ecology and Environment of the People`s Republic of China 2017). This method is applicable to various types of soil. When using this method, if sample solutions contain high OM, detection results would be interfered with, and this interference can be corrected by simultaneously measuring the absorbance at 475 nm and 380 nm. To measure soil Fe and P content, the collected samples were digested by the Ministry of Ecology and Environment of the People`s Republic of China method HJ 781–2016 (Ministry of Ecology and Environment of the People's Republic of China 2016) with minor modifications. Briefly, approximately 0.2 g of each soil sample was weighed into a Teflon beaker and 5 mL HCl was added. Then, these Teflon beakers were heated at 140 °C for 15 min on a hot plate. After

digestion, the liquid was cooled to 50 °C and 5 mL HNO_3, 5 mL HF, and 3 mL $HClO_4$ were added, and the mixture was heated at 140 °C for 1 h with a cap cover and another 2 h with the cap open. Afterwards, another 3 mL HNO_3, 3 mL HF, and 1 mL $HClO_4$ were added and the liquid was heated at 140 °C for 1 h with a cap cover, then the liquid was kept heating at 140 °C with the cap open. When the liquid was almost completely evaporated, 2 mL HNO_3 was added to dissolve the residues. After cooling to room temperature, the digested liquid was diluted with ultrapure water to 100 mL and filtered with a 0.45-µm cellulose acetate membrane filter. Finally, soil Fe and P content were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 8000, PerkinElmer, America).

Total arsenic analysis in soils and plants

Total As (tAs) content in soil samples was determined according to Zhang et al. (2018b). Approximately 0.2 g of each soil sample was digested with 12 mL aqua regia (HCl + HNO_3, 3:1, v/v) at 100 °C for 120 min. After cooling to room temperature, the digested solution was carefully transferred in a volumetric flask and brought to a volume of 100 mL with ultrapure water followed by filtration with a 0.45-µm cellulose acetate membrane filter. Then, the As contents in soil samples were measured using ICP-OES.

For plant samples, tAs content was determined as reported by Ma et al. (2017). Briefly, approximately 0.1 g plant powders were digested with the addition of 8 mL HNO_3 and 2 mL H_2O_2 in a microwave digestion system (MDS-6G, Sineo Microwave Chemistry Technology Co., Ltd., Shanghai, China). The digestion program was as follows: 10 min to 120 °C, 10 min to 190 °C, and 30 min at 190 °C. After cooling to room temperature, the digested solution was diluted to 25 mL with ultrapure water and then filtered with 0.45-µm cellulose acetate membrane filters before analysis. The tAs was determined by inductively coupled plasma mass spectrometry (ICP-MS, 7700×, Agilent Technologies Inc., America). The polyatomic interference on m/z 75 from argon chloride (i.e., $40Ar35Cl^+$) was minimized by a collision/reaction cell in the helium mode.

Arsenic fractionation in soils

A five-step extraction method was applied to extract arsenic (As) from soils based on the Shiowatana method (Shiowatana et al. 2001) with a minor modification. This method is applicable to most soils, especially for studies on the phytoavailability of As in soils. However, Fe- and Al-associated As might not be fully extracted by this method. The sequential extraction procedures were as follows. (Step 1)

Approximately 1 g soil sample and 30 mL ultrapure water were added into a 50-mL plastic centrifugal tube. After shaking for 16 h at 25 °C, the samples were centrifuged at 3000 rpm for 15 min to obtain the supernatant, which was filtered with 0.45-µm cellulose acetate membrane filters to determine the water-soluble–extractable As (water-soluble As). (Step 2) The remaining residue from step 1 was washed with 30 mL ultrapure water and centrifuged at 3000 rpm for 15 min, then the washing solution was discarded. The residue was resuspended with 30 mL of 0.5 M NaHCO$_3$ and shaken for 16 h at 25 °C then centrifuged as in step 1. The supernatant was collected and filtered with 0.45-µm cellulose acetate membrane filters. This fraction represents the sodium bicarbonate–extractable As (surface-adsorbed As). (Step 3) The remaining residue from step 2 was washed as in step 2. Afterward, the residue was resuspended with 30 mL of 0.1 M NaOH and shaken for 16 h at 25 °C, then centrifuged as in step 1. The supernatant was acidified with HNO$_3$ and filtered with 0.45-µm cellulose acetate membrane filters. This fraction represents the sodium hydroxide–extractable As (Fe- and Al-associated As). (Step 4) The remaining residue from step 3 was washed as in step 2. Afterwards, the residue was resuspended with 30 mL of 1 M HCl and shaken for 16 h at 25 °C, then centrifuged as in step 1. The supernatant was collected and filtered with 0.45-µm cellulose acetate membrane filters. This fraction represents the hydrochloric acid–extractable As (carbonate-bound As). (Step 5) The remaining residue from step 4 was oven-dried at 60 °C for 48 h and ground. Then, the residual As content was determined as described in section "Total arsenic analysis in soils and plants".

Quality control in element analysis

The calibration of the instruments was conducted on a daily basis by using standards. A method blank was included in each analytical batch. Strict quality assurance and control of element analysis were conducted by using the certified reference materials GBW07410, GBW07311, and GBW10048 (purchased from the Chinese CRM/RM information center, Beijing, China). The recoveries for these reference materials were 92–121% for As, and 94–96% for Fe, except the recovery of GBW07311 for P which was 59–68%. The accuracy, precision, and repeatability of metal contents were 106%, 13%, and 10% for As, 95%, 0.4%, and 0.6% for Fe, and 64%, 6.9%, and 5.2% for P, respectively. The accuracy of the SEP was verified by a comparison of the difference between the sum of the As content in the individual phase and the soil tAs content. The recovery and accuracy of SEP were 81–102% and 90%, respectively, showing a satisfactory quality control.

Statistical analysis

The potential soil bioavailable As was represented by the bioavailable fraction of As, calculated as Eq. 1.

$$\text{The bioavailable fraction of As} = \frac{\text{The sum of first two fractions of Shiowatana SEP}}{\text{Soil tAs}} \quad (1)$$

The actual soil bioavailable As was represented by the BF and BF$_{available}$, calculated as Eq. 2 and Eq. 3, respectively. They are both capable of evaluating the ability of plants to accumulate As from soils.

$$BF = \frac{\text{As concentration in plant tissues}}{\text{Soil tAs}} \quad (2)$$

$$BF_{available} = \frac{\text{As concentration in plant tissues}}{\text{The sum of first two fractions of Shiowatana SEP}} \quad (3)$$

To identify the dominant soil parameters in an area, all BF and BF$_{available}$ values of sampling plants were used to establish SMLR equations. The normality of data was tested by the Shapiro–Wilk test with a significance level at $p < 0.05$. However, pH, the sum of first two fractions, bioavailable fraction of As, BF, and BF$_{available}$ did not conform to the normal distribution. Therefore, Spearman's correlation analysis was employed to determine the relationships between soil parameters and potential and actual bioavailable As, with significance levels at $p < 0.05$ and $p < 0.01$. The empirical models to predict the two types of soil bioavailable As based on soil parameters were constructed through SMLR analysis. Five assumptions were preliminary checked: normality, linearity, independence, homogeneity of variance, and multicollinearity. For normality, the residuals conform to normal distribution. For linearity, there should be a linear relationship between the dependent variable and the independent variable, which was checked by a scatter diagram. For independence, there should be no autocorrelation between residuals, which was checked by the Durbin-Watson test. For homogeneity of variance, the variance of the residuals is homogeneous, which was checked by a scatter diagram. For multicollinearity, there should be no multicollinearity between the independent variables, which was checked by the value of the variation inflation factor. The stepping criteria employed for entry was based on a significance level of 0.05 and for removal was based on a significance level of 0.10. The quality of the models was evaluated on the basis of the coefficient of determination (R^2). All data were log- or log(V + 1)- transformed (V is variable and V + 1 was to avoid the negative number when log-transformed). Statistical analyses were performed by SPSS 26 for windows. The graphical work was completed using Origin 2019 software.

Results

Soil parameters

Selected soil parameters are shown in Fig. S1. The soil pH varied from 4.71 to 8.04. Seventeen sites have a pH ranging from 6.00 to 8.00 and only four sites have a pH below 6.00, indicating that almost all the soils are neutral. The content of OM varied from 37.63 to 64.75 $g \cdot kg^{-1}$, and the value of CEC ranged from 20.34 to 121.01 $mmol \cdot kg^{-1}$. In addition, the soil Fe and P content varied from 23.25 to 49.96 $g \cdot kg^{-1}$ and 303.89 to 1267.77 $mg \cdot kg^{-1}$, respectively.

As content and As fractionation in soil

The tAs content in soils ranged from 10.16 to 459.60 $mg \cdot kg^{-1}$ (Fig. S1). There was a large variation in soil tAs content among sampling sites, especially in sites around the mining area and tailings dam. In sampling sites around this area, soil tAs content was in the range of 10.16 to 448.60 $mg \cdot kg^{-1}$ with an average of 105.14 $mg \cdot kg^{-1}$. In the sampling sites from the downwind area of the mining area, soil tAs content varied from 51.76 to 459.60 $mg \cdot kg^{-1}$, with an average of 229.17 $mg \cdot kg^{-1}$.

Figure S2 shows the results of As sequential extractions. The water-soluble As was extracted in the first step and accounted for a small portion of the total extracted As, ranging from 0 to 2.88%. The second fraction represented surface-adsorbed As in soils and represented a relatively small fraction of the total extracted As, ranging from 1.99 to 10.38%. In the third step, Fe- and Al-associated As was extracted from soil and constituted a relatively large part of the total extracted As, ranging from 17.76 to 54.31%. The

fourth fraction was the carbonate-bound As, and the proportion of this fraction varied greatly, from 0.23 to 28.99%. The residual As was determined in the fifth fraction and represented the largest fraction of the total extracted As for most soil samples, ranging from 33.35 to 75.19%. As recovery for the five-step extraction procedure (the ratio of the sum of all fractions to the soil tAs content) was in the range of 81.47 to 102.43%.

According to Wan et al. (2017), the first two fractions of Shiowatana SEP represent the bioavailable As in soils; thus, the bioavailable fraction of As (the ratio of the sum of first two fractions to soil tAs) was used to represent the potential soil bioavailable As in this study. As shown in Fig. S2, the bioavailable fraction of As in sampled soils ranged from 1.77 to 11.43%. Soils with higher tAs content tended to show also a higher value in the sum of first two fractions (Fig. 2a), even if the distribution of the percentage of As bioavailable fraction showed no correlation with soil tAs content (Fig. 2b). Basically, the bioavailable fraction of As showed an increasing trend with increasing soil pH value (Fig. 3). Similarly, the bioavailable fraction of As essentially increased with the increase of soil OM content in most sites (Fig. 3). There was no obvious trend observed in the relationship between the bioavailable fraction of As and soil CEC value or soil P content (Fig. 3). The bioavailable fraction of As showed a reducing trend with increasing soil Fe content, following two different patterns (Fig. 3).

As concentration in plants

The plant tAs content varied greatly within the sampling sites and plant species (Fig. S3). In general, *Pteris vittata* showed the highest As concentration among the collected plant samples. *Daucus carota Linn. var. sativa* was collected
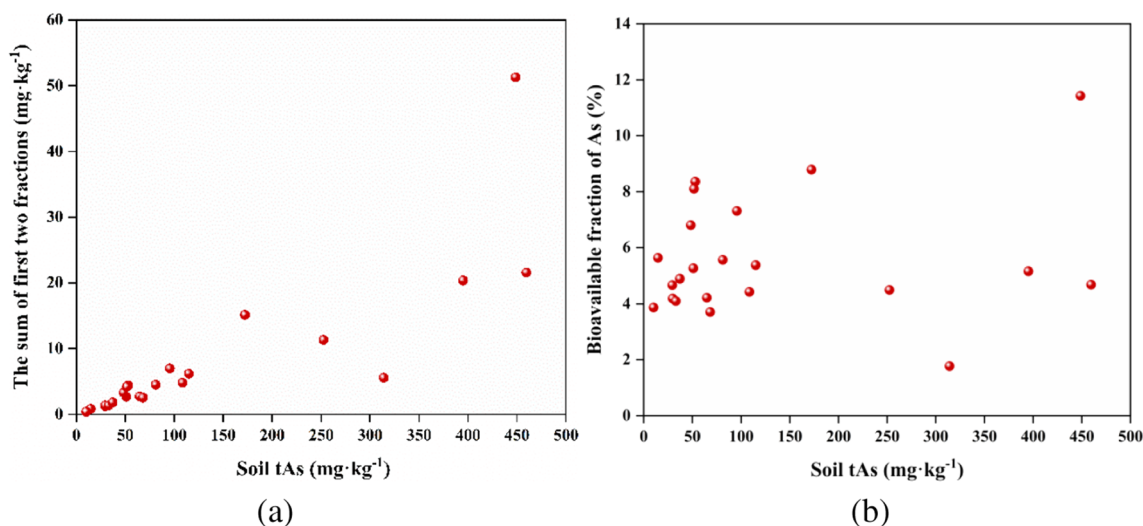

Fig. 2 Relationships between the sum of first two fractions (**a**); bioavailable fraction of As (**b**) and soil tAs
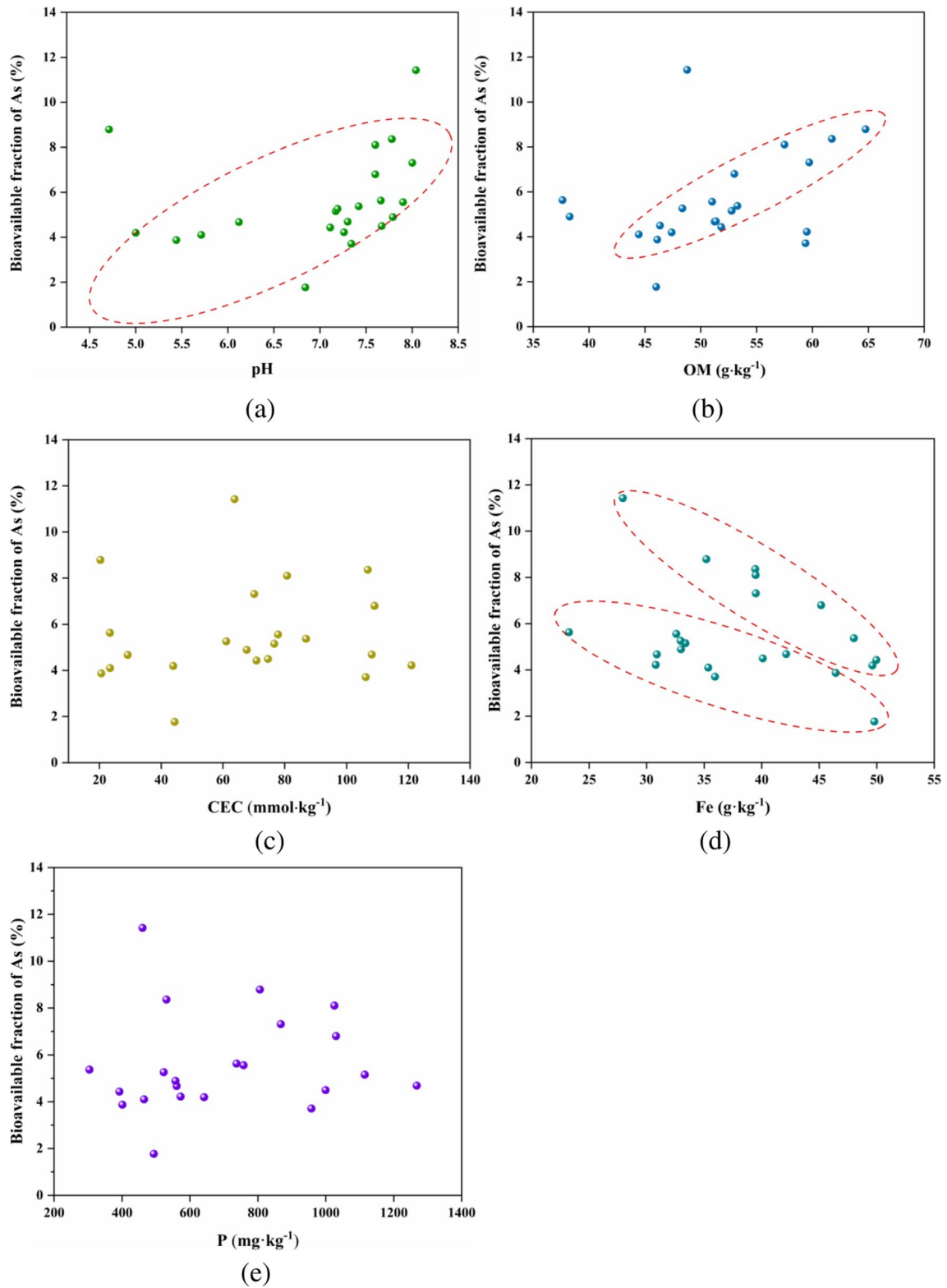
Fig. 3 Relationships between the potential soil bioavailable As and pH (**a**), OM (**b**), CEC (**c**), soil Fe content (**d**), and soil P content (**e**)

at the S20 site, where the soil tAs content was the highest among the sampling sites, and the tAs concentration of the plant was also the highest among the sampled vegetables. *Fortunella margarita* (Lour.) fruit was collected at the S22 site, where the soil tAs content was 51.76 mg·kg^{-1}; however, no As was detected in the fruit. Despite they were all collected at the S3 site, *Ipomoea aquatica* showed a higher tAs concentration than *Capsicum annuum* and *Lablab purpureus* (Linn.). As shown in Fig. S4, the BF values of *Pteris vittata* and *Ipomoea aquatica* stem were both greater than 1. Especially, the *Pteris vittata* leaf of sites S2 and S6 showed BF values of 5.23 and 5.27, respectively. For other plant samples, the BF value ranged in the range 0.00–1.01. Among vegetables, the leaf (and stem) samples presented a higher BF value (0.00 to 1.01) than the fruit samples (0.00 to 0.02). BF$_{available}$ of plants varied from 0.01 to 17.87 and presented a similar pattern with BF value.

Discussion

Effect of soil parameters on potential soil bioavailable As

In collected soils, the fraction of bioavailable As was generally low, and the predominant As fractions were Fe- and Al-associated As and residual As (Fig. S2). Since soil tAs content was positively correlated with the sum of first two fractions ($r = 0.953$, $p < 0.01$, Table 1) rather than with the bioavailable fraction of As, soil tAs content might not be the decisive factor affecting potential soil bioavailable As. In fact, the potential bioavailability of As in soil is mainly determined by soil physical and chemical parameters (Farooq et al. 2016; Masscheleyn et al. 1991). As shown in Fig. 3, potential soil bioavailable As showed different correlation patterns with pH, OM, and Fe content, which implied these soil parameters might have effects on potential soil bioavailable As. Shen et al. (2020) reported an exponential

increase in potential soil bioavailable As with increasing soil pH from 6.89 to 7.81. Likewise, Chen et al. (2020) found that potential bioavailable As was higher in alkaline soil than in acidic soil. In this study, the bioavailable fraction of As also basically increased with the rise of soil pH value. A significant positive correlation between the bioavailable fraction of As and pH ($r = 0.543$, $p < 0.01$, Table 1) was observed. Soil pH can influence potential As availability by affecting the adsorption and desorption of As on soil particles (Masscheleyn et al. 1991). In an adsorption experiment, Fan et al. (2020) found that the adsorption equilibrium amount for a black soil for As(V) significantly decreased with the increase of pH from 3.00 to 10.00. The reason behind this is the accumulation of OH$^-$ in soil as a result of pH increase. Since As is predominantly present in soils as oxyanions, it tends to be adsorbed by soil particles with positive charge in acid soil (Jiang et al. 2014; Wan et al. 2017). However, the rising amount of OH$^-$ can enhance the generation of hydroxylic functional groups on the soil particle surface to promote the increase of electrostatic repulsion of As, and compete with As for the adsorption sites, thus reducing the adsorption of As on soil particles (Goh and Lim 2004; Jiang et al. 2014). The relationship between the potential bioavailable As and soil pH in the present work basically matched well with this pattern, whereas some sites behaved differently, indicating that other parameters are likely to affect the potential soil bioavailable As besides pH.

Soil OM also plays an important role in potential soil bioavailable As and its effect on potential soil bioavailable As is more complex than pH. Williams et al. (2011) concluded that OM has dual effects on potential soil As bioavailability. On the one hand, As could be bound to OM through cation bridges or directly binding with functional groups of OM forming insoluble complexes, thus reducing As mobility in soils (Buschmann et al. 2006; Caporale et al. 2018; Wang and Mulligan 2006). On the other hand, OM could compete with As for adsorption sites and combine with As to form water-soluble complexes, thus decreasing the absorption

Table 1 Correlations between the sum of first two fractions, bioavailable fraction of As, soil tAs content, and soil properties (*$p < 0.05$, **$p < 0.01$, bold and italic correlation coefficient)

	The sum of first two fractions	Bioavailable fraction of As (%)	Soil tAs	pH	OM	CEC	Soil Fe	Soil P
The sum of first two fractions	1.000							
Bioavailable fraction of As (%)	0.422	1.000						
Soil tAs	*0.953***	0.181	1.000					
pH	0.300	*0.543***	0.213	1.000				
OM	0.420	0.414	0.333	0.079	1.000			
CEC	0.336	0.115	0.355	*0.456**	*0.528**	1.000		
Soil Fe	0.104	−0.356	0.152	−0.306	0.062	0.115	1.000	
Soil P	0.255	0.203	0.205	0.177	0.300	0.379	−0.100	1.000

of As on soil particles (Wang and Mulligan 2006). In this study, the increase of potential soil bioavailable As with the increase of soil OM content in most sampling sites suggested that OM was a vital parameter controlling the release of As on soil particles in the local area. However, no significant correlation was found between the potential soil bioavailable As and OM (Table 1). Wang and Mulligan (2009) found that the introduction of HA (chosen as a model soil OM) at a low dosage decreased the potential soil bioavailable As under acidic conditions while increased As mobility under alkaline conditions. The inhibition of As mobilization by adding HA under acidic conditions could be attributed to the formation of insoluble complexes and/or the increase of adsorption sites. However, under alkaline conditions, HA and As tend to form water-soluble complexes in the presence of metal cations, and the adsorption sites would be reduced. In addition, the adsorption of OM on soil particles increases the repulsion between soil particles or OM surfaces and As anions (Wang and Mulligan 2009). Thus, the effect of soil OM on potential soil bioavailable As may depend also on soil pH.

Since Fe oxides/hydroxides have a great capacity to adsorb As and generally are the dominant adsorption sites for As in soils (Fitz and Wenzel 2002; Suda and Makino 2016), the soil Fe content has been regarded as another important parameter affecting potential soil bioavailable As. It implies that soils with higher Fe content would provide more adsorption sites for As thus decreasing the potential soil bioavailable As, which was also the case in the studied area. The different patterns observed in the relationship between the bioavailable fraction of As and soil Fe content (Fig. 3) might be ascribed to the contribution of other soil parameters (i.e., pH and OM content). As shown in Fig. 3, despite a similar Fe content, soils possessing higher pH and/or OM content presented higher As mobility. Higher pH and/or OM content would promote the desorption of As resulting in higher As mobility in soils as discussed above. However, the soils in sites S18 and S19 were behaved differently. The pH value was higher in site S18 than in site S1, and the content of OM and Fe was similar in these two sites, but the bioavailable fraction of As was far lower in site S18 than in site S1. In fact, soil from site S18 presented the lowest As potential bioavailable fraction among all the collected soils. Compared with sites S11 and S22, site S19 showed a similar pH value and OM content but lower Fe content. However, the potential bioavailable As in site S19 was the lowest among these three sites. Notably, the proportion of

As partitioning in the residual fraction was predominant among all fractions in the soil of site S18 (68.25%) and S19 (75.19%). Generally, the binding strength of As with soil fractions is gradually increasing with progress in sequential extractions, which means that the As extracted in the later fractions is more stable than that in the former (Kim et al. 2014). The residual As, extracted in the final step of SEP, is the most stable As fraction in soils and can hardly be absorbed by plants in the natural environment (Du et al. 2020; Zhang et al. 2018a). Therefore, a large amount of As sequestrated in residual fraction resulted in a low content of bioavailable As (F1 and F2), Fe- and Al-associated As (F3), and carbonate-bound As (F4) in soil. Despite a similar proportion of residual fraction, the soils possessing a lower Fe content and a higher pH and OM content tended to present a higher potential bioavailable fraction of As. Thus, only a small proportion of potential bioavailable As was observed in soils of sites S18 and S19.

The SMLR equation was built unsuccessfully only based on pH, OM, CEC, soil Fe, and P content; thus, the As residual fraction was also used to build the equation (Table 2). Soil pH was included in the equation, whereas soil OM was not, which further confirmed that the effect of soil OM on potential soil bioavailable As depended on soil pH. Soil P was also included in the equation, which could be due to P competing with As for adsorption sites in soil (Anawar et al. 2018), leading to the increase in the potential soil bioavailable As. Soil Fe was not included in the equation, indicating that the effect of soil Fe on potential soil bioavailable As might not be significant as the proportion of residual fraction As, soil pH, and P content.

Effect of soil parameters on actual soil bioavailable As

Pteris vittata presented the highest BF and $BF_{available}$, which were far beyond all the collected vegetables. As an As hyperaccumulating plant, *Pteris vittata* has a better ability to uptake, translocate, accumulate, and tolerate As, even at extremely high As concentrations, compared with common plants (Fayiga and Saha 2016). The other collected vegetables were non-hyperaccumulating plants with a much lower As enrichment capacity than *Pteris vittata*. As shown in Fig. S3, the tAs content of *Pteris vittata* was dozens to thousands of times higher than that of other vegetables. Hence, *Pteris vittata* was not involved in building SMLR equations.

Table 2 Prediction equations for the bioavailable fraction of As calculated by stepwise multiple linear regression (SMLR)

	Regression equations	R^2	p	n[a]	Eq
Soil	$\lg(\text{the bioavailable fraction of As} + 1) = 0.040\lg pH + 0.022\lg P - 0.240\lg(F5\%^a + 1) - 0.026$	0.69	<0.001	22	4

[a]F5%: the proportion of residual fraction

Such a high BF value of *Pteris vittata* was in agreement with the report of Ma et al. (2018). These authors found that the BF value of *Pteris vittata* leaves was in the range of 3.58 to 5.51 in a field experiment, which was much higher than previous reports (Yang et al. 2018) also sampled at Shimen realgar mine area (the BF value of *Pteris vittata* leaves was 0.65 to 2.16). In another study of the Shimen realgar mine, the BF value of *Pteris vittata* was reported to be 3.11 to 4.22 at the tailing dam (Zhu et al. 2010) (site S6 was near the tailing dam). Han et al. (2020) documented that the senescing fronds and mature fronds accumulated higher As concentration than the young fronds, indicating a difference in As accumulation of *Pteris vittata* in fronds with different maturity. Therefore, the differences in *Pteris vittata* BF values between this study and previous ones might be attributed to the distinct soil parameters and/or plant growth status in sampled sites.

In the present study, the BF values of vegetable plants were very close to the results reported by Yang et al. (2018) (the BF value of vegetables varied from 0.0003 to 0.20). Among the collected vegetables, leafy vegetables (leaves and stems, *Ipomoea aquatica*, *Ipomoea batatas* (L.) Lam.,

Allium fistulosum L., *Allium tuberosum* Rottler ex Spreng., *Daucus carota* Linn. var. *sativa* Hoffm.) showed higher BF values than fruit vegetables (fruits, *Capsicum annuum* L., *Lablab purpureus* (L.) Sweet, *Vigna unguiculata* (L.) Walp., and *Fortunella margarita* (Lour.) Swingle), which was also observed by Huang et al. (2006). It indicated different As accumulation abilities among plant species and tissues. As shown in Table 3, there was a significant correlation between BF and CEC ($r = -0.569$, $p < 0.01$), BF and soil Fe content ($r = -0.644$, $p < 0.01$), $BF_{available}$ and CEC ($r = -0.563$, $p < 0.01$), and $BF_{available}$ and soil Fe content ($r = -0.594$, $p < 0.01$). BF and/or $BF_{available}$ showed significant correlation with soil parameters (CEC and soil Fe) only in *Ipomoea* family. It suggested that CEC and soil Fe content might have an effect on the actual soil bioavailable As for *Ipomoea* family. To further figure out the dominant soil parameters affecting the actual soil bioavailable As, SMLR equations of BF and $BF_{available}$ including also these parameters (i.e., pH, OM, CEC, soil Fe, and P content) were built in this study. As shown in Table 4, R^2 increased with decreasing species of vegetables and R^2 of equations in *Ipomoea* family was greater than 0.7. This result highlighted the different behavior of different plant species in As transfer from soil to plant. Soil Fe content was the only soil parameter included in the equations of vegetable BF values in all vegetables range, leafy and fruit vegetables range, and leafy range. It suggested that soil Fe content was a main parameter affecting As accumulation by native vegetables in the sampling area. Ding et al. (2015) and Chen et al. (2020) also documented the vital role of soil Fe oxides in affecting plant As content. However, some studies reported that other soil parameters rather than soil Fe content were the dominant parameters affecting plant As accumulation (Dai et al. 2019; Yao et al. 2021). The difference might be attributed to the plant species and soil type investigated in different studies (Dai et al. 2019). Considering different vegetable species rather than only one single plant species, the soil type might be more important in this issue. In this study, soil Fe content was far higher than that in the study of Dai et al. (soil Fe oxide content was 0.05–0.19 $g \cdot kg^{-1}$) (Dai et al. 2019), which meant

Table 3 Correlations between BF, $BF_{available}$, and soil properties (*$p < 0.05$, **$p < 0.01$, bold and italic correlation coefficient)

	pH	OM	CEC	Soil Fe	Soil P
All vegetables					
BF	0.053	−0.158	−0.103	−0.255	0.195
$BF_{available}$	−0.002	−0.247	−0.137	−0.212	0.111
Leafy and fruit vegetables					
BF	0.082	−0.173	−0.197	−0.311	0.177
$BF_{available}$	0.007	−0.285	−0.246	−0.250	0.045
Leafy vegetables					
BF	−0.056	−0.291	−0.306	−0.363	0.188
$BF_{available}$	−0.111	−0.417	−0.326	−0.364	0.046
Ipomoea family					
BF	−0.022	−0.411	***−0.569****	***−0.644****	0.014
$BF_{available}$	−0.144	−0.549	***−0.563****	***−0.594****	−0.175

Table 4 Prediction equations for BF and $BF_{available}$ calculated by stepwise multiple linear regression (SMLR)

	Regression equations	R^2	p	n^{a}	Eq
All vegetables	$lg(BF+1) = -0.267lgFe + 0.441$	0.21	0.008	32	5
	$lg(BF_{available}+1) = -1.792lgOM + 3.220$	0.18	0.015	32	6
Leafy and fruit vegetables	$lg(BF+1) = -0.300lgFe + 0.488$	0.25	0.010	26	7
	$lg(BF_{available}+1) = -1.410lgFe + 2.342$	0.26	0.008	26	8
Leafy vegetables	$lg(BF+1) = -0.505lgFe + 0.820$	0.44	0.003	18	9
	$lg(BF_{available}+1) = -1.986lgOM - 1.853lgFe + 6.466$	0.62	0.001	18	10
Ipomoea family	$lg(BF+1) = -0.567lgOM - 0.517lgFe + 1.805$	0.77	0.001	13	11
	$lg(BF_{available}+1) = -2.678lgOM - 2.430lgFe + 8.560$	0.86	<0.001	13	12

[a]n: number of vegetable samples

that plenty of adsorption sites could be provided for As in our sampling areas. This was supported by the high fraction of Fe- and Al-associated As (the residual As could barely release As, thus it was not included). Therefore, soil Fe content was the main parameter affecting BF in this study. This was also the case of the *Ipomoea* family (*Ipomoea batatas* (L.) Lam. and *Ipomoea aquatica* Forssk.) vegetables, which were the most numerous plants collected in our sampling campaign. Based on Eq. 11 (Table 4), OM was another main parameter affecting As accumulation by the *Ipomoea* family in this area. The $BF_{available}$, calculated based on the sum of first two fractions instead of soil tAs, was more efficient in addressing the As assimilation capacity of plants. Similar to the regression equations of BF, the regression equations of $BF_{available}$ also contained the soil Fe content (Table 4), indicating the dominant role of soil Fe oxides/hydroxides in affecting plant's As uptake from the soil. OM was also included in the regression equations of $BF_{available}$. It implies that the effect of soil OM on actual soil bioavailable As was also significant enough to affect the transfer of As from soil to plant in the sampling area. In addition, CEC was not included in any SMLR equations of BF and $BF_{available}$, indicating that the effect of CEC on the actual soil bioavailable As was not as significant as soil Fe or OM content.

Conclusions

In this study, two different soil bioavailable As pools, the potential soil bioavailable As and the actual soil bioavailable As, were considered, and the effect of different soil parameters on these two soil bioavailable As pools in an As-contaminated area was studied. In this area, despite a similar proportion of As fractionating in the residual fraction, soils possessing a lower Fe content, and higher pH and OM content tended to present a higher potential soil bioavailable As. Importantly, soil pH and P content were the dominant parameters affecting the potential soil bioavailable As in the sampling area. BF and $BF_{available}$ varied due to the different plant species and soil parameters. Soil Fe and OM were the most important soil parameters affecting the actual soil bioavailable As in the sampling area. Hence, the dominant soil parameters affecting the two soil bioavailable As pools were different. To regulate the transfer of As from soil to the plant, studies should be focused on the soil parameters that significantly influence the actual soil bioavailable As. Hence, in the investigated area, for food safety purposes, Fe oxides and OM can be applied to soils to bind As, while for phytoremediation purposes, measures should be taken to enhance the release of As from Fe oxides and OM into soil. Notably, soil is a complex medium and presents characteristics other than pH, OM, CEC, Fe, and P content which might influence As behavior; therefore, other potential governing parameters might have been missed in this study. In addition, we only focused on plant species that local residents cultivated. These deficiencies might limit the applicability of our findings. Hence, with the expanding scope of soil parameters, plant species, and other environmental factors, the investigation of long-term environmental and health effects of As transfer from soil to plants, and the investigation of the interaction of plants and soils are needed in the future.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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