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Uptake of heavy metals by crops near a mining field: Pathways from roots and leaves

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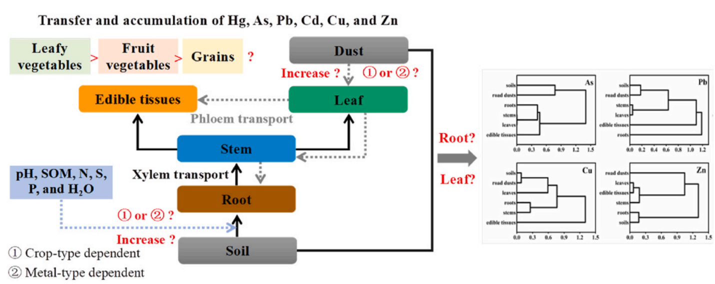
HIGHLIGHTS

- Leafy crops have a stronger propensity to uptake and accumulate Hg, As, and Zn.
- Coexisting metals, N and P may inhibit the transfer of Cd and Cu to rice grains.
- Pb accumulation is independent of soil property, dust input and crop type.
- Hierarchical cluster analysis identifies the uptake pathway of different metals.
- Zn uptake in fruit and grain crops is mainly dust input via phloem of leaves.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal uptake and distribution in crops have been demonstrated to be highly variable and depending on the metal of interest and the crop type. However, no consensus is reached regarding the primary factor controlling metal uptake in crops. This study thus comparably investigated Hg, As, Zn, Pb, Cd and Cu uptake and distribution in three crops grown in a watershed near a copper mining field located in Yunnan, Southwestern China. The bioconcentration factor (*BCF*) and translocation factor (*TF*) were statistically compared for the same metal across different crops. Leafy crops had a stronger propensity to accumulate Hg, As and Zn than fruit crops. The ability of grain crops to accumulate Cd and Cu was much lower than leafy and fruit crops. The three crops all tended not to accumulate Pb in their edible tissues. The DTPA extracted metal concentrations were not statistically correlated with the metal concentrations in crop edible tissues. It is thus not practical to predict metal uptake of Hg, As, Pb and Zn through their available concentrations in soils. The contents of nitrogen and phosphorus, and competing metal ions present in paddy soil decreased the accumulation of Cu and Cd in rice grains. By means of hierarchical cluster analysis, the high accumulation of Zn in the edible tissues of fruit and grain crops was mainly due to dust inputs via phloem transport from leaves. This is why *BCF*(Zn) was the highest among the six metals for these two

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crops. For leafy crops, the accumulation of Hg, Cd and Zn in leaves was mainly through soil inputs by roots. Our findings serve as a scientific basis for the selection of crops in areas with high background of heavy metals.

1. Introduction

According to the reports of International Labour Organization, world mining production reached 17.9 billion metric tons in 2019. Asia was responsible for 59% of the world's total mining production, with China leading in 32 different commodities (ILO, 2021). Human health and the environment are still at risk from food contaminated with metals (Wen et al., 2022). This is especially the case near stream basins in mining fields. In the processes of mining and smelting, waste water and dust containing metals are easily discharged into the environment including surface water, ground water, and agricultural soils (Liu et al., 2013). Metals with high background values in mining fields can easily be absorbed by crops and be accumulated in their edible tissues following fertilization and irrigation of the soil and atmospheric deposition (Qin et al., 2021). Consumption of these crops may result in toxicity or serious health problems to animals and human beings via bio-magnification within the food chain (Chen et al., 2021). However, in complex natural conditions, many factors such as crop species and environmental factors may act simultaneously in determining the metal accumulation in crops which always leads to crop-dependent or metal-dependent variations. It thus seems necessary to explicitly understand the impacts of these factors on uptake, transport and accumulation of metals in various types of crops growing along stream basins in mining fields. The findings from such studies could be used to further assess the risks of crop safety and determine the management strategies to be taken in these areas.

Due to the difference in physiological metabolism, various types of crops may differ greatly in their ability to take up, transfer and accumulate metals from soils. Säumel et al. (2012) reported that Zn concentrations in green beans, tomato, potato, kahlrabi, and carrots were significantly lower than the concentrations in leafy crops. With the characteristics of fast growth, large leaf area (Zhang et al., 2021), close to the ground and high transpiration rate (Zhou et al., 2016), the available metals absorbed by leafy crops from the soils may be more easily transferred to their leaves through the xylem under the action of transpiration pull as compared with other types of crops (Li et al., 2015).

Additionally, soil properties, such as pH, dissolved organic matter (DOM), nitrogen, phosphorus, and sulfur contents, are closely relevant to metal speciation and their bio-availability (Hou et al., 2019; Tian et al., 2018), and subsequently determine the amounts of metal being transferred to the edible tissues of crops. It is worth noting that the chemical speciation of different metals may vary a lot, even under the same soil environmental factors. For example, H^+ in acidic soils may occupy the sorption sites on the surface of soil particles, leading to the release of Cd from relatively stable fractions and increasing Cd extractability (Wen et al., 2020). In contrast, Pb can easily form Pb–Al–P minerals with highly active amorphous Al at a low soil pH (Zhang et al., 2021), resulting in its low mobility. Different metal ions have different binding affinities with ligands (e.g., anions or DOMs) in soil solution. For example, the stabilities of complexes formed between humic acid and metal ions were in the order of Cu > Fe > Pb > Ni > Co > Ca > Cd > Zn > Mn > Mg (Pandey et al., 2000). This would lead to great differences in chemical species of Cu and Mg, and thus Cu uptake by crops could be substantially inhibited by DOMs.

Metal accumulation in edible tissues of crops is not only associated with root uptake and xylem transport, but also originates from foliar uptake and phloem transport (Clemens and Ma, 2016; Page and Feller, 2015). Atmospheric deposition or road dust may be another important reason for the elevated metal concentrations in crops (Zhou et al., 2021). In addition to the dust deposited to the soil and its indirect absorption, metals may also directly enter the leave cells through stomates or aqueous pores in cuticles (Shahid et al., 2017; Schönherr, 2006). In that case, the translocation of metals through phloem would also determine metal accumulation in crop edible tissues. Various leaf characteristics control the direct absorption of metals, such as leaf surface roughness, stomatal density and leaf area (Grazia et al., 2009). As compared with leafy crops, wheat leaves are rough. This may be the reason why the Cd content in wheat grains increased when spraying Cd on the leaves (Li et al., 2020). Based on the above discussion, metal accumulation in crops may be enhanced with rough leaves, and the metals could be accumulated in the edible tissues via phloem transport. To test the hypothesis, the transport and accumulation of Hg, As, Pb, Cd, Cu, and Zn were investigated in 9 different crops grown near a stream basin in a mining field of Yunnan Province, Southwestern China, with a focus on the crop- or metal-dependent variations.

2. Materials and methods

2.1. Study area and sample collection

Soil and crop samples were obtained from the Haojia River Basin, Mouding County, Yunnan Province, which is adjacent to a medium Cu mine. This Cu mine is mainly engaged in Cu ore mining, and Cu, Pb, and Zn processing and smelting. It is located in a north subtropical monsoon climate zone with an annual average temperature of 15.8 °C and a mean annual precipitation around 872 mm. Samples were collected from farmlands of the five natural villages along the Haojia River Basin, including different crops (n = 560), and soils (n = 81). The sampling sequence from the upstream to the downstream was Xinqiao Village (25°36′68.82″ N, 101°60′39.44″ E), Maichong Village (25°35′22.29″ N, 101°61′23.26″ E), Chenjia Village (25°35′24.25″ N, 101°62′ 08.06″ E), Wangjia Village (25°35′34.05″ N, 101°63′20.53″ E), and Lijiawan Village (25°35′33.72″ N, 101°63′94.19″ E).

The selection of sampling varieties of crops depended on local diet and planting habits, primarily including rice, maize, pepper, eggplant, bitter cabbage, leek, shallot, coriander and radix isatidis. Among them, there were no rice, coriander and radix isatidis grown in Lijiawan Village, no radix isatidis in Xinqiao Village, no shallot and coriander in Chenjia Village, and no radix isatidis in Wangjia Village. To facilitate further analysis, these crops were divided into three types according to previous studies (Chen et al., 2021; Dennis et al., 2021), namely leafy (bitter cabbage, leek, shallot, coriander and radix isatidis), fruit (pepper and eggplant) and grain crops (rice and maize). At harvest season (autumn, 2020), several plants of the same species from each plot were collected and mixed to obtain a sample for chemical analysis. The roots, stems, leaves and edible tissues of these plants were stored separately in polyethylene bags at 4 °C. Due to their small biomass, leafy crops were only decomposed into above- and under-ground tissues. The farmland soils were collected while collecting crop samples. Because the farmland in this watershed is distributed along the main road, the dust on the roadside close to the soil sampling sites was sampled (from the curb stone into the road for 1 m) according to the method of Bi et al. (2018). Three natural villages, e.g., Xinqiao, Maichong, and Lijiawan Village, were selected to represent the upper, middle and lower reaches of Haojia River Basin. The sampling area for dust should avoid intersections and road sections near the construction site and bus stops. During collecting, leaves, cigarette butts, weeds and domestic garbage should be avoided as well.

2.2. Sample analysis and quality control

The crop samples were cleaned using deionized water to remove dust and soil. Different parts of the crop samples were dried in an oven at 65 °C until the sample weight remained the same. All samples were then ground to fine powder using a DLF-55 S stainless steel grinder (Dingli Instrument, China), passed through a sieve (<0.42 mm), and kept in a clean polyethylene container. Half g of the prepared sample was acid-digested using concentrated HNO_3 and $HClO_4$ (5:1, *v/v*) in a Multiwave 3000 (Anton Paar, Austria) for 2 h at 180 °C. Digested samples were then diluted to 50 mL using 2% HNO_3 before metal analysis. Total Hg and As in crop samples were determined by an AFS-8510 atomic fluorescence spectrometer (Haiguang Instrument, China), and total Pb, Cd, Cu and Zn were determined by an AA-6880 atomic absorption spectroscopy (Shimadzu, Japan).

The collected soil and dust samples were air-dried at room temperature, ground to fine powder using an agate mortar and pestle, and passed through sieves (<2 mm, <0.149 mm, <0.074 mm), then kept in clean polyethylene containers respectively. Soil pH was measured in a 1:2.5 of soil:water suspension using a PB-10 glass electrode (Sartorius, Germany). Soil organic matter (SOM) was determined using the acid dichromate oxidation method (Zhang et al., 2021). The total contents of N and S in soils were measured by a Vario MICRO cube elemental analyzer (Elementar, Germany). The total contents of P in soils were determined using the rapid perchloric acid digestion method (Sommers and Nelson, 1972). Available P (Olsen-P) was extracted from the soil with HCl and NH_4F (Jiang et al., 2014), and then measured by 6300 inductively coupled plasma optical emission spectrometer (Thermo Fisher Scientific, USA). The dried and sieved soil and dust samples were digested with 10 mL aqua regia for 2 h at 95 °C, and then diluted to 50 mL using ultra-pure water for total Hg and As determination. Soil and dust samples were also digested with a mixture of HCl–HNO_3–HF–$HClO_4$ and filtered with a 0.45 μm membrane for total Pb, Cd, Cu and Zn determination. Bioavailable fractions of Hg, As, Pb, Cd, Cu and Zn were obtained from the soil samples using a DTPA solution (Meng et al., 2021) including 0.1 M TEA, 0.01 M $CaCl_2$ and 0.005 M DTPA (pH = 7.3). The mixture was shaken at around 200 r min^{-1} for 2 h under room temperature, then was centrifuged at 3000 rpm for 10 min and filtered through a 0.45 μm membrane for determination of the bioavailable fractions. Instruments used for metal analysis of soil and dust samples were similar to those used for the crop analyses. Certified reference materials for soil (GBW07456 and GBW07404) and certified reference materials for crop samples (GBW10045 and GBW10015) were also analyzed with the samples. The mean recoveries of standard reference materials were 90–110% for Hg, As, Pb, Cd, Cu, Zn, proving the accuracy of the results.

2.3. Data analysis

The bioconcentration factor (*BCF*) is the ratio between the metal concentration in edible tissues of crops (mg kg^{-1} dry weight) and the metal concentration in soil (Mu et al., 2020). The *BCF* was calculated for each crop sample to quantify its bioaccumulation ability for metals from soil. As shown in Formulas 1 and 2, BCF_{total} and $BCF_{available}$ for individual metals were calculated based on total and bioavailable (quantified using DTPA solution) concentrations, respectively (Adamoa et al., 2014).

$$BCF_{available} = C_{edible\ tissues} / C_{available} \tag{1}$$

$$BCF_{total} = C_{edible\ tissues} / C_{total} \tag{2}$$

where $C_{edible\ tissues}$ represents the total concentration of metals in edible tissues of different crops, mg kg^{-1}; C_{total} represents the total concentration of metals in soil, mg kg^{-1}; $C_{available}$ represents the available concentration of metals in soil, mg kg^{-1}.

To compare metal transfer in crops, e.g., from roots to edible tissues (Formula 3), from soils to roots (Formula 4), and from dusts to leaves (Formula 5), the translocation factors (*TF*) were determined as follows (Ye et al., 2012).

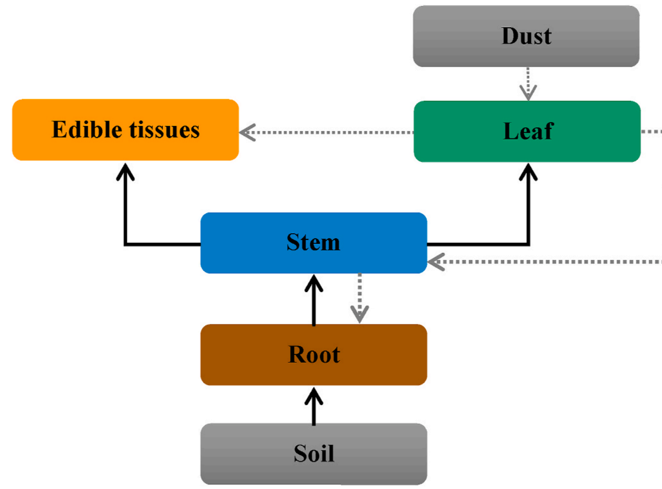

Fig. 1. Diagram of the transport pathway of metals within crops. Solid lines represent the xylem transport process and the dotted lines represent the phloem transport process. For leafy crops, the edible tissues are their leaves.

$$TF = C_{edible\ tissues} / C_{roots} \tag{3}$$

$$TF_r = C_{roots} / C_{available} \tag{4}$$

$$TF_l = C_{leaves} / C_{road\ dusts} \tag{5}$$

where C_{roots} represents the concentrations of metals in plant roots, mg kg^{-1}; C_{dusts} represents the metal concentration in road dusts, mg kg^{-1}; C_{leaves} represents the concentrations of metals in plant leaves, mg kg^{-1}.

Theoretically, xylem transport always plays a key role in transferring metals from underground tissues to above-ground tissues via water transpiration (Uraguchi et al., 2009; Xin et al., 2014). However, phloem transport should not be ignored in metal allocation (Cao et al., 2020), especially when metals can enter the crop through foliar uptake (see Fig. 1). We used hierarchical cluster analysis (HCA) to qualitatively and quantitatively compare the similarity between variables through statistical organization and dendrogram display (Zhang et al., 2018). To screen off the variations of background values and those in different crop tissues, the concentration percentage of each metal in soils, road dusts, roots, stems, leaves, or edible tissues to the total concentration of six metals were calculated using Equation (6). Dendrograms were then established based on 'distance' by HCA to determine the similarities between the concentration percentages of metals in edible tissues of the three crops and those in other parts of crops or in environmental media.

$$Percentage\ (\%) = C_{Mi} \Big/ \sum C_{Mi} \times 100\% \tag{6}$$

where C_{Mi} represents the concentration of Hg, As, Pb, Cd, Cu or Zn, mg kg^{-1} in a media; $\sum C_{Mi}$ represents the sum of concentrations of all 6 metals in the same media, mg kg^{-1}. The HCA of variables is defined by a stepwise algorithm which merges two variables with the least dissimilarity at each step. Dissimilarities between clusters of variables was defined by the average dissimilarity or average linkage method in this study.

The SPSS 26.0 statistical software package (International Business Machines Corporation, USA) was used to process the data, and the Origin 8.0 software (Origin Lab, USA) was used for drawing. Variables were analyzed using one-way analysis of variance (ANOVA) to test significant differences (5% level) in *BCF*s and *TF*s. Pearson correlation coefficients were calculated to determine the relationships: 1) between DTPA-extracted metals in soil and soil properties, metal concentrations in roots or edible tissues; 2) between metal concentrations in roots and

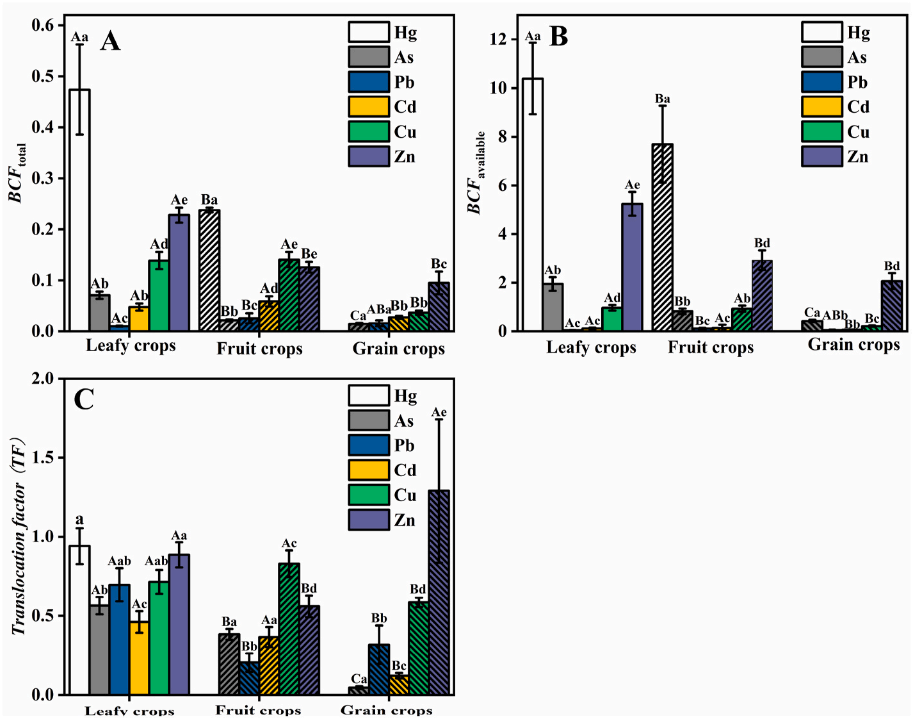

Fig. 2. Transfer factors (*TFs*) and bio-concentration factors (*BCFs*) of the six metals (Hg, As, Pb, Cd, Cu and Zn) in three types of crops in the studied region. $BCF_{total} = C_{edible\ tissues}/C_{total}$. $BCF_{available} = C_{edible\ tissues}/C_{available}$. $TF = C_{edible\ tissues}/C_{roots}$. The statistical difference was expressed as marked letters at $p < 0.05$ according to the one-way ANOVA test. The concentrations of Hg in edible tissues of grain crops and in roots or edible tissues of fruit crops were lower than the detection limit, and thus were not presented here. Capital letters represent the comparison of averaged values of *BCF* and *TF* for the same metal across different crops. Lower letters represent the comparison of averaged values of *BCF* and *TF* for different metals in the same crop.

in edible tissues.

3. Results and discussion

3.1. Varying enrichment of the six metals in different crops

The values of BCF_{total}, $BCF_{available}$ and *TF* of the investigated metals are summarized in Fig. 2. Generally, no difference was observed between BCF_{total} and $BCF_{available}$ in quantifying metal bioaccumulation by crops from the soils. For example, leafy crops had significantly higher BCF_{total} and $BCF_{available}$ for Hg, As and Zn than fruit and grain crops in the studied region (Fig. 2A and B), which was not found for *TFs* of grain crops. This result indicated that leafy crops had a stronger propensity to transfer and accumulate Hg, As and Zn than fruit crops. However, no significant difference was found in BCF_{total} or $BCF_{available}$ between leafy and fruit crops for Cd and Cu, but they were both significantly higher than the values for grain crops. This trend was consistent with the *TFs* for Cd and Cu (Fig. 2C), indicating that the ability of grain crops to accumulate Cd and Cu from soils was significantly lower as compared to the other two crops. In contrast, for Pb, the averaged BCF_{total} or $BCF_{available}$ of fruit crops was significantly higher than the values of leafy crops. This finding did not coincide with the *TFs* for Pb (see Fig. 2C). One explanation for the difference between the accumulation of Pb and of other metals may be the much lower Pb concentrations in edible tissues of the three crops than in the corresponding soils (in the form of both total and available concentrations), resulting in a small *BCF* value and slight variations between *BCFs* of different crops. In other words, although the available concentrations of Pb in soils were high, the three crops did not necessarily absorb that much of Pb. It is believed that most Pb uptake by plants would be detained in roots because of the binding of Pb to ion-exchangeable sites on the cell wall and the extracellular precipitation in the form of Pb-carbonated deposits in the cell wall (Yang et al., 2015). The other explanations such as modulation of uptake by different soil properties and metal inputs from dusts (hypothesis) would be further discussed in Sections 3.2 and 3.3.

The transfer and accumulation of metals in crops also varied with metal type. As shown in Fig. 2A, the values of BCF_{total} followed the order ($p < 0.05$) of Hg > Zn > Cu > As ≈ Cd > Pb, Hg > Cu ≈ Zn > Cd > As > Pb, and Zn > Cu ≈ Cd > As ≈ Pb ≫ Hg for leafy, fruit, and grain crops, respectively. These findings indicated that Hg had the highest potential to be accumulated in the edible tissues of leafy and fruit crops, while Pb had the lowest accumulation potential among the investigated metals. For grain crops, the accumulation potential of Zn in edible tissues was the highest, while the accumulation potential of Hg was very low with Hg concentrations below the detection limit of 0.01 mg kg^{-1}. The reason was that the soil moisture content was relatively high for the grain crops especially for rice, and Hg species are mostly insoluble Hg^0 or HgS (Schuster and Lindqvist, 1991; Zárate-Valdez et al., 2006), which restrained Hg absorption by rice roots and accumulation in rice. The accumulation potential of Zn in edible tissues of the three crops was in the first or second place of the six metals, possibly because Zn is necessary for plant growth and development such as photosynthesis, ATP synthesis and various enzymatic reactions (Ghori et al., 2019). Similarly, the transfer or accumulation potential of Cu was always higher than that of Cd for the three crops, which can be also explained by the internal concentrations of essential elements regulated in plants (Zaranyika and Nyati, 2017).

3.2. Impacts of soil properties on metal transfer and accumulation

Pearson correlation analysis was conducted to understand the relationships between metal transfer or accumulation and soil properties. The results are presented in Tables 1, S1, S2 and S3. For Hg, As, Pb and Zn, no significant correlation was found between available metal concentrations in the soil and metal concentrations in edible tissues of the three crops (see Table S2). Thus, the accumulation of Hg, As, Pb and Zn in crops was not determined by their bio-available forms in the soils. However, it was observed that the available Cd, Cu and Zn in leafy crops, Cu and Zn in fruit crops, Pb, Cd and Zn in grain crops were positively related to the accumulated As in different crops. Previous studies have observed a synergistic interaction between As and Cd in solution culture (such as Cao et al., 2007). The negatively charged surface of the plasma membrane can be neutralized by the adsorbed Cd^{2+}, resulting in the increased concentration of anionic metal(loid) As at the root surface and

Table 1
Results of Pearson correlation analysis (the *r* value) between available metal concentrations in the soil and the main soil properties.

Crops	Available metal concentration	Soil properties						
		pH	SOM	N	S	AP	TP	Soil moisture content
Leafy crops ($n = 372$)	Available Hg	−0.38[b]	−0.48[b]	−0.38[b]	−0.28[a]	−0.68[b]	−0.57[b]	−0.61[b]
	Available As	−0.47[a]	−0.40[a]	−0.13	0.43[b]	−0.22	−0.43[b]	−0.06
	Available Pb	0.62[b]	−0.09	−0.21	0.49[b]	0.44[b]	0.20	0.74[b]
	Available Cd	−0.29[a]	0.21	0.21	−0.57[b]	−0.42[b]	−0.09	−0.78[b]
	Available Cu	−0.08	0.54[b]	0.50[b]	−0.39[b]	−0.04	0.21	−0.52[b]
	Available Zn	−0.54[b]	0.14	0.21	−0.52[b]	−0.47[b]	−0.20	−0.82[b]
Fruit crops ($n = 90$)	Available Hg	−0.26	−0.44[a]	−0.35	−0.27	−0.62[b]	−0.52[b]	−0.53[b]
	Available As	−0.47[b]	−0.36	−0.09	0.39[a]	−0.20	−0.41[a]	−0.03
	Available Pb	0.63[b]	−0.24	−0.36	0.47[b]	0.35	0.08	0.71[b]
	Available Cd	−0.28	0.32	0.32	−0.55[b]	−0.37[a]	0.00	−0.79[b]
	Available Cu	−0.13	0.60[b]	0.56[b]	−0.40[a]	−0.03	0.24	−0.57[b]
	Available Zn	−0.54[b]	0.29	0.35	−0.50[b]	−0.38[a]	−0.09	−0.81[b]
Grain crops								
Rice ($n = 66$)	Available Hg	0.28	−0.45	−0.48	−0.42	−0.53	−0.58[a]	−0.26
	Available As	0.23	−0.34	−0.52	−0.29	−0.45	−0.48	0.02
	Available Pb	0.21	−0.50	−0.71[b]	−0.41	−0.61[a]	−0.76[b]	−0.33
	Available Cd	0.18	−0.50	−0.70[a]	−0.43	−0.60[a]	−0.79[b]	−0.43
	Available Cu	−0.08	−0.25	−0.51	−0.49	−0.37	−0.60[a]	−0.24
	Available Zn	0.06	−0.38	−0.61[a]	−0.46	−0.49	−0.70[a]	−0.31
Maize ($n = 32$)	Available Hg	−0.26	−0.44	−0.35	−0.27	−0.62[a]	−0.52[a]	−0.53[a]
	Available As	−0.47	−0.36	−0.10	0.39	−0.20	−0.41	−0.03
	Available Pb	0.63[a]	−0.24	−0.36	0.47	0.35	0.08	0.71[b]
	Available Cd	−0.28	0.32	0.32	−0.55[a]	−0.37	0.01	−0.79[b]
	Available Cu	−0.13	0.60[a]	0.55[a]	−0.40	−0.03	0.24	−0.55[a]
	Available Zn	−0.54[a]	0.29	0.35	−0.50	−0.38	−0.09	−0.81[b]

[a] Indicates a statistically significant correlation when $p < 0.05$.
[b] Indicates a statistically significant correlation when $p < 0.01$. SOM indicates the amount of soil organic matter. AP indicates the available concentration of phosphorus in the soil. TP indicates the total concentration of phosphorus in the soil.

more chance of being taken up by the plant roots.

Significantly negative correlations were found for Cd and Cu between available metal concentrations in the soil and metal concentrations in edible tissues of rice namely rice grains (Table S2). Similarly, significantly negative correlations also occurred between Cd or Cu concentrations in rice roots and in rice grains (see Table S3). Significant negative correlations were also found between Cd/Cu and other metal concentrations in soils, rice roots, and the accumulated concentrations.

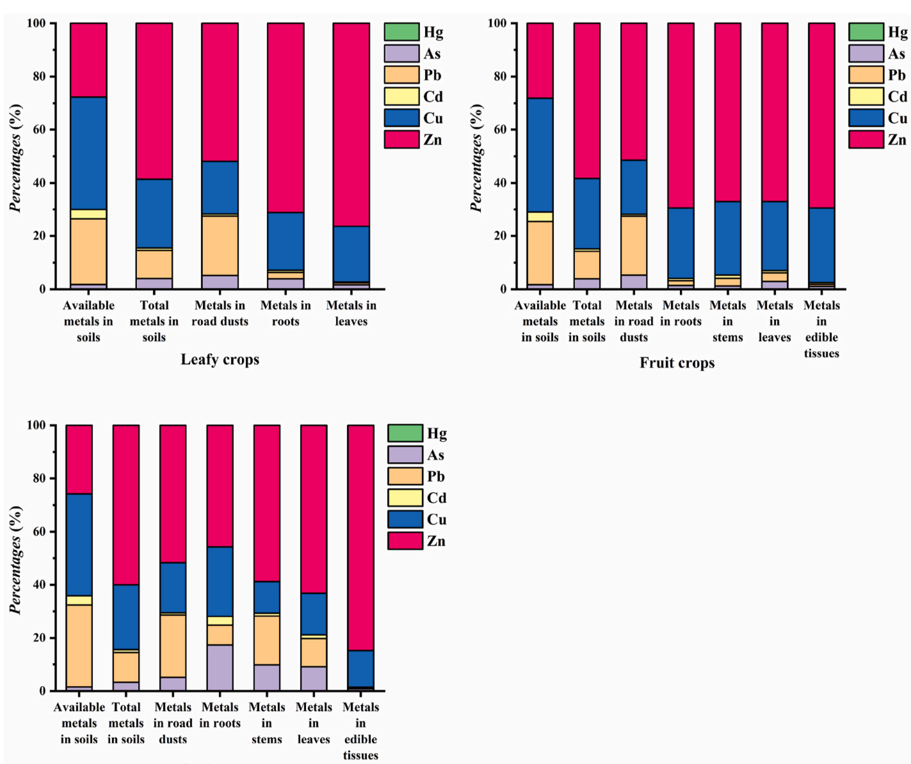

Fig. 3. Percentages of the total or available concentration of each metal in soils, road dusts, roots, stems, leaves, or edible tissues of the three crops to the total concentration of six metals namely Hg, As, Pb, Cd, Cu and Zn.

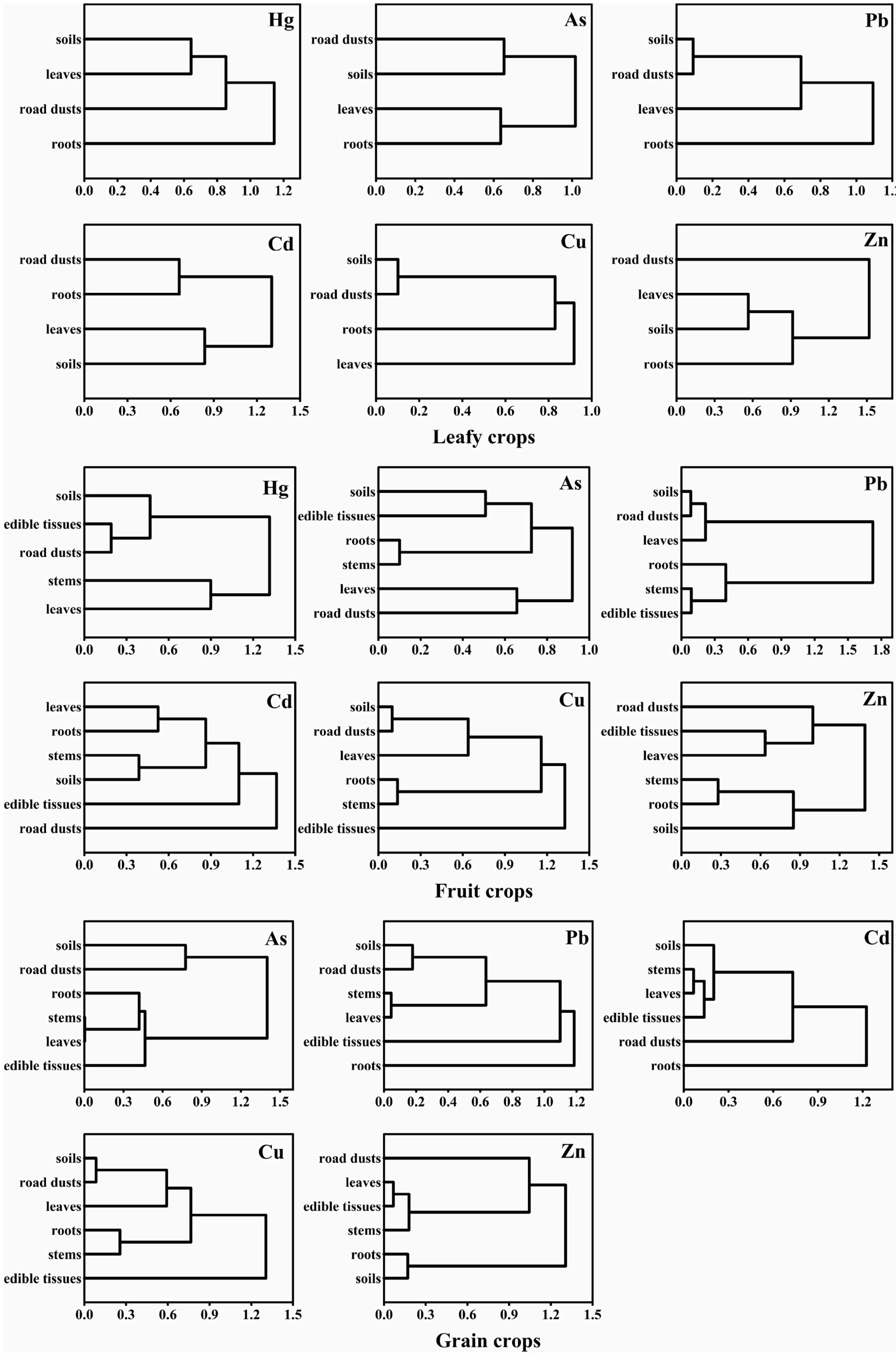

Fig. 4. Dendrograms of the similarity of metal percentages distributed in soils, road dusts, roots, stems, leaves, and edible tissues of the three crops using the HCA approach. Hg was not detected in edible tissues of grains at a detection limit of 0.01 mg kg^{-1}.

For instance, Cu and Zn in soils negatively related to Cd accumulation in rice grains, whereas Zn, Cd and Pb in soils negatively related to Cu accumulation (Table S2). Furthermore, Hg, Pb, Cu, and Zn in rice roots negatively related to Cd accumulation in rice grains, whilst Hg, As, Pb, Cd and Zn in roots negatively related to Cu accumulation (Table S3). These observations implied that competitive effects among metals may inhibit the transfer and accumulation of Cd and Cu in rice. This interactive effects may increase with the increased concentrations of existing ions (Liu et al., 2017), resulting in the negative correlations observed in Tables S2 and S3. However, the available concentrations of Cd/Cu and other metals in soil were all positively correlated with Cd/Cu concentrations in rice roots (Table S1). Thus, the above metals may compete with Cd or Cu to transport after entering rice root. Roots seemed to be also a barrier for rice to protect its edible tissues from the accumulation or harms caused by Cd and Cu, which coincides with the finding of Lux et al. (2011).

As shown in Table 1, the correlation between selected soil physicochemical properties and available metals varied with metal and crop types. For rice, the available concentration of Cd in paddy soil was negatively correlated with N content ($r = -0.7^*$), available ($r = -0.60^*$) and total concentrations ($r = -0.79^{**}$) of P. The available concentration of Cu was also found to negatively correlate with total P concentrations in paddy soil ($r = -0.60^*$). On the one hand, available P such as phosphate may form precipitates with metal ions in soil solution (Bolan et al., 2014; Feng et al., 2020). On the other hand, the concentration of total P was 15 times higher than the available P concentration (see Fig. S1). The insoluble phosphate minerals which were included in the assessment of total P, are able to adsorb metal ions and reduce their availability (Bolan et al., 2003). To our knowledge, N in soil mainly affects the soluble content of metals by changing soil pH. For example, the application of N (as urea) decreased the soluble plus exchangeable fractions of Pb and Cd by 6–46% and 1–7%, and the soil pH increased from 4.6 to 5 (Tu et al., 2000). These findings proved that soil properties can affect the bioavailable forms of Cd and Cu in soil, and influenced the accumulation of these two metals in rice grains.

3.3. Metal inputs from soils or dusts?

According to Sections 3.1 and 3.2, BCF(Pb) was found to be lowest among the six metals, and the accumulation of Pb in edible tissues of the three crops was not significantly associated with its available concentrations in soil. Similar results were also found in the distribution or proportion of Pb in various environmental media and different tissues of the three crops (Fig. 3). For example, the concentration of Pb in soil accounted for 30% of the summed concentration of the six metals, while it dropped to less than 5% in the edible tissues of the grains. Because no significant correlation was found between the accumulations of Pb and other metals in Table S2, the interactions between metals can be ruled out. The HCA approach was used to statistically compare the similarity of the Pb distribution in various environmental media and different tissues of crops, as well as the uptake pathways. As shown in Fig. 4, the highest similarity was found between the concentration percentage of Pb in soil and its percentage in dust, and they were similarly clustered with edible tissues of the three crops. This result indicated that Pb in soil and road dusts may both contribute to the accumulated Pb in the three crops. The self-protection mechanism of plants may have restricted Pb accumulation. It has been reported that Pb ($EC_{50} = 184$ μM) was much more toxic than Zn ($EC_{50} = 260$ μM) in reducing the root length of lettuce (Lamb et al., 2010). Plants would purposely reduce the transport of such highly toxic metals. This was why the value of TF_r(Pb) was only 14% of TF_r(Zn) for leafy crops (Fig. S2).

Also in Fig. 4, the highest similarity was found between the concentration percentage of Zn in edible tissues of grain crops and its percentage in leaves, followed by stems and road dusts. Similarly, for fruit crops, the highest similarity was found between the concentration percentage of Zn in edible tissues and its percentage in leaves, followed by road dusts. These findings thus testified our hypothesis about the importance of leaf uptake for metal accumulation, especially for Zn in edible tissues of grain and fruit crops. This also explained why *BCF*(Zn) ranked at the first or second places for grain and fruit crops (see Section 3.1). Besides, the concentration percentage of Hg in edible tissues of fruit crops showed the highest similarity with its percentage in road dusts, which also suggested the important metal input from road dusts. For leafy crops, the accumulation of Hg, Cd and Zn in leaves was mainly associated with soil inputs, while the accumulation of As, Cu and Pb was highly related to both soil and dust inputs. The high accumulation of Hg, As and Zn in leafy vegetables (Section 3.1) may be more related to their high transpiration rate (Zhou et al., 2016).

4. Conclusions

This study systematically investigated the uptake and distribution of Hg, As, Zn, Pb, Cd and Cu in three types of crops in a watershed near a copper mining field located in Yunnan, Southwestern China. Leafy crops have a stronger propensity to transfer and accumulate Hg, As and Zn than fruit crops, as suggested by their significantly higher values of *BCF* and *TF*. According to Pearson correlation analysis, soil properties including N content, P content and competing metal ions negatively related to the accumulation of Cu and Cd in rice. By means of the statistical HCA approach, the high accumulation of Zn in edible tissues of fruit and grain crops was mainly due to dust inputs via phloem transport from leaves, which testified our hypothesis.

Our investigation suggested that the high background concentrations of metals may not necessarily lead to more metal accumulated in all crops. Leafy crops tended to accumulate Hg, As and Zn. The uptake, transport and accumulation of Cd and Cu in rice were negatively related to N and P contents in soil, and to some of the coexisting metals in plants. The accumulation of Pb was the lowest among the six metals in three crops which can be attributed to the barrier effect of plant roots. Our findings are useful for explaining variations of metal accumulation and properly selecting crops to be cultured along stream basins near a mining field.

Author contributions statement

Yang Liu: Methodology, Formal analysis, Writing - original draft, Writing - review & editing. Ruicai Zhang: Methodology, Formal analysis, Investigation, Writing - original draft. Bo Pan: Formal analysis, Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration. Hao Qiu: Writing - review & editing. Jing Wang: Writing - review & editing. Junyuan Zhang: Investigation. Xuekui Niu: Resources. Liping He: Resources. Wenmin Qian: Resources. Willie J. G.M. Peijnenburg: Writing - review & editing.

Declaration of competing 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138215.

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