Environmental Pollution 300 (2022) 118927

Contents lists available at ScienceDirect

Environmental Pollution

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

Understanding the translocation and bioaccumulation of cadmium in the Enshi seleniferous area, China: Possible impact by the interaction of Se and Cd☆

Chuanyu Chang [a,b], Hua Zhang [a,*], Fang Huang [b], Xinbin Feng [a]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China
[b] CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, 230026, China

ARTICLE INFO

Keywords:
Cadmium
Selenium
Translocation
Interaction
Co-exposure risk
Enshi

ABSTRACT

Selenium (Se) plays an indispensable role in minimizing cadmium (Cd) hazards for organisms. However, their potential interactions and co-exposure risk in the naturally Se–Cd enriched paddy field ecosystem are poorly understood. In this study, rice plants with rhizosphere soils sampled from the Enshi seleniferous region, China, were investigated to resolve this confusion. Here, translocation and bioaccumulation of Cd showed some abnormal patterns in the system of soil-rice plants. Roots had the highest bioaccumulation factors of Cd (range: 0.30–57.69; mean: 11.86 ± 14.32), and the biomass of Cd in grains (range: 1.44–127.70 μg, mean: 36.55 ± 36.20 μg) only accounted for ~10% of the total Cd in whole plants (range: 14.67–1363.20 μg, mean: 381.25 ± 387.57 μg). The elevated soil Cd did not result in the increase of Cd concentrations in rice grains ($r^2 = 0.03$, $p > 0.05$). Most interestingly, the opposite distribution between Se and Cd in rice grains was found ($r^2 = 0.24$, $p < 0.01$), which is contrary to the positive correlation for Se and Cd in soil ($r^2 = 0.46$, $p < 0.01$). It is speculated that higher Se (0.85–11.46 μg/g), higher Se/Cd molar ratios (mean: 5.42 ≫1; range: 1.50–12.87), and higher proportions of reductive Se species (IV, 0) of the Enshi acidic soil may have the stronger capacity of favoring the occurrence of Se binding to Cd ions by forming Cd–Se complexes ($Se^{2-} + Cd^{2+} = CdSe$) under reduction conditions during flooding, and hence change the Cd translocation from soil to roots. Furthermore, the negative correlation ($r^2 = 0.25$, $p < 0.05$) between the Cd translocation factor ($TF_{whole\ grains/root}$) and the roots Se indicates that Cd translocation from the roots to rice grains was suppressed, possibly by the interaction of Se and Cd. This study inevitably poses a challenge for the traditional risk assessment of Cd and Se in the soils-crops-consumers continuum, especially in the seleniferous area.

1. Introduction

As a trace element, cadmium (Cd) is toxic for organisms in terrestrial ecosystems (Rahman and Singh, 2019). Due to the strong mobility of Cd in the ecosystem of cropland, it is easily taken up and bioaccumulated in edible parts of crops (Hu et al., 2020). Excessive Cd can negatively affect the growth of crops, leading to physiological disorders of metabolism and even deterioration in the quality of agricultural products (Ismael et al., 2019). Rice, as the staple food, is a key source of Cd intake for people in South China (Song et al., 2017). Cadmium has a long half-life and can be highly accumulated in the human kidney and liver; thus long-term intake of Cd-contaminated grains may induce health problems (Baba et al., 2013).

Due to the extensive economic development model in the past, many environmental problems involving heavy metal contamination were brought about in China Mainland (Zhao et al., 2015). Currently, the main pollutants affecting the soil environmental quality of agricultural land in China are heavy metals, of which Cd is the primary one, underlined in the “China Ecological Environment Status Bulletin 2020”. Cd pollution in the agroecosystem is particularly serious in Southern China (Mu et al., 2019), which is attributed to the local geological background, industrial activities, or agricultural activities (Wang et al., 2019a). A field investigation revealed that the Cd concentrations of rice grains in a Cd-contaminated area in Hunan Province reached 0.69 μg/g

☆ This paper has been recommended for acceptance by Su Shiung Lam.
* Corresponding author.
E-mail address: zhanghua@mail.gyig.ac.cn (H. Zhang).

https://doi.org/10.1016/j.envpol.2022.118927
Received 31 July 2021; Received in revised form 25 January 2022; Accepted 28 January 2022
Available online 29 January 2022

(Chen et al., 2018), which is equivalent to that in the rice cultivation region in Japan where “itai-itai disease” occurs. What is more worrying is that rice accounts for 56% of Chinese residents’ total Cd intake (Song et al., 2017), posing a threat to food security and people’s health.

Selenium is a necessary nutrient element for humans. As the core of selenoenzyme, it plays a part in scavenging free radicals and antagonizing heavy metal toxicity (Rayman, 2012). However, most of the area is in a state of Se deficiency in China (Dinh et al., 2018), causing the intake of total Se for people to be generally less than the reference value (60 μg/day) (Li et al., 2014), recommended by the Chinese Nutrition Society. Interestingly, Se biofortification or Se functional agriculture is emerging to increase the Se levels in agricultural products (rice, wheat, eggs, tea) to improve the nutrient status for Se-deficient population (Schiavon et al., 2020), especially in typical seleniferous areas, such as Enshi, Ankang, Shitai, and Yichun in China.

The mitigating effect of Se on Cd biological toxicity was generally confirmed in rats by improving Cd-induced oxidative stress (Jihen et al., 2009) or forming protein-bound complexes (Gasiewicz and Smith, 1976). The adverse effect of Cd on rice plants could be mitigated by Se fertilization has been shown by many pot experiments. The key mechanism is that Se chelates Cd metal ions in soil (Huang et al., 2018) or in rice plants (Feng et al., 2021). The interactions of Cd and Se in the soil are mainly manifested in that Se changes the geochemical distribution of different fractions of Cd in the soil and reduces the content of soluble Cd (Huang et al., 2018). The formed insoluble substance of CdSe ($K_{sp} = 4 \times 10^{-35}$), less bioavailable for plants (Navarro et al., 2012), might be responsible for the reduction of soluble Cd in soils (Shanker et al., 1995). In rice plants, Se may regulate Cd transport genes of Nramp5 (Zhou et al., 2021) or HMA3 (Huang et al., 2021) in the tissue of roots and then restain Cd translocation from roots to other tissues. Furthermore, chelation of Cd by Se was also found in corn leaves (Zhang et al., 2019). Although numerous studies of Se on Cd were reported, the impact of Cd on Se translocation in rice plants seems not so significant (Huang et al., 2017; Zhang et al., 2019).

Enshi, located in central China, is known as the “World Capital of Selenium”. The soil Se concentrations range from 0.5 to 47.7 μg/g and rice Se levels vary from 0.084 to 9.67 μg/g (Sun et al., 2010). The naturally higher soil Se is mainly attributed to the wide distribution of shales with high Se in Enshi (Chang et al., 2019a). However, as the associated heavy metal of Se, Cd (geomean: 4.8 μg/g) is also enriched in local shales based on the literature analysis (Chang et al., 2019b). Subsequently, the weathering of parent rocks containing Cd might result in the highly accumulated Cd in the soil (Yu et al., 2018; Chang et al., 2019b). A recent study revealed that the Cd in soil was 0.93 ± 1.63 μg/g and even exceeded 10 μg/g at some sites of Enshi (Yu et al., 2020). Therefore, the Enshi area is a naturally high Se and Cd geological background area. To achieve agricultural development and rural revitalization, Se-functional agriculture is being promoted by the local governments. Although the biogeochemistry of Se has been well investigated, the interaction of Se and Cd and their co-exposure risk in such paddy field ecosystems are poorly understood. Understanding the interaction of Cd and Se and their co-exposure risk in the local farmland system is helpful for further implementation of environmental risk governance and the high-quality development of Se-functional agriculture. It was previously reported that the accumulation of Cd in corns, collected from the natural Se–Cd rich upland soils of the Wumeng Mountain area of Guizhou province, were inhibited when soil bioavailable Se:Cd molar ratios greater than 0.7 (Zhang et al., 2019). Considering the Se (IV) has a stronger ability to antagonize Cd than Se (VI) under flooded conditions (Wan et al., 2016) and Se (IV) accounts for 19% of total Se in paddy soil of Enshi (Qin et al., 2017), this study hypothesizes that a possible Se–Cd interaction may occur to control Cd accumulation in rice and may affect Cd or Se risk assessment in the natural paddy ecosystem of Enshi. To address the abovementioned concerns, co-located soil and rice plants were then sampled. This study aims to provide a more profound implication with regard to the environmental risks of Cd and Se at this natural seleniferous area. It may serve as a valuable reference for stakeholders, including environmental protection agencies in China and globally.

2. Materials and methods

2.1. Study area

Enshi has a humid subtropical monsoon climate with abundant rainfall and four distinct seasons. The annual average precipitation is ~1600 mm, and the average annual temperature in the territory is 16.2 °C (Qin et al., 2013). The Se ore and Se-rich stone coal resources containing abundant vanadium, molybdenum, cadmium, and other metal elements are mainly produced in Permian silicon-bearing carbonaceous shale (Yao et al., 2002). The trace metals of copper, zinc, plumbum, and so on were reported in a previous study, showing non-polluted farmland soil, apart from the Cd and Se (Chang et al., 2019b). Se-enriched agricultural products have been vigorously promoted with rapidly developed Se functional agriculture in this area in recent years.

2.2. Sample collection and preparation

24 sites of rice plants and the corresponding rhizosphere soils were sampled from the Enshi region (Figure S1, N = 24) in September 2016, in which the total soil Se, extracted bioavailable Se, soil pH, and organic carbon (SOC) were previously reported (Chang et al., 2019a) and directly used for this study. To further look into the potential Cd–Se interaction, different rice tissues (including roots, stems, leaves, husks, and grains, were subjected to Cd analysis. Sequential chemical extraction procedures for fractions of soil bioavailable Cd have been given previously, where ultrapure water was applied to abstract the fraction of water-soluble and 1 M $MgCl_2$ was used to take out the exchangeable Cd (Chang et al., 2019b). The extracted solutions were firstly filtered with 0.45 μm filter membranes (JINTENG®) to avoid the influence of possible particulate impurities on the following analysis. Then the solution samples were tested by ICP-MS (Nexion 300X, PerkinElmer) after being diluted by ultrapure water.

Analysis of Cd in soil and plants tissues. 0.05–0.1 g of soil sample was digested with the distilled 3.4 mL of HNO_3 and 0.6 mL of HF, and 0.1–0.15 g of plant sample was digested with the distilled 3.0 mL of HNO_3 at 160 °C for 38 and 20 h in 15 mL of Teflon bombs respectively. After digestion, 2 mL of 30% (v/v) H_2O_2 were added to the cooled bombs, then placed at the platen heater (~90 °C), to evaporate the solutions to be nearly dry. Then, 3 mL of distilled HNO_3 and 2 mL of ultrapure water were supplemented to the bombs, placed in an oven at 160 °C for 8 h (Chang et al., 2019b). After cooling, the solution was diluted and detected by ICP-MS. Before the test, the diluted solutions were filtered with a 0.45 μm filter membrane. To ensure the quality of the experiment, standard reference materials of GBW10020 (citrus leaf) and GBW07405 (GSS-5, yellow-red soil) were used during the digestion process of samples. The analysis results of standard reference materials for GBW07405 is 0.42 ± 0.03 μg/g (0.38–0.46 μg/g; reference value: 0.45 μg/g); and the analysis result for GBW10020 is 0.18 ± 0.01 μg/g (0.17–0.20 μg/g; reference value: 0.17 μg/g). The mean recovery of Cd for GBW07405 and GBW10020 are all ranged within 90–110%. The relative variance was within 10% for all sample duplicates.

2.3. Bioaccumulation and translocation factors

The bioaccumulation factors (BAFs), mainly used to evaluate the ability of different parts of plants to accumulate the related elements in rhizosphere soil, were calculated using the following equation:

$$BAF_{rice\ tissue} = C_{rice\ tissue}/C_{soil} \tag{1}$$

where $C_{rice\ tissue}$ represents the concentrations of Cd in rice tissue and C_{soil} indicates the concentrations of Cd in the soil.

The translocation factors (TF_S), characterizing the migration ability of elements between rice tissues, were calculated as:

$$TF_{tissue1/tissue2} = C_{tissue1/Ctissue2} \quad (2)$$

where $C_{tissue1}$ is the concentration of Cd in rice tissue 1 and $C_{tissue2}$ is the concentration of Cd in rice tissue 2.

2.4. Statistical analysis

The software of IBM SPSS Statistics 22 was utilized to perform correlation analysis. Correlation coefficient (r) and significance probability (p) values were given during the regression fits. T-tests, showing the significant difference of concentrations and bioaccumulation factors of Cd in plants tissues, also were calculated. Additionally, Microsoft Office 2013 and Origin 2021 were used to perform graphics drawings. Since no significant correlations were found between the major metal elements in soil and Cd in rice, the only impact of Se on Cd translocation and bioaccumulation was discussed in the study.

3. Results and discussion

3.1. The total and bioavailable Cd in soils

The total Cd concentrations of paddy soil samples varied from 0.35 to 2.67 μg/g (mean:1.28 ± 0.62 μg/g), which is comparable to a recent soil investigation study (range: 0.12–21.95 μg/g, mean: 0.93 ± 1.63 μg/g) (Yu et al., 2020), but ten times higher than the natural background of Cd in Chinese soil (0.097 μg/g, Wei et al., 1991). The soil in Enshi is acidic, with a mean pH of 5.33 ± 0.46 (Chang et al., 2019a). The lower soil pH may result from the decomposition of organic matter in soil and shales, which was revealed by the negative correlation between pH and organic matter ($r^2 = 0.25$, $p < 0.01$) (Chang et al., 2019a). The mean concentration of soil Cd seriously exceeded the risk screening values (0.3 μg/g, pH ≤ 5.5), and one-third of soil samples reached the risk intervention values (1.5 μg/g, pH ≤ 5.5) for paddy soil contamination set by the Chinese government (GB 15618-2018).

The Cd species of water-soluble and exchangeable are deemed as the most bioavailable for plants (Ma and Rao, 1997). The concentrations of water-soluble Cd ranged from 0.79 to 22.66 ng/g (mean: 7.50 ng/g), while the proportions varied largely from 0.09% to 1.12% (mean: 0.61%) (Chang et al., 2019b). A positive correlation between the water-soluble and the total soil Cd was found (Table S1, $p < 0.01$), which indicates that total soil Cd defines the level of water-soluble Cd. However, a significant negative relationship was found between the proportions of water-soluble Cd to the pH values ($r^2 = 0.53$, $p < 0.01$), revealing that pH largely affects the release of water-soluble Cd from the soil. It is also observed that the proportion of water-soluble Cd at pH ~4.8 is ten times higher than that at pH ~7; this finding is comparable to a recent study, which found that the decreased pH results in a sharp increase of the soluble Cd (Wang et al., 2019a). The specific mechanism for the increased water-soluble Cd with increasing soil acidity may be controlled by the interaction of Cd fractions, the competition between Cd^{2+} and other metal ions (Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}), and the desorption or adsorption process (Dou et al., 2020). Additionally, the concentrations of exchangeable Cd varied from 0.21 to 1.36 μg/g (mean: 0.52 ± 0.29 μg/g), and its proportions varied from 27.14% to 58.21% (mean: 41.23%) (Chang et al., 2019b), comparable to those in other acidic soils (Wang et al., 2019b). A positive correlation between exchangeable and total soil Cd is also observed (Table S1, $r^2 = 0.90$, $p < 0.01$), which still indicates that exchangeable Cd was primarily controlled by the total soil Cd. However, the weaker negative correlation of pH and the proportions of exchangeable Cd to total Cd ($r^2 = 0.22$, $p = 0.02$), implying that the effect of pH on exchangeable Cd is weaker than that on water-soluble Cd.

3.2. The pattern of Cd bioaccumulation in rice

The concentrations, bioaccumulation factors, and biomass of Cd in rice plants are given in Fig. 1. It is easily known that rice roots have the highest Cd concentrations (range: 0.22–32.63 μg/g; mean: 11.31 ± 10.30 μg/g) among all rice tissues, followed by stems (range: 0.10–17.98 μg/g; mean: 5.90 ± 5.73 μg/g), bran (range: 0.067–5.33 μg/g; mean: 1.59 ± 1.61 μg/g), polished rice (range: 0.028–1.89 μg/g; mean: 0.74 ± 0.71 μg/g), leaves (range: 0.023–2.34 μg/g; mean: 0.56 ± 0.62 μg/g), and husks (range: 0.003–1.54 μg/g; average: 0.31 ± 0.38 μg/g) (Fig. 1a). Roots had the highest BAFs (range: 0.30–57.69; mean: 11.86 ± 14.32), followed by stems (range: 0.062–26.45; mean: 6.72 ± 8.45), bran (range: 0.052–7.50; mean: 1.77 ± 2.28), polished rice (range: 0.02–3.54; mean: 0.84 ± 1.11), leaves (range: 0.01–2.93; mean: 0.63 ± 0.86), and husks (range: 0.0009–1.93; mean: 0.35 ± 0.51) (Fig. 1a). The highest bioaccumulation capacity of Cd in rice roots is attributed to its special roles in adsorbing, retaining, and transporting Cd from soils to roots and from roots to shoots. The root is generally deemed as the main tissue that absorbs Cd for rice plants (Smolders, 2001). Cd^{2+} adsorption from the soil solutions by rice roots cells is primarily controlled by *OsNramp5* that located in the outer and endodermis of the roots (Sasaki et al., 2012). A feasible measure was introduced to decrease the Cd in rice by inhibiting the Cd absorption by rice roots through genetic mutation of the *OsNramp5* (Wang et al., 2019c). Furthermore, Once Cd^{2+} enters the roots, biochemical reactions that detoxify Cd in rice are induced. Like *OsHMA3*, located in the vacuoles of roots, can transport Cd ions into the vacuoles (Miyadate et al., 2011) and the ions can be further chelated by free sulfhydryl groups, ultimately resulting in large bioaccumulation of Cd in roots (Zhang et al., 2013). Experimental studies also have been proved that overexpression of *OsHMA3* can effectively elevate Cd retention in roots (Sasaki et al., 2014) and markedly decrease migration of Cd from rhizosphere to ground tissues (Lu et al., 2019).

Interestingly, the concentrations and BAFs of rice leaves were slightly lower than those in polished rice (t-test, $p = 0.045$), which was a little different from the previous result (root > stem > leaf > rice grain) (Liu et al., 2020), potentially indicating a stronger translocation capacity of Cd from leaves to grains via the phloem during the filling stage. The significantly lower concentrations and BAFs of Cd in the polished rice than in bran were found (t-test, $p < 0.01$), indicating that Cd was intensively distributed along the outside of rice grains, which agrees well with the μ-XRF evidence (Gu et al., 2020). More interestingly, a recent study found no correlations between Cd levels in bran and polished rice (Gu et al., 2020); however, a higher positive correlation was found in the present field study (Table S1, $r^2 = 0.92$, $p < 0.01$), which may imply similar water management measures for the sampling sites, because largely varied water management may change the supplementation of Cd from the pore water and ultimately affect the Cd distribution in grains (Gu et al., 2020).

The Cd biomass in rice tissues differs with concentrations and BAFs. As Fig. 1b shows, the varying trend of Cd biomass in the whole plants was as follows: whole plants (range: 14.67–1363.20 μg, mean: 381.25 ± 387.57 μg) > stems (range: 2.28–686.77 μg, mean: 195.56 ± 215.47 μg) > roots (range: 2.39–447.69 μg, mean: 127.97 ± 126.77 μg) > polished rice (range: 1.44–127.70 μg, mean: 36.55 ± 36.20 μg) > leaf (range: 0.15–45.11 μg, mean: 7.57 ± 10.57 μg) > bran (range: 0.29–27.53 μg, mean: 7.44 ± 7.88 μg) > husk (range: 0.02–31.78 μg, mean: 6.16 ± 7.69 μg). Nearly half of the total Cd was stored in the stems (51.3%), followed by roots (33.6%), polished rice (9.6%), leaves (2%), bran (2%), and husks (1.6%) (Fig. 1c). Given the much lower Cd biomass in rice grains than in other tissues, the Cd migration from stems or roots to grains was inferred to be inhibited extraordinarily. It was reported that nodes in stems play a role in preventing Cd from being transported to rice grains (Yamaguchi et al., 2012), which can partly explain the higher Cd

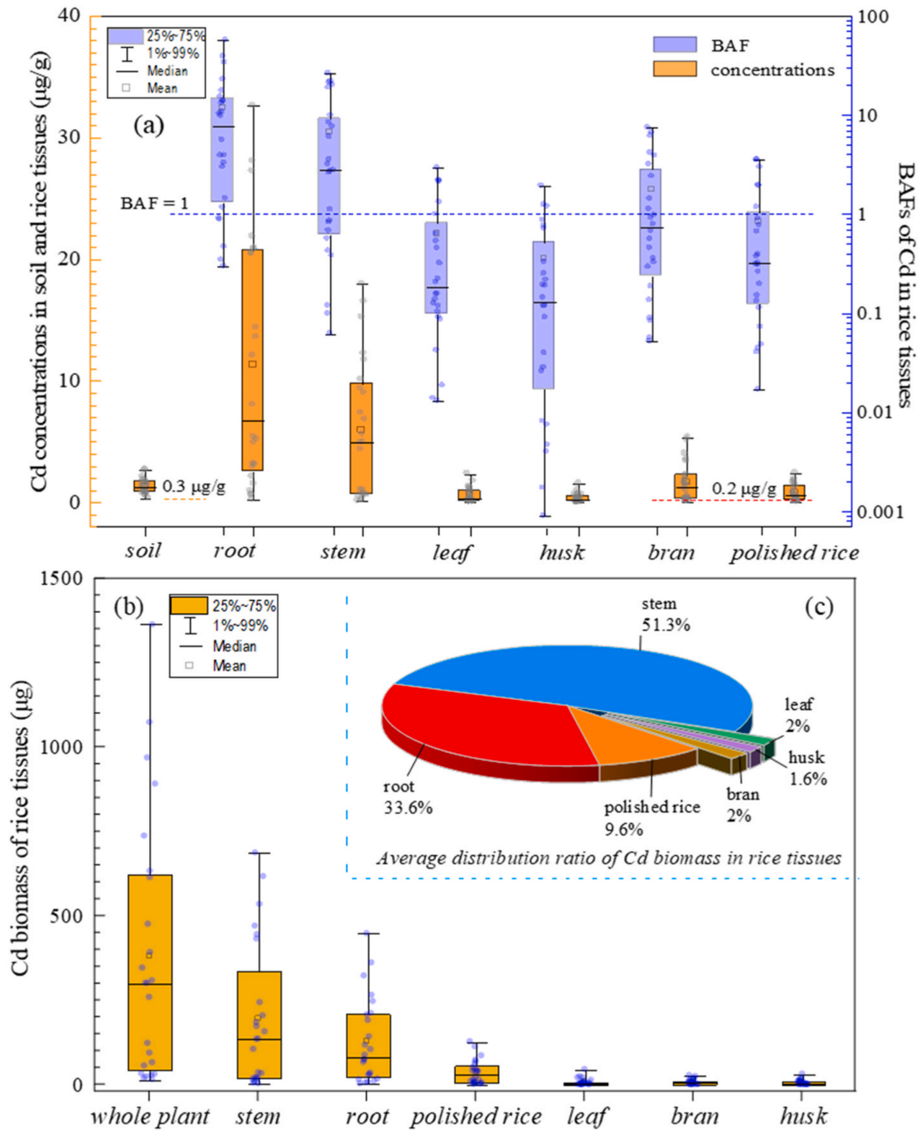

Fig. 1. Bioaccumulation patterns of concentrations, BAFs, and biomass of Cd in rice tissues collected in the Enshi seleniferous area.

bioaccumulation in stems. The Cd biomass in bran accounts for approximately 1/6 of the whole Cd in grains, meaning that a milling process would be feasible in reducing the Cd content in rice grains.

3.3. Se versus Cd in soils and rice tissues

Se-rich black shale was recognized as the potential source of Se in the soil (Chang et al., 2019a). Black shale is a special sedimentary rock abundant in organic matter and heavy metals (Duan et al., 2020), and its weathering and degradation by natural geological processes or anthropogenic activities may give rise to the heavy metals being released into the ambient (Yu et al., 2011). In this study, the Cd in soil was positively correlated with the soil Se ($r^2 = 0.46$, $p < 0.01$, Figure S3a), which indicates that Se and Cd may have the same source and Cd also derived from the Se-rich black shale.

The concentrations of Se in polished rice varied widely from 0.09 to 1.88 μg/g (average: 0.59 ± 0.42 μg/g), higher than the standards of Se-rich rice set by China (0.04–0.3 μg/g, GB 22499-2008) (Chang et al., 2019a). The average of Cd in the polished rice was 0.74 ± 0.71 μg/g (range: 0.028–1.89 μg/g), two-thirds of which exceeded the limit standard for rice in China (0.2 μg/g, GB 2762—2017). Here, it is worth emphasizing that the levels of Cd were inversely correlated to those of Se in the rice grains ($r^2 = 0.24$, $p < 0.01$) (Fig. 2, Table S2). Three points (the empty dots in Fig. 2, that was not included into the regression analysis) abnormally deviated from the fitted curve; however, the underlying causes still need to be further explored, given the complexity of field research. Similarly, inverse correlations of Se and Cd in other aerial tissues were also observed (Figure S3), which is contrary to the positive correlation of Se and Cd in soil ($r^2 = 0.46$, $p < 0.01$).

3.4. Preliminary risk assessment for Cd/Se co-exposure in the polished rice

In terms of the Chinese guidelines for Se-rich rice (40–300 ng/g, GB 22499-2008) and limits of Cd contamination in rice (<200 ng/g, GB 2762—2017), six types of polished rice could be characterized as: low Se/high Cd, low Se/low Cd, rich Se/high Cd, rich Se/low Cd, high Se/high Cd, and high Se/low Cd (Fig. 2). Only the rice type with rich Se/low Cd represents no intake risk for the locals, whereas other types still pose a risk to varying degrees. Notably, nearly all Se:Cd molar ratios of rice samples with rich Se/high Cd were lower than 1, possibly implying the limited ability for Se antagonizing with Cd when this type of rice is consumed by the locals. Low Se/high Cd or rich Se/high Cd types of rice are exceptionally harmful, representing a particularly excessive Cd

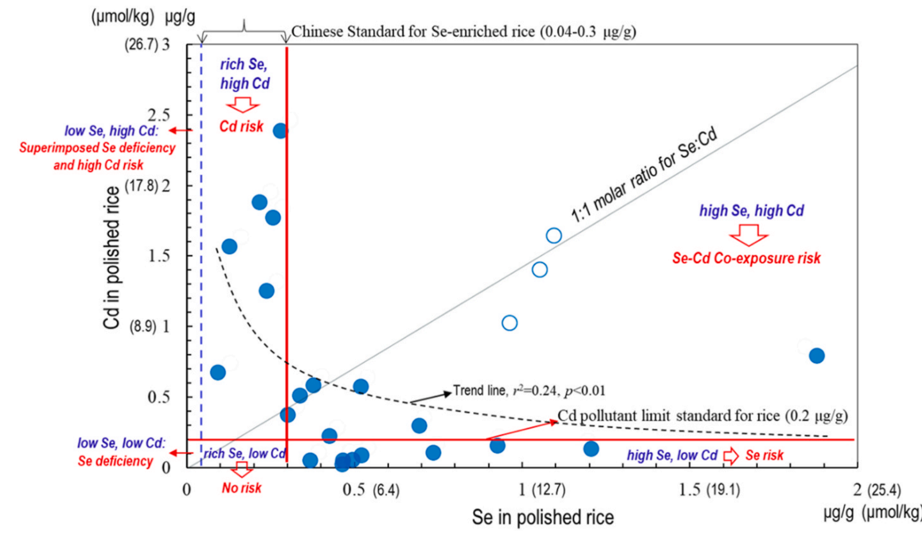

Fig. 2. Se versus Cd in the polished rice of Enshi samples.

intake risk. The high Se/low Cd rice may indicate a potential Se exposure risk due to the ample Se intake, approximately 252 ± 184 μg/day by consumption of rice (Chang et al., 2019b). Although selenosis would hardly occur based on the current Se intake levels in this study (selenosis generally involves Se intake >800 μg/day), long-term intake of high Se rice still should be avoided to control the total Se intake to not exceed 400 μg/day, as recommended by the Nutrition Society of China. However, it is hard to give a definite conclusion regarding such high Se/high Cd rice samples due to the lack of risk assessment criteria for high Se–Cd co-exposure for human bodies. The harmful effects of Cd on organisms could be mitigated by adequate Se intake (Chen et al., 2020). Generally, the total Cd intake, less than 60 μg/day, is safe for humans with 60 kg body weight (WHO, 1972). To avoid the adverse effect of long-term intake of Cd-containing rice (~315 μg/day for the locals, Huang et al., 2013) on the health, locals should be advised to limit ingesting much rice with excessive Cd (>0.2 μg/g), especially for rice with a Se:Cd molar ratio <1. The low Se/low Cd rice only indicates Se deficiency but was not found in the Enshi samples. Since the levels of Cd in rice can not be predicted by Cd in soil, the traditional knowledge for Cd risk analysis in rice is challenging. According to preliminary discussions above, the intake risk of these six types of rice grains might be ranked as follows: low Se/high Cd > rich Se/high Cd > high Se/high Cd > high Se/low Cd > low Se/low Cd > rich Se/low Cd. However, more practical investigations involving different Cd/Se co-exposure groups should be carried out to clarify the inference.

3.5. *Impact of Se on Cd translocation in soil-rice plants and possible mechanisms*

Soil is considered as the major source of Se in rice tissues (Qin et al., 2013). The Se and Cd in polished rice are all positively correlated to their levels in roots ($r^2 = 0.77$, $p < 0.01$, for Se; $r^2 = 0.74$, $p < 0.01$, for Cd), indicating that both Se and Cd in polished rice are contributed by roots that taking up Se and Cd from the soils. Interestingly, no positive correlations between Cd in soil and rice or between bioavailable Cd fractions and rice were found in the collected Enshi samples (Figure S2), which contradicts the general result, that a good correlation of Cd in rice grains and soil solutions was observed (Wen et al., 2020). The increased total or bioavailable Cd did not result in a subsequent increase in Cd in rice but rather showed a decreasing trend (Figure S2) in the study.

Selenium shows a robust impact on decreasing the Cd mobility in soils and the uptake capacity by roots (Affholder et al., 2019). In previous soil culture experiments, applying only 0.5 μg/g of sodium selenite reduced the transport capacity of Cd from the soils to the iron plaque of roots by 71%, and the Cd concentrations in rice dropped by 44.4% (Hu et al., 2014). It is worth noting that the soil Se concentrations range from 0.85 to 11.46 μg/g in this study (Chang et al., 2019a), even higher than the added Se mentioned above. It is speculated that strong interactions of Se and Cd may exist in the Enshi acidic paddy soils (Fig. 3). The unusual non-correlation between Cd in soils and rice tissues (Table S1) may indicate that uptake and mobility of Cd from soils to roots were largely inhibited. Under flooded conditions, species transformation of Se from the high valence to low valence ($SeO_4^{2-} \rightarrow SeO_3^{2-} \rightarrow Se^0 \rightarrow Se^{2-}$) generally occurs in the soil-water system (Wang et al., 2019d). In the cornfield rich in Se and Cd, the antagonistic effect of Se on Cd was found in corn plants, especially when the bioavailable Se:Cd molar ratio (range: 0.4–1.1) of the soil >0.7 (Zhang et al., 2019), whereas the soil Se:Cd molar ratio averagely reached 5.42 (range: 1.50–12.87) in this study. A negative linear correlation between the Se:Cd molar ratios of soils and the concentrations of Cd in rice was found ($r^2 = 0.15$, $p = 0.058$), which resembles that of the study on corn by Zhang et al. (2019). However, the threshold effect between the soil Se:Cd molar ratio and the bioaccumulation of Cd was not found in this study, which differs from the previous corn study. The lack of threshold effect here might be ascribed to the much higher soil Se and Se:Cd molar ratios than the study by Zhang et al. (2019). In addition, the Se(IV) and elemental Se(0) account for 19–44% and 6.1–14.9% of the total soil Se respectively in Enshi (Qin et al., 2017). Thus, it may provide a considerable abundance of reductive Se to interact with Cd and form Cd–Se complexes in soils.

Selenium also plays a part in immobilizing Cd among plants tissues by direct or indirect interactions with Cd. Here, a negative correlation of roots Se and TF ($C_{polished\ rice}/C_{root}$) was found ($r^2 = 0.25$, $p < 0.05$, Fig. 4a), indicating that Cd translocation from roots to polished rice was inhibited by the increased roots Se. Se(IV) is the major available species for rice roots taking up Se from acidic soil under flooded conditions (Li et al., 2010). After being taken up by rice roots, selenite (Se^{+4}) may rapidly be reduced into organic Se (Li et al., 2008), like the form of C–Se–C (Zhao et al., 2013), then complicated CdSe/CdS inert complexes may be formed in tissues. The increased Se not only brings about selenocysteine and selenoproteins rich in selenols (-SeH) but also induces the increased formation of glutathione (GSH) (Srivastava et al., 2009) and phytochelatins (PCs) (Wan et al., 2016). These substances rich in sulfhydryl (-SH) functional groups have a strong ability to chelate Cd ions (Yadav, 2010). Additionally, –SH groups can also be replaced by -SeH groups due to the higher chemical activity of –SeH (Arnér, 2010). PC with -SeH can preferentially chelate Cd^{2+} to form Cd–Se inert substances, which are then transported to vacuoles to restrict the mobility of Cd from roots to grains (Ismael et al., 2019; Riaz et al., 2021). The

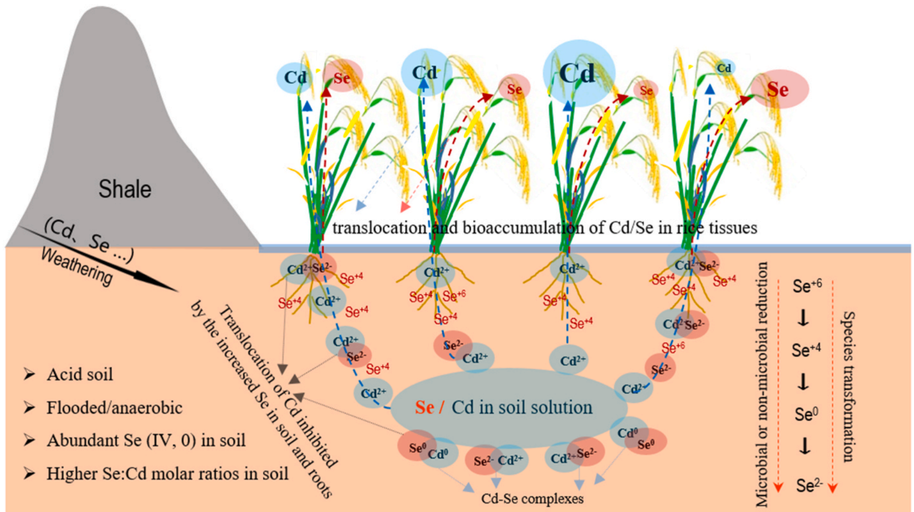

Fig. 3. Translocation and potential interactions of Se and Cd in the rice paddy ecosystem of Enshi seleniferous area.

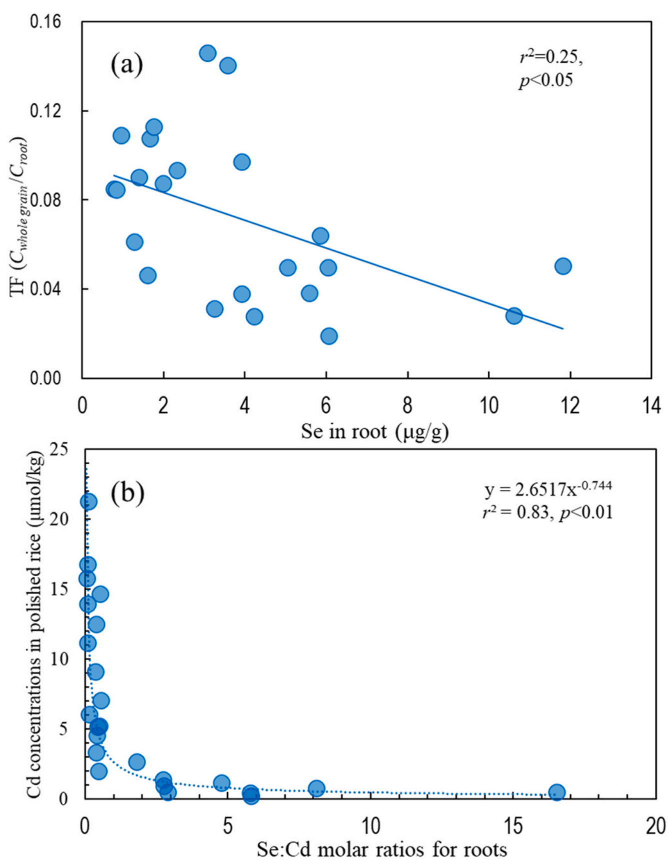

Fig. 4. (a) Impact of root Se on TF($C_{whole\ grain}/C_{root}$) of Cd; (b) Impact of root Se: Cd molar ratios on Cd concentrations in polished rice collected from Enshi samples.

inhibitory impact of the increased Se on Cd mobility causes a certain amount of Cd retention in roots and a reduction in seeds, as found in this study (Fig. 2, Figure S3) and the oilseed rape study by Zhao et al. (2019). More interestingly, a significant negative correlation was found between the Cd in rice seeds and the Se:Cd molar ratios of roots ($r^2 = 0.83$, $p < 0.01$, Fig. 4b), which demonstrates that the rapidly increased Se relative to Cd largely affected Cd translocation from roots to rice seeds. As Fig. 4b shows, there would be an active Se–Cd interaction when the root Se:Cd molar ratio was <3:1, while weaker at > 3:1. However, the hydroponic experiment by Guo et al. (2021) finds that the interaction of Se and Cd may get weaker at Se:Cd molar ratio greater than 1. These may indicate that the Se–Cd interaction in roots is somewhat different between the field and hydroponics study. Additionally, selenomethionine was found to combine with Cd in corn leaves by using the HPLC-ICPMS technique (Zhang et al., 2019). Also, deeper identification on the Cd or Se species should be done to compare enough this study to the previous corn study in the following work.

4. Conclusions and environmental implications

The unusual translocation and bioaccumulation patterns of Cd in the shale-soil-rice system are worthy of attention in the Enshi region. In this study, the acidic soil environment, the higher total Se, reductive Se species, and molar ratios of Se:Cd, may favor the interaction of Cd with Se in the system of soil and rice plants. The increased Se levels in soil and roots greatly affect the geochemical fate of Cd, which may primarily result in the inverse distribution of Se and Cd in polished rice at this natural seleniferous area. The rice with high Cd/insufficient Se may have a very higher food safety risk. Unfortunately, this type of rice is not easily identified by determining the soil Cd based on the observed non-positive correlation between Cd in soils and rice. Therefore, the necessary investigation of Cd in the rice paddy ecosystem is suggested to be conducted to avoid the production of Se-rich rice but containing high levels of Cd. The real added-value of the study is that it enlightens us to ponder how to formulate a scientific risk assessment method to take a new look at the risks of Cd in the paddy soils-crops-consumers chain, considering the interaction of Cd and Se. More practical fieldwork and direct evidence are needed to deeply reveal the antagonism actions of Cd and Se along with this chain. One point is that toxicity or bioaccessibility of Cd, no matter in local foods or humans, may be weakened by the presence of Se. Some primary investigations found that the Cd-induced nephrotoxicity might be alleviated by Se in the residents of Enshi (Chen et al., 2020) and Shitai (Yang et al., 2021). In addition, direct characterization on Se–Cd complexes, such as by XANES, μ-XRF, and UHPLC-Q-Exactive Orbitrap MS evidence will be expected to more deeply reveal the mechanism of Se antagonizing Cd in this naturally Se and Cd enriched area. Many scientific studies still need to be conducted to better serve the local eco-environment, functional agriculture, and people's health.

Author statement

Chuanyu Chang: Conceptualization, Methodology, Software, Data curation, Funding acquisition, Writing – original draft, Writing-Reviewing and Editing. Hua Zhang: Funding acquisition, Supervision, Writing- Reviewing and Editing. Fang Huang: Resources. Xinbin Feng: Resources, Writing-Reviewing and 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.

Acknowledgments

This research was funded by the State Key Laboratory of Environmental Geochemistry (SKLEG 2021209), the China Postdoctoral Science Foundation (2021M703057), the National Natural Science Foundation of China (41573125), and the Metal Stable Isotope Geochemistry Lab in the University of Science and Technology of China (USTC). This study also thanks the editor and five anonymous reviewers for their constructive suggestions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.118927.

References

Affholder, M.-C., Flöhr, A., Kirchmann, H., 2019. Can Cd content in crops be controlled by Se fertilization? A meta-analysis and outline of Cd sequestration mechanisms. Plant Soil 440, 369–380.
Arnér, E.S.J., 2010. Selenoproteins—what unique properties can arise with selenocysteine in place of cysteine? Exp. Cell Res. 316, 1296–1303.
Baba, H., Tsuneyama, K., Yazaki, M., Nagata, K., Minamisaka, T., Tsuda, T., Nomoto, K., Hayashi, S., Miwa, S., Nakajima, T., Nakanishi, Y., Aoshima, K., Imura, J., 2013. The liver in itai-itai disease (chronic cadmium poisoning): pathological features and metallothionein expression. Mod. Pathol. 26, 1228–1234.
Chang, C., Yin, R., Wang, X., Shao, S., Chen, C., Zhang, H., 2019a. Selenium translocation in the soil-rice system in the Enshi seleniferous area, Central China. Sci. Total Environ. 669, 83–90.
Chang, C., Yin, R., Zhang, H., Yao, L., 2019b. Bioaccumulation and health risk assessment of heavy metals in the soil-rice system in a typical seleniferous area in Central China. Environ. Toxicol. Chem. 38, 1577–1584.
Chen, H., Yang, X., Wang, P., Wang, Z., Li, M., Zhao, F.J., 2018. Dietary cadmium intake from rice and vegetables and potential health risk: a case study in Xiangtan, southern China. Sci. Total Environ. 639, 271–277.
Chen, J., He, W., Zhu, X., Yang, S., Yu, T., Ma, W., 2020. Epidemiological study of kidney health in an area with high levels of soil cadmium and selenium: does selenium protect against cadmium-induced kidney injury? Sci. Total Environ. 698, 134106.
Dinh, Q., Cui, Z., Huang, J., Tran, T., Wang, D., Yang, W., Zhou, F., Wang, M., Yu, D., Liang, D., 2018. Selenium distribution in the Chinese environment and its relationship with human health: a review. Environ. Int. 112, 294–309.
Dou, W.Q., An, Y., Qin, L., Lin, D.S., Zeng, Q.N., Xia, Q., 2020. Advances in effects of soil pH on cadmium form. Soils 52, 439–444.
Duan, Y., Yang, Z., Yu, T., Yang, Q., Liu, X., Ji, W., Jiang, H., Zhuo, X., Wu, T., Qin, J., Wang, L., 2020. Geogenic cadmium pollution in multi-medians caused by black shales in Luzhai, Guangxi. Environ. Pollut. 260, 113905.
Feng, R., Zhao, P., Zhu, Y., Yang, J., Wei, X., Yang, L., Liu, H., Rensing, C., Ding, Y., 2021. Application of inorganic selenium to reduce accumulation and toxicity of heavy metals (metalloids) in plants: the main mechanisms, concerns, and risks. Sci. Total Environ. 771, 144776.
Gasiewicz, T.A., Smith, J.C., 1976. Interactions of cadmium and selenium in rat plasma in vivo and in vitro. BBA-Gen Subjects 428, 113–122.
Gu, Y., Wang, P., Zhang, S., Dai, J., Chen, H.P., Lombi, E., Howard, D.L., van der Ent, A., Zhao, F.J., Kopittke, P.M., 2020. Chemical speciation and distribution of cadmium in rice grain and implications for bioavailability to humans. Environ. Sci. Technol. 54, 12072–12080.
Guo, Y., Mao, K., Cao, H., Ali, W., Lei, D., Teng, D., Chang, C., Yang, X., Yang, Q., Niazi, N.K., Feng, X., Zhang, H., 2021. Exogenous selenium (cadmium) inhibits the absorption and transportation of cadmium (selenium) in rice. Environ. Pollut. 268, 115829.
Hu, B., Xue, J., Zhou, Y., Shao, S., Fu, Z., Li, Y., Chen, S., Qi, L., Shi, Z., 2020. Modelling bioaccumulation of heavy metals in soil-crop ecosystems and identifying its controlling factors using machine learning. Environ. Pollut. 262, 114308.
Hu, Y., Norton, G.J., Duan, G., Huang, Y., Liu, Y., 2014. Effect of selenium fertilization on the accumulation of cadmium and lead in rice plants. Plant Soil 384, 131–140.
Huang, B., Xin, J., Dai, H., Zhou, W., 2017. Effects of interaction between cadmium (Cd) and selenium (Se) on grain yield and Cd and Se accumulation in a hybrid rice (Oryza sativa) system. J. Agric. Food Chem. 65, 9537–9546.
Huang, H., Li, M., Rizwan, M., Dai, Z., Yuan, Y., Hossain, M.M., Cao, M., Xiong, S., Tu, S., 2021. Synergistic effect of silicon and selenium on the alleviation of cadmium toxicity in rice plants. J. Hazard Mater. 401, 123393.
Huang, Q., Xu, Y., Liu, Y., Qin, X., Huang, R., Liang, X., 2018. Selenium application alters soil cadmium bioavailability and reduces its accumulation in rice grown in Cd-contaminated soil. Environ. Sci. Pollut. Res. 25, 31175–31182.
Huang, Y., Wang, Q., Gao, J., Lin, Z., Banuelos, G.S., Yuan, L., Yin, X., 2013. Daily dietary selenium intake in a high selenium area of Enshi, China. Nutrients 5, 700–710.
Ismael, M.A., Elyamine, A.M., Moussa, M.G., Cai, M., Zhao, X., Hu, C., 2019. Cadmium in plants: uptake, toxicity, and its interactions with selenium fertilizers. Metallomics 11, 255–277.
Jihen, E.H., Imed, M., Fatima, H., Abdelhamid, K., 2009. Protective effects of selenium (Se) and zinc (Zn) on cadmium (Cd) toxicity in the liver of the rat: effects on the oxidative stress. Ecotoxicol. Environ. Saf. 72, 1559–1564.
Li, S., Banuelos, G.S., Wu, L., Shi, W., 2014. The changing selenium nutritional status of Chinese residents. Nutrients 6, 1103–1114.
Li, H.F., McGrath, S.P., Zhao, F.J., 2008. Selenium uptake, translocation and speciation in wheat supplied with selenate or selenite. New Phytol. 178, 92–102.
Li, H.F., Lombi, E., Stroud, J.L., McGrath, S.P., Zhao, F.J., 2010. Selenium speciation in soil and rice: influence of water management and Se fertilization. J. Agric. Food Chem. 58, 11837–11843.
Liu, N., Jiang, Z., Li, X., Liu, H., Li, N., Wei, S., 2020. Mitigation of rice cadmium (Cd) accumulation by joint application of organic amendments and selenium (Se) in high-Cd-contaminated soils. Chemosphere 241, 125106.
Lu, C., Zhang, L., Tang, Z., Huang, X.Y., Ma, J.F., Zhao, F.J., 2019. Producing cadmium-free Indica rice by overexpressing OsHMA3. Environ. Int. 126, 619–626.
Ma, L.Q., Rao, G.N., 1997. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. J. Environ. Qual. 26, 259.
Miyadate, H., Adachi, S., Hiraizumi, A., Tezuka, K., Nakazawa, N., Kawamoto, T., Katou, K., Kodama, I., Sakurai, K., Takahashi, H., Satoh-Nagasawa, N., Watanabe, A., Fujimura, T., Akagi, H., 2011. OsHMA3, a P1B-type of ATPase affects root-to-shoot cadmium translocation in rice by mediating efflux into vacuoles. New Phytol. 189, 190–199.
Mu, T., Wu, T., Zhou, T., Li, Z., Ouyang, Y., Jiang, J., Zhu, D., Hou, J., Wang, Z., Luo, Y., Christie, P., Wu, L., 2019. Geographical variation in arsenic, cadmium, and lead of soils and rice in the major rice producing regions of China. Sci. Total Environ. 677, 373–381.
Navarro, D.A., Bisson, M.A., Aga, D.S., 2012. Investigating uptake of water-dispersible CdSe/ZnS quantum dot nanoparticles by Arabidopsis thaliana plants. J. Hazard Mater. 211–212, 427–435.
Qin, H.B., Zhu, J.M., Liang, L., Wang, M.S., Su, H., 2013. The bioavailability of selenium and risk assessment for human selenium poisoning in high-Se areas, China. Environ. Int. 52, 66–74.
Qin, H.B., Zhu, J.M., Lin, Z.Q., Xu, W.P., Tan, D.C., Zheng, L.R., Takahashi, Y., 2017. Selenium speciation in seleniferous agricultural soils under different cropping systems using sequential extraction and X-ray absorption spectroscopy. Environ. Pollut. 225, 361–369.
Rahman, Z., Singh, V.P., 2019. The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. Environ. Monit. Assess. 191, 419.
Rayman, M.P., 2012. Selenium and human health. Lancet 379, 1256–1268.
Riaz, M., Kamran, M., Rizwan, M., Ali, S., Parveen, A., Malik, Z., Wang, X., 2021. Cadmium uptake and translocation: synergetic roles of selenium and silicon in Cd detoxification for the production of low Cd crops: a critical review. Chemosphere 273, 129690.
Sasaki, A., Yamaji, N., Ma, J.F., 2014. Overexpression of OsHMA3 enhances Cd tolerance and expression of Zn transporter genes in rice. J. Exp. Bot. 65, 6013–6021.
Sasaki, A., Yamaji, N., Yokosho, K., Ma, J.F., 2012. Nramp5 is a major transporter responsible for manganese and cadmium uptake in rice. Plant Cell 24, 2155–2167.
Schiavon, M., Nardi, S., Dalla Vecchia, F., Ertani, A., 2020. Selenium biofortification in the 21(st) century: status and challenges for healthy human nutrition. Plant Soil 1–26.
Shanker, K., Mishra, S., Srivastava, S., Srivastava, R., Dass, S., Prakash, S., Srivastava, M. M., 1995. Effect of selenite and selenate on plant uptake of cadmium by kidney bean (Phaseolus mungo) with reference to Cd—Se interaction. Chem. Speciat. Bioavailab. 7, 97–100.
Smolders, E., 2001. Cadmium uptake by plants. Int. J. Occup. Med. Environ. Health 14 (2), 177–183.
Song, Y., Wang, Y., Mao, W., Sui, H., Yong, L., Yang, D., Jiang, D., Zhang, L., Gong, Y., 2017. Dietary cadmium exposure assessment among the Chinese population. PLoS One 12, e0177978.
Sun, G.X., Xiao, L., Williams, P.N., Zhu, Y.G., 2010. Distribution and translocation of selenium from soil to grain and its speciation in paddy rice (Oryza sativa L.). Environ. Sci. Technol. 44, 6706–6711.
Srivastava, M., Ma, L.Q., Rathinasabapathi, B., Srivastava, P., 2009. Effects of selenium on arsenic uptake in arsenic hyperaccumulator Pteris vittata L. Bioresour. Technol. 100, 1115–1121.
Wan, Y., Yu, Y., Wang, Q., Qiao, Y., Li, H., 2016. Cadmium uptake dynamics and translocation in rice seedling: influence of different forms of selenium. Ecotoxicol. Environ. Saf. 133, 127–134.

Wang, P., Chen, H., Kopittke, P.M., Zhao, F.J., 2019a. Cadmium contamination in agricultural soils of China and the impact on food safety. Environ. Pollut. 249, 1038–1048.
Wang, J., Wang, P.M., Gu, Y., Kopittke, P.M., Zhao, F.J., Wang, P., 2019b. Iron-Manganese (Oxyhydro)oxides, rather than oxidation of sulfides, determine mobilization of Cd during soil drainage in paddy soil systems. Environ. Sci. Technol. 53, 2500–2508.
Wang, T., Li, Y., Fu, Y., Xie, H., Song, S., Qiu, M., Wen, J., Chen, M., Chen, G., Tian, Y., Li, C., Yuan, D., Wang, J., Li, L., 2019c. Mutation at different sites of metal transporter gene OsNramp5 affects Cd accumulation and related agronomic traits in rice (Oryza sativa L.). Front. Plant Sci. 10, 1081.
Wang, D., Xia, X., Wu, S., Zheng, S., Wang, G., 2019d. The essentialness of glutathione reductase GorA for biosynthesis of Se(0)-nanoparticles and GSH for CdSe quantum dot formation in Pseudomonas stutzeri TS44. J. Hazard Mater. 366, 301–310.
Wei, F.S., Chen, J.S., Wu, Y.Y., Zheng, C.J., 1991. Study on the background contents on 61 elements of soils in China. Chin. J. Environ. Sci. 12, 12–19 (In Chinese with English abstract).
Wen, Y., Li, W., Yang, Z., Zhuo, X., Guan, D.X., Song, Y., Guo, C., Ji, J., 2020. Evaluation of various approaches to predict cadmium bioavailability to rice grown in soils with high geochemical background in the karst region, Southwestern China. Environ. Pollut. 258, 113645.
WHO, 1972. WHO. Evaluation of certain food additives and the contaminants mercury, lead, and cadmium. In: Additives, SRotJFWECoF. (Ed.), World Health Organization Technical Report Series No. 505, FAO Nutrition Meetings Report Series No. 51. Geneva, Switzerland, 1972.
Yadav, S.K., 2010. Heavy metals toxicity in plants: an overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. South Afr. J. Bot. 76, 167–179.
Yamaguchi, N., Ishikawa, S., Abe, T., Baba, K., Arao, T., Terada, Y., 2012. Role of the node in controlling traffic of cadmium, zinc, and manganese in rice. J. Exp. Bot. 63, 2729–2737.
Yang, R., He, Y., Luo, L., Zhu, M., Zan, S., Guo, F., Wang, B., Yang, B., 2021. The interaction between selenium and cadmium in the soil-rice-human continuum in an area with high geological background of selenium and cadmium. Ecotoxicol. Environ. Saf. 222, 112516.
Yao, L., Gao, Z., Yang, Z., Long, H., 2002. Origin of seleniferous cherts in yutangba Se deposit, southwest Enshi, Hubei province. Sci. China, Ser. A D 45, 741–754.
Yu, C., Peng, B., Peltola, P., Tang, X., Xie, S., 2011. Effect of weathering on abundance and release of potentially toxic elements in soils developed on Lower Cambrian black shales, P. R. China. Environ. Geochem. Health 34, 375–390.
Yu, T., Yang, Z., Wang, R., Zeng, Q., Hou, W., 2018. Characteristics and sources of soil selenium and other elements in typical high selenium soil area of Enshi. Soils 50, 1119–1125 (In Chinese with English abstract).
Yu, T., Hou, W., Hou, Q., Ma, W., Xia, X., Li, Y., Yan, B., Yang, Z., 2020. Safe utilization and zoning on natural selenium-rich land resources: a case study of the typical area in Enshi County, China. Environ. Geochem. Health 42, 2803–2818.
Zhang, C., Yin, X., Gao, K., Ge, Y., Cheng, W., 2013. Non-protein thiols and glutathione S-transferase alleviate Cd stress and reduce root-to-shoot translocation of Cd in rice. J. Plant Nutr. Soil Sci. 176, 626–633.
Zhang, Z., Yuan, L., Qi, S., Yin, X., 2019. The threshold effect between the soil bioavailable molar Se:Cd ratio and the accumulation of Cd in corn (Zea mays L.) from natural Se-Cd rich soils. Sci. Total Environ. 688, 1228–1235.
Zhao, F.J., Ma, Y., Zhu, Y.G., Tang, Z., McGrath, S.P., 2015. Soil contamination in China: current status and mitigation strategies. Environ. Sci. Technol. 49, 750–759.
Zhao, Y., Hu, C., Wu, Z., Liu, X., Cai, M., Jia, W., Zhao, X., 2019. Selenium reduces cadmium accumulation in seed by increasing cadmium retention in root of oilseed rape (Brassica napus L.). Environ. Exp. Bot. 158, 161–170.
Zhao, J., Hu, Y., Gao, Y., Li, Y., Li, B., Dong, Y., Chai, Z., 2013. Mercury modulates selenium activity via altering its accumulation and speciation in garlic (Allium sativum). Metallomics 5, 896–903.
Zhou, J., Zhang, C., Du, B., Cui, H., Fan, X., Zhou, D., Zhou, J., 2021. Soil and foliar applications of silicon and selenium effects on cadmium accumulation and plant growth by modulation of antioxidant system and Cd translocation: comparison of soft vs. durum wheat varieties. J. Hazard Mater. 402, 123546.