



Selenium translocation in the soil-rice system in the Enshi seleniferous area, Central China



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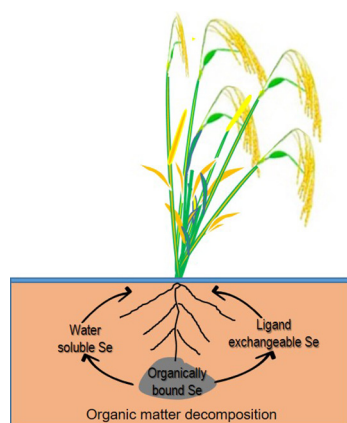
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HIGHLIGHTS

- Translocation of Se in soil-rice system is affected by organic matter.
- Organic matter decomposition promotes the transformation of O-Se to W-Se and L-Se.
- W-Se, L-Se and O-Se are the major sources of Se in rice tissues.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 December 2018

Received in revised form 26 February 2019

Accepted 28 February 2019

Available online 1 March 2019

Editor: Daniel CW Tsang

Keywords:

Selenium

Soil

Rice

Transformation

Translocation

Enshi, China

ABSTRACT

Rice is an important source of selenium (Se) exposure; however, the transformation and translocation of Se in the soil-rice system remain poorly understood. Here, we investigated the speciation of Se in Se-rich soils from Enshi, Central China and assessed which Se species is bioavailable for rice grown in Enshi. Extremely high Se concentrations (0.85 to 11.46 mg/kg) were observed in the soils. The soil Se fractions, which include water-soluble Se (0.2 to 3.4%), ligand-exchangeable Se (4.5 to 15.0%), organically bound Se (57.8 to 80.0%) and residual Se (6.1 to 32.9%), are largely controlled by soil organic matter (SOM) levels. Decomposition of SOM promotes the transformation of organically bound Se to water-soluble Se and ligand-exchangeable Se, thereby increasing the bioavailability of Se. The bioaccumulation factors (BAFs) of Se decrease in the following order: roots (0.84 ± 0.30) > bran (0.33 ± 0.17) > leaves (0.18 ± 0.09) > polished rice (0.14 ± 0.07) > stems (0.12 ± 0.07) > husks (0.11 ± 0.07). Selenium levels in rice plants are affected by multiple soil Se fractions in the soil. Water-soluble, ligand-exchangeable and organically bound Se fractions are the major sources of Se in rice tissues.

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1. Introduction

Selenium (Se) is a naturally occurring metalloid element that is essential to human health in trace amounts (suggested adequate dietary requirement level of 40 µg/day) but is toxic in excess (>800 µg/day) (Yang and Xia, 1995; Zhang et al., 2014a). In organisms, Se acts as an antioxidant preventing the degeneration of biological membranes and plays a crucial role in reducing the incidence of cancer and cardiovascular disease (Navarro-Alarcón and López-Martínez, 2000; Rayman, 2012). Selenium deficiency causes Keshan disease (which leads to myocardial necrosis) and Kashin-Beck disease (which leads to atrophy, degeneration, and necrosis of cartilage tissue in joints), whereas Se poisoning causes hair and nail loss and disorders of the nervous system (Rayman, 2012; Natasha et al., 2018).

The average crustal abundance of Se is low (0.05 µg/g) (Fordyce, 2013); however, organic-rich sedimentary rocks (e.g., mudstones, coals and shales) can be rich in Se (Zhu et al., 2014). Selenium has five oxidation states (+6, +4, 0, −1, and −2). Selenium mainly occurs in reduced states in rocks. Weathering of rocks converts Se to oxidized species (e.g., SeO_3^{2-} and SeO_4^{2-}) and releases Se to the environment (Winkel et al., 2011; Zhu et al., 2014). A positive correlation between Se concentrations in soils and geological parent materials is often observed (Dhillon and Dhillon, 2014; Kulp and Pratt, 2004; Schilling et al., 2015). Seleniferous area can be found in many countries including Australia, China, India, Ireland and the USA (Dhillon and Dhillon, 2003), especially in Punjab, India (Dhillon and Dhillon, 2014; Eiche et al., 2015) and Enshi, China (Zhu et al., 2008). As the “selenium capital of China”, Enshi is the world’s sole independent selenium deposit (Zhu, 2004). Toxic levels of Se have been reported in shales and soils in Enshi (Zheng et al., 1992; Zhu et al., 2008). In the 1960s, Se poisoning in the local population of Enshi, which was caused by a large amount of selenium intake over short periods of time, attracted much attention around the world (Yang et al., 1983; Zhu et al., 2008).

High levels of Se have been reported in plants (e.g., rice, wheat, corn and mustard) grown in Se contaminated sites (Zhu and Zheng, 2001; Wang et al., 2012; Sharma et al., 2014; Eiche et al., 2015; Cui et al., 2018; Both et al., 2018; Shen et al., 2019; Qin et al., 2013). Rice, a staple, has been demonstrated to be the most important source of human exposure to Se in Enshi and Wanshan, China (Qin et al., 2013; Zhang et al., 2014a). Selenium is not an essential element for plant (White, 2018), but it can regulate metabolic and physiological processes during rice growth (Andrade et al., 2018; Gao et al., 2018; Yin et al., 2019). Although studies have shown that plant leaves can absorb Se from the atmosphere (Haygarth et al., 1993; Haygarth et al., 1995; Terry et al., 2000), it is commonly believed that the uptake of Se from soil is the dominant pathway contributing to Se levels in plants (Haygarth et al., 1995; Qin et al., 2013; Zhang et al., 2014b). The bioavailability of Se in soil, however, is controlled by its chemical speciation or fraction (Wadgaonkar et al., 2018; Dinh et al., 2018a). According to the chemical extraction method, Se in soil can be divided into four fractions: water-soluble Se (W-Se), ligand-exchangeable Se (L-Se), organically bound Se (O-Se), and residual Se (R-Se) (Qin et al., 2012; Schilling et al., 2014; Zhang et al., 2014b). Among these fractions, W-Se and L-Se, which mainly consist of soluble or partially soluble Se compounds, are of great concern due to their large bioavailability (Chao and Sanzalone, 1989; Kulp and Pratt, 2004; Zhang et al., 2014b). O-Se represents Se species that are bound to organic matter (Kulp and Pratt, 2004; Qin et al., 2012; Séby et al., 1997) and is the dominant fraction of Se in Enshi soils (Qin et al., 2012; Qin et al., 2013; Qin et al., 2017). However, the bioavailability of O-Se remains unclear due to the strong binding of Se by organic matter. R-Se, which includes sulfide-, Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se species, is less concerning due to its low bioavailability (Qin et al., 2013).

The transformation of Se in soils is controlled by many factors such as pH and total organic carbon (TOC) which further affect the

translocation of Se in plants (Wang et al., 2017, 2018, 2019; Dinh et al., 2017). To date, the transformation and translocation of Se in the soil-rice system, especially in areas with high background Se levels, remains not well understood. In this study, co-located rice plants were collected at Se-rich sites in Enshi. Soil Se fractions and geochemical parameters (pH and TOC) were measured to determine the mechanism of Se transformation in soils. Selenium concentrations and mass distributions in rice tissues (roots, stems, leaves and grains) were also investigated. Through correlation analysis of Se concentrations between rice tissues and soil Se fractions, this study aimed to specify which soil Se fractions are bioavailable for rice.

2. Materials and methods

2.1. Study area, sampling and sample preparation

Enshi, located in Hubei Province, Central China (Fig. 1), has a subtropical monsoon climate, with hot summer and cold winter. The annual temperature and annual precipitation in Enshi are 16 °C and ~1600 mm, respectively (Qin et al., 2013). Carbonaceous shale and carbonaceous chert strata are the major source rocks of Se in Enshi (Zhu, 2004). The Se-rich rocks in Enshi have been mined for many years. Mining and weathering have caused intense Se release into the environment (Zhu, 2004; Zhu et al., 2008). Extremely high levels of Se have been observed in soils, sediments, plants, and human hair (Dinh et al., 2018b; Huang et al., 2013; Qin et al., 2013; Zheng et al., 1992).

In September 2016, rice plants and soils were collected at 24 sites in Enshi. The locations (longitude and latitude) of the sampling sites are recorded and shown in Fig. 1. At each site, three 2 × 2 m plots were established for sample collection. At each plot, three rice plants and corresponding rhizosphere soils (0–20 cm depth) were randomly sampled. The subsamples from the three plots were mixed as a composite sample. Samples were sealed in plastic bags before their delivery to the laboratory. Soil samples were freeze-dried (−79 °C), crushed, homogenized, and sieved at 200 mesh. For rice plants, different tissues (roots, stems, leaves and grains) were separated, washed thoroughly with tap water followed by 18.2 MΩ water (Milli-Q® Integral system), dried in an oven (35 °C) and weighed. The grain samples were further separated into hulls, bran, and polished rice. Rice tissue samples were then powdered using a grinding machine (IKA®A11 basic). Before each sample was prepared, the machine was cleaned with alcohol to avoid cross-contamination. All soil and rice tissue samples were sealed in polyester plastic bags and stored at room temperature.

2.2. Chemical analysis

All chemical analyses were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (SKLEG-IGCAS). Soil pH was determined by a PHS-3C pH meter, and TOC and total sulfur (TS) concentrations were determined by an elemental analyser (vario MACRO cube) (Qin et al., 2012; Wang et al., 2013).

Total Se concentrations (TSe) of the soil and rice tissue samples were measured using a previous method (Zhu et al., 2008). Briefly, approximately 50 mg of the soil samples and approximately 0.1 to 0.2 g of the rice tissue samples were weighed into 15 mL Teflon bombs. For the soil samples, 2.5 mL of 16 mol/L HNO_3 and 0.5 mL of 57 mol/L HF were added into the bombs. For the rice tissue sample, 3 mL of 16 mol/L HNO_3 was added. Each bomb was placed in a steel can and heated on a hot plate at 150 °C for 16 h, when the solution was clear. Thereafter, the bombs were removed from their cans, had their tops screwed open, were supplemented with 2 mL of 30% (v/v) H_2O_2 , and were heated on a hot plate (90 °C) until the solution was evaporated to near dryness. The residual solution was added to 3 mL of 6 mol/L HCl and heated in a water bath (95 °C) for 2 h. The final solution was diluted to 15 mL with 18.2 MΩ water for hydride generation atomic

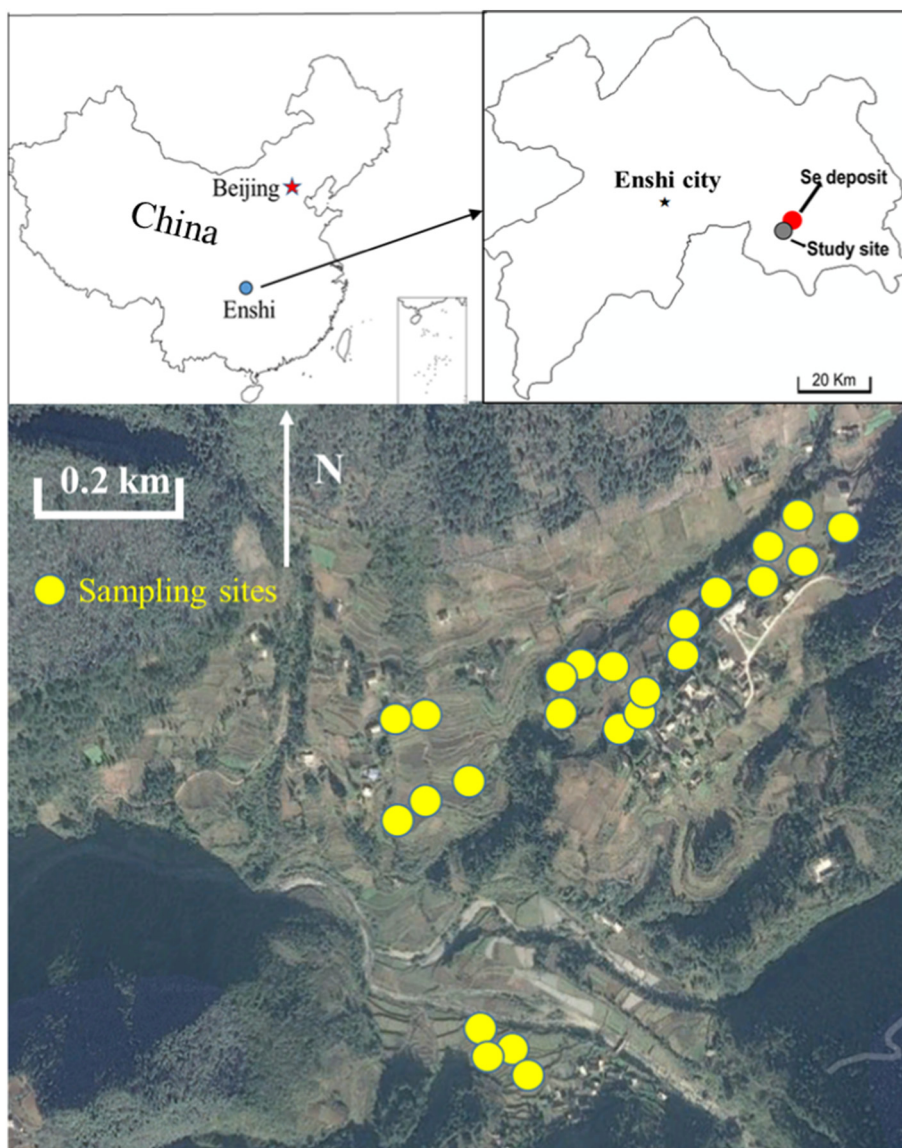


Fig. 1. A sketch map showing the study area and sampling sites.

fluorescence spectrometry analysis (LC-AFS 9700, BJHG, China). Standard reference materials (SRMs) GBW07405 and GBW10020 and sample replicates were included for the quality control. Recoveries of TSe were 88.9% to 104.9% for the SRMs, and the relative standard deviation of sample duplicates was within 10%.

A previously standardized sequential extraction method was used to investigate the major soil Se fractions (Qin et al., 2012). The four soil Se fractions W-Se, L-Se, O-Se and R-Se were extracted and analysed following the steps summarized in Table 1. The sequential extraction resulted in good recoveries (90 to 110%) compared to the TSe concentrations of soils.

2.3. Statistical analysis

Correlation analyses were performed using Origin 2017 software. Correlation coefficients (r) and significance probabilities (p) were computed for linear regression fits according to Pearson correlation analysis. Structural equation modelling (SEM) was performed by IBM SPSS Amos 25 to determine the uptake of different soil Se fractions by rice. Graphical analyses were performed by Origin 2017 and Microsoft Office 2013.

3. Results and discussion

3.1. TSe, TOC, TS and pH of soil

The TSe concentrations of the sampled soils ranged from 0.85 to 11.46 mg/kg, which are within the range of previous results for Enshi soils (Fordyce et al., 2000; Sun et al., 2010; Tan et al., 2002) but much higher than the geochemical background of soils in China (0.29 mg/kg) (Wei et al., 1991). Based on their environmental risk, the TSe levels of the sampled soils can be classified into five categories: deficient (<0.125 mg/kg), low (0.125–0.175 mg/kg), medium (0.175–0.4 mg/kg), high (0.4–3 mg/kg) and excessive (>3 mg/kg) (Zhang et al., 2014b). In this study, 29% of the soil samples had high Se levels (0.4–3 mg/kg), and 71% of exceeded 3 mg/kg, indicating severe Se pollution in Enshi.

The TS and TOC concentrations of the Enshi soils ranged from 0.013 to 0.059% and 1.60 to 2.69%, respectively, which are comparable to previous results for Enshi soils (Fordyce et al., 2000; Zhu and Zheng, 2001). No correlations were found between TS and TOC ($p > 0.05$), or between TS and TSe ($p > 0.05$). The SOM content was estimated to range from 2.77 to 4.63% according to the conversion coefficient between SOM

Table 1
Sequential extraction procedure for Se fractionation in soil samples collected from Enshi, China.
(Modified from Qin et al., 2012 and Zhang et al., 2014b).

Steps	Se fractionation	Method description
1	Water-soluble Se	Approximately 0.3 g of soil was weighed into a 15 mL centrifuge tube, and 6 mL of 18.2 MΩ water was added. The tube was shaken using a Vortex-Genie mixer for 5 min and by a reciprocating shaker (180 strokes/min) for 2 h. Then, the tube was centrifuged (3500 rpm) for 30 min, and the supernatant was transferred to a new 15 mL tube. Another 6 mL of 18.2 MΩ water was added to the original centrifuge tube, and the above operation was repeated. The supernatant was mixed with the supernatant acquired the first time and filtered (0.45 μm, PES, JIN TENG®) for Se concentration analysis.
2	Ligand-exchangeable Se	Six mL of 0.1 M KH ₂ PO ₄ solution was added to the tube containing residual solids from Step 1. The tube was shaken by a Vortex-Genie mixer for 5 min and by a reciprocating shaker (180 strokes/min) for 2 h. Then, the tube CC was centrifuged (3500 rpm) for 30 min, and the supernatant was transferred to a new 15 mL tube. Another 6 mL of 0.1 M KH ₂ PO ₄ solution was added to the original centrifuge tube, and the above operation was repeated. The supernatant was mixed with that acquired the first time and filtered (0.45 μm) for Se concentration analysis.
3	Organically bound Se	Six mL of 0.1 M NaOH solution was added to tube containing residual solids from step (2). The tube was shaken by a reciprocating shaker (180 strokes/min) for 30 min and heated by water bath (90 °C) for 2 h. After cooling to room temperature, the tube was centrifuged (3500 rpm, 25 min). The supernatant was decanted to a new 15 mL tube. Then, 6 mL of 18.2 MΩ water was added to the original centrifuge tube, and the above operation was repeated. The supernatant was mixed with that acquired the first time and filtered (0.45 μm) for Se concentration analysis.
4	Residual Se	The residual solids from Step 3 were digested (using the method for soil TSe analysis) for Se concentration analysis.

and TOC (SOM/TOC = 1.724) (Rowell, 2014). The SOM of the Enshi soils was generally higher than that of Chinese farmland soils (2.465%) (Yang et al., 2017). Organic matter has a strong affinity for Se in soils (Alemi et al., 1991; Dinh et al., 2017; Gustafsson and Johnsson, 1992). As shown in Fig. 2, a positive correlation between TOC and TSe concentrations ($r = 0.81, p < 0.01$) was observed for soil and shale samples. Fresh (or less weathered) shales from Enshi showed much higher TOC and TSe concentrations than soils and weathered shales in Enshi. While the black shales in Enshi contain a substantial amount of minerals, high TOC contents were reported (0.57 to 46.3%) (Zhu et al., 2014). Although plants can be an important source of SOM, the weathering of shales contributes a substantial amount of organic matter and Se to the soil. Selenium in black shales can be released to nearby soils when black shales are exposed to weathering (Zhu et al., 2014).

The soil pH ranged from 4.8 to 7.06. Except for a few samples that were neutral, the Enshi soils were acidic. In the long term, the decaying of organic matter increases the release of CO₂ into soils, which tends to decrease soil pH (McCauley et al., 2009; Yun et al., 2016). As mentioned above, high organic matter levels were observed in the Enshi soils and shales. The low pH values in the Enshi soils are thought to result from organic matter decay in soil and shales. This hypothesis can be supported by the significantly negative correlation between pH and SOM in the Enshi soils ($r = 0.52, p < 0.01$).

3.2. Selenium fractions in soil

The concentrations and proportions of the four Se fractions in soils are shown in Fig. 3. The correlations in concentrations between different

Se fractions are summarized in Table 2. The W-Se concentration ranged from 0.008 to 0.175 mg/kg, which is much higher than that reported for farmland soils in China (0.006 mg/kg) (Tan et al., 2002). The proportion of W-Se varied from 0.23% to 3.37%, with a mean value of 1.14%, which is lower than that reported for farmland soils in China (2.23%) (Tan et al., 2002). A significant positive correlation in concentrations between W-Se and soil TSe ($r = 0.71, p < 0.01$) was observed. However, the proportion of W-Se decreased significantly with increasing soil TSe concentrations ($r^2 = 0.53, p < 0.01$). This relationship is most likely due to the high SOM contents in high-Se soils. SOM, which has a strong affinity for Se, may have decreased the formation of W-Se in the Enshi soil, causing the significantly negative correlation between the proportion of W-Se and SOM ($r = 0.60, p < 0.01$). High SOM contents result in high decomposition rates and therefore low pH values (McCauley et al., 2009; Yun et al., 2016). At low pH, the transformation of soluble selenate to partially soluble selenite occurs (Schilling et al., 2015; Winkel et al., 2011), which further decreases the formation of W-Se. This relationship is supported by the significantly positive correlation between the proportion of W-Se and soil pH ($r = 0.66, p < 0.01$).

L-Se ranged from 0.10 to 1.45 mg/kg and accounted for 4.48 to 15.00% of the TSe in the soil, which is similar to previous results for Enshi soils (Qin et al., 2012; Qin et al., 2013). Like the correlation between W-Se and TSe, a significant positive correlation was observed between the concentrations of L-Se and soil TSe ($r = 0.91, p < 0.001$), but the proportion of L-Se was negatively correlated with soil TSe concentrations ($r^2 = 0.36, p < 0.01$). Because the proportion of L-Se and SOM is negatively correlated ($r = 0.79, p < 0.01$), it is hypothesized

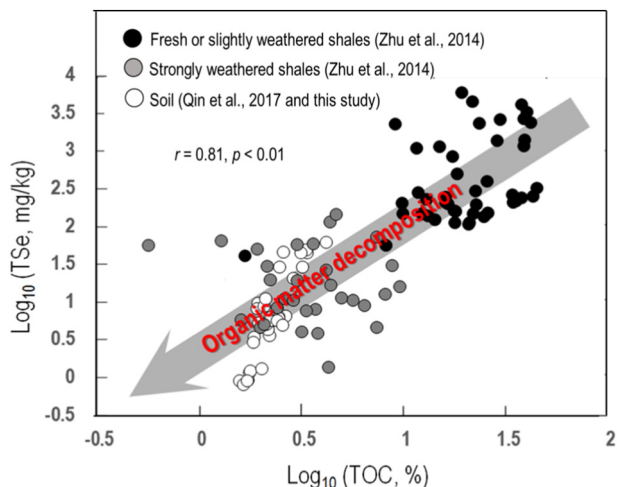


Fig. 2. Total Se and TOC contents in soils and shales from Enshi, China.

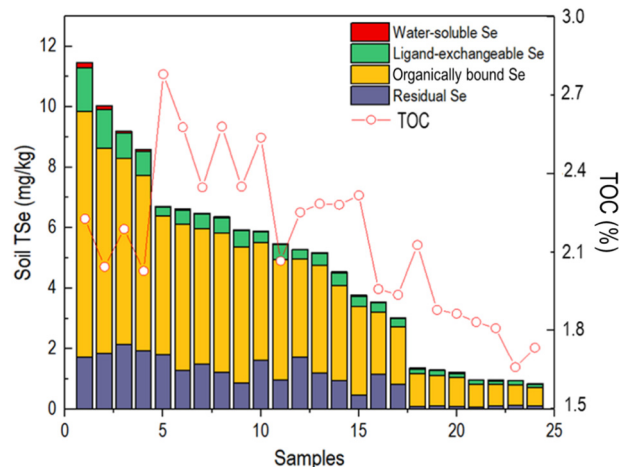


Fig. 3. Distribution of soil TSe concentrations and soil Se fractions for soils collected from Enshi, China.

Table 2
Pearson's correlation matrix for TSe concentrations in rice tissues and soils collected from Enshi, China.

	Water-soluble Se	Ligand-exchangeable Se	Organically bound Se	Residual Se	Roots	Stems	Leaves	Husks	Bran	Polished rice
Total Se	0.71**	0.91**	0.99**	0.91**	0.87**	0.81**	0.82**	0.82**	0.84**	0.89**
Water-soluble Se		0.90**	0.72**	0.45*	0.83**	0.68**	0.75**	0.72**	0.87**	0.84**
Ligand-exchangeable Se			0.91**	0.71**	0.93**	0.78**	0.82**	0.79**	0.89**	0.90**
Organically bound Se				0.87**	0.88**	0.83**	0.83**	0.83**	0.85**	0.89**
Residual Se					0.67**	0.63**	0.68**	0.67**	0.66**	0.73**
Roots						0.75**	0.72**	0.76**	0.80**	0.84**
Stems							0.88**	0.93**	0.88**	0.92**
Leaves								0.94**	0.94**	0.95**
Husks									0.94**	0.96**
Bran										0.98**

Note: Factors in the first column on the left are independent variables, and factors in the top row are dependent variables.

Significance level:

* $p < 0.05$;

** $p < 0.01$.

that SOM may also play a vital role in suppressing the formation of L-Se. A weak correlation was observed between the proportion of L-Se and soil pH ($r = 0.41$, $p = 0.04$), suggesting that pH has a minor effect on L-Se.

O-Se ranged from 0.61 to 8.11 mg/kg, with a proportion of 57.8 to 80.0%, indicating that it is the dominant soil Se fraction in Enshi soils. This result is consistent with previous results from both Se-rich soils (56–81%) (Qin et al., 2017) and Se-deficient soils (80%) (Wang et al., 1988). The concentrations of O-Se and soil TSe were significantly positively correlated ($r = 0.99$, $p < 0.01$). As shown in Fig. 4A, positive correlations were observed between concentrations of O-Se and W-Se and between concentrations of O-Se and L-Se, which indicate that O-Se may be the major source of W-Se and L-Se (Kikkert and Berkelaar, 2013; Läuchli, 2015; Qin et al., 2013). As shown in Fig. 4B, the proportions of L-Se and W-Se increased as the SOM decreased.

Decaying organic matter during weathering affects the SOM levels, which may promote the transformation of O-Se to W-Se and L-Se.

R-Se ranged from 0.46 to 2.15 mg/kg, accounting for 6.05 to 32.86% of the soil TSe in Enshi. Positive correlations were observed between concentrations of R-Se and other Se fractions (W-Se, L-Se and O-Se) (Table 2). The proportion of R-Se and SOM were positively correlated ($r = 0.60$, $p < 0.01$), suggesting that SOM may play an important role in the formation of R-Se. In our study, the proportions of W-Se and L-Se decreased as the SOM increased, whereas no clear correlation was observed between the proportion of O-Se and SOM ($r = 0.14$, $p = 0.53$). This result indicates that W-Se and L-Se may transform to R-Se at high SOM levels.

3.3. Distribution of Se in rice tissues

The TSe concentration of rice tissues decreased in the following order: roots (0.77 to 11.82 mg/kg), bran (0.31 to 4.67 mg/kg), leaves (0.12 to 3.06 mg/kg), polished rice (0.09 to 1.88 mg/kg), stems (0.09 to 1.35 mg/kg) and husks (0.15 to 0.89 mg/kg). A similar pattern of TSe distribution was observed in rice tissues in a previous study (Sun et al., 2010). Notably, the mean TSe concentration for polished rice (0.59 mg/kg) significantly exceeded the limits of Se in foodstuffs (0.3 mg/kg) (USDA, 2006), indicating a high risk for local residents. The mass of Se in rice tissues was calculated by multiplying the mass of the tissue by its TSe concentration. The mass of Se showed large variations in roots (9.8 to 93.2 μg), polished rice (5.3 to 89.6 μg), stems (3.2 to 36.0 μg), leaves (1.4 to 27.0 μg), husks (2.1 to 11.6 μg) and bran (1.6 to 20.0 μg). As shown in Fig. 5A, roots contained much more Se than ground tissues, which agrees well with a previous study that demonstrated that root Se is difficult to translocate to other plant tissues (Huang et al., 2015).

Significantly positive correlations were observed between root TSe concentrations and W-Se concentrations ($r = 0.83$, $p < 0.01$) and between root TSe concentrations and L-Se concentrations ($r = 0.93$, $p < 0.01$). Roots are the tissue that absorb most Se from the soil. W-Se and L-Se fractions are the most bioavailable for roots, given that the two fractions are mainly composed of soluble Se compounds (Läuchli, 2015; Li et al., 2008; Zhu et al., 2009). Interestingly, a significantly positive correlation was also observed between root TSe concentrations and O-Se concentrations ($r = 0.88$, $p < 0.01$). This result may either support O-Se as the primary source of W-Se and L-Se or indicate that a substantial amount of O-Se can be absorbed by rice (Kikkert and Berkelaar, 2013; Läuchli, 2015). Considering that W-Se, L-Se and O-Se fractions account for most Se in soils (Qin et al., 2013; Qin et al., 2017), they are likely the major sources of Se absorbed by rice.

Positive correlations in the concentrations between rice tissues were observed (Table 2). More importantly, TSe concentrations in plant tissues were unexceptionally significantly correlated with root TSe concentrations ($r = 0.72$ to 0.84, $p < 0.01$). This result again confirms

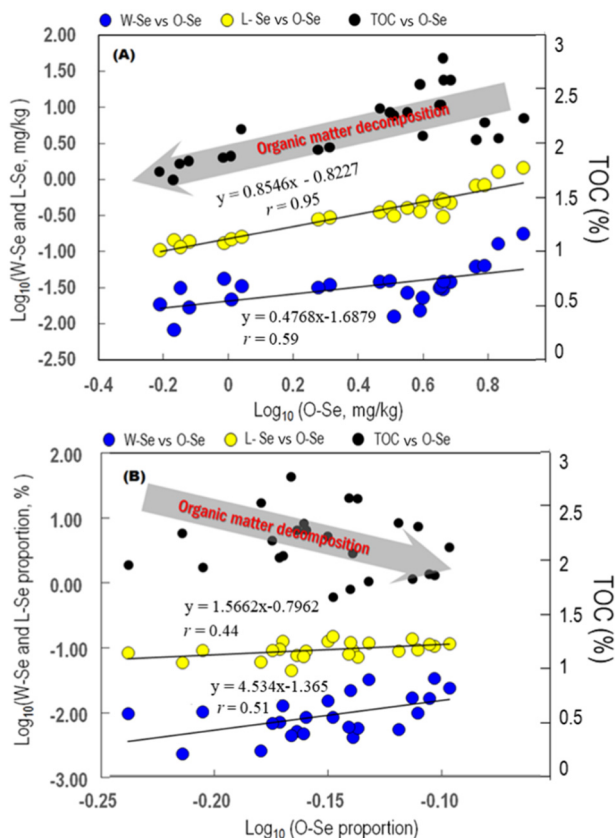


Fig. 4. Correlations between concentrations (A) and proportions (B) of O-Se and W-Se and of O-Se and L-Se in soils collected from Enshi, China.

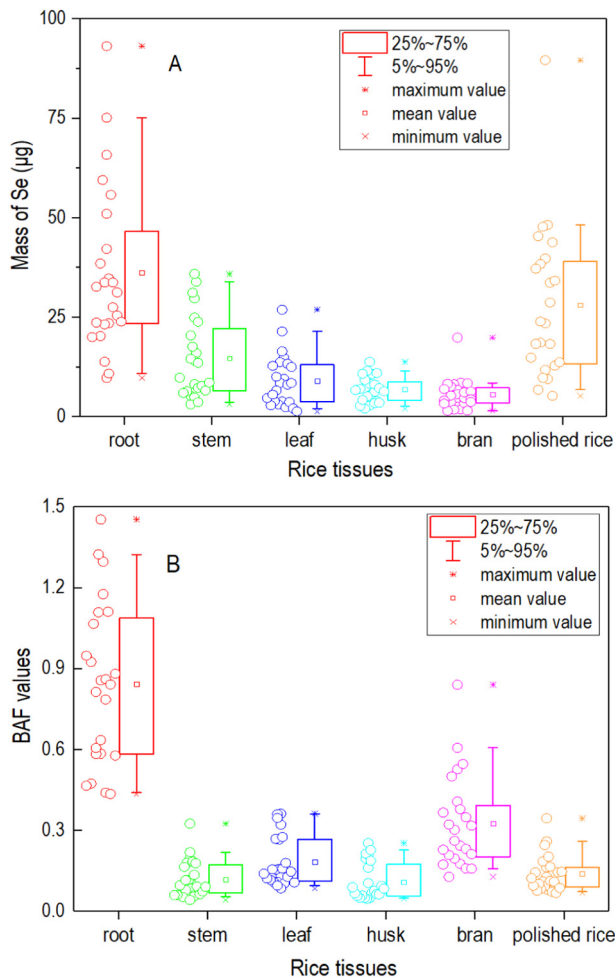


Fig. 5. Mass of Se accumulation (A) and BAFs of Se (B) in rice tissues collected from Enshi, China.

that the uptake of soil Se by roots is the major pathway contributing Se to rice plants.

3.4. Selenium bioaccumulation capability of rice tissues

The Se bioaccumulation factors (BAFs) for rice tissues were calculated by dividing the TSe concentrations of rice tissues by the TSe concentrations of their paired soils. As shown in Fig. 5B, the Se BAFs for roots (0.44 to 1.45) were much higher than those for bran (0.13 to 0.84), leaves (0.09 to 0.36), polished rice (0.07 to 0.35), stems (0.04 to 0.33) and husks (0.05 to 0.25). In this study, roots had the highest BAF values, which is consistent with the fact that the uptake of soil Se by roots is the major pathway contributing Se to rice plants (Haygarth et al., 1995; Qin et al., 2013). The low BAFs of plant tissues (stems, leaves, polished rice, and husks) suggest that a substantial amount of Se can be barred during the transport of Se from root to aboveground tissues. Interestingly, compared to polished rice, bran showed a higher BAF value. This result indicates that Se is relatively enriched in the surface layer of brown rice, which has been demonstrated in previous studies using synchrotron X-ray fluorescence techniques (Carey et al., 2012; Williams et al., 2009).

3.5. Using structural equation modelling to understand the uptake of soil Se by rice

SEM is a multivariate statistical analysis technique that is used to analyse structural relationships. This technique, which incorporates

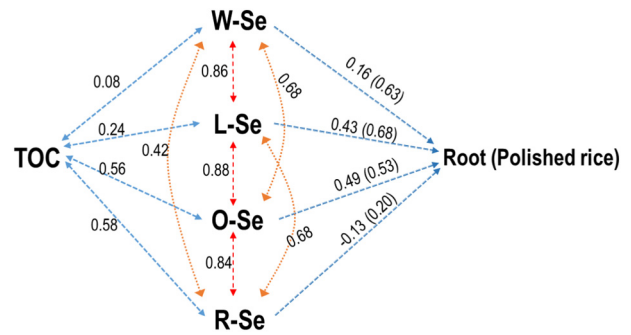


Fig. 6. Structural equation model showing the interactive effects between TOC, soil Se fractions, root and polished rice Se concentrations. Two-way arrows indicate two variables interacting with each other; one-way arrows indicate the contribution of independent variables to a dependent variable.

factor analysis and multiple regression analysis, is commonly used to analyse the structural relationship between measured variables and latent constructs. In this study, SEM was used to analyse the uptake of soil Se by rice. As shown in Fig. 6, Se concentrations of four soil Se species and TOC were assigned as the independent variables, and the TSe concentrations of rice root and polished rice were assigned as dependent variables. According to the model output, positive effects were observed among the four soil Se fractions, which suggests that the transformation of Se may occur dynamically. More importantly, significantly positive interactive effects between TOC and soil Se fractions (W-Se, L-Se, O-Se, and R-Se) were observed, suggesting that organic matter is an important factor controlling the transformation of Se in Enshi soils. More interestingly, the contributions of W-Se, L-Se, and O-Se for root and polished rice were 0.16, 0.43, 0.49 and 0.63, 0.68, and 0.53, respectively (Fig. 6), which is consistent with our earlier conclusion that W-Se, L-Se and O-Se fractions are directly available Se sources for rice absorption.

4. Conclusions

As a trace element, Se plays an important role in human health both in positive and negative directions, depending on the amount of Se consumed. In nature, Se is released into the environment mainly via weathering and anthropogenic mining of Se-rich rocks. The environmental fate of Se cannot be simply evaluated by Se concentrations. The chemical speciation of Se largely controls the bioavailability of Se. This study demonstrated that the decomposition of organic matter may promote the transformation of O-Se into more bioavailable species (e.g., W-Se and L-Se fractions). The decomposition of organic matter may be beneficial in areas deficient in Se because it increases the bioavailability of Se; however, in Enshi, this effect may increase the human risk of Se poisoning due to the high background Se levels. According to this study, it appears that rice uptakes not only W-Se and L-Se but also O-Se. This finding differs from previous study that proposed W-Se might be the major Se fraction absorbed by plants (Zhang et al., 2014b). The application of X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques can provide additional insights into the geochemical fate of heavy metals (e.g., Tl and U) in soils and sediments (Liu et al., 2017, 2018, 2019; Aguilar-Carrillo et al., 2018). Further XRD and SEM studies on Enshi soils are worthy of future research to better understand the transformation and translocation of Se in soil-rice systems.

Acknowledgements

This research was financed by the National Key Research and Development Program of China (2017YFD0800302) and the Natural Science Foundation of China (41573125). Runsheng Yin was funded

by the Chinese Academy of Sciences through the Hundred Talent Plan. The authors would also like to thank the anonymous reviewers for their constructive comments that significantly improved the quality of the manuscript.

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