



Microscale Investigation into Selenium Distribution and Speciation in Se-Rich Soils from Enshi, China

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Abstract

In this study, we investigated the distribution and chemical speciation of Se in Se-rich soil by using micro-focused X-ray absorption near-edge structure (μ -XANES) spectroscopy coupling with X-ray fluorescence (μ -XRF) mapping. The microscale distribution showed that Se is heterogeneously distributed in the soil from seleniferous areas in Enshi, China. Se K-edge μ -XANES analysis suggested that Se is mainly present as Se(IV), organic Se(-II) or Se(0) species in Se-rich agricultural soil. The findings from this study would help improve the understanding of the fate, mobility, bioavailability, and biogeochemical cycling of Se in the seleniferous soil environment.

Keywords Selenium · Speciation · μ -XRF-XANES · Microscale distribution · Seleniferous soil · Enshi

Selenium (Se) is of growing interest as an essential trace element for human beings. Nonetheless, excessive Se intake could induce human Se poisoning in Se-laden ecosystems, such as seleniferous areas in China and India (Hira et al. 2004; Lenz and Lens 2009; Qin et al. 2013). The maximum daily dietary Se intake for adults is set at 400 $\mu\text{g day}^{-1}$ (WHO and FAO 2004). It has been demonstrated that the consumption of cereals and vegetables make a great contribution to human daily Se intake (Hira et al. 2004; Qin et al. 2013). Se level in crops is strongly controlled by Se bioavailability in agricultural soils (Qin et al. 2013, 2017a; Winkel et al. 2015), and thus Se speciation in soils is critical for the assessment of potential health risk for human Se intake.

Se occurs in several oxidation states (-II, 0, IV, and VI) and organic forms in the environment. Se(VI) is highly mobile and is weakly retained by soil particles due to its high solubility, whereas Se(IV) has a great affinity for soil minerals (e.g., iron oxides) and organic matter (Lenz and Lens 2009; Winkel et al. 2015; Qin et al. 2012, 2017a). Selenide (Se(-II)) and elemental Se(0) are thermodynamically favorable species under reducing conditions (Lenz and Lens 2009). Additionally, organic Se derived from plant litters could also be preserved in soils (EI Mehdawi et al. 2015; Qin et al. 2017a). Given that different Se species has distinct mobility and bioavailability, the identification of Se speciation in soils is important for better understanding of the fate and biogeochemical behavior of Se in the soil environment.

Sequential chemical extractions have been widely applied to characterize Se fractionation in geological and environmental samples, although this indirect approach has some drawbacks such as the nonspecific dissolution of different extractant (Wright et al. 2003; Kulp and Pratt 2004; Qin et al. 2017a). X-ray absorption near-edge structure (XANES) spectroscopy can nondestructively determine chemical speciation of Se in solid samples (Ryser et al. 2005, 2006; Wiramanaden et al. 2010; Matamoros-Veloza et al. 2014; Qin et al. 2017a, b). However, limited XANES investigation have been performed in soils due to low Se concentrations. Micro-focused XANES coupling with X-ray fluorescence (μ -XRF-XANES) techniques are more powerful, which can provide additional insights into the micromorphology and chemical speciation

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of heterogeneous soil samples, allowing for more information on Se biogeochemical cycling in the soil environment (Ryser et al. 2005, 2006; Qin et al. 2017b, 2020).

Enshi Prefecture of Hubei Province, China, is a typical Se-rich area, where a number of studies have investigated soil Se levels and environmental effects (e.g., Zhu et al. 2008). In the present study, we carried out in-situ μ -XRF-XANES analysis to reveal the distribution, speciation, and host phase of Se in the soil at the microscale and to improve our understanding of the fate, migration, and bioavailability of Se in the seleniferous soil environment.

Materials and Methods

The soil samples at near-surface (0–30 cm) were collected from Se-rich areas of Enshi, China (Qin et al. 2017a). In this study, a thin section of the agricultural soil sample was prepared for μ -XRF-XANES measurements. This soil sample contains 7% clay, 36% silt, and 57% sand. The total Se concentration in this sample was 20.9 mg/kg (Qin et al. 2017a). In brief, the freeze-dried soil sample was embedded in a high purity epoxy resin and then double-face polished to a thickness of $\sim 40 \mu\text{m}$ (Qin et al. 2017b, 2020).

The μ -XRF mapping and μ -XANES experiments were performed at BL4A at KEK-PF (Tsukuba, Japan). The soil thin section was mounted on a sample holder oriented at 45° to the incident beam, whose intensity was fixed at 12.9 keV. The fluorescence X-rays from the soil sample were determined by a Si-SDD. Se K-edge μ -XANES spectra for several

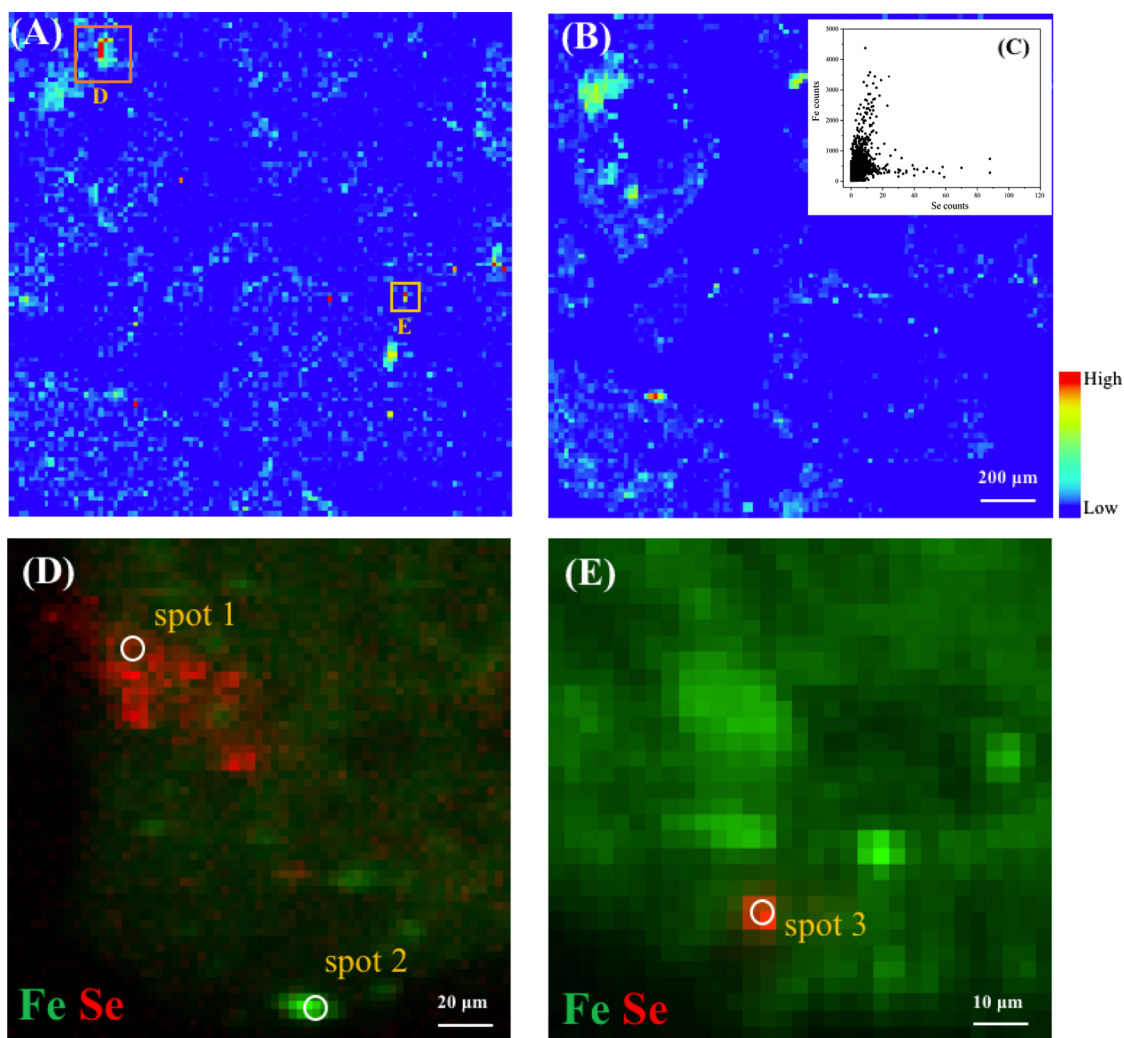


Fig. 1 μ -XRF maps showing the elemental distribution in the soil. **a–c** shows the μ -XRF maps of Se and Fe, and the correlation between Se and Fe in the scan area; **d, e** shows bicolor maps of Se (red) and

Fe (green) in the soil. The open circles indicate spots of interest for further Se μ -XANES measurements

spots in the soil sample were collected in fluorescence mode. Se XANES spectra of standard materials, including NaHSeO_3 (Wako, Japan), Na_2SeO_4 (Wako, Japan), elemental Se (Wako, Japan), and L-selenocystine (SeCys, C-Se-Se-C, Acros Organics Co.) were recorded in transmission mode.

The XANES data were analyzed using the REX2000 software (Rigaku Co. Ltd.). The background was removed from the raw data by a spline smoothing method. Linear combination fitting (LCF) was conducted to obtain quantitative information of Se speciation. Details of the XANES analysis are similar to those described previously (e.g., Qin et al. 2017a, 2020).

Results and Discussion

Figure 1 shows the distribution maps of Se and Fe in the soil thin section obtained by μ -XRF mapping. It was observed that Se distribution is non-uniform in the scan areas, with the presence of some Se hotspots with high Se intensities (Fig. 1). These observations indicate that Se is highly heterogeneously distributed in the seleniferous soils from Enshi. Moreover, the distribution of Se hotspots seemed to not overlap with Fe-rich particles in the examined soil, as

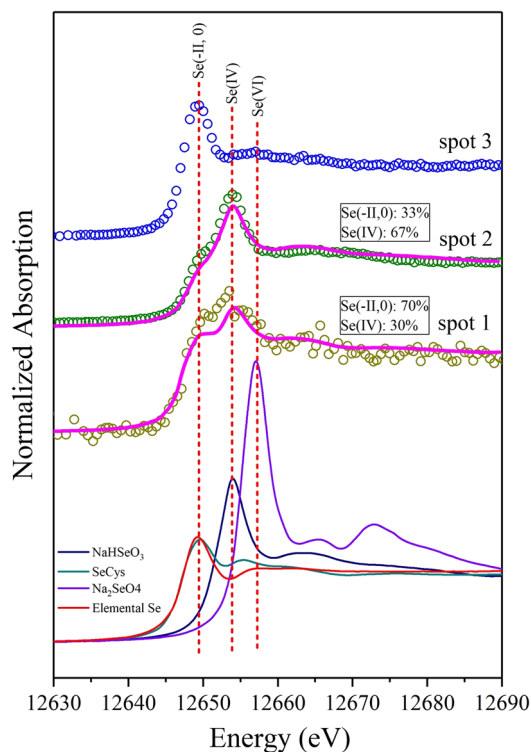


Fig. 2 Se K-edge μ -XANES spectra for interested spots (marked by open circles in Fig. 1) in the soil. Dotted lines are spectra obtained by experiments, and solid lines for the spots are calculated spectra by the LCF analysis

was reflected by the correlation between Se and Fe (Fig. 1c). This fact likely implies that Se is also hosted by other phases in seleniferous agricultural soils from Enshi in addition to Fe-containing minerals.

Selenium K-edge μ -XANES spectra of the spots of interest and reference materials are given in Fig. 2. In this study, Se(-II, 0) was used to represent the oxidation state of reduced Se forms, because of the similar peak energy between organic Se(-II, SeCys) and Se(0) (Fig. 2). However, the peak position is sensitive to distinguish Se(VI), Se(IV), and Se(-II, 0) species (e.g., Ryser et al. 2006; Wiramanaden et al. 2010; Qin et al. 2017b). For the examined spots, the peak energies of their μ -XANES spectra were located between those for Se(IV) and Se(-II, 0) forms, indicating that Se in the soil was present as Se(-II, 0) or Se(IV), or a mixture of the two species. By contrast, the contribution of Se(VI) species appeared to be very small. These results are not surprising because Se(VI) tends to form outer-sphere complexes and has a lower affinity to soil particles, resulting in much less presence of Se(VI) in the soil (Harada and Takahashi 2008; Qin et al. 2017b).

Quantitative analysis of Se μ -XANES spectra showed that 30% of Se is present as Se(IV) species in the spot 1, and the percentage of Se(IV) is much higher (67%) in the spot 2 with a higher Fe intensity (Figs. 1 and 2). It has been demonstrated that Se(IV) associated with Fe(III) (oxyhydr)oxides is the dominant speciation in the soils developed after pyritic shale materials (Strawn et al. 2002; Ryser et al. 2006) and the contaminated soils from abandoned Au–Ag–Te mine tailings (Qin et al. 2017b). The results strongly suggest that Se(IV) can be associated with Fe(III) (oxyhydr)oxides in soils, which can be well explained by the formation of stable inner-sphere surface complexes (Harada and Takahashi 2008; Qin et al. 2017b).

Interestingly, only Se(-II, 0) species was identified in the spot 3 that has a great Se intensity (Figs. 1 and 2), likely indicating different formation pathway, mobility, and bio-availability of Se compared with those for spots 1 and 2. Despite featureless characteristics of Se XANES spectra among Se(0), organic and inorganic Se(-II), several evidences can be used to reveal possible Se speciation in the spot 3. One possibility is that Se is mainly present as inorganic selenide/sulfide Se(-II), because Se can substitute for sulfur (S) in pyrite structure or occur as the FeSe_x form (Matamoros-Velozta et al. 2014; Zhu et al. 2012). However, Se seemed to not coexist with Fe in the spot 3 (Fig. 1e). Hence, we can exclude the predominant occurrence of inorganic selenide/sulfide Se(-II) in the soil.

The most possible Se(-II, 0) form in the soil is organic Se(-II), considering that Se-rich corns were planted in this soil. This can be supported by the combination of sequential extractions and bulk XANES results, showing that Se in this soil occurs as 44% Se(IV) and 56% organic Se(-II)

species (Qin et al. 2017a). Likewise, previous studies have documented that organic Se in soils can be derived from Se-rich plant litters or parent materials (Ryser et al. 2005; El Mehdawi et al. 2015; Qin et al. 2017a). Thus, organic Se(-II) is likely the predominant speciation in the soil particles. However, it should be noted that the occurrence of elemental Se is also highly possible in soils due to microbial activities and agricultural practices (Zhu et al. 2012), although the contribution of Se(0) in this soil is likely limited compared with organic Se(-II) (Qin et al. 2017a). Further study such as EXAFS analysis is needed to confirm the existence of elemental Se(0) in the soil.

In this study, we reveal microscale speciation distribution in the soils from seleniferous areas in Enshi, China by the μ -XRF-XANES technique. Our study provides direct spectroscopic evidence for the presence of organic Se(-II) in Se-rich soils. This finding has a significance for the understanding of Se bioavailability and for the assessment of ecological risk in the seleniferous soil environment, considering that organic Se is more readily taken up by crops.

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