

Understanding the mechanisms controlling selenium bioavailability in soils

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Objective

Establish the effect of pH on selenium (Se) interaction with soil organic matter alone, and in combination with Fe-oxides, to understand the fixation mechanisms of Se. The Se redox products will be analysed by X-ray absorption spectroscopy (XAS), using the XANES (X-ray Absorption Near-Edge Structure) region to identify Se oxidation state and coordination, and the EXAFS (Extended X-ray Absorption Fine-Structure) region to elucidate the local structure.

Introduction

Selenium is an essential trace element whose benefits include cancer prevention, anti-viral effects, improved cognition and immune system function. There is a clear link between Se speciation and bioavailability. Alongside the need to investigate Se in terms of dietary deficiency we must also consider the long-lived ^{79}Se isotope, a fission product of ^{235}U , which is of primary concern regarding radioactive waste disposal.

Methods

Selenium K-edge adsorption data was obtained at the Diamond Light Source (Oxford) for selenite (Se(IV)) and selenate (Se(VI)) adsorbed on Ca-humate, Ca-humate with Fe(III), and goethite (at pH 6 and pH 4) and two soils; DYG (pH 3.9, 11.4% Org-C) and SRG (pH 7.04, 5.7% Org-C). Data was collected on beamline I20 for a range of adsorbed Se concentrations. Samples comprised moist slurries held between kapton windows and run in a liquid N_2 cryostat. Spectra for aqueous standards of Se(VI) and Se(IV) and elemental Se^0 were also collected.

Results

Soil organic matter predominantly comprises humin, humic acid and fulvic acid. Results from a humic acid (HA) dynamics experiment, where HA suspensions at both pH 4 and 6 were spiked with $^{77}\text{Se(IV)}$ and $^{77}\text{Se(VI)}$, demonstrated that both Se(IV) and Se(VI) undergo removal from solution at pH 4 (20°C) in the presence of HA alone, and HA in combination with Mn(III) and Fe(III) (Fig. 1), forming the basis for the XAS experiment.

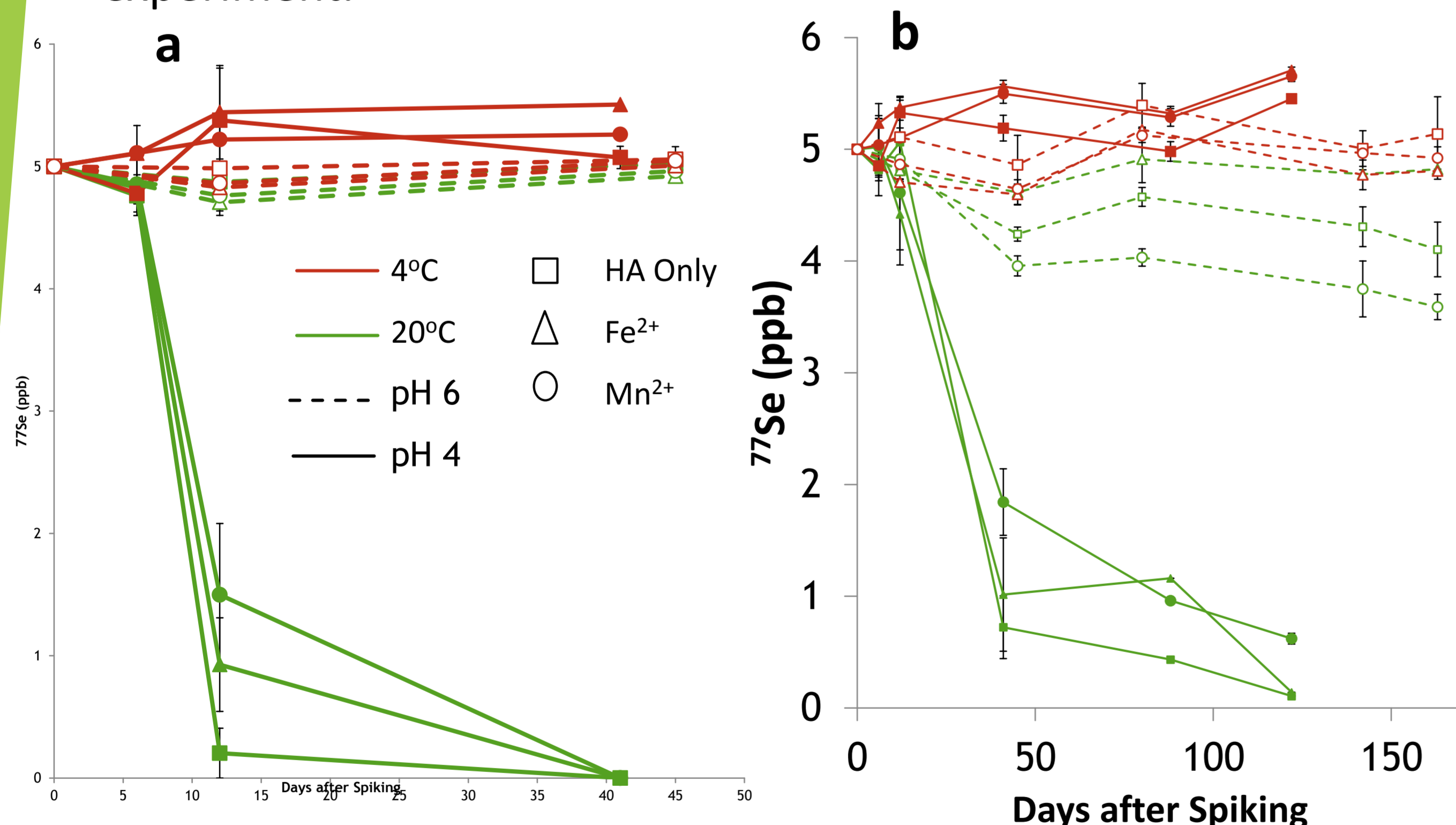


Fig. 1. (a) Loss of Se(IV) and (b) Se(VI) through binding to humic acid (0.2 g L^{-1}) at pH 4 and 6, and at 20°C and 4°C, when spiked with 5 ppb Se(IV). Additions of Fe^{2+} , Mn^{2+} and HA only were included.

XANES

The Se K-edge data collected throughout the experiment was high quality, but did show some evidence of reduction of Se in the beam. Linear combination fitting of the XANES spectra demonstrated that Se was reduced to some extent in nearly all soil, Ca-humate and goethite samples at pH 4, either from Se(VI) to Se(IV), or Se(IV) to Se(0), and in one case from Se(VI) to Se(0) (Table 1). The goethite samples retained Se as both Se(IV) and Se(VI), but Se(VI) showed significant reduction to Se(IV). In the Ca-humate samples spiked with either Se(IV) or Se(VI) virtually all Se was present as Se(0).

Table 1. Linear combination fitting results for all samples with measurable Se K-edge XANES spectra.

Sample	Linear combination XANES (%)		
	Se(IV)	Se(VI)	Se(0)
HA Se(IV)	23.0	2.9	74.1
HA Se(VI)	11.7	11.2	77.1
HA+ Fe(III) Se(IV)	71.5	28.5	0.0
HA+ Fe(III) Se(VI)	72.2	27.8	0.0
Goethite Se(IV)	96.9	0.0	3.1
Goethite Se(VI)	50.5	45.2	4.4
SR-G Se(IV)	85.5	0.0	14.5
SR-G Se(VI)	84.4	0.0	15.6
DY-G Se(IV)	12.8	2.9	84.2

EXAFS

In the EXAFS spectra analysis the Fourier transform magnitude (Fig. 2) was dominated by a strong peak at $\sim 1.5 \text{ \AA}$, which arose from backscattering of the oxygen atoms in the coordination sphere. Beyond this, in many samples, there was also a peak at $\sim 2.2 \text{ \AA}$ which can be fitted with Se-Se paths with a length of 2.34 \AA confirming the presence of elemental Se(0). In the Ca-humate samples that received additions of Fe(III) there was a small/weak peak at $2.9\text{-}3.3 \text{ \AA}$ that could be fitted to an Se-Fe path suggesting the formation of ternary complexes with Fe when incorporated into Ca-humate.

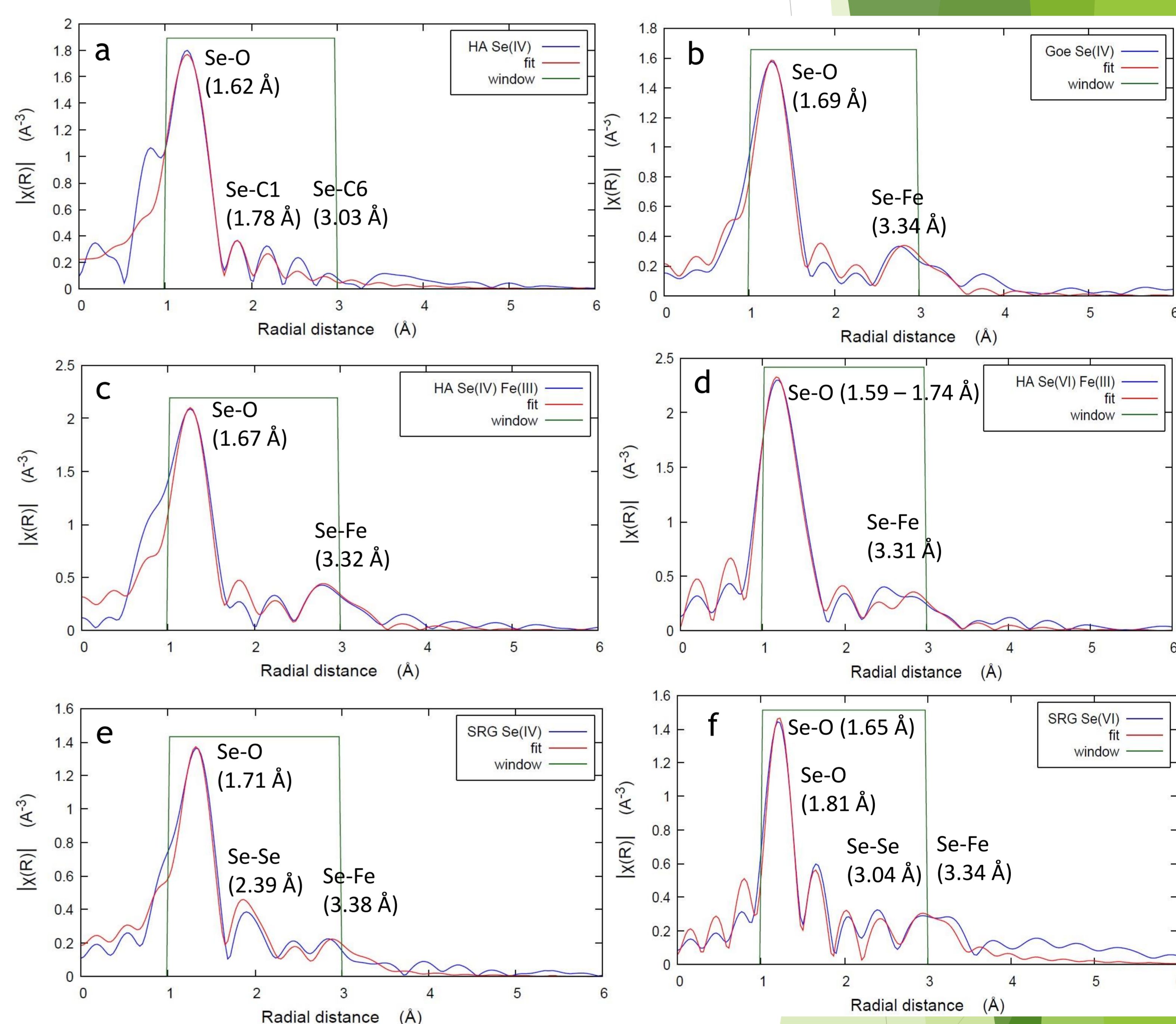


Fig. 2. Se K-edge EXAFS spectra (a, b, c, d, e, f) for a selection of samples. HA alone with Se(IV) (a), goethite with Se(IV) (b), HA with Fe(III) and Se(IV) (c), HA with Fe(III) and Se(VI) (d), SRG soil with Se(IV) (e) and SRG soil with Se(VI) (f). HA with Se(VI) and DYG soils not included as data was only appropriate for XANES.

Conclusions

The capability of HA alone and HA in combination with Fe(III) to reduce both Se(IV) and Se(VI) to Se(0) is demonstrated here alongside the ability of goethite to bind Se(IV) and reduce Se(VI) to Se(IV). Selenite reduction by HA has been shown previously however, to the best of our knowledge, this is the first demonstration of Se(VI) reduction to Se(0) by HA alone. The experiment showed significant reduction and binding of Se at pH 4, but not at pH 6. There was evidence that the addition of Fe(III) to HA samples results in the formation of cation bridges in the adsorption of Se(IV) and Se(VI), in contrast to the HA only samples where Se showed association with phenolic groups.