# Quantitative speciation of selenium in soils using

## X-ray absorption spectroscopy

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### Abstract (For Chemical Abstracts only, not to be included in the journal).

Selenium contamination of soils is a significant problem in parts of the Western United States, but until recently our knowledge of the oxidation state and coordination chemistry of selenium in soils has been based on indirect chemical analyses. We demonstrate the use of Se K-edge X-ray absorption spectroscopy (XAS) to quantitatively speciate selenium in soils from the Kesterson Reservoir in California, USA without any pretreatment. The majority of the selenium is present in the relatively immobile elemental form. XAS provides an important new tool for assessing the potential environmental impact of selenium contamination.

#### Introduction

The importance of selenium as a naturally occurring, potentially toxic trace element in various natural and agricultural environments has received considerable attention during the past 60 years (1,2). The recent Se contamination of Kesterson Reservoir (Merced County, California, USA) with agricultural drainage waters, and the resulting wildlife mortalities, impaired reproduction, and deformities, highlights the need for accurate Se speciation (3-8), as the valence and coordination of Se radically affects its mobility, bioavailability and toxicity (9,10). However, relatively little direct information has been forthcoming; studies of Se in soil and groundwater systems have, to date, provided direct speciation only in the aqueous and gaseous phases (5-13), which account for only about 10% of the total Se in Kesterson Reservoir soils, mainly present as aqueous Se(VI). The occurrence of Se(IV) and Se(0) in the remaining adsorbed and solid phases of Se has been inferred from a variety of selective extraction techniques (5-13), but chemical change caused by the treatments, together with the inability to distinguish adsorption from precipitation (14-18) make these indirect analyses less than optimal.

Synchrotron-radiation based X-ray absorption spectroscopy (XAS) methods are well-established for probing local structural and electronic environments in a variety of systems (19). The ability of XAS to probe specific elements within a complex system, all states of matter and a wide concentration range make it highly suitable as a tool to study contaminants in soils and sediments. In particular, for many elements XAS can be carried out essentially in situ on undisturbed bulk samples under ambient conditions. Furthermore, extended X-ray absorption fine structure (EXAFS) can be used to distinguish adsorption from precipitation at mineral surfaces (20-22). In contrast, the near-edge region of the XAS spectrum has been little used in environmental speciation, and potentially can probe much lower levels of contaminants than those feasible by EXAFS. The sensitivity of near-edge XAS is critically dependent upon the chemical composition of individual samples; under very favorable circumstances concentrations as low as 500 ppb are detectable (in an unrefined oil sample; Pickering, I.J. and Prince, R.C., unpublished), however for soil samples practical limits are somewhat higher (ca. 10 ppm). The fine structure in the edge region is dependent upon the electronic environment of the absorbing atom, and hence is very sensitive to both the valence and coordination environment of the species (19, 23-25). Although this structure is often difficult to interpret rigorously, the edge can readily be used as a fingerprint to identify species (26), and quantitative analyses of mixtures of species can be obtained by fitting with a linear combination of reference spectra, as previously demonstrated for sulfur speciation (27-30). We show here that similar approaches allow quantitative analyses of selenium contaminated samples from Kesterson Reservoir, and therefore demonstrate the utility of XAS edge-fitting analysis as a tool for quantitative speciation of contaminants in environmental systems.

#### Materials and Methods

Reference samples were prepared from their reagent-grade chemicals (except for red, monoclinic elemental selenium which was synthesized by slow evaporation of a solution of gray metallic Se in  $CS_2$ ), either as a powder diluted with BN or as an aqueous solution. Samples from Kesterson Reservoir include soils from a former evaporation pond (from the 0-0.05 and 0.05-0.15 m depth intervals of an area formerly vegetated with cattails, *Typha latifolia*), and one mushroom (*Agaricus bernardii*). Samples from a laboratory experiment which simulated Se contamination of sediments by ponding waters with an initial Se distribution of 98% Se(VI) and 2% Se(IV) over previously uncontaminated soils were also studied. Se K-edge XAS data were collected on beamlines 4-2 and 4-3 of the Stanford Synchrotron Radiation Laboratory using Si(220) double crystal monochromators with an upstream vertical aperture of 1 mm. The spectra of concentrated samples were collected in transmittance using N<sub>2</sub>-filled ion chambers. For dilute soil samples, Se K<sub>a</sub> fluorescence was collected using a Canberra 13-element germanium detector. The spectrum of hexagonal Se was collected simultaneously with each data set for energy calibration, with the first inflection of its absorption edge taken to be 12658 eV. Background subtraction and normalization were carried out according to established procedures (*19*).

#### Results and discussion

The Se K-edge spectra of several structurally well-characterized reference compounds are shown in Figure 1, together with their second derivative spectra. It is apparent that the edges are sensitive to the selenium valence; edge energy increases with the formal oxidation state due to increased effective nuclear charge as valence electrons are removed. Additionally, the intense feature above the edge, formally a  $1s \rightarrow 4p$  transition, gains intensity as valence increases, which is attributable to a decrease in population of the valence 4p levels. Figure 1 also demonstrates that the edges are sensitive to variations in local environment, including crystalline and aqueous forms of the same ion and different elemental allotropes. Quantitative analysis using edge spectra consists of least squares fits of linear combinations of spectra of standards to the spectrum of the unknown. As a control, edge-fitting analyses were performed for aqueous selenite-selenate solution mixtures which were independently analyzed by hydride generation atomic absorption spectroscopy (AAS) (31), and the results of these are shown in Figure 2. The excellent correspondence between the data and the fit, and the agreement between these and the results from AAS show that XAS is a viable tool for quantitative speciation of selenium.

The results of XAS edge-fitting analyses for the Kesterson and laboratory samples are given in Figures 3 and 4, again showing good agreement between data and fit. A variety of standards were tested as possible components of-the unknown, but, where present, the aqueous forms of selenate and selenite gave better fits than the respective solid forms, and fits using monoclinic selenium were superior to

those using the hexagonal form. The major phase in both of the Kesterson soil samples (Figure 3) is determined to be monoclinic elemental selenium, with a minor component, fitted as aqueous selenite, being slightly more abundant for the deeper fraction. The spectrum of the mushroom sample is consistent with an organoselenium species, and the fit result indicates a predominantly (>70%) selenomethionine-like species. The laboratory sediment samples (Figure 4) fit well to mixtures of aqueous selenate, selenite and elemental selenium, displaying a systematic total selenium reduction with time. The importance of various microbes in mediating Se reduction in sediments has been investigated by others (32-35).

This XAS study provides direct evidence for the presence of elemental selenium in contaminated soils from the Kesterson Reservoir and in laboratory soil simulations. Elemental selenium is far less mobile than the more oxidized forms observed, and its transport through the soil profile and in groundwaters is strongly retarded. The kinetics of Se reduction ultimately control selenium mobility and the extent of groundwater contamination, and these experiments suggest that the kinetics are relatively rapid (within a few days after flooding of soils). Reduction of selenium to Se(0) also diminishes its bioavailability, thus lessening the detrimental impact on wildlife. The presence of organo-selenium species similar to selenomethionine in mushrooms from Kesterson Reservoir has implications for the movement of selenium up the food chain, although mushrooms comprise a very small fraction of the area's biomass.

Our study of selenium in natural soils demonstrates the utility of XAS for *in situ* study of trace element contaminants in soils and organisms, and in principal this method can be applied to any element with an absorption edge at an accessible energy. In particular, information from XAS on the oxidation state and molecular environment of Se in all phases of the soil complements total selenium concentrations provided by conventional analysis techniques and does not require elaborate extraction procedures that may alter the chemical form of selenium. This type of element-specific information is essential for understanding the basic chemistry, geochemical cycling, impacts, and management of environmental contaminants.

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#### Figure captions

Figure 1. Se K-edge XAS spectra (A) and corresponding second derivative (B) for selected selenium standards: (a) FeSe; (b) elemental selenium (grey hexagonal); (c) elemental selenium (red monoclinic); (d) SeS<sub>2</sub>; (e) selenocystine (R-Se-Se-R); (f) selenomethionine (R-Se-H); (g) SeO<sub>2</sub>; (h) Na<sub>2</sub>SeO<sub>3</sub>; (i) SeO<sub>3</sub><sup>2-</sup> (aq); (j) Na<sub>2</sub>SeO<sub>4</sub>; (k) SeO<sub>4</sub><sup>2-</sup> (aq).

**Figure 2.** Se K-edge XAS edge fit results for two selenite-selenate aqueous mixtures. The points are the data, solid line the total fit, and the dashed and dotted lines the aqueous selenate and selenite components. The second derivative fits are shown in the insets. Fitting analyses were carried out separately for the edges (E) and their derivatives (D) and the results compared as percentage aqueous selenite (balance aqueous selenate). E: (a) 72.2 (b) 27.0; D: (a) 72.2 (b) 27.9; results from AAS: (a) 67 (b) 27.

Figure 3. Se K-edge XAS edge fit results. (a) and (b) Kesterson soils, 0-0.05 and 0.05-0.15m, respectively; (c) mushroom. The points are the data, and solid line the total fit. The second derivative fits are shown in the insets. The dotted and dashed lines show the components of the fits. The fit results for the edge (E) and the derivative (D) are expressed as E(D) as follows: (a) 97(94)% monoclinic elemental selenium, balance aqueous selenite; (b) 86(84)% monoclinic elemental selenium, balance aqueous selenite; (b) 86(84)% monoclinic elemental selenium, balance aqueous selenite; (c) 71(92)% selenomethionine, 11(7)% aqueous selenite, balance selenocystine. The samples were previously analyzed for total Se concentrations by conventional x-ray fluorescence spectrometry (*36*), yielding the following concentrations (mg.kg<sup>-1</sup> (air dry mass)): (a)  $344\pm17$ , (b)  $41\pm2$ , (c)  $509\pm20$ . Note that the concentrations of the soil samples are higher than average values from Kesterson Reservoir, which for surface soil is about 10 mg kg<sup>-1</sup>.

**Figure 4.** Se K-edge XAS edge fitting analysis results for laboratory soil samples ponded for the following times (days): (a) 0.2; (b) 1.0; (c) 3.7; (d) 50. See Fig. 3 for key. Edge-fitting results give: (a) 95(93)% aqueous selenate, balance aqueous selenite; (b) 65(64)% aqueous selenate, balance aqueous selenite; (c) 65(64)% aqueous selenite, balance monoclinic elemental selenium; (d) 100(100)% monoclinic elemental selenium. This experiment simulated major features of Kesterson Reservoir sediment contamination by seleniferous agricultural drainage waters, in which saline pond waters containing an initial Se concentration of 240 g.m<sup>-3</sup> (98% Se(VI) and 2% Se(IV)) infiltrated through anoxic sediments. Details will be provided in Tokunaga, T.K.; Pickering, I.J.; Brown, G.E. Jr.; submitted to *Soil Sci. Soc. Am. J.*.



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