Environmental Pollution xxx (2017) 1–11

Contents lists available at ScienceDirect

Environmental Pollution

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

Selenium speciation in phosphate mine soils and evaluation of a sequential extraction procedure using XAFS☆

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ARTICLE INFO

Article history:
Received 9 March 2017
Received in revised form
17 July 2017
Accepted 22 July 2017
Available online xxx

Keywords:
Selenium
Speciation
Sequential extraction procedure
XANES

ABSTRACT

Selenium is a trace element found in western US soils, where ingestion of Se-accumulating plants has resulted in livestock fatalities. Therefore, a reliable understanding of Se speciation and bioavailability is critical for effective mitigation. Sequential extraction procedures (SEP) are often employed to examine Se phases and speciation in contaminated soils but may be limited by experimental conditions. We examined the validity of a SEP using X-ray absorption spectroscopy (XAS) for both whole and a sequence of extracted soils. The sequence included removal of soluble, PO_4-extractable, carbonate, amorphous Fe-oxide, crystalline Fe-oxide, organic, and residual Se forms. For whole soils, XANES analyses indicated Se(0) and Se(-II) predominated, with lower amounts of Se(IV) present, related to carbonates and Fe-oxides. Oxidized Se species were more elevated and residual/elemental Se was lower than previous SEP results from ICP-AES suggested. For soils from the SEP sequence, XANES results indicated only partial recovery of carbonate, Fe-oxide and organic Se. This suggests Se was incompletely removed during designated extractions, possibly due to lack of mineral solubilization or reagent specificity. Selenium fractions associated with Fe-oxides were reduced in amount or removed after using hydroxylamine HCl for most soils examined. XANES results indicate partial dissolution of solid-phases may occur during extraction processes. This study demonstrates why precautions should be taken to improve the validity of SEPs. Mineralogical and chemical characterizations should be completed prior to SEP implementation to identify extractable phases or mineral components that may influence extraction effectiveness. Sequential extraction procedures can be appropriately tailored for reliable quantification of speciation in contaminated soils.

1. Introduction

Selenium is a trace element found in elevated concentrations in seleniferous regions. In soils where bioavailable forms are present, toxic levels can accumulate in vegetation. In particular, foraging livestock exhibit Se toxicity following ingestion of Se-hyperaccumulators, such as western aster *Symphyotrichum ascendens* (Lindl.); (Davis et al., 2012; Fessler et al., 2003).

Seleniferous soils throughout the western US are attributed to mining of the Phosphoria Formation and reclamation practices. Associated waste rock contain reduced Se species, selenide (Se(-II)) and elemental Se (Se(0)), which are not immediately soluble (Desborough et al., 1999). Weathering promotes their oxidation to soluble species, selenate (Se(VI)) and selenite (Se(IV)); (McNeal and Balistrieri, 1989). Selenate is more bioavailable, while Se(IV) is typically strongly sorbed onto mineral surfaces, such as clays, oxides, and carbonates (Duc et al., 2006; Goldberg and Glaubig, 1988; Hayes et al., 1987; Masscheleyn et al., 1990; Rajan, 1979; Su and Suarez, 2000).

Selenium bioavailability is a function of soil pH, redox

Abbreviations: LCF, Linear Least-Squares Combination Fitting; SEP, Sequential Extraction Procedure; XANES, X-ray Absorption Near Edge Structure.

☆ This paper has been recommended for acceptance by Prof. W. Wen-Xiong.

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http://dx.doi.org/10.1016/j.envpol.2017.07.071
0269-7491/

conditions, and mineralogy (Geering et al., 1968; USEPA, 1996). Often, examining total concentrations is considered inappropriate when evaluating bioavailability (Tessier et al., 1979). Instead, sequential extraction procedures (SEP) are employed to estimate soluble, exchangeable, mineralogical, and organic phases using progressively stronger reagents. These fractions will often differ greatly in their potential bioavailability. Sequential extractions are easily accomplished and employ accessible chemical reagents. However, SEPs are often criticized for being operationally defined. Several limitations authors have noted include: issues with target element and solid-phase chemical properties (Martin et al., 1987), lack of reagent specificity for target phases (Jouanneau et al., 1983), partial dissolution of target elements (Sulkowski and Hirner, 2006), and redistribution of solubilized elements (Qiang et al., 1994; Shan and Chen, 1993).

In contrast to SEP protocols and methods, synchrotron-sourced spectroscopic techniques provide detailed insight into trace element mineralogical and organic phase associations in soils. Several authors have demonstrated the usefulness of X-ray absorption fine structure (XAFS) techniques for directly comparing SEP results and using this to evaluate their validity for target phases. Previous studies have indicated mobile species are better estimated using SEPs, which are often overlooked using XAFS (Scheinost et al., 2002). Scheinost et al. (2002) examined Zn in smelter-contaminated soils using a combination of XAFS and a SEP. The SEP failed to identify Zn associated with several mineral phases due to precipitation and nonspecific dissolution during extractions. While the SEP was not able to accurately target particular Zn phases, it was, however, able to better estimate mobilized species not identified by XAFS (Scheinost et al., 2002). Qin et al. (2014) compared results from a SEP modified from Kulp and Pratt (2004) and XAFS for Se in seleniferous soils. They also determined SEP results provided useful information related to bioavailable Se fractions not observed in XAFS spectra. The authors noted distinct differences in conclusions drawn from the Se XAFS vs. SEP data. They observed overestimation of Se(0) and underestimation of Se(-II) by the SEP. In combination, the techniques are complementary and provide improved information for trace element speciation identification and quantification (Qin et al., 2014).

Previous research on soil Se demonstrated synchrotron-sourced X-ray techniques, especially XAFS, are reliable for probing local structures and electronic environments under a wide range of concentrations for bulk samples (Pickering et al., 1995; Koningsberger and Prins, 1988). The main portion of generated spectra used was X-ray absorption near edge structure (XANES) region, which occurs between −20 and + 50 eV below and above the absorption edge, providing information about elemental oxidation states, associated ligands, and immediate coordination environments (Pickering et al., 2013). XANES is ideal for analyzing speciation in soils because it can be completed in situ with minimal pretreatments (Scheinost et al., 2002).

Seleniferous soils within the western US are dominated by Se(-II), Se(0) and Se(IV); (Oram et al., 2008; Pickering et al., 1995; Ryser et al., 2006; Weres et al., 1989). This includes both Blackfoot River, ID sediments and soils from Conda phosphate mine, located near the sites for this current study (Oram et al., 2008; Ryser et al., 2006). This has been confirmed by several synchrotron-based investigations, which have demonstrated the role of geomorphological setting on primary mineral oxidation and subsequent weathering products. For example, within the Kesterson Reservoir, XAFS results indicated varying Se phases based on geomorphological setting. Selenium species present in a former evaporation pond indicated a predominance of Se(0) with Se(IV) as a minor component (Pickering et al., 1995).

This work aimed to improve understanding of Se speciation in soils systems and to increase reliability of SEPs for estimating bioavailable Se fractions. Demonstrating usefulness and shortcomings of SEPs is important from a research perspective because they are widely used techniques with possible limitations that reduce their validity. The combination of SEP and synchrotron-based techniques can provide more reliable information regarding Se solid-phases. An evaluation of this procedure will also prove useful from a regulatory perspective and for future remediation efforts. The objectives of this work were to:

(1) Examine Se solid-state speciation in bulk phosphate mine soils
(2) Evaluate a SEP for solid-phase specificity formulated for Se in soils using XAFS
(3) Suggest SEP modifications using results gleaned from XAFS data, determined by its accuracy for examining target phases

2. Materials & methodology

2.1. Soil samples

Soils were collected from three previously reclaimed phosphate mines near Soda Springs, ID, USA. Mine reclamation was completed prior to 1996. Soil samples were collected at a depth of 0–20 cm. This was chosen due to a shallow calcic horizon below this depth, indicating the presence of a wetting front above the water table. Soil plots examined at Gay Mine by Booth (1980), located near Sites A and B, received annual precipitation levels between 36 and 41 cm. Water ponding was also observed from snowmelt. There is speculation that reducing conditions are possible near our study locations after snowmelt.

The three sites, labeled A, B and C, were reclaimed using middle waste shale material from the Phosphoria Formation. Y-shaped sampling transects were established with center points in locations where high Se levels were presumed to occur, based on the presence of Se-hyperaccumulating vegetation. Transect lines were extended 30 m in three directions, and soil samples were collected every 6 m (16 samples per site). Samples were dried and sieved to 8-mesh (2 mm). Soil mineralogy was determined by powder X-ray diffraction (XRD) using a PANalytical Xpert Pro MPD (Westborough, MA) with Cu kα radiation and a scan rate of 0.02° Θ, from 5 to 90° 2Θ. XPowder software was employed to conduct peak searches (Martin-Ramos, 2004). Reference d-spacing and relative intensities were obtained from the ICDD library card database.

Samples were chosen for XANES analysis based on total Se data, determined through a soils digestion using a mixture of HNO_3, H_2O_2, and HCl (Hossner, 1996). For the intial twenty soils collected, Site A soils were lowest in Se (22.9–37.1 mg kg^{-1}), Site B soils were highest (117–435 mg kg^{-1}), and Site C soils were moderate (3.73–106 mg kg^{-1}).

Prior to XAFS analyses, a SEP described by Amacher (2010) and modified from Martens and Suarez (1997) was employed (Table 1). Extracts were analyzed for Se using ICP-AES (SPECTRO Analytical Instruments, Inc., Mahwah, NJ). This procedure accounts for 1) water-soluble, 2) PO_4-extractable, 3) carbonate-associated, 4) amorphous Fe-oxide-associated, 5) organic, and 6) residual/elemental Se phases. To substantiate results from whole soils analyses, six soil samples (seven subsamples each) from the initial twenty soils were re-analyzed under a stepwise SEP approach using XANES (Table 2A and B).

Prior to XANES analyses, samples were air-dried and sieved to 325-mesh (<45 μM). Twenty whole soils were analyzed by bulk in-situ XANES. The six soils used in the second analysis were prepared similarly as whole soils.

Please cite this article in press as: Favorito, J.E., et al., Selenium speciation in phosphate mine soils and evaluation of a sequential extraction procedure using XAFS, Environmental Pollution (2017), http://dx.doi.org/10.1016/j.envpol.2017.07.071