



Sorption and speciation of selenium in boreal forest soil



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ARTICLE INFO

Article history:

Received 20 April 2016

Received in revised form

3 August 2016

Accepted 4 August 2016

Keywords:

Selenite and selenate

Soil

Speciation

Sorption

HPLC–ICP–MS

ABSTRACT

Sorption and speciation of selenium in the initial chemical forms of selenite and selenate were investigated in batch experiments on humus and mineral soil samples taken from a 4–m deep boreal forest soil excavator pit on Olkiluoto Island, on the Baltic Sea coast in southwestern Finland. The HPLC–ICP–MS technique was used to monitor any possible transformations in the selenium liquid phase speciation and to determine the concentrations of selenite and selenate in the samples for calculation of the mass distribution coefficient, K_d , for both species. Both SeO_3^{2-} and SeO_4^{2-} proved to be resistant forms in the prevailing soil conditions and no changes in selenium liquid phase speciation were seen in the sorption experiments in spite of variations in the initial selenium species, incubation time or conditions, pH, temperature or microbial activity. Selenite sorption on the mineral soil increased with time in aerobic conditions whilst the opposite trend was seen for the anaerobic soil samples. Selenite retention correlated with the contents of organic matter and weakly crystalline oxides of aluminum and iron, solution pH and the specific surface area. Selenate exhibited poorer sorption on soil than selenite and on average the K_d values were 27–times lower. Mineral soil was more efficient in retaining selenite and selenate than humus, implicating the possible importance of weakly crystalline aluminum and iron oxides for the retention of oxyanions in Olkiluoto soil. Sterilization of the soil samples decreased the retention of selenite, thus implying some involvement of soil microbes in the sorption processes or a change in sample composition, but it produced no effect for selenate. There was no sorption of selenite by quartz, potassium feldspar, hornblende or muscovite. Biotite showed the best retentive properties for selenite in the model soil solution at about pH 8, followed by hematite, plagioclase and chlorite. The K_d values for these minerals were 18, 14, 8 and 7 L/kg, respectively. It is proposed that selenite sorption is affected by the structural Fe(II) in biotite, which is capable of inducing the reduction of SeO_3^{2-} to Se(0). Selenite probably forms a surface complex with Fe(III) atoms on the surface of hematite, thus explaining its retention on this mineral. None of the minerals retained selenate to any extent.

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1. Introduction

The rationale for the final disposal of spent nuclear fuel from our current nuclear power plants in Finland is based on the spent fuels being placed in a specially built underground repository without any reprocessing. Olkiluoto has been selected as the final disposal site and currently the final repository is being built at depths between 400 and 450 m in the granitic bedrock of the Olkiluoto site on the coast of the Baltic Sea in southwestern Finland (Posiva,

2009). The KBS-3 final disposal concept targets on the isolation of the fuel from its environment by the host bedrock and engineered barriers made up of copper canisters with cast-iron inserts and bentonite buffers surrounding the canisters. The copper canisters are expected to retain their integrity at least for the first 100 000 years, allowing the safe decay of the short-lived radionuclides (Posiva, 2013a; Raiko, 2005). However, if the copper canisters malfunction, radionuclides could escape from the repository into the near-field geosphere and further migrate into far-field environment (intact bedrock), overburden and biosphere. The scenario of a possible leakage of the copper canisters and subsequent release and migration of especially long-lived radionuclides is a factor of great importance in safety assessment of spent nuclear fuel (Posiva, 2013a).

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^{79}Se is one of the long-lived, high priority classified radionuclides according to its possible future radiation dose for man (Hjerpe et al., 2010), its physical half-life of 3.27×10^5 years (Jörg et al., 2010) and occurrence as an anionic species with a low level of interaction with mineral phases and thereby potentially high bioavailability. ^{79}Se is a fission product of ^{235}U and ^{239}Pu , but it is mainly produced via the activation of the impurity component ^{78}Se found in the reactor construction materials and fuel itself by the reaction $^{78}\text{Se}(n,\gamma)^{79}\text{Se}$. Also, the contamination of air, soil or groundwater with stable selenium is produced in multiple human activities such as coal and fossil fuel combustion, the refining of crude oil, and the mining and agricultural irrigation of selenium rich soils (Barceloux, 1999). The average topsoil selenium content is estimated to be 0.33 mg/kg on a world-wide basis (Kabata-Pendias, 2011), whilst the typical range is 0.01–2 mg/kg even though concentrations as high as 1250 mg Se/kg can be encountered in seleniferous soils (Oldfield, 2002). In Olkiluoto soil, selenium is enriched in humus (34 ± 30 mg/kg) and its content in the mineral soil remains rather unchanged irrespective of soil depth (14 ± 13 mg/kg) (Lusa et al., 2009).

Selenium chemistry bears a significant resemblance to that of sulfur, and like sulfur, selenium can form compounds in multiple oxidation states including –II, –I, 0, +IV and +VI. In well-oxidized environments, the most frequently encountered inorganic Se species is selenate, $\text{Se}(+\text{VI})\text{O}_4^{2-}$, which is reduced into selenite, $\text{Se}(+\text{IV})\text{O}_3^{2-}$ in somewhat less oxidizing conditions. Upon conditions becoming more reducing, elemental selenium (0) is formed. Selenides (–II), either H_2Se or insoluble metal selenides, are produced only in highly reducing environments (Masscheleyn and Patrick, 1993). Together with selenium species transformations (Dowdle and Oremland, 1998; Kenward et al., 2006; Lortie et al., 1992; Losi and Frankenberger, 1998), soil microbes form organoselenium compounds through microbial assimilation. In these reactions selenate and selenite are reduced to selenide and incorporated into the organic molecules forming groups of seleno-amino acids (e.g. selenocysteine and selenomethionine), methyl selenides (e.g. $(\text{CH}_3)_2\text{Se}$) and methyl selenones (e.g. $(\text{CH}_3)_2\text{SeO}_2$) (Masscheleyn and Patrick, 1993). Of the various chemical forms of selenium, the oxyanions selenate and selenite are considered to be the most mobile ones and biogeochemically significant.

In addition to the chemical form of selenium and the ambient redox potential, the behavior of selenium in the environment is influenced by several factors such as solution composition and pH, soil mineralogy and organic matter content (Coppin et al., 2009; Février et al., 2007; Fujikawa and Fukui, 1997; Goldberg and Glaubig, 1988; Pezzarossa et al., 1999; Vuori et al., 1989). Solution pH directly affects the mineral surface hydroxyl groups ($\text{M}-\text{OH}$; $\text{M}=\text{Si}$, Al , Fe , Mg , etc.), which are protonated ($\text{M}-\text{OH}_2^+$) and deprotonated ($\text{M}-\text{O}^-$) according to their pK_a values (Essington, 2004). $\text{Si}-\text{OH}$, a typical hydroxyl group met on soil minerals, has pK_a value of approximately 3 and remains in its deprotonated form on the environmentally relevant pH scale exhibiting only cation retention. $\text{Al}-\text{OH}$ and $\text{Fe}-\text{OH}$ groups, however, have pK_a values of approximately 8–9, and thus these groups remain in their protonated form on a wide pH range in soils and play an important role in anion inner and outer sphere complexation. The sorption of polyprotic acid anions such as selenate (pK_{a1} –3 and pK_{a2} 1.7) and selenite (pK_{a1} 2.6 and pK_{a2} 8.4 (ANDRA, 2009)) are at their maximum at low pH values (Essington, 2004), as observed in multiple studies conducted with e.g. minerals, peat and soil (Goldberg and Glaubig, 1988; Lee et al., 2011; Neal et al., 1987). When the solution pH has increased and reached the pK_a value of the acid, the retention of the species can decrease drastically with further increase in pH (Ervanne et al., 2015; Essington, 2004; Fujikawa and Fukui, 1997; Lee et al., 2011). However, even though both selenium oxyanions

are retained by an ion exchange mechanism (outer sphere complexation) (Martinez et al., 2006; Peak and Sparks, 2002), selenite also forms inner sphere monodentate or bidentate mononuclear or binuclear surface complexes with Al and Fe atoms on goethite, hematite, magnetite and hydrous aluminum oxide (Duc et al., 2003; Hayes et al., 1987; Martinez et al., 2006; Missana et al., 2009; Peak, 2006). Surface complexation is favored even at rather high pH values due to aforementioned tendency of $\text{Al}-\text{OH}$ and $\text{Fe}-\text{OH}$ groups to retain their basic character (Essington, 2004).

A well-documented observation is the stronger retention of selenite on the solid phase compared with selenate (Duc et al., 2003; Goldberg and Glaubig, 1988). On the other hand, enrichment of both species is found on soil layers rich in organic matter (Coppin et al., 2009; Lusa et al., 2009; Pezzarossa et al., 1999). The retention mechanism is proposed to go through microbial reductive incorporation of selenium preferentially on low-molecular-weight humic substances (Gustafsson and Johnsson, 1994). Even though organic soil fractions tend to have higher sorption capacities for selenium, it has also been suggested that selenium sorption on organic matter is indirect and proceeds via association with aluminum and iron oxides or clays within the organic matter matrix (Coppin et al., 2009).

High performance liquid chromatography equipped with a direct connection to inductively coupled plasma mass spectrometer (HPLC–ICP–MS) has been widely used in speciation analysis e.g. of iodide, arsenic and selenium from soil extracts and water samples (Shimamoto et al., 2010; Stroud et al., 2012; Tolu et al., 2011; Vassileva et al., 2001) due to its efficient online separation of the chemical species and quantification at the sub parts per million ($\mu\text{g}/\text{L}$) level (B'Hymer and Caruso, 2006). The analytical limit of detection for HPLC–ICP–MS has been found to range from 25 ng Se/L to 4 μg Se/L (Ohta et al., 2011; Stroud et al., 2012; Tolu et al., 2011; Vassileva et al., 2001).

In the present investigation, the sorption and speciation of selenium on humus and mineral soil from the Olkiluoto site was studied by batch sorption experiments. The speciation analysis of selenium was carried out with HPLC–ICP–MS. The research aimed to gain insight into the site-specific retention of selenium on Olkiluoto soil and liquid phase speciation changes taking place in the studied soil system. Also, the effect of time, incubation conditions, pH, microbes, temperature and minerals on selenium liquid phase speciation and sorption were investigated.

2. Materials and methods

2.1. Soil sampling and characterization

Our sampling site, Olkiluoto Island, is situated on the coast of the Baltic Sea in southwestern Finland. Here, a final repository for Finnish spent nuclear fuel is being built. An excavator–dug soil pit was sampled from five different depths extending from 0.70 m below the soil surface to the depth of 3.40 m in the vicinity of the bedrock surface. Organic humus samples were taken from the vicinity of the excavator pit. The sample pit was encoded as OL–KK20, in which OL refers to Olkiluoto and 20 to the pit number. Parallel aerobic and anaerobic samples were collected from each depth. Aerobic humus and mineral soil samples were taken with a shovel and conserved in plastic bags. A special soil corer (Eijkelkamp 04.16) designed to prevent exposure to air was used in the sampling of anaerobic samples into two stainless steel tubes. Aerobic soil samples were transferred to a laboratory and stored at ambient conditions. Anaerobic samples were placed into a nitrogen filled glovebox and preserved without any pretreatment.

The soil characterization has been described previously elsewhere (Söderlund et al., 2015, 2016) and is only reviewed here. The

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