



Sorption of radioiodide in an acidic, nutrient-poor boreal bog: insights into the microbial impact



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ABSTRACT

Batch sorption experiments were conducted to evaluate the sorption behaviour of iodide and the microbial impact on iodide sorption in the surface moss, subsurface peat, gyttja, and clay layers of a nutrient-poor boreal bog. The batch distribution coefficient (K_d) values of iodide decreased as a function of sampling depth. The highest K_d values, 4800 L/Kg dry weight (DW) (geometric mean), were observed in the fresh surface moss and the lowest in the bottom clay (geometric mean 90 mL/g DW). In the surface moss, peat and gyttja layers, which have a high organic matter content (on average 97%), maximum sorption was observed at a pH between ~4 and 5 and in the clay layer at pH 2. The K_d values were significantly lower in sterilized samples, being 20-fold lower than the values found for the unsterilized samples. In addition, the recolonization of sterilized samples with a microbial population from the fresh samples restored the sorption capacity of surface moss, peat and gyttja samples, indicating that the decrease in the sorption was due to the destruction of microbes and supporting the hypothesis that microbes are necessary for the incorporation of iodide into the organic matter. Anoxic conditions reduced the sorption of iodide in fresh, untreated samples, similarly to the effect of sterilization, which supports the hypothesis that iodide is oxidized into I_2/HIO before incorporation into the organic matter. Furthermore, the K_d values positively correlated with peroxidase activity in surface moss, subsurface peat and gyttja layers at +20 °C, and with the bacterial cell counts obtained from plate count agar at +4 °C. Our results demonstrate the importance of viable microbes for the sorption of iodide in the bog environment, having a high organic matter content and a low pH.

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1. Introduction

Spent nuclear fuel from the Finnish nuclear power reactors is planned to be disposed of in a deep bedrock repository in the crystalline bedrock on Olkiluoto Island, located on the southwest coast of Finland. The coastline of the Olkiluoto area is changing due to on-going post-glacial land uplift in the region (Haapanen et al., 2013). Within six millennia, Olkiluoto Island will develop into an inland site, during which time new bogs will form in the area. The formation of new bogs will take place during the same time period as, according to biosphere safety assessment calculations, the possible releases from the deep spent nuclear fuel repository would be able to reach the biosphere if the nuclear waste canisters were to lose their integrity. Thus, Lastensuo bog has been chosen as an analogous biotope in biosphere safety assessment for the long-lived

radionuclides present in spent nuclear fuel. ^{129}I is among the most important radionuclides in the long-term safety assessments due to its very long half-life of 15.7 My, large inventory in spent nuclear fuel and high mobility. In addition, iodine is highly biophilic and bioaccumulates in humans, especially in the thyroid glands, through the food chain or inhalation (Xu et al., 2011a).

Several factors affect the migration and sorption of iodine in the geosphere, including its chemical speciation, organic matter content, mineral properties, redox potential, pH and microorganisms (Assemi and Erten, 1994; Evans and Hammad, 1995; Sheppard et al., 1995; Ashworth et al., 2003; Ashworth and Shaw, 2006; Li et al., 2012). Iodine is predominantly retained in soil organic matter (SOM) (Bostock et al., 2003; Yamaguchi et al., 2010; Xu et al., 2011a; Li et al., 2012; Xu et al., 2013), and microorganisms have been reported to affect the sorption of iodine in several studies (e.g. Bunzl and Schimmack, 1988; Muramatsu et al., 1990; Assemi and Erten, 1994; Evans and Hammad, 1995; Yamaguchi et al., 2010; Li et al., 2011, 2012; Xu et al., 2013).

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Major iodine species found in environmental systems include iodide (I^-), iodate (IO_3^-), molecular iodine (I_2) and organo-iodine (Muramatsu et al., 1990; Muramatsu and Yoshida, 1999; Li et al., 2012; Xu et al., 2013; Kaplan et al., 2014), of which organo-iodine forms a major proportion of iodine in a number of environments with a high organic matter content (Xu et al., 2013). Iodine is considered to occur as I^- in anoxic, waterlogged environments with a low organic matter content and as IO_3^- in oxic environments (Yuita, 1992; Ashworth et al., 2003; Ashworth and Shaw, 2006; Li et al., 2012). Iodide is assumed to remain stable over typical pH and Eh ranges because of its thermodynamically unfavourable oxidation via single-step electron transfer without a strong oxidant (Li et al., 2012). Abiotic oxidants such as MnO_2 and Fe_2O_3 can oxidize iodide, but the importance of these reactions is limited under environments with a low pH (<5) (Xu et al., 2011b). Humic substances can act as oxidizing agents for iodide (Keller et al., 2009), but in SOM the oxidation of iodide is linked to soil microbial activity (Bunzl and Schimmack, 1988; Evans and Hammad, 1995; Koch-Steindl and Pröhl, 2001; Li et al., 2012), involving extracellular enzymes excreted from the microbial cells (Bunzl and Schimmack, 1988; Muramatsu et al., 1990; Sheppard and Hawkins, 1995; Yoshida et al., 1998).

In organic soils, iodide oxidation can produce numerous highly reactive intermediates, and it has been shown in multiple studies that iodide must be oxidized into an intermediate such as I_2 or hypiodous acid (HIO) in order to interact with soil organic matter through iodination (Warner et al., 2000; Reiller et al., 2006; Schlegel et al., 2006; Li et al., 2012; Xu et al., 2013). Especially in oxidizing, acidic environments such as bogs, I_2 is formed (Li et al., 2012; Xu et al., 2013; Kaplan et al., 2014), and in aqueous solutions I_2 is readily hydrolysed to HIO by the reaction $I_2 + H_2O \leftrightarrow HIO + I^- + H^+$ (Nagy et al., 2003). As the dissociation constant (pK_a) of HIO is 10.4 (Bichsel and von Gunten, 2000), its undissociated form, IO^- , can be ignored in acidic environments. Consequently, it is expected that I_2 /HIO reacts with organic matter to form organo-iodine compounds (Yamaguchi et al., 2010; Xu et al., 2011a; Li et al., 2012; Seki et al., 2013; Xu et al., 2013). Furthermore the volatilization of iodide as I_2 or CH_3I from peat has been reported to be negligible, less than 0.2% (Sheppard and Hawkins, 1995).

Based on their studies on stable ^{127}I and radioactive ^{129}I at the Savannah River Site, Xu et al. (2011a) suggested that iodine is incorporated into SOM via covalent C–I bonds. Recently, Xu et al. (2013) demonstrated that iodide is catalytically oxidized into reactive iodine species (e.g. I_2 or HIO) by peroxides, and at the same time fulvic acid is oxidized by peroxides into more aliphatic and less aromatic compounds on which reactive iodine is bound to form new organo-iodine compounds (Xu et al., 2013). Xu et al. (2013) reported that in 91% of the total of 129 identified organo-iodine compounds, iodine was covalently bound to the newly-produced organic components. The identified organo-iodine compounds were distributed between three classes: unsaturated hydrocarbons > lignin > protein (Xu et al., 2013). Xu et al. (2013) also found that ~69% of the identified organo-iodine species contained nitrogen, presumably in the form of $-NH_2$ or $-NHCO$ groups, which are ring activating groups, enhancing the electrophilic substitution in ortho and para directions. Shetaya et al. (2012) found no evidence for $^{129}I^-$ oxidation to $^{129}IO_3^-$ in topsoil and subsoil samples from the East Midlands of England, but the formation of soluble ^{129}I -org species was rapid.

In the mineral soils, important functional surface groups are found in silicate and oxide minerals. In these minerals, the most abundant functional surface groups are the hydroxyl groups associated with mineral-forming metals, such as silicon, aluminium, iron and magnesium. These M–OH groups are amphoteric,

protonating to positively charged $M-OH_2^+$ at low pH values and deprotonating to negatively charged $M-O^-$ at higher pH levels. Simple anions, such as iodide, typically sorb on the positively charged groups by outer-sphere complexation to form $M-OH_2^+ I^-$, while oxoanions, such as iodate sorb by ligand exchange (inner-sphere complexation) to form $M-IO_3$. Thus, the hydroxyl groups on the mineral surfaces prefer iodate over iodide as iodide sorbed by outer-sphere complexation is readily exchangeable. The pH range in which a mineral is able to take up anions depends on the acidity of the mineral-forming metal. The siloxane group remains in the unprotonated Si–OH form over the whole environmentally relevant pH region and is thus not able to take up anions. The most important hydroxyl groups with respect to anion sorption are those associated with iron and aluminium, which remain protonated up to a pH of about 8. At pH values below 5, the most important inorganic iodine sorbents are iron oxides, while at a pH from 5 to 7, aluminium oxides dominate (Whitehead, 1974; Um et al., 2004).

In this study, the sorption of radioiodide on bog samples (*Sphagnum* moss, peat, gyttja and clay) from the Lastensuo bog was examined in both unsterilized and sterilized samples. Elovich kinetics and pseudo-second-order models were used to evaluate the effects of temperature and sterilization on the sorption kinetics of iodide. In addition, the bacterial peroxidase activity found in the sorption batch experiment samples was determined and the correlation between iodide uptake in peat and microbial peroxide activities was assessed. The primary motivation of our study was to assess the sorption characteristics of iodine in an acidic bog for the long-term safety evaluation of the final disposal of spent nuclear fuel and to evaluate the microbial impact on the sorption of iodide.

2. Materials and methods

2.1. Sampling site, sample pretreatment, and peat and bog water analysis

Our sampling area, Lastensuo, is situated on the western coast of Finland, about 30 km northeast of the Olkiluoto repository area. This raised, ombrotrophic, bog is surrounded by hummocky till soils and has a surface area of 440 ha (Mäkilä and Grundström, 2008; Haapanen et al., 2013). The maximum thickness of the peat layer is approximately 6 m and the surface level is 44–48 m above sea level. The bottom soil below the peat layers consists of clay and sand derived from a former seabed. In the middle parts of the bog, gyttja (mud formed from decomposed peat) is found on top of the clay layer (Mäkilä and Grundström, 2008). The mire types found in the centre parts of the bog are treeless or near-treeless *Sphagnum fuscum* bog, *S. fuscum* pine bog, ridge hollow pine bog and hollow bog (Mäkilä and Grundström, 2008). Towards the margins of the bog, the mire types change through low sedge bog and cotton grass pine bog to tall sedge pine fen and forested peatland. The main peat types found in Lastensuo include *Sphagnum* peat (58%), sedge-moss peat (8%), sedge peat (19%) and few-flowered sedge (15%) (Mäkilä and Grundström, 2008). According to radiocarbon dating, peat accumulation in the mire started 5300 years ago and the overall average peat accumulation rate has been 1.08 mm/a (Mäkilä and Grundström, 2008).

The bacterial community of the bog profile mainly consists of Acidobacteria and Proteobacteria in the surface moss and Acidobacteria in the peat layers, with growing abundances of Chloroflexi, Verrucomicrobia and Spirochaeta at greater depth (Tsitko et al., 2014). The gyttja layer and bottom clay have greater bacterial diversity than the peat layers, and in addition to Acidobacteria they also contain Verrucomicrobia, Chloroflexi, Bacteroidetes, Spirochaeta and OP8 groups. The number of bacteria/g DW sample

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