



## Factors affecting the sorption of cesium in a nutrient-poor boreal bog



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### ABSTRACT

<sup>135</sup>Cs is among the most important radionuclides in the long-term safety assessments of spent nuclear fuel, due to its long half-life of 2.3 My and large inventory in spent nuclear fuel. Batch sorption experiments were conducted to evaluate the sorption behavior of radiocesium (<sup>134</sup>Cs) in the surface moss, peat, gyttja, and clay layers of 7-m-deep profiles taken from a nutrient-poor boreal bog. The batch distribution coefficient ( $K_d$ ) values of radiocesium increased as a function of sampling depth. The highest  $K_d$  values, with a geometric mean of 3200 L/kg dry weight (DW), were observed in the bottom clay layer and the lowest in the 0.5–1.0 m peat layer (50 L/kg DW). The maximum sorption in all studied layers was observed at a pH between 7 and 9.5. The *in situ*  $K_d$  values of <sup>133</sup>Cs in surface *Sphagnum* moss, peat and gyttja samples were one order of magnitude higher than the  $K_d$  values obtained using the batch method. The highest *in situ*  $K_d$  values (9040 L/kg DW) were recorded for the surface moss layer. The sterilization of fresh surface moss, peat, gyttja and clay samples decreased the sorption of radiocesium by 38%, although the difference was not statistically significant. However, bacteria belonging to the genera *Pseudomonas*, *Paenibacillus*, *Rhodococcus* and *Burkholderia* isolated from the bog were found to remove radiocesium from the solution under laboratory conditions. The highest biosorption was observed for *Paenibacillus* sp. VO-1-LW and *Pseudomonas* sp. PS-0-L isolates. When isolated bacteria were added to sterilized bog samples, the removal of radiocesium from the solution increased by an average of 50% compared to the removal recorded for pure sterilized peat. Our results demonstrate that the sorption of radiocesium in the bog environment is dependent on pH and the type of the bog layer and that common environmental bacteria prevailing in the bog can remove cesium from the solution phase.

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## 1. Introduction

Nuclear energy production results in spent nuclear fuel, which in Finland will be disposed of in a deep bedrock repository in the crystalline bedrock on Olkiluoto Island, located in southwestern Finland (Posiva, 2012). The long-term safety of the repository is based on several barriers, such as the copper sheeted waste canister, the bentonite clay protecting the canister and the bedrock of the repository (KBS-3 model, SKB, 1983a,b). However, if the waste canisters were to lose their integrity, radionuclides could escape from the repository. The dissolution of radionuclides from the spent nuclear fuel into the groundwater and their potential migration into the overburden may finally result in the

contamination of the biosphere. Due to significant land uplift on the west coast of Finland, within six millennia Olkiluoto Island will develop into an inland site, and during this period new bogs will form in the area (Haapanen et al., 2013). The formation of new bogs will occur in the same time period in which, according to safety assessment calculations, the first possible emissions from the deep bedrock repository to the surface ecosystems would be possible if the nuclear waste canisters were to leak (Posiva, 2012).

Among the most important radionuclides in long-term safety assessments is <sup>135</sup>Cs, due to its long half-life of 2.3 My and large inventory in spent nuclear fuel (Helin et al., 2010). As an alkali metal, cesium is potentially highly soluble and it occurs in the spent nuclear fuel essentially in the instant release fraction (IRF), which represents the fraction of safety-relevant radionuclides that will be released from the spent nuclear fuel at a faster dissolution rate than the matrix. Cesium is a relatively rare element in soils and typical

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concentrations of stable cesium ( $^{133}\text{Cs}$ ) are approximately 5 mg/kg (Sparks, 2003). In aqueous solutions, cesium is present as free  $\text{Cs}^+$  ions and its speciation is unaffected by changes in the pH or redox conditions (Lieser and Steinkopff, 1989). In soils, cesium is typically sorbed by outer-sphere complexation, but in clay and mica minerals cesium also forms inner-sphere complexes (Bostick et al., 2002; Chang et al., 1993; Zhuang et al., 2003). Cesium is also found on the surfaces of iron, manganese and aluminum oxides, as well as in organic matter. The selectivity of cesium sorption on these materials is, however, substantially lower than on clay and mica minerals.

In organic matter, Cs sorption is expected on the deprotonated weakly acidic carboxylic groups (R-COOH) and alcoholic and phenolic -OH groups (Sparks, 2003; Paasonen-Kivekäs et al., 2009; Tan, 2003). These groups are amphoteric and deprotonate in alkaline conditions, enabling cesium sorption onto the resulting negatively charged groups through electrostatic interactions. As the conditions in bogs are acidic, limited sorption of cesium on the organic matter is expected under *in situ* pH conditions.

Biological adsorption and desorption processes are analogous to mineralogical processes (Anderson et al., 2011). Bacterial surfaces have several extracellular functional groups, on which adsorption is possible. These groups include carboxylic, phosphate, phosphodiester and hydroxyl sites, which deprotonate as pH increases. The microorganisms show considerable variety in their ability to accumulate  $\text{Cs}^+$  and microbial  $\text{Cs}^+$  accumulation is generally accompanied by a stoichiometric exchange for intracellular  $\text{K}^+$  (Avery, 1995). Only limited data are available on the biosorption of cesium by bacteria. Sasaki et al. (2002) have reported biosorption  $K_d$  values below 100 L/kg after one to 120 days of incubation for cesium using anaerobic iron- and sulfate-reducing bacterial mixtures and Ngwenya and Chirwa (2010) reported a maximum uptake value of 238 mg/g bacterial biomass (dry weight) for sulfate-reducing bacteria. Luk'yanova et al. (2008) reported that bacteria isolated from deep groundwater, including among others *Pseudomonas fluorescens* C50-1, *Pseudomonas stutzeri* 116-1-1, *Pseudomonas putida* C49-2, *Sphingomonas panii* 116-2-2 and *Acinetobacter johnsonii* C61-2, did not sorb radiocesium ( $^{137}\text{Cs}$ ). On the contrary, the exopolymers (PFCO2) produced from *P. fluorescens* C-2 have been reported to remove Cs ( $^{133}\text{Cs}$ ) from an aqueous solution (Mao et al., 2011).

In this study, the sorption of radiocesium ( $^{134}\text{Cs}$ ) on bog samples (surface *Sphagnum* moss, peat, gyttja and clay) from an acidic, nutrient-poor boreal bog was examined in dried and undried fresh samples, as well as in sterilized fresh samples. In addition, the *in situ*  $K_d$  values for  $^{133}\text{Cs}$  were obtained from 1 M ammonium acetate extraction and the measurement of  $^{133}\text{Cs}$  in bog water. In addition, the removal of cesium from the solution by *Pseudomonas* sp. PS-0-L, *Pseudomonas* sp. T5-6-I, *Burkholderia* sp. K5-6-SY, *Rhodococcus* sp. B6-7-CB, *Paenibacillus* sp. B6-7-W and *Paenibacillus* sp. V0-1-LW isolated from the surface *Sphagnum* moss, peat, gyttja and clay samples (Lusa et al., 2015a) was examined using 1% Tryptone broth and sterilized bog samples in model bog water solution as the nutrient media. The studies on the sorption behavior of cesium have been previously focused especially on clays and agricultural and forest soils. Knowledge about the cesium sorption in bog environment/on peat (e.g. Absalom et al., 1995) and cesium biosorption is however scarce (e.g. Sasaki et al., 2002). The primary motivation of our study was to assess the sorption characteristics of cesium in an acidic bog and the effect of microbiota on the cesium sorption in this boreal environment. Comprehensive information about the cesium sorption behavior in the bog environment is crucial for the long-term safety evaluation of the final disposal of spent nuclear fuel as bogs will be important ecotypes in the repository area in the future.

## 2. Materials and methods

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

Our sampling site, Lastensuo bog, is a nutrient-poor, ombrotrophic bog located on the western coast of Finland. Lastensuo bog represents the mire type expected to be found in the Olkiluoto area in the future, and has therefore been chosen as an analogous biotope in biosphere safety assessment for the long-lived radionuclides present in spent nuclear fuel (Haapanen et al., 2011). The surface level of the bog is 44–48 m above sea level and the area of the bog is 440 ha (Mäkilä and Grundström, 2008). Peat accumulation in this bog, according to radiocarbon dating, started 5300 years ago and the average peat accumulation rate is 1.1 mm/a, leading to a maximum thickness of the peat layer of 6 m (Mäkilä and Grundström, 2008; Haapanen et al., 2013). The bottom soil below the peat layers consists of clay derived from a former seabed and gyttja is found on top of the clay layer (Mäkilä and Grundström, 2008). The center parts of the bog consist of treeless or near-treeless *Sphagnum fuscum* bog, *S. fuscum* pine bog, ridge hollow pine bog and hollow bog, while at the edges of the bog, low sedge bog, cotton grass pine bog, tall sedge pine fen and forested peatland are found (Mäkilä and Grundström, 2008). The main peat types include *Sphagnum* peat (58%), sedge peat (19%) and few-flowered sedge (15%) (Mäkilä and Grundström, 2008). Acidobacteria and Proteobacteria in the surface moss and Acidobacteria in the peat layers, with growing abundances of Cloroflexi, Verrucomicrobia, Bacteroidetes, Spirochaeta and OP8 groups at greater depths, are the main bacterial populations found in the Lastensuo bog profile (Tsitko et al., 2014).

Discontinuous depth-wise samples of peat were obtained from four sampling points located in the middle part of the bog (61°17'31", 21°50'22", WGS84 coordinate system). Samples were taken from different representative layers between the depths of 0.5 and 7.0 m during two sampling campaigns in 2011 and in 2013. In 2011 samples from the depths of 0.5–6.0 m were obtained for the batch and *in situ*  $K_d$  value determinations using a stainless steel peat corer with a nest length of 50 cm, a diameter of 5 cm and a sampling interval of 0.5 m ("MacCauley sampler"). The sampling layers with 0.5 m intervals were 0.5–1.0 m, 1.5–2.0 m, 2.5–3.0 m, 3.5–4.0 m, 4.5–5.0 m and 5.5–6.0 m. The samples were taken into 1-L plastics bags, brought to the laboratory in cool bags and dried at room temperature. In addition bog water samples from the surface and the depths of 0.5–1.0 m, 2.5–3.0 m and 5.5–6.0 m were separated from the peat by filtering through Whatman® filter paper with a pore size of 11 µm at the sampling site. In the laboratory, the bog water samples were further filtered through a membrane filter with a pore size of 0.45 µm (Whatman ME membrane filter, Whatman plc, Maidstone, Kent, UK). pH of the bog water was measured from the filtered samples and the analysis of dissolved organic carbon (DOC) was carried out in the Finnish Forest Research Institute (Metla) (Table 1). The major cations Na, Mg, K and Ca, were determined from the bog water using ICP-MS (Agilent 7500ce, Agilent Technologies, Inc., Santa Clara, CA, USA) and the major anions,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , using IC (ion chromatography). Based on the measured cation and anion concentrations, simulated bog water used in the determination of  $K_d$  values from the experimental batch samples was prepared (Table 1).

In 2013 additional samples for the microbial and biosorption studies and pH studies were obtained from representative depths between 0.5 and 7.0 m using a stainless steel peat corer with a nest length of 50 cm, a diameter of 15 cm and a sampling interval of 0.5 m. The sampled layers were the same as those retrieved in 2011 sampling, with the exception of one additional layer from 6.5 to

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