



Geochemical controls of iodine uptake and transport in Savannah River Site subsurface sediments



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ABSTRACT

Because iodine-129 has a half-life of nearly 16 million years, poses major health threats, and can be mobile in the environment, it is important to use the best estimates for kinetics of sorption in risk assessment models. Previous work estimating the iodine sorption has not allowed for samples to reach full equilibrium and field studies have reported significant fractions of up to three major species of iodine; therefore, further research into the kinetics of iodine sorption to sediments is warranted. The objective of this study is to investigate the kinetics of iodine sorption in the presence of subsurface upland sediments and wetland sediments from an area within an ¹²⁹I plume at the Savannah River Site in Aiken, SC. Batch sorption studies for these systems took longer than 8 weeks to reach equilibrium, which is significant as previous studies did not reach such timescales. In addition, experiments were conducted under oxic and anoxic conditions. Results confirm that there are three species present in these systems (iodide, iodate, and organo-iodine) with a majority as organo-iodine species at equilibrium for systems with high organic matter content. It is notable that the anoxic conditions exhibited reduced sorption for the iodate species to wetland sediment with high organic matter.

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1. Introduction

1.1. Study site

From 1955 until 1988, low level nuclear waste was disposed of in unlined seepage basins at the F-Area of the Savannah River Site (SRS). Two curies of ¹²⁹I were estimated to be disposed of in these seepage basins during operations (Killian et al., 1985). In 1988, the basins were closed following addition of limestone and blast furnace slag and covered with a low permeability engineered cover to minimize rainwater infiltration. Limestone was added to aid in the precipitation of cationic radionuclides that had been released from the basins and slag material, with its high iron sulfide content, was added to reduce the radionuclides to less mobile forms (Li et al., 2011).

The remediation efforts resulted in a modest pH increase of 0.7 units from the initial pH in 1988 of approximately 3.0 (Kaplan et al., 2011). This pH increase resulted in decreased aqueous concentrations of the cationic radionuclides within the system. How-

ever, the iodine species existed as negatively charged ions in the form of I⁻ and IO₃⁻ (Otosaka et al., 2011). In response to the pH increase within the system, the levels of ¹²⁹I have steadily increased for the well closest to the seepage basin with a concentration of 200 pCi/L measured in 1993 and a current concentration between 400 and 1000 pCi/L (14.8 and 37 Bq/L) depending on the location. The greatest concentration of ¹²⁹I measured was 1060 pCi/L (39.2 Bq/L) (Kaplan et al., 2011). The contaminant plume has now reached a downstream wetland along Four Mile Branch creek. The ¹²⁹I concentration increase in the plume may be attributed to the pH increase at the source and within the plume resulting from limestone additions during the seepage basin closure and remediation; thus, there is a clear need to understand the influence of pH on ¹²⁹I mobility in SRS sediments. In addition to pH effects, the speciation of iodine is changing from iodide (I⁻) to iodate (IO₃⁻) as it leaves the basins and approaches the wetland, as described by Otosaka et al. (2011).

The EPA Maximum Contaminant Limit (MCL) is 1 pCi/L (0.037 Bq/L) or 4 mrem/yr (400 mSv/yr) for ¹²⁹I. This low MCL is based on the dose conversion factor of 1.06 × 10⁻⁷ Sv/Bq (EPA, 2002). Therefore, release of even small amounts of radioiodine can result in a significant risk. Although ¹²⁹I comprised only 0.00002% of the total radioactivity released from the seepage

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basins at SRS, it represents 13% of the offsite risk (Kantelo et al., 1990). It is a concern for disposal and human health reasons because of its half-life of nearly 16 million years and because iodine taken into the body will accumulate in the thyroid. The objective of this study was to conduct batch sorption isotherms with relevant sediments from SRS under both oxic and anoxic conditions to better refine the sorption terms of risk assessment models for the site.

1.2. Iodine geochemistry

Iodine can be found as an anion in various oxidation states ranging from -1 to $+7$. The most common species in natural organic matter (NOM)-free aqueous systems are reduced iodide (I^-) [-1] and oxidized iodate (IO_3^-) [$+5$] (Schwehr and Santschi, 2003; Santschi and Schwehr, 2004; Schwehr et al., 2009). Examination of theoretical iodine Eh–pH relationships as described by Baas-Becking et al. (1960) and Ootosaka et al. (2011) indicate that iodide should be the major species under the Eh and pH conditions of the F-Area groundwater. However, it is noteworthy that organo-iodine species are not currently included in geochemical speciation databases. The organo-iodine species have not been well defined and thermodynamic stability constants are not available, therefore standard thermodynamic databases cannot accurately describe the wetland system at SRS. Furthermore, most speciation models assume equilibrium conditions which may not persist in the SRS F-Area subsurface particularly near the wetland environment due to steep chemical gradients from previous acidic waste disposal and current remediation efforts.

Iodine sorption rate and mobility is greatly determined by its oxidation and speciation. Iodate has been shown to sorb significantly more than iodide which has been utilized as a nonreactive tracer in previous studies (Hu et al., 2005; Zhang et al., 2011). In addition, iodate has been shown to reduce to iodide due to the presence of natural reductants such as Fe(II) in clays (Hu et al., 2005). Furthermore, the sorption reaction of iodate is slower than that of iodide species, which leads to the theory that IO_3^- is first reduced to HIO and then to I^- unless a reaction with natural organic matter (NOM) is occurring (Schwehr and Santschi, 2003; Santschi and Schwehr, 2004; Steinberg et al., 2008; Schwehr et al., 2009; Xu et al., 2011a,b, 2012, 2013; Zhang et al., 2011).

Sorption of iodine species by NOM has been established as a major factor for iodine binding to sediments and soils by iodine binding to aromatic moieties in NOM (Cosgrove, 1970; Schlegel et al., 2006; Steinberg et al., 2008; Xu et al., 2011a,b, 2012, 2013). The reduction of IO_3^- species to HIO by diphenolic moieties analogous to hydroquinone may allow the iodine species to undergo aromatic substitution into the NOM forming organo-iodine species (Schwehr and Santschi, 2003; Santschi and Schwehr, 2004; Steinberg et al., 2008; Schwehr et al., 2009; Xu et al., 2011a,b, 2012; Zhang et al., 2011). Organo-iodine species have been found to be a major fraction of total iodine in aqueous environmental systems at ambient conditions (Schwehr et al., 2009; Zhang et al., 2011; Xu et al., 2011a, 2012). In addition, Oktay et al. (2001) found that 70–85% of the iodine in the Mississippi River was associated with colloidal organic matter. The incorporation of iodine species into NOM may greatly affect its transport in groundwater systems because organo-iodine was previously determined to have greater retardation than inorganic iodine species (Hu et al., 2005; Xu et al., 2011a; Zhang et al., 2011). For example, in a study by Hu et al. (2005) 4-iodoaniline (representative of organo-iodine species) exhibited a retardation factor of 25.9 versus 1.0 for iodide in a SRS subsurface soil with 2.3% NOM. The study concluded that the NOM content of a system may be a factor in transport of organo-iodine species.

2. Materials and methods

2.1. Description of SRS sediments

Two clean sediments from SRS were utilized for the sorption studies: a subsurface, red-clayey sand from the F-Area at SRS referred to throughout as upland and a wetland sediment sample from Four Mile Branch wetland at SRS referred to as wetland (Table 1). The wetland soil was stored hydrated at 4°C while the upland sediment was stored dried at room temperature.

2.2. Preparation of stock and standards for iodide and iodate

The iodide (I^-) stock was prepared by dissolving a solid potassium iodide (High Purity Standards) and the iodate (IO_3^-) stock was prepared by dissolving a solid potassium iodate (Alfa Aesar, ACS grade) in distilled-deionized H_2O (DDI). The solution was stored in an amber bottle at 4°C and the concentration was verified each time samples were analyzed on the inductively coupled plasma mass spectrometer (ICP-MS) Thermo X series II. In addition to ICP-MS analysis, the concentration of the iodide and iodate stock solutions was analyzed by use of an iodide probe (Orion Sure-Flow 9653BN, Thermo Scientific). For the iodate stock solution, an aliquot was first measured with the iodide probe to show the absence of iodide, then the aliquot was acidified by addition of HCl and reduced to iodide with $NaHSO_3$ prior to analysis with the iodide probe to confirm the concentrations measured by ICP-MS.

2.3. Iodide and iodate sorption techniques

2.3.1. Sample preparation techniques

Batch sorption experiments were performed in 15 mL (BD Falcon) polypropylene, conical tubes containing 0.01 M NaCl and 25 g/L of upland or wetland sediments and a total volume of 10 mL with varying concentrations of iodate and iodide. Initially, pH dependent isotherms were prepared at a concentration of 10,000 $\mu\text{g/L}$ and 1000 $\mu\text{g/L}$ iodate with wetland sediment. The different total concentrations yielded different K_d values and thus implied that sorption was non-linear. Therefore, concentration isotherms were completed for concentrations of 500, 1000, 2000, 5000, and 10,000 $\mu\text{g/L}$ iodate at pH values of 4.83 ± 0.14 and 4.58 ± 0.19 for the upland and wetland sediments, respectively. These acidic pH levels are typical of SRS sediments, which are on average about pH 5.5 (Dixon et al., 1997). Additional pH isotherms were completed for iodate at 1000 $\mu\text{g/L}$ for upland sediments and iodide at 1000 $\mu\text{g/L}$ for upland and wetland sediments for comparison under oxic (atmospheric) conditions and anoxic conditions (within a glovebox (Coy Laboratories) with a 98%/2% nitrogen/hydrogen gas mix). For the samples in the variable pH and concentration experiments, the pH of each tube was adjusted at the time the sediment suspensions were spiked with the allotted iodide or iodate and re-adjusted on day 3. After day 3, all samples were

Table 1
Summary of significant characteristics of SRS sediments.

Parameter	Upland subsurface sediment (SRS upland)	Four Mile Branch wetland sediment (SRS wetland)
Sand/silt/clay (% by weight)	57.9/40.6/1.6	85.5/11.7/2.8
Textural classification	Sandy loam	Loamy sand
Equilibrium pH	4.55	4.1
Point of zero charge pH	5.65	4.01
Organic carbon content (% by weight)	1.2	9.7
Water content (% by weight)	–	43

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