



## Sorption and transport of iodine species in sediments from the Savannah River and Hanford Sites

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Received 1 June 2004; received in revised form 28 April 2005; accepted 3 May 2005

### Abstract

Iodine is an important element in studies of environmental protection and human health, global-scale hydrologic processes and nuclear nonproliferation. Biogeochemical cycling of iodine is complex, because iodine occurs in multiple oxidation states and as inorganic and organic species that may be hydrophilic, atmophilic, and biophilic. In this study, we applied new analytical techniques to study the sorption and transport behavior of iodine species (iodide, iodate, and 4-iodoaniline) in sediments collected at the Savannah River and Hanford Sites, where anthropogenic <sup>129</sup>I from prior nuclear fuel processing activities poses an environmental risk. We conducted integrated column and batch experiments to investigate the interconversion, sorption and transport of iodine species, and the sediments we examined exhibit a wide range in organic matter, clay mineralogy, soil pH, and texture.

The results of our experiments illustrate complex behavior with various processes occurring, including iodate reduction, irreversible retention or mass loss of iodide, and rate-limited and nonlinear sorption. There was an appreciable iodate reduction to iodide, presumably mediated by the structural Fe(II) in some clay minerals; therefore, careful attention must be given to potential interconversion among species when interpreting the biogeochemical behavior of iodine in the environment. The different iodine species exhibited dramatically different sorption and transport behavior in three sediment samples, possessing different physico-chemical properties, collected from different depths at the Savannah River Site. Our study yielded additional insight into processes and mechanisms affecting the geochemical cycling of iodine in the environment, and

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provided quantitative estimates of key parameters (e.g., extent and rate of sorption) for risk assessment at these sites.

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*Keywords:* Iodine; Sorption; Transport; Sediment

## 1. Introduction

Iodine is an essential micronutrient in animals and humans, necessary for the production of thyroid hormones and for the proper functioning of the thyroid gland, and deficiencies can lead to severe metabolic disorders. As reported by the World Health Organization in 1999, iodine deficiency is a significant public health problem in 130 countries, with one-third of the world's population estimated to be at risk. Furthermore, because radioactive iodine is concentrated in the human thyroid (e.g., [Vanmiddlesworth et al., 2000](#)), an uncontrolled release of radioactive iodine could constitute a direct threat to human populations.

Iodine has one stable isotope,  $^{127}\text{I}$ , and 25 radioactive isotopes that include 10 fission products with very short half-lives ranging from minutes to a few hours. Two radionuclides ( $^{131}\text{I}$  and  $^{129}\text{I}$ ) are particularly of environmental concern. Following a nuclear accident (such as the one at Chernobyl) or an intentional radiological release,  $^{131}\text{I}$  would be an acute contaminant because of its short half-life of 8.05 days and a high specific activity. Having a long half-life ( $1.57 \times 10^7$  years),  $^{129}\text{I}$  is an important fission product with a fission yield of 0.9% from uranium-235 and 1.6% from plutonium-239. Nuclear-fuel reprocessing facilities constitute the major source of  $^{129}\text{I}$  released in the environment. Up until 1998, a total of 2300 kg of  $^{129}\text{I}$  was discharged in the marine environment by two European facilities at La Hague in France and Sellafield in England, an amount that is 50 times the total release from nuclear weapon tests ([Hou et al., 2000](#); [Fréchou and Calmet, 2003](#)). From 1944 through 1972, the plutonium-production operation at the Hanford Site in Washington released about 260 kg of  $^{129}\text{I}$  into the air. In comparison, the operation of production reactors from 1953 to about 1990 at the Savannah River Site (SRS) in South Carolina released about 32 kg of  $^{129}\text{I}$  into the air.

As the only naturally occurring radioactive isotope of iodine,  $^{129}\text{I}$  can also be produced by cosmic-ray interactions with xenon in the upper atmosphere and by spontaneous fission of uranium-238 in the geosphere. Anthropogenic inputs of  $^{129}\text{I}$  have overwhelmed the natural inventory, increasing the hydrospheric  $^{129}\text{I}/^{127}\text{I}$  ratio from  $1.5 \times 10^{-12}$  during the pre-nuclear era up to  $10^{-10}$ – $10^{-4}$  ([Moran et al., 1998](#); [Fréchou and Calmet, 2003](#); [Kekli et al., 2003](#)). This change in the ratio creates an opportunity for the application of anthropogenic  $^{129}\text{I}$  as an environmental tracer, originally proposed by [Edwards \(1962\)](#), to examine a variety of processes including ocean circulation, biogeochemical cycling, and regional hydrologic (e.g., atmosphere, surface water, and groundwater) processes (e.g., [Moran et al., 1999](#); [Oktay et al., 2001](#)).

Iodine exhibits complex geochemical behavior. With oxidation states ranging from  $-1$  to  $+7$ , the predominant states in aqueous systems are  $-1$  (iodide,  $\text{I}^-$ ) and  $+5$  (iodate,  $\text{IO}_3^-$ ). The iodine species exhibit unique hydrophilic, atmophilic, and biophilic characteristics ([Fuge and Johnson, 1986](#)). The fate and transport of iodine in aqueous

environments is dictated by its chemical speciation. In reducing environments, aqueous iodine usually occurs as the mobile monovalent anion,  $I^-$ . Under more oxidizing conditions, iodine is present as the more reactive  $IO_3^-$ , which can lead to retarded transport through interaction with clays and organic matter.

Coexistence of various inorganic and organic iodine species, in different proportions, has been reported in various environments (Liss et al., 1973; Couture and Seitz, 1983; Yuita, 1992, 1994; Yamada et al., 1999; Muramatsu and Ohmono, 1988; Baker et al., 2001). However, there are conflicting reports regarding the extent of sorption for  $I^-$  and  $IO_3^-$ . While  $I^-$  is often considered to undergo limited sorption, and is in fact employed as a nonreactive tracer (Turin et al., 2002), an increasing body of evidence indicates appreciable sorption of  $I^-$  in a variety of geologic media (Sheppard et al., 1996; Yoshida et al., 1998; Kaplan, 2003). Interconversion of iodine species may, to some extent, contribute to the conflicting results. In addition, few publications address the fate and transport of organic iodine compounds.

Organically bound iodine can be a significant fraction of total iodine in aqueous systems and in the atmosphere. For example, methyl iodide is an important gaseous form of iodine in the marine atmosphere and in releases from nuclear fuel reprocessing facilities, while dissolved organo-I compounds comprise up to 50% of total iodine in aqueous samples from estuaries, rivers, and rain (Santschi and Schwehr, 2004).

The research objectives of this study are to understand the environmental fate and transport of iodine species (i.e., iodide, iodate, and 4-iodoaniline), particularly the extent and rate of interaction of these iodine species with geologic media from two nuclear facilities in the U.S. Department of Energy (DOE) complex, where release of radionuclides including  $^{129}I$  has occurred (NRC, 2000). We investigated the conversion of iodate to iodide and the associated implications. Such knowledge is critical for a defensible environmental safety assessment of nuclear waste disposal. The results of our work are expected to contribute to the application of  $^{129}I$  as an intrinsic tracer to examine biogeochemical cycling and to the detection of possible illicit proliferation of nuclear materials.

## 2. Materials and methods

### 2.1. Materials

We obtained four uncontaminated sediments from SRS in South Carolina and the Hanford Site in Washington for laboratory tests (Table 1). These locations represent a vast contrast in geologic and climatologic variability (NRC, 2000). SRS has a humid subtropical climate with annual rainfall of 91–112 cm, and geology representative of Atlantic Coastal Plain. In contrast, the Hanford Site is located in an arid region with an average annual rainfall of only 16 cm and a stratigraphy consisting of bedded alluvial plain sediments with sands and gravels. Three SRS sediment samples were collected at different depths, providing an opportunity to examine sorption and transport of iodine species in a vertical sediment core. The wide range in sample types provided us with an opportunity to examine the influence of organic matter, clay mineralogy, soil pH, and texture on the

Table 1  
Information and properties of samples used in this study

Name	Units	SRS surface soil	SRS subsoil	SRS aquifer	Hanford sediment
Description		Surface soil	Composite of sediments collected over 3-m span 12 m below surface	Aquifer	Composite of core samples 9–12 m below surface in the S-SX tank farm
Location		Aiken, SC	Aiken, SC	Aiken, SC	Richland, WA
pH	(1:1) DI water	4.90	5.36	5.42	8.46
Organic matter	(%)	2.3	0.072	0.013	0.060
Particle size	Sand (%)	87.6	76.7	97.2	89.0
	Silt (%)	2.9	3.5	0.9	7.9
	Clay (%)	9.5	19.8	1.9	3.1
Cation exchange capacity	(meq/100 g)	1.3	1.8	0.064	7.4
Anion exchange capacity	(meq/100 g)	0.27	4.0	0.15	0.0071
Iron	(g/kg, oxalate ext.)	0.32	0.20	0.036	0.94
Iron	(g/kg, CBD ext.)	2.5	16	7.3	3.3
Aluminum	(g/kg, oxalate ext.)	0.38	0.37	0.0081	0.46
Aluminum	(g/kg, CBD ext.)	0.97	2.5	0.42	0.28
Clay mineralogy <sup>a</sup>		HIV, kaolinite	kaolinite, goethite, HIV	goethite, kaolinite, HIV	smectite, chlorite, mica

CBD ext. = citrate–bicarbonate–dithionite extraction; oxalate ext. = ammonium oxalate extraction; HIV = hydroxyl interlayered vermiculite; I = illite or weathered mica.

<sup>a</sup> Data from Seaman et al. (1996) for SRS samples and Zachara et al. (2002) for Hanford sample.

transport behavior of iodine species. All sample properties were measured according to standard procedures (Klute, 1986; Sparks, 1996) and are presented in Table 1.

In addition to the above samples, clay minerals including kaolinite from Edgar, FL, illite from Rochester, NY, vermiculite from Sanford, NC, and montmorillonite from Panther Creek, CO were purchased from Ward's Natural Sciences in Rochester, NY. The only pretreatment we performed was to crush these minerals using a mortar and pestle so that they could pass through a 63  $\mu\text{m}$  sieve. Iodine chemicals (including KI, KIO<sub>3</sub> and 4-iodoaniline; all with purity >99%) were purchased from Aldrich Chemical Co. in Milwaukee, WI. The 4-iodoaniline (chemical formula IC<sub>8</sub>H<sub>4</sub>NH<sub>2</sub>) was used as a representative refractory organic iodine species. All iodine solutions were prepared using 18 M $\Omega$  deionized water from a NANOpure Infinity Water Purification System from Barnstead International, Dubuque, IA, and stored in amber glass bottles.

## 2.2. Column and batch tests

Glass columns—either from Kontes in Vineland, NJ (2.5 cm inner diameter, 15.0 cm) or Omnifit in Boonton, NJ (1.5 cm inner diameter, 10.0 cm long)—were incrementally packed with the air-dried sediment (<2 mm) to obtain a uniform bulk density. The packed columns were slowly wetted from the bottom with an electrolyte solution, consisting of

different concentrations of  $\text{CaCl}_2$  dependent upon the test purpose, to establish saturation. Approximately 100 column pore volumes of electrolyte solution pumped through the column prior to the transport study.

The methods employed for the miscible displacement studies were similar to those used in previous experiments (e.g., Hu and Brusseau, 1998). We connected an HPLC pump (Model 301 from Alltech Associates Inc., Deerfield, IL) to the column, and placed a three-way valve in-line to facilitate switching between treatment solutions. Both iodide and iodate, with an initial concentration of either  $1 \times 10^{-5}$  or  $1 \times 10^{-4}$  M, were simultaneously injected into the column to study their transport behavior. In some sediments (e.g., the SRS surface sample), a single iodine species was also examined to investigate the potential reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ .

We also studied the transport of tritium (activity 30 kBq/L) so that we could compare the transport behavior of tritium and iodine species in the column studies. Column effluents were collected with an automated fraction collector (Retriever 500, ISCO Inc., Lincoln, NE) for chemical analysis as described below. For 4-iodoaniline transport experiments, the solution was allowed contact only with glass or stainless steel to avoid potential interaction of organoiodine with plastics in the column system. When borosilicate glass tubes were used, we did not observe any mass loss of this organoiodine; however, we did observe a 20% loss of 4-iodoaniline (tested for a concentration of  $10^{-4}$  M) stored in polypropylene tubes for 7 days.

Supplementary batch tests, in accordance with the ASTM method D4646-87 (1998), were conducted to investigate conversion of  $\text{IO}_3^-$  and  $\text{I}^-$  in contact with sediments or clay minerals. A solution to solid ratio of 4:1 was employed instead of the 20:1 ratio specified in the ASTM method. (This was done because a ratio of 20:1 is unrealistically high when compared to that commonly encountered under field conditions). We conducted duplicate blank treatments (adding only  $10^{-5}$  M  $\text{Cl}^-$ ) and triplicate treatments of either iodide ( $10^{-5}$  M  $\text{I}^-$  and  $10^{-5}$  M  $\text{Cl}^-$ ) or iodate ( $10^{-5}$  M  $\text{IO}_3^-$  and  $10^{-5}$  M  $\text{Cl}^-$ ) for each sediment or clay mineral. We also prepared control samples in the same manner with  $\text{I}^-$  or  $\text{IO}_3^-$  solution but no solid sample material. These treatments were carried out to discern the potential reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ .

### 2.3. Analyses of iodine species

We used a Dionex Corp. (Sunnyvale, CA) ion chromatography (IC) DX-600 system to analyze  $\text{I}^-$  and  $\text{IO}_3^-$ , as well as other common anions, using a hydroxide gradient method developed by Hu and Moran (in press). The system includes a GP50 gradient pump, an ED50A electrochemical detector in conductivity mode, and an AS50 autosampler with a thermal compartment for temperature control. For separation purposes, we used an IonPac AG17 guard column in conjunction with an IonPac AS17 analytical column, and with an anion self-regenerating suppressor that operated at 248 mA in recycled-water mode. The guard and analytical columns, both maintained at 35 °C, were 4 mm inner diameter, and 50 mm long. We employed an EG50 eluent generator with an EGC-KOH cartridge and a continuously regenerated anion trap column to achieve a gradient separation by producing a varying concentration of KOH (from deionized water) over the run at a flow rate of 1.0 mL/min.

To measure low (sub-ppb) concentrations of  $I^-$ , we used the ED50A electrochemical detector in pulsed amperometric mode, with silver working electrode and Ag/AgCl reference electrode, after separation using IonPac AG11 and IonPac AS11 columns. Iodide separation was achieved with 50 mM nitric acid eluent under an isocratic flow of 1.5 mL/min (Dionex, 2004). We used a 25  $\mu$ L injection loop size for sample analyses for both

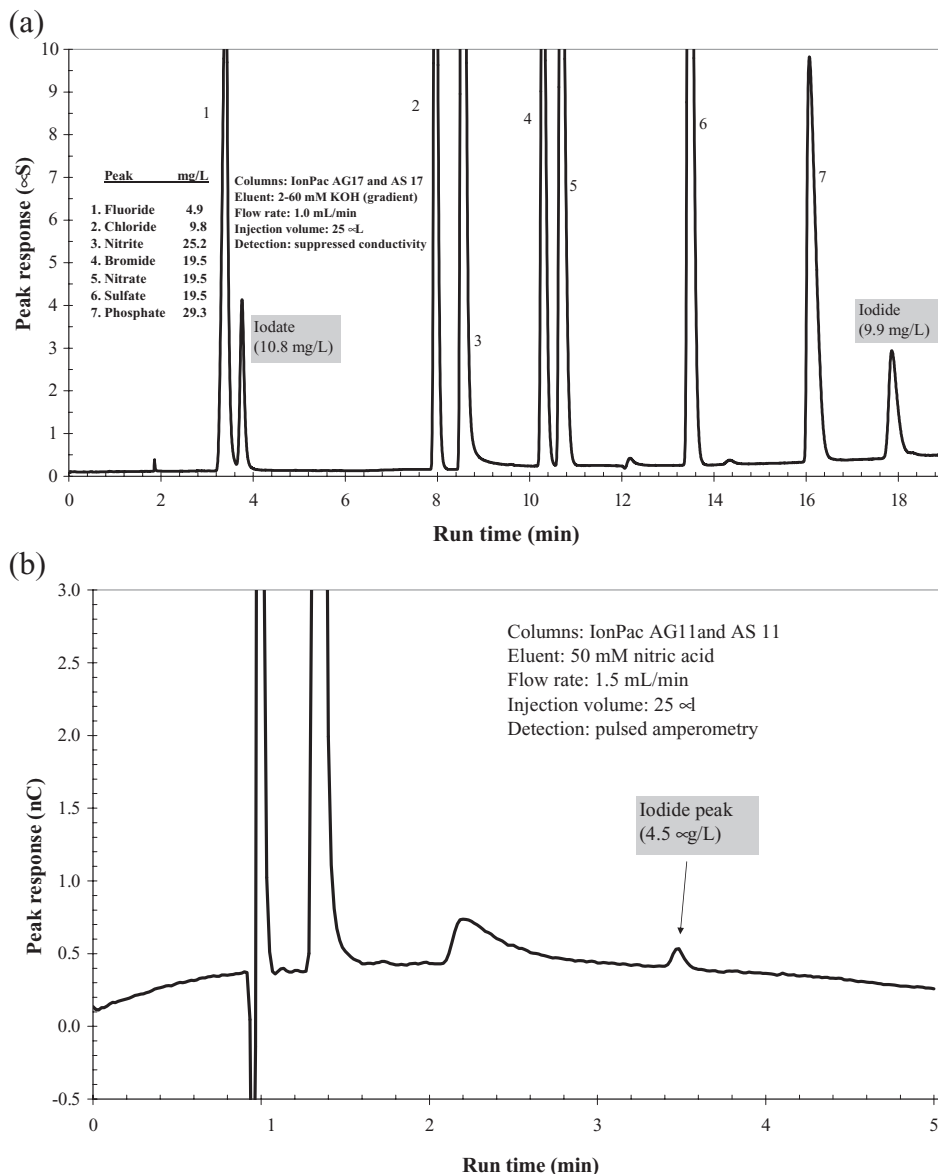


Fig. 1. IC chromatogram for (a) conductivity detection ( $\mu$ S: microsiemens) of iodate, iodide, and other common inorganic anions, and (b) by amperometric detection for low-level detection of iodide (nC: nanocoulomb).

conductivity and amperometry detection and Dionex PeakNet 6.2 software for system control, data collection, and processing.

Measurement of 4-iodoaniline was carried out using a quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) system (Hewlett Packard 4500, Agilent Technologies, Palo Alto, CA). The ICP-MS was operated at a forward power of 1400 W with argon flow rates of 16, 1.0, and 0.9 L/min, respectively, for plasma, auxiliary gas, and carrier gas flows. The column effluent sample was spiked with 20  $\mu\text{g/L}$  internal standard elements for iodine-127 analysis. A rinse solution of 10% methanol was used between samples to mitigate potential memory effects. For ICP-MS analysis of total iodine (in this study, introduced as 4-iodoaniline), we tested several internal standards (Y-89, Rh-103, In-115, Tb-159, and Bi-209) to examine potential matrix effects introduced by the effluent samples collected from column transport studies. Rh-103 consistently stood out as the best choice for all samples types, and was therefore used in the iodine data reduction.

### 3. Results and discussion

#### 3.1. Analyses of iodine species by ion chromatography

Employment of recently developed, specialized ion chromatographic methods was a key factor in obtaining the experimental results described here. As shown in Fig. 1a, under a hydroxide gradient condition at a range of 2 to 60 mM KOH, one can use conductivity detection to resolve and quantify  $\text{IO}_3^-$  and  $\text{I}^-$ , as well as other common anions such as fluoride, chloride, and sulfate. This method has a detection limit of 21.7 for  $\text{IO}_3^-$  and 19.9  $\mu\text{g/L}$  for  $\text{I}^-$  (Hu and Moran, *in press*).

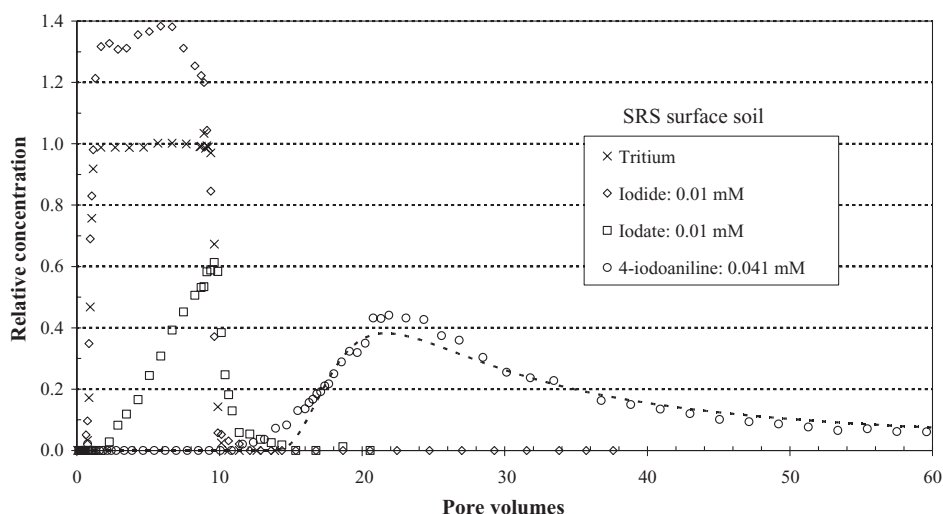


Fig. 2. Breakthrough curves of tritium and iodine species in a column homogeneously packed with Savannah River Site surface soil. The input pulse for tritium, iodide, and iodate is 8.7 column pore volumes and 14.7 pore volumes for 4-iodoaniline. The dashed line is the simulation result for the transport of 4-iodoaniline.

At lower concentrations, the amperometric method provides a fast, with a run time less than 4 min, and sensitive way to determine  $I^-$  concentration. We followed the experimental conditions for pulsed amperometric detection, published by Dionex (2004), with an example chromatogram shown in Fig. 1b. Fluoride, chloride, bromide, and iodate all elute well before iodide. Amperometric detection with a silver electrode is highly specific for iodide, with a measured method detection limit of 0.6  $\mu\text{g/L}$ . Minimal memory effect was observed, as evidenced by a measured apparent iodide concentration only 0.005% for the first non-iodide-containing sample injected immediately after a high-concentration (100 mg/L) iodide standard.

### 3.2. Conversion of iodate to iodide

Fig. 2 shows breakthrough curves for  $I^-$  and  $IO_3^-$ , which were simultaneously injected, in a column packed with SRS surface soil (results for transport of 4-iodoaniline are discussed later). It is evident that the eluted iodide is more than that pumped into the column, with a mass recovery of 129%, compared to 100% for tritium. Both conductivity and amperometric methods confirm the larger mass recovery for  $I^-$ . The breakthrough

Table 2  
Mass recovery and sorption parameters from column experiments<sup>a</sup>

		Input concentration	Mass recovery	$R_f$	$k_2$ (1/h)	$F$
SRS surface soil	Tritium	30 kBq/L	1.00	0.95		
	Iodide	$1 \times 10^{-5}$ M	0.94	0.93		
	Iodide	$1 \times 10^{-4}$ M	0.66	0.99		
	Iodate	$1 \times 10^{-5}$ M	0.83	2.92		
	Iodate	$1 \times 10^{-4}$ M	0.97	2.29		
	4-iodoaniline	$4 \times 10^{-5}$ M	0.53	25.9	0.027	0.82
SRS subsoil	Tritium	30 kBq/L	0.99	1.06		
	Iodide	$1 \times 10^{-5}$ M	0.56	5.50		
	Iodide	$1 \times 10^{-4}$ M	1.03	6.30		
	Iodate	$1 \times 10^{-5}$ M	0.00	NA <sup>b</sup>		
	Iodate	$1 \times 10^{-4}$ M	0.00	NA <sup>b</sup>		
	4-iodoaniline	$1 \times 10^{-5}$ M	1.12	0.97		
SRS aquifer	Tritium	30 kBq/L	0.99	1.00		
	Iodide	$1 \times 10^{-5}$ M	1.00	1.35		
	Iodide	$1 \times 10^{-4}$ M	0.95	1.31		
	Iodate	$1 \times 10^{-5}$ M	>0.80 <sup>c</sup>	16.2	0.23	0.22
	Iodate	$1 \times 10^{-4}$ M	>0.72 <sup>c</sup>	7.92	0.49	0.22
	4-iodoaniline	$1 \times 10^{-5}$ M	1.04	0.90		
Hanford sediment	Tritium	30 kBq/L	0.95	1.14		
	Iodide	$1 \times 10^{-5}$ M	1.00	1.33		
	Iodide	$1 \times 10^{-4}$ M	1.01	1.05		
	Iodate	$1 \times 10^{-5}$ M	0.99	1.93		
	Iodate	$1 \times 10^{-4}$ M	1.06	1.41		

<sup>a</sup> The parameters for sorption kinetics ( $k_2$  and  $F$ ) and nonlinear sorption (Freundlich  $N$ ) are not available for the breakthrough curves that can be described by linear equilibrium assumption (e.g., with minimal sorption) and that have apparent irreversible retention or conversion of iodine species (e.g., in SRS subsoil).

<sup>b</sup> NA: not available because there is no breakthrough for iodate in the experimental conditions.

<sup>c</sup> Incomplete recovery because of limited experimental duration.



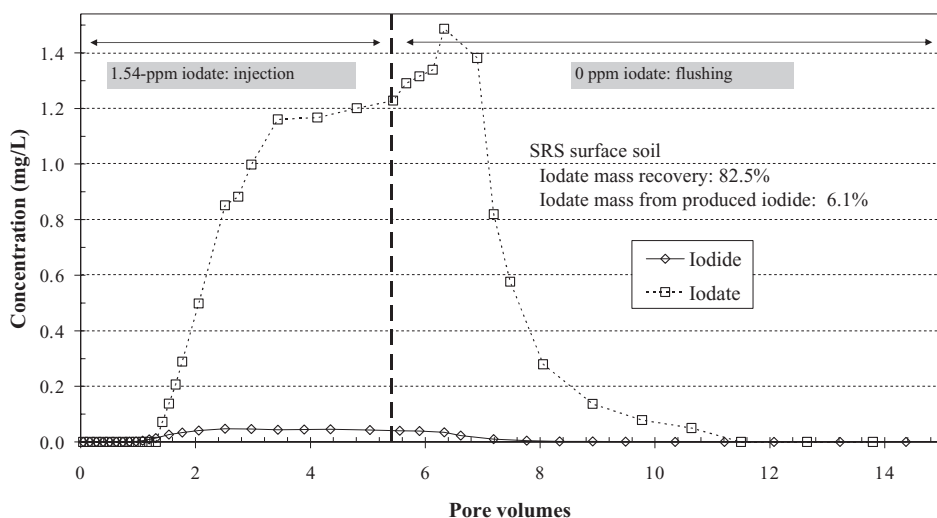


Fig. 3. Breakthrough curves for transport of iodate only in SRS surface soil column.

curve obtained by pumping  $\text{I}^-$  alone produced a steady-state plateau lower than the inlet concentration and a corresponding mass recovery of 94% (Table 2), implying that a portion of  $\text{I}^-$  is irreversibly retained. The sorption of  $\text{I}^-$ , with or without simultaneous transport of  $\text{IO}_3^-$ , in the SRS surface soil is small, with a retardation factor of about 0.93, as compared to 0.95 for tritium (Table 2). The retardation factor and mass recovery are calculated by moment analysis of the breakthrough curves.

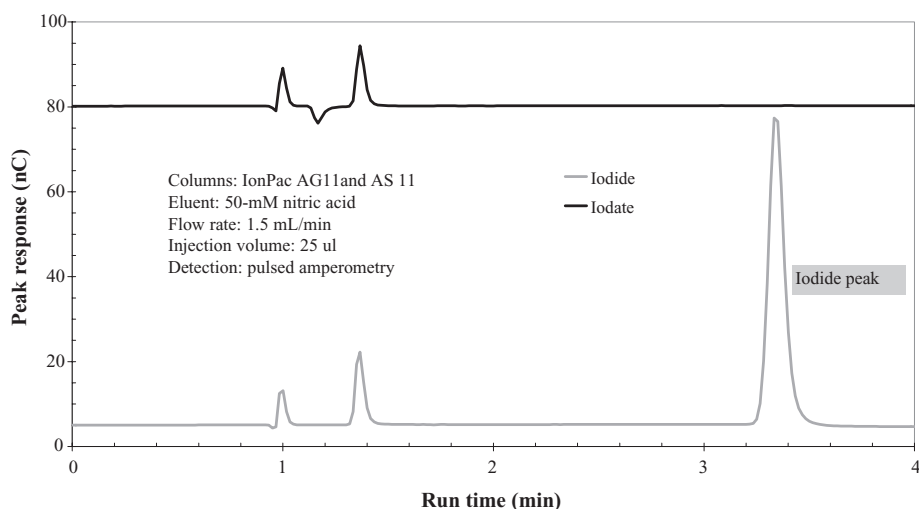


Fig. 4. IC chromatograms with amperometric detection for the standard solutions of  $1 \times 10^{-5}$  M iodate or iodide in  $5 \times 10^{-6}$  M  $\text{CaCl}_2$  to show the nonresponse to iodate at the iodide peak location. We adjusted the position of the baseline in the plotting, but the magnitude of the peak signal response in the y-axis has not been altered.

We also conducted a transport experiment of  $\text{IO}_3^-$  at a concentration of  $10^{-5}$  M (1.54 mg/L; see Fig. 3). While the  $\text{IO}_3^-$  concentration in the column effluent was quantified by conductivity detection,  $\text{I}^-$  production was monitored by the more sensitive amperometric method. It is apparent that production of  $\text{I}^-$  takes place after the appearance of  $\text{IO}_3^-$ . The effluent mass recovery for  $\text{IO}_3^-$  is 82%, the corresponding  $\text{IO}_3^-$  portion from produced  $\text{I}^-$  is calculated to be 6.1%, and the remainder (about 12%) is retained irreversibly in the

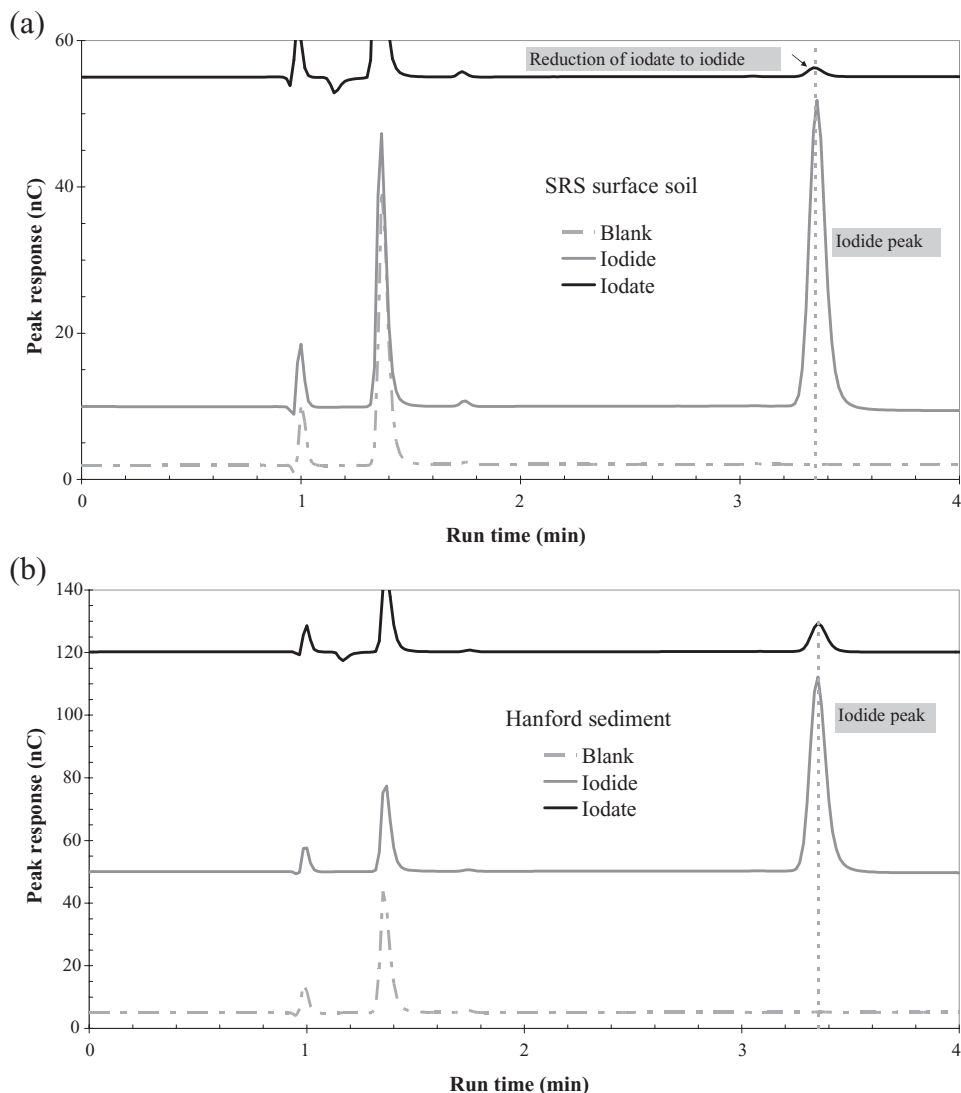


Fig. 5. IC chromatograms with amperometric detection for the (a) SRS surface soil and (b) Hanford sediment samples with three treatments (blank:  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ; iodide:  $1 \times 10^{-5}$  M iodide in  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ; and iodate:  $1 \times 10^{-5}$  M iodate in  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ).

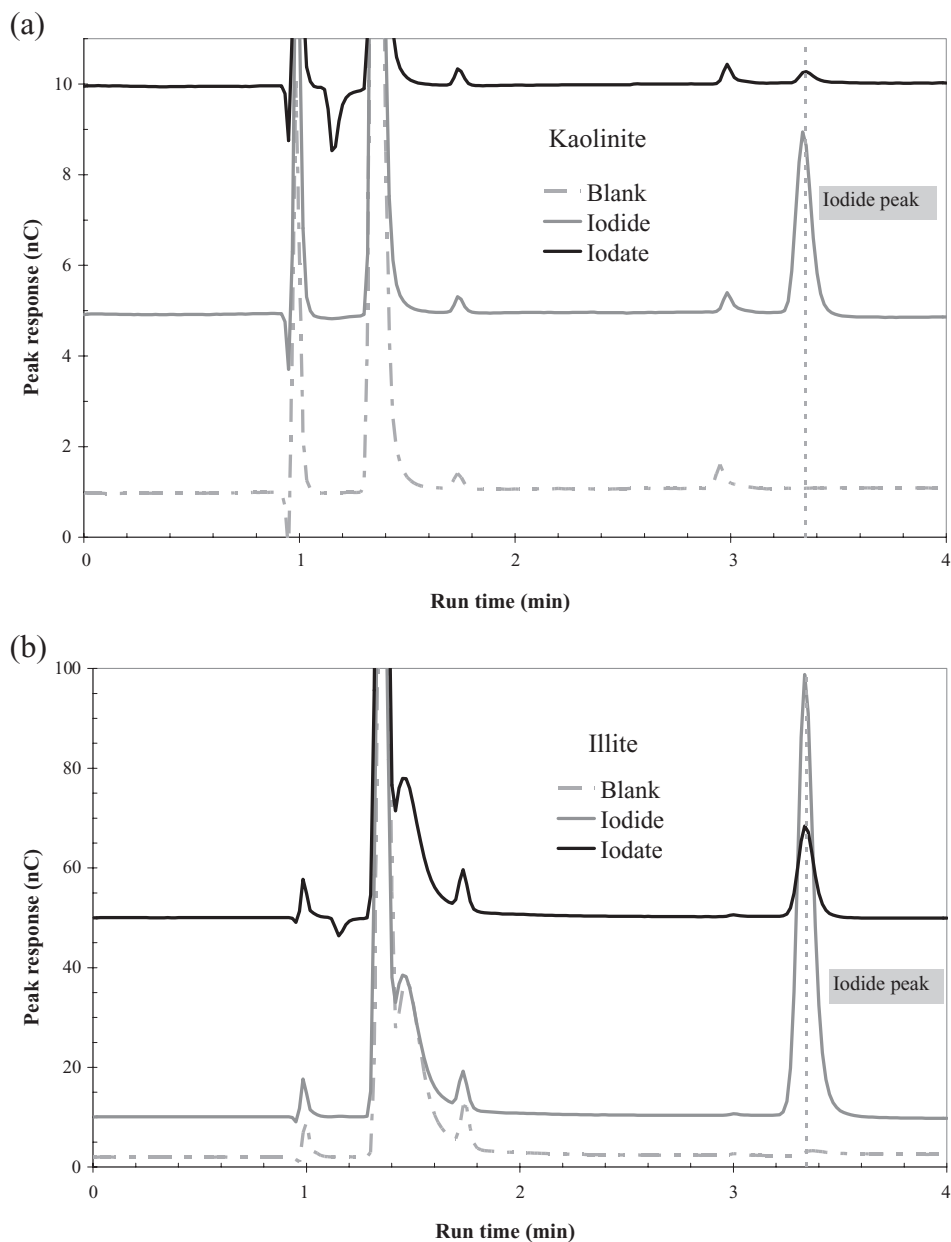


Fig. 6. IC chromatograms with amperometric detection for the (a) kaolinite and (b) illite mineral samples with three treatments (blank:  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ; iodide:  $1 \times 10^{-5}$  M iodide in  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ; iodate:  $1 \times 10^{-5}$  M iodate in  $5 \times 10^{-6}$  M  $\text{CaCl}_2$ ).

sample column or lost as volatile iodine ( $I_2$ ) during the reduction. In contrast to the low retention of  $I^-$  in SRS surface soil,  $IO_3^-$  exhibits delayed transport with some sorption (Fig. 2), which will be discussed later. As  $IO_3^-$  is transported through the SRS surface soil column, a fraction of sorbed  $IO_3^-$  is converted to  $I^-$ , which quickly elutes from the column because of its minimal interaction with the solids.

We carried out batch experiments to examine the surface-mediated  $IO_3^-$  reduction in the presence of the four sediments from the SRS and Hanford Sites, as well as with several clay mineral separates that are suspected of facilitating the reduction. As discussed in Section 2.2, we conducted four treatments, including control, blank, iodide, and iodate. As shown in Fig. 4, the presence of  $IO_3^-$  does not interfere with the detection of  $I^-$ . Fig. 5 presents the results of batch experiments for SRS surface soil and Hanford sediment. Fig. 5a confirms the same  $IO_3^-$  reduction to  $I^-$  in the SRS surface soil that was observed in the column experiment. Such reduction also occurs in Hanford sediment (Fig. 5b).

Iodide was not detected during any of the blank treatments; however, this is not unexpected because the water-leachable iodide on sediment surfaces was too low to be measured under the experimental conditions, given that the total iodine content for typical soils ranges from <1 to 20 mg/kg (Whitehead, 1973; Fuge and Johnson, 1986). The organically bound iodine, which is probably present in at least the SRS surface soil sample, may not be leached or detected.

Furthermore, while the observed  $I^-$  peak height from the  $IO_3^-$  treatment indicates the magnitude of  $IO_3^-$  reduction, the difference in peak responses from the iodide treatments is related to the affinity of each sample to sorb  $I^-$ . For example, kaolinite sorbs  $I^-$  to a greater degree than does illite and therefore we observed a smaller  $I^-$  peak from the iodide treatment. On the other hand, illite exhibits a greater capacity for reducing  $IO_3^-$  to  $I^-$  (Fig. 6).

Table 3 lists the  $IO_3^-$  reduction capacity for the samples, which is calculated by the measured  $I^-$  concentration and considering the molecular weight of  $IO_3^-$  and  $I^-$ . While vermiculite is incapable of the reduction, illite, montmorillonite, and kaolinite show an appreciable capability for  $IO_3^-$  reduction. Iodate reduction in the four sediments at SRS and Hanford is probably related to the presence of these minerals, as shown from the clay mineralogy obtained by X-ray diffraction (Table 1). Though the presence of aqueous-phase reducing agents or microbes can contribute to  $IO_3^-$  reduction, they are unlikely to be factors in this study because the soil samples had been air-dried for nearly 2 years, which

Table 3  
Reduction capacity of iodate to iodide (nmol  $IO_3^-$ /g sample)<sup>a</sup>

SRS surface soil	0.80 ± 0.31
SRS subsoil	0.16 ± 0.022
SRS aquifer	1.2 ± 0.38
Hanford sediment	5.2 ± 0.48
Kaolinite	9.4 ± 1.4
Illite	14 ± 0.69
Montmorillonite	18 ± 1.5
Vermiculite	0

<sup>a</sup> Average ± standard deviation for three replicates.

is not conducive to the survival of microbes (Wollum, 1994), and the batch experiment was conducted under atmospheric conditions.

It is probable that the abiotic reduction was mediated by structural iron (Fe) present in some clay minerals. Some of the most abundant natural reductants are soil clay minerals that contain reduced forms of iron and sulfur. Such minerals have been shown to reductively transform organic and inorganic contaminants, including tetrachloroethylene, chloropicrin, and Cr(VI) (Stucki et al., 1996; Erbs et al., 1999; Cervini-Silva et al., 2000; Stucki et al., 2002; Lee and Batchelor, 2003). However, we are not aware of any published studies evaluating the capacity for clay minerals to abiotically reduce  $\text{IO}_3^-$  to  $\text{I}^-$ . Using X-ray absorption near edge structure, which requires a relatively high concentration (0.009 M iodine as  $\text{IO}_3^-$ ), Fuhrmann et al. (1998) reported that  $\text{IO}_3^-$  was reduced to what appeared to be  $\text{I}_2$  or HI vapor in the presence of pyrite; no change in the iodine redox state was observed in magnetite and biotite experiments. Fukui et al. (1996) found that  $\text{I}^-$  accounted for about 30% total iodine, with  $\text{IO}_3^-$  as the starting species, in a solution after a 14-day contact with a Japanese soil; no explanation for the reduction was offered. Muramatsu et al. (1990) reported that  $\text{IO}_3^-$  was mostly (68–95%) converted to  $\text{I}^-$  after an 8-day contact with three Japanese soils, and there was a negligible change for  $\text{I}^-$ .

Structural Fe has been investigated in various clays. The term illite was originally introduced to cover all clay-sized minerals belonging to the mica group that contain structural Fe (Sparks, 2003). Montmorillonite is an important mineral in the smectite group, and is the term that has been traditionally used for all smectite minerals. Compositional variations in the smectite group are enormous, resulting from substitution of different amounts of  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Li}^+$  and other cations in the octahedral layer, and substitution of  $\text{Al}^{3+}$ , and probably  $\text{Fe}^{3+}$ , for  $\text{Si}^{2+}$  in the tetrahedral layer. Iron is the most frequently reported element substituted in kaolinite, and the presence of structural iron has been proven using various analytical methods (Dixon, 1989). Although vermiculite is an iron-bearing mineral, we did not observe  $\text{IO}_3^-$  reduction to  $\text{I}^-$  by vermiculite, which is consistent with the nonreactivity of structural Fe(II) observed by Lee and Batchelor (2003). We cannot rule out the possibility of  $\text{IO}_3^-$  reduction to the intermediate valence states (+1, 0) of iodine, nevertheless, we did not observe any reddish brown colored solution from  $\text{I}_2$ .

We did not detect oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$ , which is consistent with results reported for Japanese soils by Muramatsu et al. (1990). However, this result is not conclusive because of the limitations in analytical methods that distinguish  $\text{IO}_3^-$  and  $\text{I}^-$  (and iodine species in general) at low concentrations in complex matrices. The IC-conductivity method can separate and quantify both  $\text{IO}_3^-$  and  $\text{I}^-$  with a reasonably low detection limit, but the aqueous phase from the batch experiments contained some impurities (most likely low-molecular-weight organic acids, such as acetate, propionate, and formate) that often interfered with the iodate peak. Using the IC-amperometric method that only detects  $\text{I}^-$ , we converted  $\text{IO}_3^-$ , which is potentially present, to  $\text{I}^-$  by adding 0.1 mL 0.1 M  $\text{NaHSO}_3$  (a reducing agent) to 1 mL solutions obtained from iodide-treatment. No significant change was observed, but this may be due to masking of a small amount of  $\text{IO}_3^-$ , if present, by a much greater amount of  $\text{I}^-$ . Overall, further development of sensitive and specific analytical methods for different iodine species in complex matrices is warranted.

### 3.3. Physicochemical properties affecting sorption and transport of iodine species

A bicontinuum model based on first-order mass transfer was used to analyze the results of the experiments, and sorption was conceptualized to occur in two (instantaneous and rate-limited) domains (Brusseau and Rao, 1989). Detailed mathematical description of the model are presented, for example, in Hu and Brusseau (1998). Four important sorption parameters are briefly mentioned here;  $R_f$  is the retardation factor that indicates the magnitude of sorption,  $F$  is the fraction of sorbent for which sorption is instantaneous,  $N$  is the Freundlich exponent which characterizes the degree of sorption nonlinearity, and  $k_2$  is first-order desorption rate coefficients ( $T^{-1}$ ). The value of  $k_2$  specifies the degree of nonequilibrium existent in the system, which decreases as  $k_2$  increases in magnitude. The retardation factor and mass recovery are calculated by moment analysis of the iodine breakthrough curve, and the size of the iodine pulse is known. The dispersion coefficient of the sediment is obtained from the tritium breakthrough curve. Other sorption parameters ( $F$ ,  $N$ , and  $k_2$ ) are fitted using FITNLE, a nonlinear least-squares program that includes nonlinear sorption (Jessup et al., 1989). Results from the column experiments for these parameters are presented in Table 2.

In all the samples, tritium exhibited ideal breakthrough with symmetrical behavior and negligible tailing (examples are shown in Figs. 2 and 7) and conservative (not retarded) transport (Table 2). Iodide sorption onto many types of geologic media has been reported to be extremely limited (Whitehead, 1974; Kaplan et al., 2000; Turin et al., 2002). We observed very limited sorption of  $I^-$  during transport in SRS surface soil, SRS aquifer, and Hanford sediment samples (Figs. 8 and 9; Table 2). However, there was significantly retarded transport of  $I^-$ , compared to tritium, in the SRS subsoil sample (Fig. 7). This

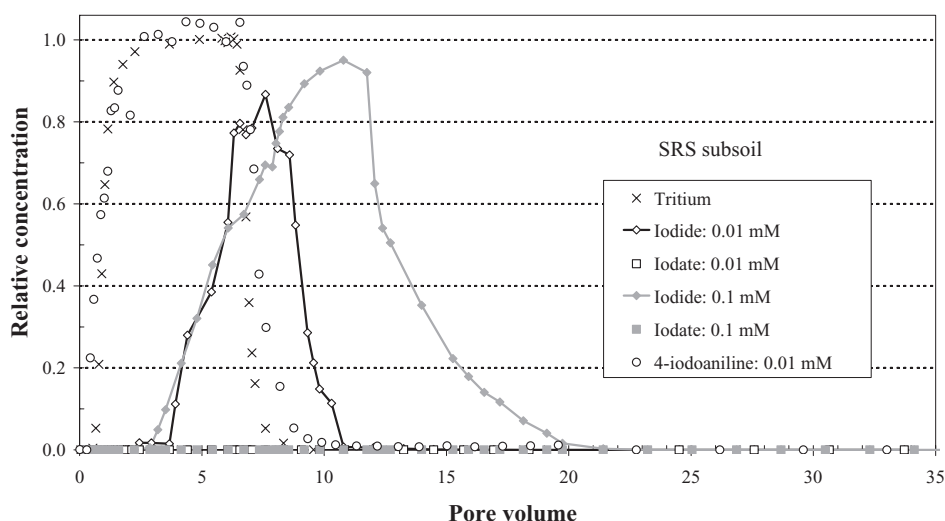


Fig. 7. Breakthrough curves for the transport of iodine species in SRS subsoil column. The input pulse for (1) the run of tritium,  $10^{-5}$  M iodide, and iodate is 5.9, (2)  $10^{-4}$  M iodide and iodate is 7.2, and (3) 4-iodoaniline is 6.1 column pore volumes, respectively.

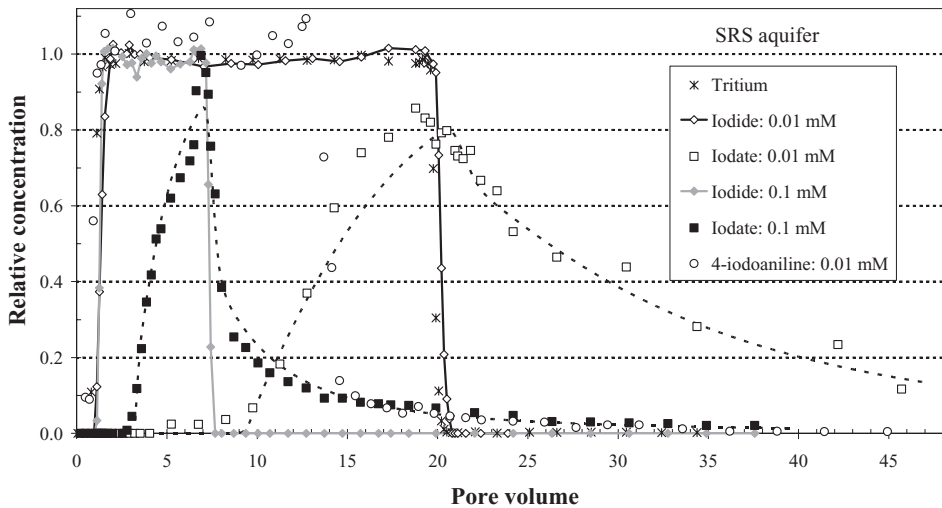


Fig. 8. Breakthrough curves for the transport of iodine species in SRS aquifer sample column. The input pulse for (1) the run of tritium,  $10^{-5}$  M iodide, and iodate is 18.8, (2)  $10^{-4}$  M iodide and iodate is 6.3, and (3) 4-iodoaniline is 14.0 column pore volumes, respectively. Dashed lines are the simulations for the transport of iodate at two initial concentrations.

sample contained an appreciable amount of iron and aluminum oxide minerals (Table 1), which possess positively charged surfaces and contribute to anion sorption, as confirmed from anion exchange capacity (AEC) measurements. Significant  $\text{I}^-$  sorption has been observed in volcanic soils (Yu et al., 1996), and  $\text{I}^-$  sorption in Japanese soils has been frequently observed (Yoshida et al., 1992, 1998). These soils contain substantial amounts

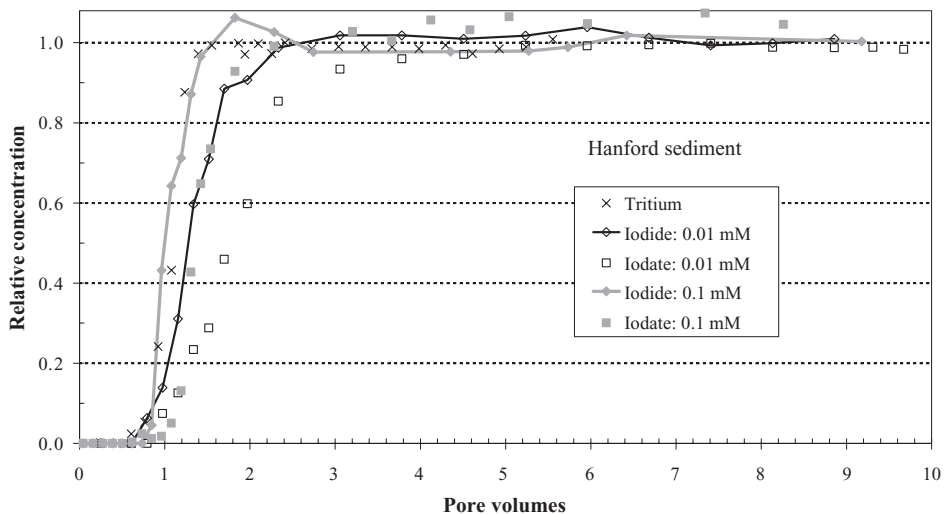


Fig. 9. Breakthrough curves for the transport of iodide and iodate in the column packed with Hanford sediment.

of imogolite, ferrihydrite, and allophane, all of which have appreciably positively charged surfaces under acidic conditions.

We used selective extraction to target the different fractions of Fe in the SRS subsoil sample. For example, citrate–bicarbonate–dithionite (CBD) extractable Fe contains crystalline iron oxide minerals such as hematite, goethite, lepidocrocite, and ferrihydrite, while ammonium oxalate ( $\text{NH}_4\text{-Ox}$ ) extraction targets noncrystalline Fe oxides, including ferrihydrite and ferrihydrite-like minerals (Loeppert and Inskeep, 1996). The CBD and  $\text{NH}_4\text{-Ox}$  extractions also remove some crystalline and noncrystalline aluminum oxide phases, respectively. The SRS subsoil had a relatively high crystalline Fe and Al oxide content from CBD extraction (Table 1). The anion sorption capacity of each geologic medium was reflected in the AEC value, which was measured according to the unbuffered salt extraction method of Summer and Miller (1996). As presented in Table 1, the SRS subsoil has a significant AEC (4.04 meq/100 g sample); more than 10 times higher than other samples.

Iodate commonly exhibits more retarded transport than iodide because it interacts more strongly with clays and organic matter (Couture and Seitz, 1983; Ticknor and Cho, 1990; Sheppard and Thibault, 1992; Yoshida et al., 1998). As discussed by Kaplan et al. (2000), the cause for the difference in  $\text{I}^-$  and  $\text{IO}_3^-$  sorptive behavior is not known but is presumably the result of the harder base nature of  $\text{IO}_3^-$ , as compared to  $\text{I}^-$ , which would favor hard–hard interactions with the hard acid sites on the mineral surfaces. The disparate sorption behavior of  $\text{I}^-$  and  $\text{IO}_3^-$  was confirmed in our study, which consistently showed greater sorption of  $\text{IO}_3^-$  than for  $\text{I}^-$ . Even in the Hanford sediment, which has a very low AEC, noticeable sorption of  $\text{IO}_3^-$  took place (Table 2).

Experiments evaluating the transport of organoiodine compounds are scarce, given the challenges associated with monitoring organoiodine compounds. In this study, we used 4-iodoaniline as a representative nonvolatile organoiodine species. As expected, we found that transport of 4-iodoaniline is different from the inorganic forms,  $\text{I}^-$  and  $\text{IO}_3^-$ , and seems to be related to the amount of organic matter in the sample. This finding is consistent with the hydrophobicity of organoiodine and its affinity for hydrophobic organic matter (Brusseau and Rao, 1989). In SRS surface soil with 2.33% organic matter, transport of 4-iodoaniline is delayed by more than 20 times, as compared to  $\text{I}^-$  (Fig. 2; Table 2). Such disparate behavior for the different iodine species needs to be considered when studying the behavior of iodine because inorganic iodine could be fixed onto macromolecular humic substances, as reported by Tikhomirov et al. (1980) and Rädlinger and Heumann (2000), and this fixation changes the physicochemical characteristics and associated fate and transport behavior of iodine. In contrast to surface soil results, 4-iodoaniline migrates without retardation, similar to tritium, in the SRS subsoil, while  $\text{IO}_3^-$  and  $\text{I}^-$  are significantly retarded (Fig. 7). This is also true for the SRS aquifer material, though the magnitude of sorption for  $\text{IO}_3^-$  and  $\text{I}^-$  is less than for SRS subsoil (Fig. 8). Both SRS subsoil and SRS aquifer samples have extremely low organic matter contents (Table 1).

Numerical fitting of the 4-iodoaniline breakthrough curve in SRS surface soil shows nonlinear (Freundlich exponent  $N$  value 0.48) and rate-limited (desorption rate coefficient  $k_2$   $0.03 \text{ h}^{-1}$ ) sorption processes. Intraorganic matter diffusion is probably responsible for the rate-limited sorption by materials containing moderate levels of organic matter (e.g.,  $>0.1\%$ ), as reported, for example, by Brusseau and Rao (1989) and Hu et al. (1995).



### 3.4. Effect of input concentration and residence time

In addition to iodine speciation, varying the input concentration also likely has an effect on iodine sorption and transport behavior. Because the sorption of both  $\text{I}^-$  (especially) and  $\text{IO}_3^-$  is related to the presence and magnitude of soil components that possess positively charged surfaces and as the positively charged surface sites are limited, the extent of sorption will probably be affected by the input concentration. Positively charged adsorption sites may exist on the edges of 2:1 clays (such as smectite and illite), on Al- and Fe-oxide surfaces, and on 1:1 clays (such as kaolinite). The number of sorption sites in variable-charge minerals is influenced by ionic strength, solution pH, and counterion valance (Seaman et al., 1996).

Ideally, one would use a concentration that is comparable to real-world situations, i.e.,  $10^{-8}$  M for stable iodine in the hydrosphere (Fuge and Johnson, 1986) and a few orders-of-magnitude lower for anthropogenic  $^{129}\text{I}$  such as in SRS (e.g., Beals and Hayes, 1995). However, for trace concentrations of  $\text{I}^-$ , usually introduced as radioactive  $^{125}\text{I}$  in laboratory experiments, in a system open to air, the  $\text{I}^-$  can be oxidized to  $\text{IO}_3^-$  (Couture and Seitz, 1983; Fuhrmann et al., 1998), which will complicate the data interpretation, considering the different sorption behavior of  $\text{I}^-$  and  $\text{IO}_3^-$ . It is not improbable that observed sorption of iodide is actually the result of conversion to  $\text{IO}_3^-$  and subsequent sorption.

At this point, we turn the discussion to the results of two iodine concentrations (0.1 mM and 0.01 mM) in the SRS sediments. We used a  $\text{CaCl}_2$  electrolyte solution with a concentration of  $\text{Cl}^-$  equivalent to the inorganic iodine species ( $\text{I}^-$  and  $\text{IO}_3^-$ ). By thus avoiding anion competition, we were able to directly examine the sorption affinity of iodine species.  $\text{I}^-$  at the two initial concentrations in SRS surface soil was not sorbed on the soil, as evidenced by the values of nearly one for the retardation factor (Table 2). However, at the higher concentration some portion of  $\text{I}^-$  is irreversibly retained by the soil, likely by its interactions with the soil organic matter, which is high in SRS surface soil. The retained iodide portion is not dissolved and mobile; this is known because the samples were also measured by ICP-MS, which measures dissolved total iodine, and showed similar results as by IC. Iodate sorption on the surface soil was similar between the two initial concentrations (Table 2), although  $\text{IO}_3^-$  reduction to  $\text{I}^-$  was more apparent at the lower concentration, indicating a limited reduction capacity of the medium. A lower initial  $\text{I}^-$  concentration in SRS subsoil produced more irreversible retention/mass loss, which is related to the sorption capacity of the subsoil. There was no breakthrough curve for  $\text{IO}_3^-$  at either concentration because of the high anion sorption capacity of the subsoil sample, as well as the greater sorption potential of  $\text{IO}_3^-$  compared to  $\text{I}^-$ .

Iodate sorption and transport in the SRS aquifer material at the two initial concentrations is well described by nonlinear and rate-limited sorption with two sorption domains (Table 2; Fig. 8). Values of  $F$ , the fraction of sorbent for which sorption is instantaneous, are the same for the two concentrations. As expected, the Freundlich  $N$  value is smaller, indicative of more nonlinearity at the higher initial concentration. The value of  $k_2$  decreases as input concentration decreases, consistent with previous findings (e.g., Hu and Brusseau, 1998). The trend of  $\text{I}^-$  and  $\text{IO}_3^-$  sorption with respect to the initial

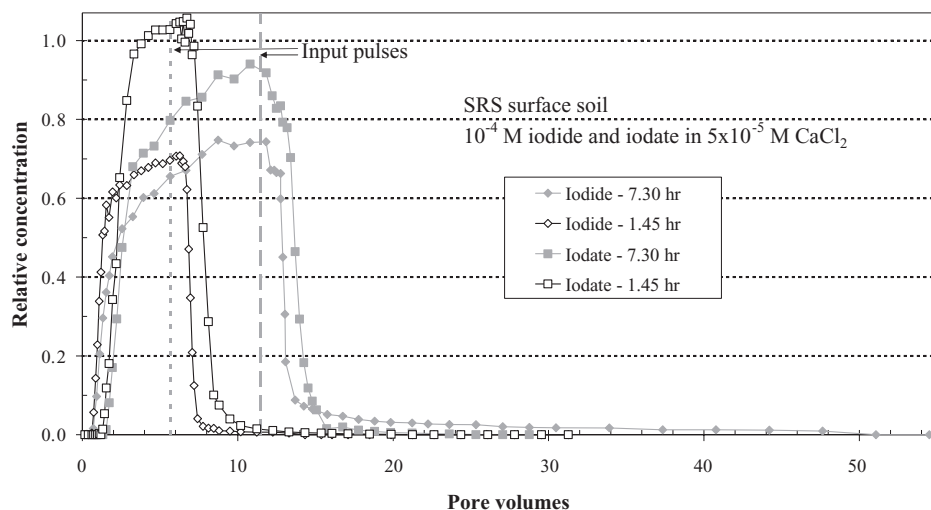


Fig. 10. The residence time effect on breakthrough curves for the transport of iodide and iodate in SRS surface soil column.

concentration seems to be consistent with the limited number of positively charged sites for sorption, as discussed above. Greater  $\text{I}^-$  sorption at a much lower ( $10^{-12}$  M) concentration for three subsurface sediments from the Hanford Site was reported by Kaplan et al. (2000).

The column experiments with the Hanford sediment did not indicate appreciable reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ , as observed in batch tests. The treatments, however, between column and batch tests are different, with the sediment-packed column having been pre-equilibrated with the same molarity of chloride before the transport experiments.

In addition—and probably more important than pretreatment—the difference in contact time between column ( $\sim 1$  h) and batch (24 h) tests, as well as the mixing condition, also affects the magnitude of  $\text{IO}_3^-$  reduction. Fig. 10 shows  $\text{I}^-$  and  $\text{IO}_3^-$  breakthrough curves for SRS surface soil for two residence times, achieved by changing the experimental pore-water velocity. We observed greater  $\text{IO}_3^-$  loss, specifically a mass recovery of 0.80 compared to 0.97, at the longer residence time, which coincides with a larger  $\text{I}^-$  mass recovery, 0.71 vs. 0.66. The retardation factor at the longer residence time is also somewhat larger (3.6 vs. 2.3) than that obtained at the shorter residence time, suggesting that, while undergoing partial conversion,  $\text{IO}_3^-$  sorption is rate-limited.

#### 4. Conclusions

Using new analytical techniques and integrated column and batch experiments, we examined the sorption and transport behavior of three iodine species (iodide, iodate, and 4-iodoaniline) in several subsurface geological media collected at SRS and the Hanford Sites. The physical and chemical processes observed include  $\text{IO}_3^-$  reduction, irreversible retention or mass loss of  $\text{I}^-$ , as well as rate-limited and nonlinear sorption.

We observed appreciable  $\text{IO}_3^-$  reduction to  $\text{I}^-$ , probably mediated by structural Fe(II), as confirmed in experiments with clay mineral separates. Examination of iodine speciation, with due attention to potential interconversion among species, is therefore essential when interpreting the environmental behavior of iodine. The different iodine species exhibit very different sorption and transport behavior in three geologic samples collected from different depths at SRS. The disparate sorption behavior of  $\text{I}^-$  and  $\text{IO}_3^-$  was confirmed in our study, which consistently showed greater sorption of  $\text{IO}_3^-$  than for  $\text{I}^-$ , while transport of 4-iodoaniline is related to the amount of organic matter in the sample, consistent with the hydrophobicity of organoiodine and its affinity for hydrophobic organic matter.

In experiments on SRS sediments at varying initial concentrations, iodate sorption on the surface soil was similar between the two initial concentrations, although  $\text{IO}_3^-$  reduction to  $\text{I}^-$  was more apparent at the lower concentration, indicating a limited reduction capacity of the medium. A lower initial  $\text{I}^-$  concentration in SRS subsoil produced more irreversible retention/mass loss, which is related to the sorption capacity of the subsoil. Iodate sorption and transport in the SRS aquifer material at two initial concentrations is well described by nonlinear and rate-limited sorption with two sorption domains and is consistent with a limited number of positively charged sites for sorption. Observed differences in iodate reduction and sorption between batch and column tests are likely due to differences in contact time. Results from this study show that anthropogenic  $^{129}\text{I}$  will have different residence times as the different species migrate through the various sediment types, which should be considered when examining processes and mechanisms affecting the geochemical cycling of iodine in the environment.

## Acknowledgements

This work was supported by the Laboratory Directed Research and Development program at Lawrence Livermore National Laboratory (LLNL). We gratefully acknowledge John Zachara of the Pacific Northwest National Laboratory for providing the Hanford sample. William Austin of Oregon State University provided assistance in analyzing some properties of the samples. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. J.C. Seaman's participation in the study was supported by the Environmental Sciences Division of the Office of Biological and Environmental Research, U.S. Department of Energy through the Financial Assistant Award no. DE-FC09-96-SR18546 to The University of Georgia Research Foundation. The authors thank Karen Rath for helpful comments.

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