

Sorption and Transport of Iodine Species in Sediments from the Savannah River and Hanford Sites

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1 **Abstract**

2 Iodine is an important element in studies of environmental protection and human health,
3 global-scale hydrologic processes and nuclear nonproliferation. Biogeochemical cycling of
4 iodine is complex, because iodine occurs in multiple oxidation states and as inorganic and
5 organic species that may be hydrophilic, atmophilic, and biophilic. In this study, we focused on
6 the sorption and transport behavior of iodine species (iodide, iodate, and 4-iodoaniline) in
7 sediments collected at the Savannah River and Hanford Sites, where anthropogenic ^{129}I from
8 prior nuclear fuel processing activities poses an environmental risk. We conducted both column
9 and batch experiments to investigate the sorption and transport behavior of iodine, and the
10 sediments we examined exhibit a wide range in organic matter, clay mineralogy, soil pH, and
11 texture.

12 The results of our experiments illustrate complex behavior with various processes
13 occurring, including iodate reduction, irreversible retention or mass loss of iodide, and rate-
14 limited and nonlinear sorption. There was an appreciable iodate reduction to iodide, presumably
15 mediated by the structural Fe(II) in some clay minerals; therefore, careful attention must be
16 given to potential interconversion among species when interpreting the biogeochemical behavior
17 of iodine in the environment. The different iodine species exhibited dramatically different
18 sorption and transport behavior in three sediment samples collected from different depths at the
19 Savannah River Site. This indicates that, when anthropogenic ^{129}I is deposited on the surface at
20 this site, the different iodine species will have different residence times as they migrate through
21 the various sediment regimes. Our study results yielded additional insight into processes and
22 mechanisms affecting the geochemical cycling of iodine in the environment, and provided
23 quantitative estimates of key parameters (e.g., extent and rate of sorption) for risk assessment at
24 these sites.

1 Key Words: iodine, sorption, transport, sediment.

2

3 **1. Introduction**

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

11 Iodine has one stable isotope, ^{127}I , and 25 radioactive isotopes that include 10 fission
12 products with very short half-lives ranging from minutes to a few hours. Two radionuclides (^{131}I
13 and ^{129}I) are particularly of environmental concern. Following a nuclear accident (such as the
14 one at Chernobyl) or an intentional radiological release, ^{131}I would be an acute contaminant
15 because of its short half-life of 8.05 days and a high specific activity.. Having a relatively long
16 half-life (1.57×10^7 years), ^{129}I is an important fission product with a fission yield of 0.9% from
17 uranium-235 and 1.6% from plutonium-239. Nuclear-fuel reprocessing facilities constitute the
18 major source of ^{129}I released in the environment. Up until 1998, a total of 2,300 kg of ^{129}I was
19 discharged in the marine environment by two European facilities at La Hague in France and
20 Sellafield in England, an amount that is 50 times the total release from nuclear weapon tests
21 (Hou et al. 2001; Fréchou and Calmet 2003). From 1944 through 1972, the plutonium-
22 production operation at the Hanford Site in Washington released about 260 kg of ^{129}I into the air.
23 In comparison, the operation of production reactors from 1953 to about 1990 at the Savannah
24 River Site (SRS) in South Carolina released about 32 kg of ^{129}I into the air.

1 ^{129}I is the only long-lived, naturally-occurring radioactive isotope of iodine. It is
2 produced by cosmic-ray interactions with xenon in the upper atmosphere and by spontaneous
3 fission of uranium-238 in the geosphere. Anthropogenic inputs of ^{129}I have overwhelmed the
4 natural inventory, increasing the hydrospheric $^{129}\text{I}/^{127}\text{I}$ ratio from 1.5×10^{-12} during the
5 pre-nuclear era up to $10^{-10} - 10^{-4}$ (Moran et al. 1998; Fréchet et al. 2003; Kekli et al. 2003). This
6 change in the ratio creates an opportunity for the application of anthropogenic ^{129}I as an
7 environmental tracer, originally proposed by Edwards (1962), to examine a variety of processes
8 including ocean circulation, biogeochemical cycling, and regional hydrologic (e.g., atmosphere,
9 surface water, and groundwater) processes (e.g., Moran et al. 1999; Oktay et al. 2001).

10 Iodine exhibits complex geochemical behavior. With oxidation states ranging from -1 to
11 $+7$, the predominant states in aqueous systems are -1 (iodide, I^-) and $+5$ (iodate, IO_3^-). The
12 iodine species exhibit unique hydrophilic, atmophilic, and biophilic characteristics (Fuge and
13 Johnson 1986). The fate and transport of iodine in aqueous environments is dictated by its
14 chemical speciation. In reducing environments, aqueous iodine usually occurs as the mobile
15 monovalent anion, I^- . Under more oxidizing conditions, iodine is present as the more reactive
16 IO_3^- , which can lead to retarded transport through interaction with clays and organic matter.

17 Coexistence of various inorganic and organic iodine species, in different proportions, has
18 been reported in various environments (Liss et al. 1973; Wolfsberg 1978; Couture and Seitz
19 1983; Yuita 1992, 1994; Yamada et al. 1999; Muramatsu and Ohmono 1988; Baker et al. 2001).
20 However, there are conflicting reports regarding the extent of sorption for I^- and IO_3^- . While I^- is
21 often considered to undergo limited sorption, and is in fact employed as a nonreactive tracer
22 (Fuhrmann et al. 2000; Turin et al. 2002), an increasing body of evidence indicates appreciable
23 sorption of I^- in a variety of geologic media (Sheppard et al. 1996; Yoshida et al. 1998; Kaplan

1 2003). Interconversion of iodine species may, to some extent, contribute to the conflicting
2 results. In addition, few publications address the fate and transport of organic iodine compounds.

3 This study focused on understanding the environmental fate and transport of iodine
4 species (i.e., iodide, iodate, and 4-iodoaniline), particularly the extent and rate of interaction of
5 these iodine species with geologic media from two nuclear facilities in the U.S. Department of
6 Energy (DOE) complex, where release of radionuclides including ^{129}I has occurred (NRC 2000).
7 We also investigated the conversion of iodate to iodide and the associated implications. Such
8 knowledge is critical for a defensible environmental safety assessment of nuclear waste disposal.
9 Our work also contributes to the application of ^{129}I as an intrinsic tracer to examine
10 biogeochemical cycling and to the detection of possible illicit proliferation of nuclear materials.

11 **2. Materials and Methods**

12 2.1 Materials

13 We obtained four uncontaminated sediments from SRS in South Carolina and the
14 Hanford Site in Washington for laboratory tests (Table 1). These locations represent a vast
15 contrast in geologic and climatologic variability (NRC 2000). SRS has a humid subtropical
16 climate with annual rainfall of 91–112 cm, and geology representative of Atlantic Coastal Plain.
17 In contrast, the Hanford Site is located in an arid region with an average annual rainfall of only
18 16 cm and a stratigraphy consisting of bedded alluvial plain sediments with sands and gravels.
19 Three SRS sediment samples were collected at different depths, providing an opportunity to
20 examine sorption and transport of iodine species in a vertical sediment core. The wide range in
21 sample types provided us with an opportunity to examine the influence of organic matter, clay
22 mineralogy, soil pH, and texture on the transport behavior of iodine species. All sample
23 properties were measured according to standard procedures (Klute 1986; Sparks 1996) and are
24 presented in Table 1.

1 In addition to the above samples, clay minerals including kaolinite from Edgar, FL, illite
2 from Rochester, NY, vermiculite from Sanford, NC, and montmorillonite from Panther Creek,
3 CO were purchased from Ward's Natural Sciences in Rochester, NY. The only pretreatment we
4 performed was to crush these minerals using a mortar and pestle so that they could pass through
5 a 63 μm sieve. Iodine chemicals (including KI, KIO_3 and 4-iodoaniline; all with purity >99%)
6 were purchased from Aldrich Chemical Co. in Milwaukee, WI. The 4-iodoaniline (chemical
7 formula $\text{IC}_8\text{H}_4\text{NH}_2$) was used as a representative refractory organic iodine species. All iodine
8 solutions were prepared using 18-M Ω deionized water from a NANOpure Infinity Water
9 Purification System from Barnstead International, Dubuque, IA, and stored in amber glass
10 bottles.

11

12 2.2 Column and Batch Tests

13 Glass columns—either from Kontes in Vineland, NJ (2.5-cm inner diameter, 15.0-cm) or
14 Omnifit in Boonton, NJ (1.5-cm inner diameter, 10.0-cm long)—were incrementally packed with
15 the air-dried sediment (<2 mm) to obtain a uniform bulk density. The packed columns were
16 slowly wetted from the bottom with an electrolyte solution (of different concentrations of CaCl_2 ,
17 depending on the test purpose) to establish saturation, with approximately 100 pore volumes of
18 electrolyte solution pumped through the column prior to the transport study.

19 The methods employed for the miscible displacement studies were similar to those used
20 in previous experiments (e.g., Hu and Brusseau 1998). We connected an HPLC pump (Model
21 301 from Alltech Associates Inc., Deerfield, IL) to the column, and placed a three-way valve in-
22 line to facilitate switching between treatment solutions. Both iodide and iodate (with an initial
23 concentration of either 1×10^{-5} or 1×10^{-4} M) were simultaneously injected into the column to

1 study their transport behavior. In some sediments (e.g., the SRS surface sample), a single iodine
2 species was also examined to investigate the potential reduction of IO_3^- to I^- .

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

11 Supplementary batch tests, in accordance with the ASTM method D4646-87 (1998), were
12 conducted to investigate conversion of IO_3^- and I^- in contact with sediment or clay minerals. A
13 solution to solid ratio of 4:1 was employed instead of the 20:1 ratio specified in the ASTM
14 method. (This was done because a ratio of 20:1 is unrealistically high when compared to that
15 commonly encountered under field conditions). We conducted duplicate blank treatments
16 (adding only 10^{-5} M Cl^-) and triplicate treatments of either iodide (10^{-5} M I^- and 10^{-5} M Cl^-) or
17 iodate (10^{-5} M IO_3^- and 10^{-5} M Cl^-) for each sediment or clay mineral. We also prepared control
18 samples in the same manner with I^- or IO_3^- solution but no solid sample material. These
19 treatments were carried out to discern the potential reduction of IO_3^- to I^- .

20 2.3 Analyses of Iodine Species

21 We used a Dionex Corp. (Sunnyvale, CA) ion chromatography (IC) DX-600 system to
22 analyze I^- and IO_3^- , as well as other common anions, using a hydroxide gradient method
23 developed by Hu and Moran (2004). The system includes a GP50 gradient pump, an ED50A
24 electrochemical detector in conductivity mode, and an AS50 autosampler with a thermal

1 compartment for temperature control. For separation purposes, we used an IonPac AG17 guard
2 column in conjunction with an IonPac AS17 analytical column, and with an anion self-
3 regenerating suppressor that operated at 248 mA in recycled-water mode. The guard and
4 analytical columns, both maintained at 35 °C, were 4-mm inner diameter, and 50-mm-long. We
5 employed an EG50 eluent generator with an EGC-KOH cartridge and a CR-ATC (continuously
6 regenerated anion trap column) to achieve a gradient separation by producing a varying
7 concentration of KOH (from deionized water) over the run at a flow rate of 1.0 mL/min.

8 To measure low (sub-ppb) concentrations of I^- , we used the ED50A electrochemical
9 detector in pulsed amperometric mode (i.e., silver working electrode and Ag/AgCl reference
10 electrode), after separation using IonPac AG11 and IonPac AS11 columns. Iodide separation was
11 achieved with 50 mM nitric acid eluent under an isocratic flow of 1.5 mL/min (Dionex 2004).
12 We used a 25 μ L injection loop size for sample analyses for both conductivity and amperometry
13 detection and Dionex PeakNet 6.2 software for system control, data collection, and processing.

14 Measurement of 4-iodoaniline was carried out using a quadrupole inductively coupled
15 plasma–mass spectrometry (ICP–MS) system (Hewlett Packard 4500, Agilent Technologies,
16 Palo Alto, CA). The ICP-MS was operated at a forward power of 1,400 W with argon flow rates
17 of 16, 1.0, and 0.9 L/min, respectively for plasma, auxiliary gas, and carrier gas flows. The
18 column effluent sample was spiked with 20 ng/L internal standard elements for iodine-127
19 analysis. A rinse solution of 10% methanol was used between samples to mitigate potential
20 memory effects. For ICP-MS analysis of total iodine (in this study, introduced as 4-iodoaniline),
21 we tested several internal standards (Y-89, Rh-103, In-115, Tb-159, and Bi-209) to examine
22 potential matrix effects introduced by the effluent samples collected from column transport
23 studies. Rh-103 consistently stood out as the best choice for all samples types, and was therefore
24 used in the iodine data reduction.

1 3. Results and Discussion

2 3.1. Analyses of Iodine Species by Ion Chromatography

3 Employment of recently developed, specialized ion chromatographic methods was a key
4 factor in obtaining the experimental results described here. As shown in Figure 1a, under a
5 hydroxide gradient condition at a range of 2 to 60-mM KOH, one can use conductivity detection
6 to resolve and quantify IO_3^- (early arrival) and I^- (late arrival), as well as other common anions
7 such as fluoride, chloride, and sulfate. This method has a detection limit of 21.7 for IO_3^- and 19.9
8 $\mu\text{g/L}$ for I^- (Hu and Moran 2004).

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

17 3.2. Conversion of Iodate to Iodide

18 Figure 2 shows breakthrough curves for I^- and IO_3^- , which were simultaneously injected,
19 in a column packed with SRS surface soil (results for transport of 4-iodoaniline are discussed
20 later). It is evident that the eluted iodide is more than that pumped into the column, with a mass
21 recovery of 129%, compared to 100% for tritium (Table 2). Both conductivity and amperometric
22 detection methods confirm the larger mass recovery for I^- . The breakthrough curve obtained by
23 pumping I^- alone produced a steady-state plateau lower than the inlet concentration and a
24 corresponding mass recovery of 94%, implying that a portion of I^- is irreversibly retained. The

1 retention of Γ^- , with or without simultaneous transport of IO_3^- , in the SRS surface soil is small,
2 with a retardation factor of about 0.93, as compared to 0.95 for tritium (Table 2). The retardation
3 factor and mass recovery are calculated by moment analysis of the breakthrough curves.

4 We also conducted a transport experiment of IO_3^- at a concentration of 10^{-5} M (1.54
5 mg/L, ppm; see Figure 3). While the IO_3^- concentration in the column effluent was quantified by
6 conductivity detection, Γ^- production was monitored by the more sensitive amperometric method.
7 It is apparent that production of Γ^- takes place after the appearance of IO_3^- . The effluent mass
8 recovery for IO_3^- is 82%, the corresponding IO_3^- portion from produced Γ^- is calculated to be
9 6.1%, and the remainder (about 12%) is retained irreversibly in the sample column or lost as
10 volatile iodine (I_2) during the reduction. In contrast to the low retention of Γ^- in SRS surface soil
11 (Figure 2), IO_3^- exhibits delayed transport with some sorption, which will be discussed later. As
12 IO_3^- is transported through the SRS surface soil column, a fraction of sorbed IO_3^- is converted to
13 Γ^- , which quickly elutes from the column because of its minimal interaction with the solids.

14 We carried out batch experiments to examine the surface-mediated IO_3^- reduction in the
15 presence of the four sediments from the SRS and Hanford Sites, as well as with several clay
16 mineral separates that are suspected of facilitating the reduction. As discussed in Section 2,
17 Materials and Methods, we conducted four treatments, including control, blank, iodide, and
18 iodate. As shown in Figure 4, the presence of IO_3^- does not interfere with the detection of Γ^- .
19 Figure 5 presents the results of batch experiments for SRS surface soil and Hanford sediment.
20 Figure 5a confirms the same IO_3^- reduction to Γ^- in the SRS surface soil that was observed in the
21 column experiment. Such reduction also occurs in Hanford sediment (Figure 5b).

22 Iodide was not detected during any of the blank treatments; however, this is not
23 unexpected because the water-leachable iodide on sediment surfaces was too low to be measured

1 under the experimental conditions, given that the total iodine content for typical soils ranges
2 from <1 to 20 mg/kg (Whitehead 1973; Fuge and Johnson 1986). The organically-bound iodine,
3 which is probably present in at least the SRS surface soil sample, may not be leached or
4 detected.

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

10 We conducted similar studies for the clay mineral separates that are important in natural
11 media, and example chromatograms for kaolinite and illite are shown in Figure 6. Table 3 lists
12 the IO_3^- reduction capacity for the samples tested. Illite, montmorillonite, and kaolinite show an
13 appreciable capability for IO_3^- reduction, while vermiculite is incapable of the reduction. Iodate
14 reduction in the four sediments at SRS and Hanford is probably related to the presence of these
15 minerals, as shown from the clay mineralogy obtained by x-ray diffraction (Table 1). While the
16 presence of aqueous-phase reducing agents or microbes can contribute to IO_3^- reduction, they are
17 unlikely to be factors in this study because the soil samples had been air-dried for nearly two
18 years, which is not conducive to the survival of microbes (Wollum 1994), and the batch
19 experiment was conducted under atmospheric conditions.

20 It is probable that the abiotic reduction was mediated by structural iron (Fe) present in
21 some clay minerals. Some of the most abundant natural reductants are soil clay minerals that
22 contain reduced forms of iron and sulfur. Such minerals have been shown to reductively
23 transform organic and inorganic contaminants, including tetrachloroethylene, chloropicrin, and

1 Cr(VI) (Stucki et al. 1996; Erbs et al. 1999; Cervini-Silva et al. 2000; Stucki et al. 2002; Lee and
2 Batchelor 2003). However, we are not aware of any published studies evaluating the capacity for
3 clay minerals to abiotically reduce IO_3^- to I^- . Using x-ray absorption near edge structure
4 (XANES), which requires a relatively high concentration (0.009 M iodine as IO_3^-), Furhrmann et
5 al. (2000) reported that IO_3^- was reduced to what appeared to be I_2 or HI vapor in the presence of
6 pyrite; no similar change in the iodine redox state was observed in magnetite and biotite
7 experiments. Fukui et al. (1996) found that I^- accounted for about 30% total iodine, with IO_3^- as
8 the starting species, in a solution after a 14-day contact with a Japanese soil; no explanation for
9 the reduction was offered. Muramatsu et al. (1990) reported that IO_3^- was mostly (68–95%)
10 converted to I^- after an 8-day contact with three Japanese soils, and there was a negligible
11 change for I^- .

12 The term illite was originally introduced to cover all clay-sized minerals belonging to the
13 mica group that contain structural Fe (Drever 1997; Sparks 2003). Montmorillonite is an
14 important mineral in the smectite group, and is the term that has been traditionally used for all
15 smectite minerals. Compositional variations in the smectite group are enormous, resulting from
16 substitution of different amounts of Mg^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , and Li^+ and other cations in the
17 octahedral layer, and substitution of Al^{3+} , and probably Fe^{3+} , for Si^{2+} in the tetrahedral layer. Iron
18 is the most frequently reported element substituted in kaolinite, and the presence of structural
19 iron has been proven using various analytical methods (Dixon 1989). Although vermiculite is an
20 iron-bearing mineral, structural Fe(II) may not be as reactive as for other soil minerals tested,
21 including montmorillonite (Lee and Batchelor 2003). In this study, we did not observe IO_3^-
22 reduction to I^- by vermiculite, which is consistent with the nonreactivity of structural Fe(II)
23 observed by Lee and Batchelor (2003). We cannot rule out the possibility of IO_3^- reduction to

1 the intermediate valence states (+1, 0) of iodine, nevertheless, we did not observe any brownish
2 colored solution (from I_2).

3 We did not detect oxidation of I^- to IO_3^- , which is consistent with results reported for
4 Japanese soils by Muramatsu et al. (1990). However, this result is not conclusive because of the
5 limitations in analytical methods that distinguish IO_3^- and I^- (and iodine species in general) at
6 low concentrations in complex matrices. The IC-conductivity method can separate and quantify
7 both IO_3^- and I^- with a reasonably low detection limit, but the aqueous phase from the batch
8 experiments contained some impurities (most likely low-molecular-weight organic acids, such as
9 acetate, propionate, and formate) that often interfered with the iodate peak. For the IC-
10 amperometric method for I^- detection, we converted IO_3^- , which is potentially present, to I^- by
11 adding 0.1 mL 0.1 M $NaHSO_3$ (a reducing agent) to 1 mL solutions obtained from iodide-
12 treatment. No significant change was observed, but this may be due to masking of a small
13 amount of IO_3^- , if present, by a much greater amount of I^- . Overall, further development of
14 sensitive and specific analytical methods for different iodine species in complex matrices is
15 warranted.

16 3.3. Physicochemical Properties Affecting Sorption and Transport of Iodine Species

17 A bicontinuum model based on first-order mass transfer was used to analyze the results
18 of the experiments, and sorption was conceptualized to occur in two (instantaneous and rate-
19 limited) domains (Brusseau and Rao 1989). Detailed mathematical description of the model are
20 presented, for example, in Hu and Brusseau (1998). Four important sorption parameters are
21 briefly mentioned here; R_f is the retardation factor that indicates the magnitude of sorption, F is
22 the fraction of sorbent for which sorption is instantaneous, N is the Freundlich exponent which
23 characterizes the degree of sorption nonlinearity, and k_2 is first-order desorption rate coefficients
24 (T^{-1}). The value of k_2 specifies the degree of nonequilibrium existent in the system, which

1 decreases as k_2 increases in magnitude. The retardation factor and mass recovery are calculated
2 by moment analysis of the breakthrough curves. Other sorption parameters are obtained using
3 FITNLE, a nonlinear least-squares program that includes nonlinear sorption (Jessup et al. 1989).
4 Results from the column experiments for these parameters are presented in Table 2.

5 In all the samples, tritium exhibited ideal breakthrough with symmetrical behavior and
6 negligible tailing (examples are shown in Figures 2 and 7) and conservative (not retarded)
7 transport (Table 2). Iodide sorption onto many types of geologic media has been reported to be
8 extremely limited (Whitehead 1974; Kaplan et al. 2000; Turin et al. 2002). We observed very
9 limited sorption of I^- during transport in SRS surface soil, SRS aquifer, and Hanford sediment
10 samples (Figures 8–10 and Table 2). However, there was significantly retarded transport of I^- ,
11 compared to tritium, in the SRS subsoil sample (Figure 7). This sample contained an appreciable
12 amount of iron and aluminum oxide minerals (Table 1), which possess positively charged
13 surfaces and contribute to anion sorption, as confirmed from anion exchange capacity (AEC)
14 measurements. Significant I^- sorption has been observed in volcanic soils (Yu et al. 1996),
15 including frequent observation of I^- sorption in Japanese soils (Yoshida et al. 1992; 1998). These
16 soils contain substantial amounts of imogolite, ferrihydrite, and allophane, all of which have
17 appreciably positively charged surfaces under acidic conditions.

18 We used selective extraction to target the different fractions of Fe in the SRS subsoil
19 sample. For example, citrate-bicarbonate-dithionite (CBD) extractable Fe contains crystalline
20 iron oxide minerals such as hematite, goethite, lepidocrocite, and ferrihydrite, while ammonium
21 oxalate (NH_4-Ox) extraction targets noncrystalline Fe oxides, including ferrihydrite and
22 ferrihydrite-like minerals (Loeppert and Inskeep 1996). The CBD and NH_4-Ox extractions also
23 remove some crystalline and noncrystalline aluminum oxide phases, respectively. The SRS
24 subsoil had a relatively high crystalline Fe and Al oxide content from CBD extraction (Table 1).

1 The anion sorption capacity of each geologic medium was reflected in the AEC value, which
2 was measured according to the unbuffered salt extraction method of Summer and Miller (1996).
3 As presented in Table 1, the SRS subsoil has a significant AEC (4.04 meq/100 g sample); more
4 than ten times higher than other samples.

5 Iodate commonly exhibits more retarded transport than iodide because it interacts more
6 strongly with clays and organic matter (Couture and Seitz 1983; Ticknor and Cho 1990;
7 Sheppard and Thibault 1992; Yoshida et al. 1998). As discussed by Kaplan et al. (2000), the
8 cause for the difference in Γ^- and IO_3^- sorptive behavior is not known but is presumably the
9 result of the harder base nature of IO_3^- , as compared to Γ^- , which would favor hard-hard
10 interactions with the hard acid sites on the mineral surfaces. The disparate sorption behavior of Γ^-
11 and IO_3^- was confirmed in our study, which consistently showed greater sorption of IO_3^- than
12 for Γ^- . Even in the Hanford sediment, which has a very low AEC, noticeable sorption of IO_3^-
13 took place (Table 2).

14 Organically-bound iodine can be a significant fraction of total iodine in aqueous systems
15 and in the atmosphere. For example, methyl iodide is an important gaseous form of iodine in the
16 marine atmosphere and in releases from nuclear fuel reprocessing facilities, while dissolved
17 organo-I compounds comprise up to 50% of total iodine in aqueous samples from estuaries,
18 rivers, and rain (Santschi and Schwer 2004). Experiments evaluating the transport of
19 organoiodine compounds are scarce, given the challenges associated with monitoring
20 organoiodine compounds. In this study, we used 4-iodoaniline as a representative nonvolatile
21 organoiodine species. As expected, we found that transport of 4-iodoaniline is different from the
22 inorganic forms, Γ^- and IO_3^- , and seems to be related to the amount of organic matter in the
23 sample. This finding is consistent with the hydrophobicity of organoiodine and its affinity for
24 hydrophobic organic matter (Brusseau and Rao 1989). In SRS surface soil with 2.33% organic

1 matter, transport of 4-iodoaniline is delayed by more than twenty times, as compared to Γ^-
2 (Figure 2 and Table 2). Such disparate behavior for the different iodine species needs to be
3 considered when studying the behavior of iodine because inorganic iodine could be fixed onto
4 macromolecular humic substances, as reported by Tikhomirov et al. (1980) and Rädlinger and
5 Heumann (2000), and this fixation changes the physicochemical characteristics and associated
6 fate and transport behavior of iodine. In contrast to surface soil results, 4-iodoaniline migrates
7 without retardation, similar to tritium, in the SRS subsoil, while IO_3^- and Γ^- are significantly
8 retarded (Figure 7). This is also true for the SRS aquifer material, though the magnitude of
9 sorption for IO_3^- and Γ^- is less than for SRS subsoil (Figure 9). Both SRS subsoil and SRS
10 aquifer samples have extremely low organic matter contents (Table 1).

11 Numerical fitting of the 4-iodoaniline breakthrough curve in SRS surface soil shows
12 nonlinear (Freundlich exponent N value 0.48) and rate-limited (desorption rate coefficient k_2
13 0.03 h^{-1}) sorption processes. Intraorganic matter diffusion is probably responsible for the rate-
14 limited sorption by materials containing moderate levels of organic matter (e.g., >0.1%), as
15 reported, for example, by Brusseau and Rao (1989) and Hu et al. (1995).

16 3.4. Effect of Input Concentration and Residence Time

17 In addition to iodine speciation, varying the input concentration also likely has an effect
18 on iodine sorption and transport behavior. Because the sorption of both Γ^- (especially) and IO_3^- is
19 related to the presence and magnitude of soil components that possess positively-charged
20 surfaces and because the positively-charged surface sites are limited, the extent of sorption will
21 probably be affected by the input concentration. Positively-charged adsorption sites may exist on
22 the edges of 2:1 clays (such as smectite and illite), on Al- and Fe-oxide surfaces, and on 1:1
23 clays (such as kaolinite). The number of sorption sites in variable-charge minerals is influenced
24 by ionic strength, solution pH, and counterion valance (Seaman et al. 1996).

1 Ideally, one would use a concentration that is comparable to real-world situations, i.e.
2 10^{-8} M for stable iodine in the hydrosphere (Fuge and Johnson 1986) and a few orders-of-
3 magnitude lower for anthropogenic ^{129}I such as in SRS (e.g., Beals and Hayes 1995). However,
4 for trace concentrations of I^- (usually introduced as radioactive ^{125}I in laboratory experiments) in
5 a system open to air, the I^- can be oxidized to IO_3^- (Couture and Seitz 1983; Fuhrmann et al.
6 1998), which will complicate the data interpretation, considering the different sorption behavior
7 of I^- and IO_3^- . It is not improbable that observed sorption of iodide is actually the result of
8 conversion to IO_3^- and subsequent sorption.

9 At this point, we turn the discussion to the results of two iodine concentrations (0.1 mM
10 and 0.01 mM) in the SRS sediments. We used a CaCl_2 electrolyte solution with a concentration
11 of Cl^- equivalent to the inorganic iodine species (I^- and IO_3^-). By thus avoiding anion
12 competition, we were able to directly examine the sorption affinity of iodine species. I^- at the
13 two initial concentrations in SRS surface soil was not sorbed on the soil (Table 2). However,
14 some portion of I^- is irreversibly retained by the soil or lost via some unknown mechanism,
15 which may be related to the concentration, because more retention/loss was noticed at the
16 higher concentration (0.1 mM). Iodate sorption was similar between the two initial
17 concentrations (Table 2), although IO_3^- reduction to I^- was more apparent at the lower
18 concentration, indicating a limited reduction capacity of the medium. A lower initial I^-
19 concentration in SRS subsoil produced more irreversible retention/mass loss, similar to what is
20 observed in SRS surface soil. There was no breakthrough curve for IO_3^- at either concentration
21 because of the high anion sorption capacity of the sample, as well as the greater sorption
22 potential of IO_3^- compared to I^- .

23 Iodate sorption and transport in the SRS aquifer material at the two initial concentrations
24 is well described by nonlinear and rate-limited sorption with two sorption domains (Table 2 and

1 Figure 9). Values of F , the fraction of sorbent for which sorption is instantaneous, are the same
2 for the two concentrations. As expected, the Freundlich N value is smaller, indicative of more
3 nonlinearity at the higher initial concentration. The value of k_2 decreases as input concentration
4 decreases, consistent with previous findings (e.g., Hu and Brusseau 1998). The trend of Γ^- and
5 IO_3^- sorption with respect to the initial concentration seems to be consistent with the limited
6 number of positively-charged sites for sorption, as discussed above. Greater Γ^- sorption at a much
7 lower (10^{-12} M) concentration for three subsurface sediments from the Hanford Site was reported
8 by Kaplan et al. (2000).

9 The column experiments with the Hanford sediment did not indicate the appreciable
10 reduction of IO_3^- to Γ^- , as observed in batch tests. The treatments, however, between column and
11 batch tests are different, with the sediment-packed column having been pre-equilibrated with the
12 same molarity of chloride before the transport experiments.

13 In addition - and probably more important than pretreatment - the difference in contact
14 time between column (~ 1 hr) and batch (24 hrs) tests, as well as the mixing condition, also
15 affects the magnitude of IO_3^- reduction. Figure 11 shows Γ^- and IO_3^- breakthrough curves for
16 SRS surface soil for two residence times, achieved by changing the experimental pore-water
17 velocity. We observed greater IO_3^- loss, specifically a mass recovery of 0.80 compared to 0.97,
18 at the longer residence time, which coincides with a larger Γ^- mass recovery, 0.71 vs. 0.66. The
19 retardation factor at the longer residence time is also somewhat larger (3.6 vs. 2.3) than that
20 obtained at the shorter residence time, suggesting that, while undergoing partial conversion, IO_3^-
21 sorption is rate-limited.

22 **4. Conclusions**

23 In this study, we examined the sorption and transport behavior of three iodine species
24 (iodide, iodate, and 4-iodoaniline) in several subsurface geological media collected at SRS and

1 the Hanford Site, where anthropogenic ^{129}I from prior fuel processing activities poses an
2 environmental concern. The geologic media display significant differences in organic matter
3 content, clay mineralogy, soil pH, and texture. We conducted both column and batch
4 experiments to investigate the complex sorption and transport processes that occur, which
5 include IO_3^- reduction, irreversible retention or mass loss of I^- , and rate-limited and nonlinear
6 sorption.

7 We observed appreciable IO_3^- reduction to I^- , probably mediated by structural Fe(II), in
8 experiments with certain clay minerals. We also considered other experimental variables, such as
9 the initial iodine concentration. Examination of iodine speciation, with due attention to potential
10 interconversion among species, is essential when interpreting the environmental behavior of
11 iodine. The different iodine species exhibit very different sorption and transport behavior in three
12 geologic samples collected from different depths at SRS. Consequently, anthropogenic ^{129}I has
13 different residence times as the different species migrate through the various sediment types.
14 Results obtained from this study yield valuable insight into processes and mechanisms affecting
15 the geochemical cycling of iodine in the environment and provide key parameters (rate of
16 transport and extent of sorption) for risk assessment at these sites.

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Figure Legends

- Figure 1 IC chromatogram for (a) conductivity detection (μS : microsiemens) of iodate, iodide, and other common inorganic anions, and (b) by amperometric detection for low-level detection of iodide (nC: nanocoulomb).
- Figure 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.
- Figure 3 Breakthrough curves for transport of iodate only in SRS surface soil column.
- Figure 4 IC chromatograms with amperometric detection for the standard solutions of 1×10^{-5} M iodate or iodide in 5×10^{-6} M 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.
- Figure 5 IC chromatograms with conductivity detection for the (a) SRS surface soil and (b) Hanford sediment samples with three treatments (blank: 5×10^{-6} M CaCl_2 ; iodide: 1×10^{-5} M iodide in 5×10^{-6} M CaCl_2 ; and iodate: 1×10^{-5} M iodate in 5×10^{-6} M CaCl_2).
- Figure 6 IC chromatograms with conductivity detection for the (a) kaolinite and (b) illite mineral samples with three treatments (blank: 5×10^{-6} M CaCl_2 ; iodide: 1×10^{-5} M iodide in 5×10^{-6} M CaCl_2 ; iodate: 1×10^{-5} M iodate in 5×10^{-6} M CaCl_2).

- Figure 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.
- Figure 8 Breakthrough curves for the transport of iodide and iodate in SRS surface soil column. The input pulses vary among the tests, as indicated by the vertical lines in the graph.
- Figure 9 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.
- Figure 10 Breakthrough curves for the transport of iodide and iodate in the column packed with Hanford sediment.
- Figure 11 The residence time effect on breakthrough curves for the transport of iodide and iodate in SRS surface soil column.

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	(oxalate ext.)	0.32	0.20	0.036	0.94
Iron	(CBD ext.)	2.5	16	7.3	3.3
Aluminum	(oxalate ext.)	0.38	0.37	0.0081	0.46
Aluminum	(CBD ext.)	0.97	2.5	0.42	0.28
Clay mineralogy ^a		HIV, kaolinite	kaolinite, goethite, HIV	goethite, kaolinite, I	smectite, chlorite, mica

CBD ext. = citrate-bicarbonate-dithionite extraction

oxalate ext. = ammonium oxalate extraction

HIV = hydroxyl interlayered vermiculite

I = illite or weathered mica

^a Data from Seaman et al. (1996) for SRS samples and Zachara et al. (2002) for Hanford sample.

Table 2. Mass recovery and sorption parameters from column experiments. ^a

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

^a 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).

^b NA: not available because there is no breakthrough for iodate in the experimental conditions.

^c Incomplete recovery because of limited experimental duration.

Table 3. Reduction capacity of iodate to iodide (nano mol IO_3^-/g sample). ^a

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

^a Average \pm standard deviation for three replicates.

Figure 1

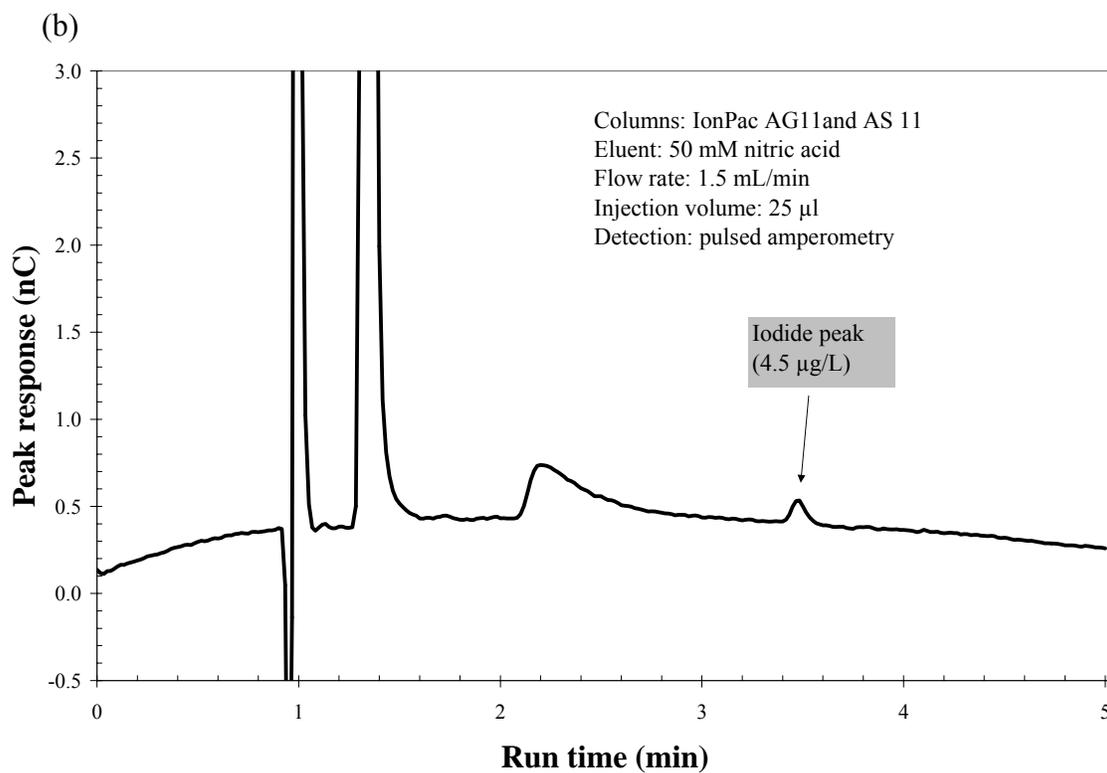
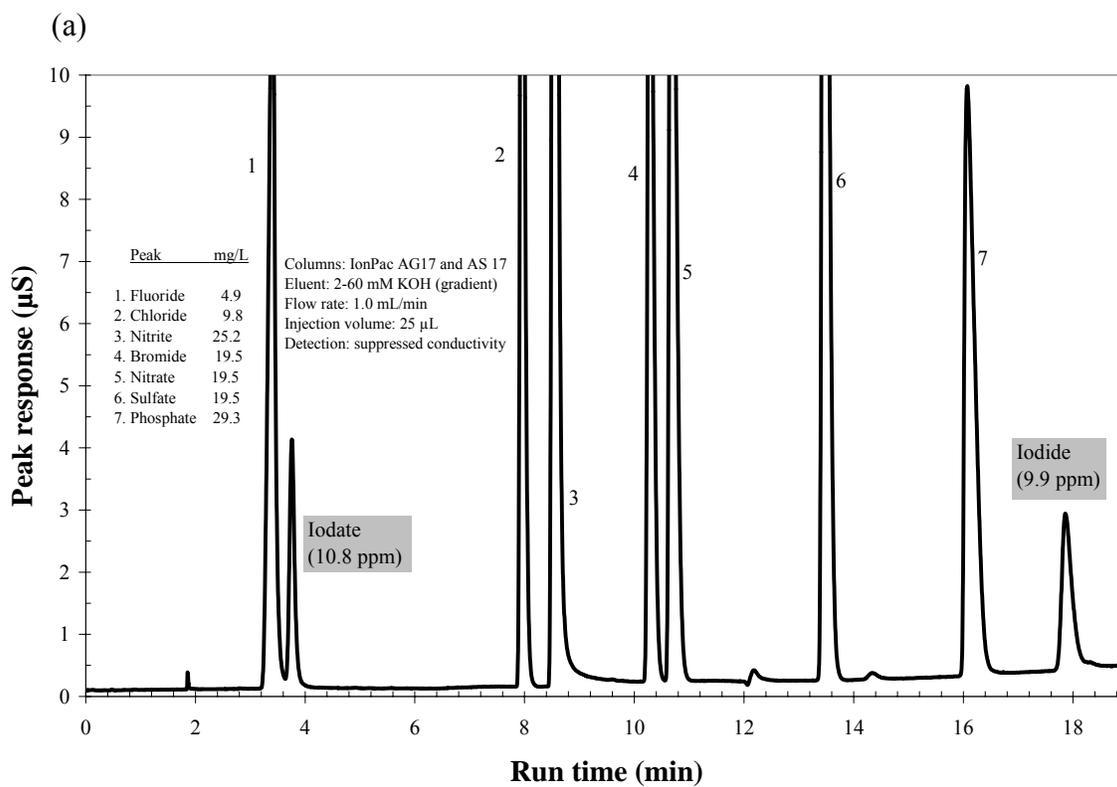


Figure 2

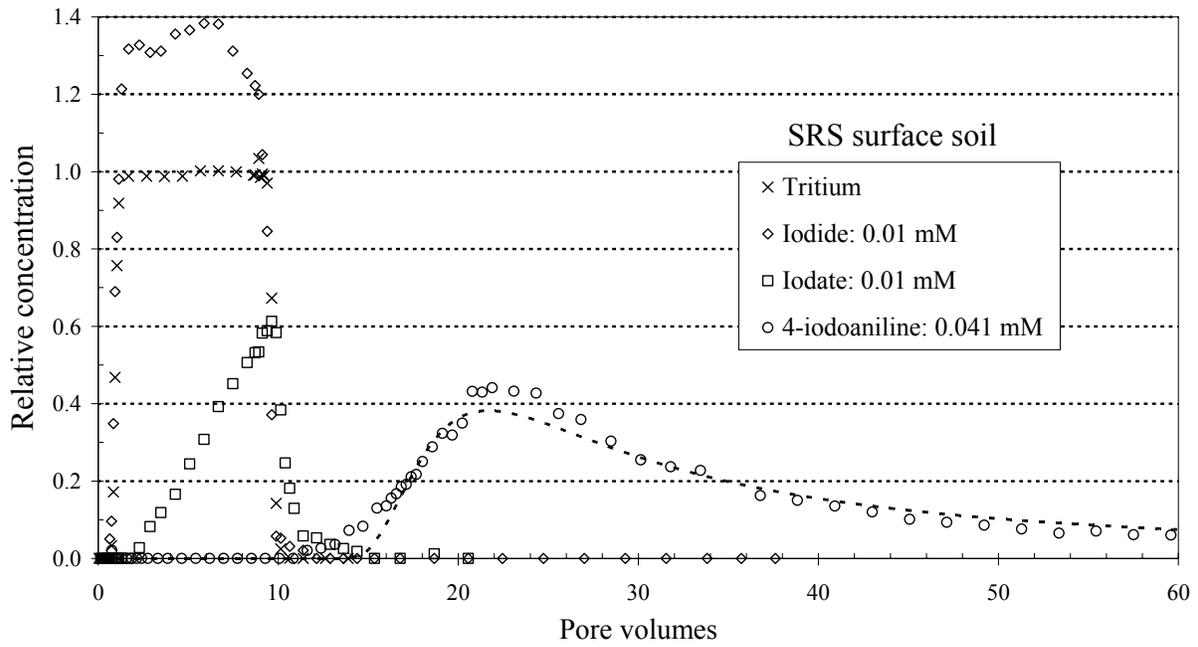


Figure 3

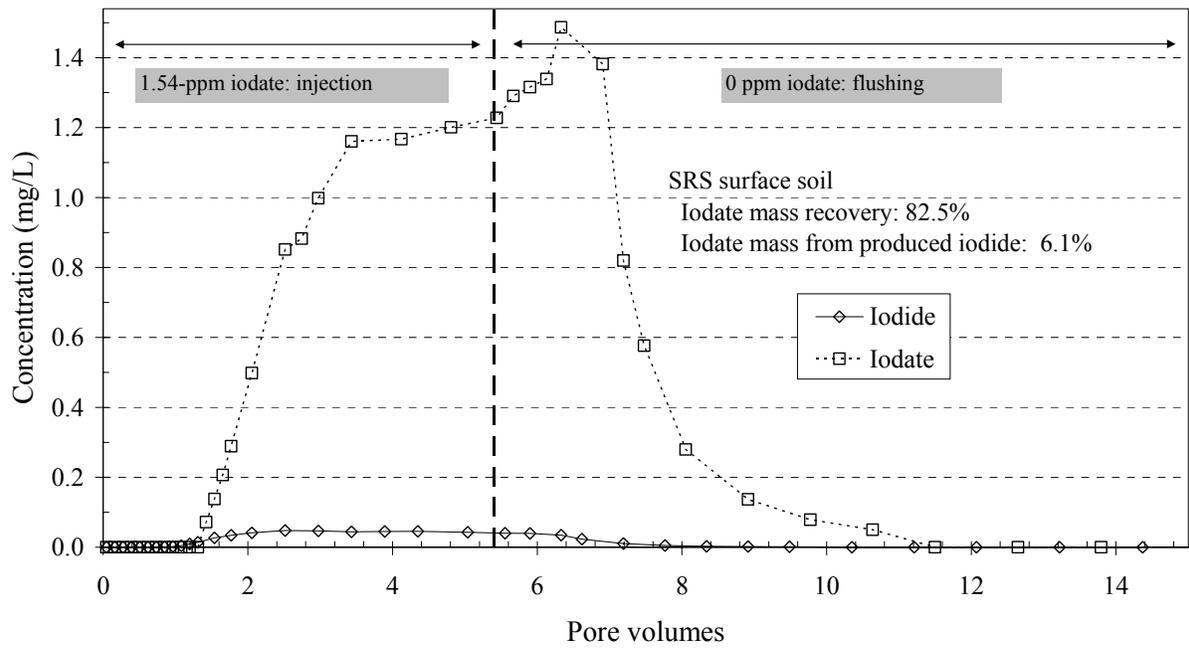


Figure 4

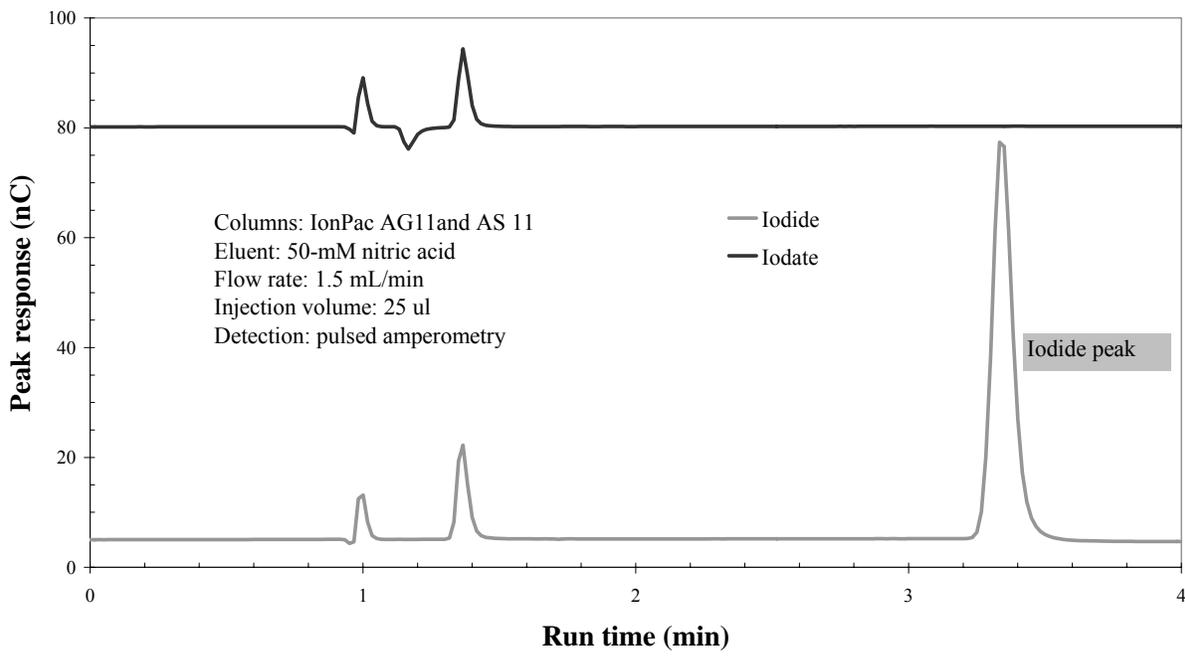


Figure 5

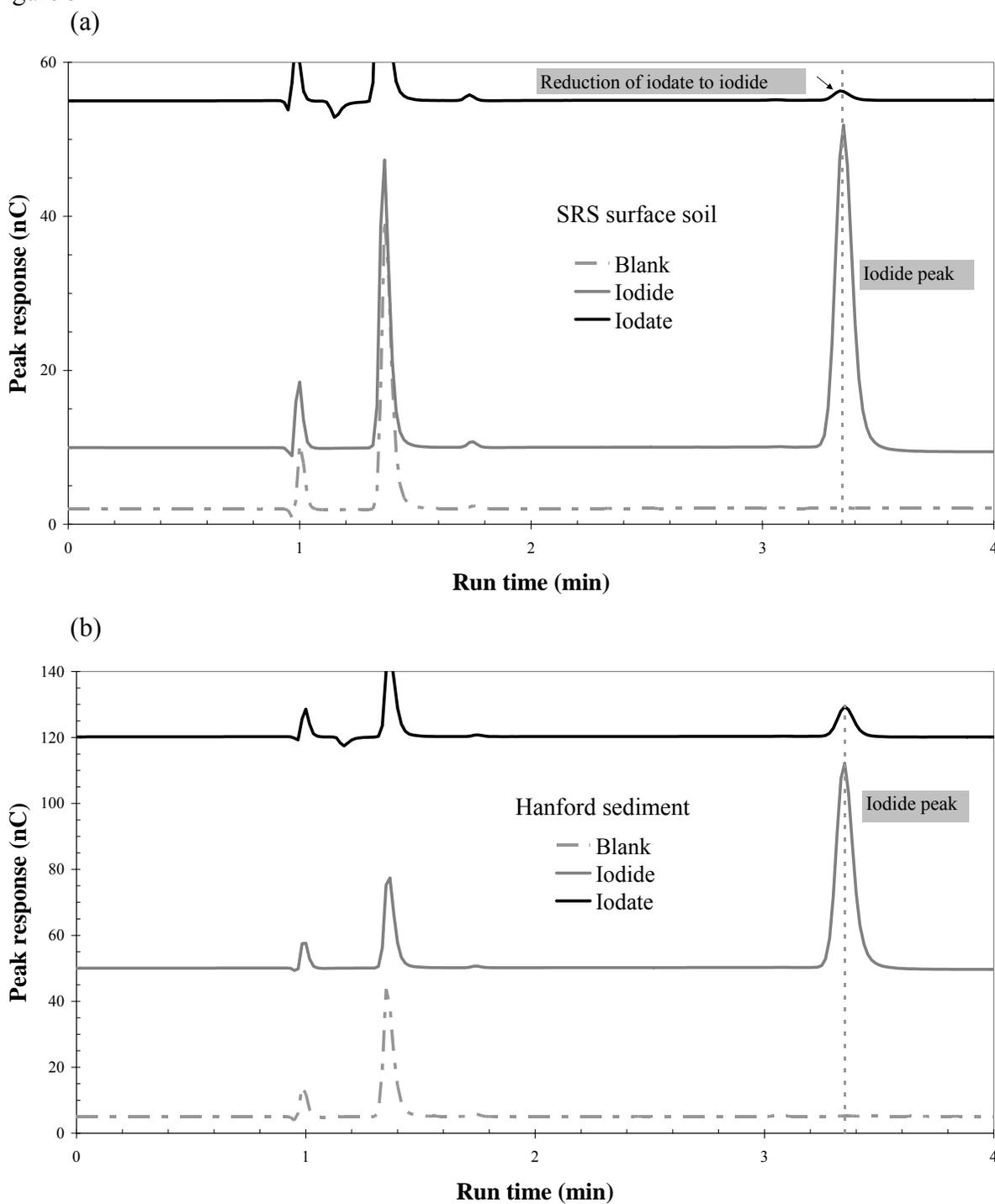


Figure 6
(a)

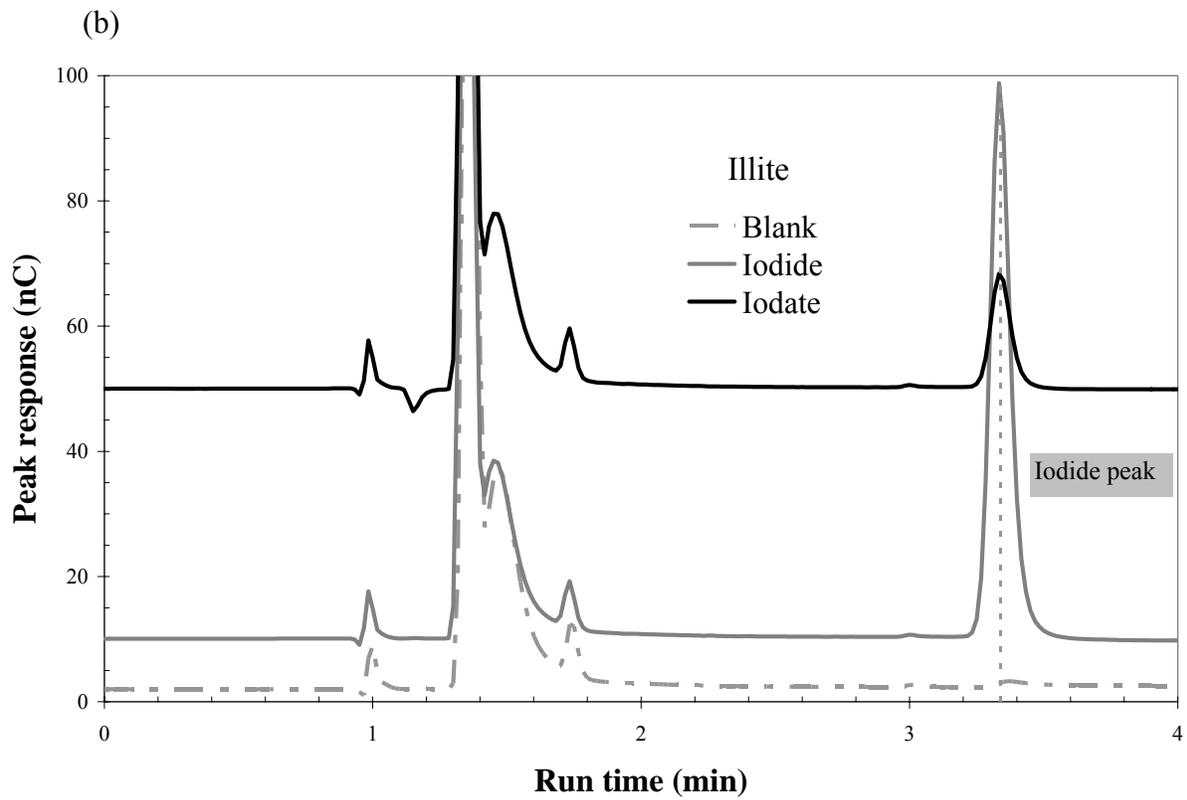
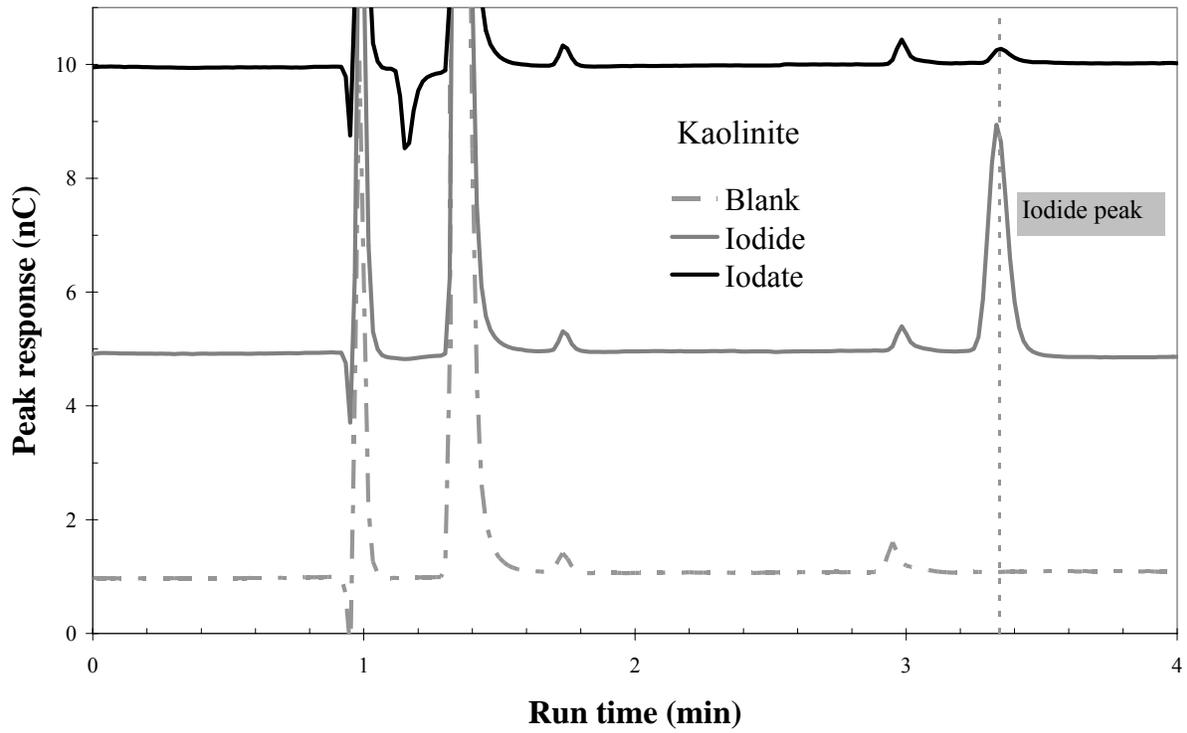


Figure 7

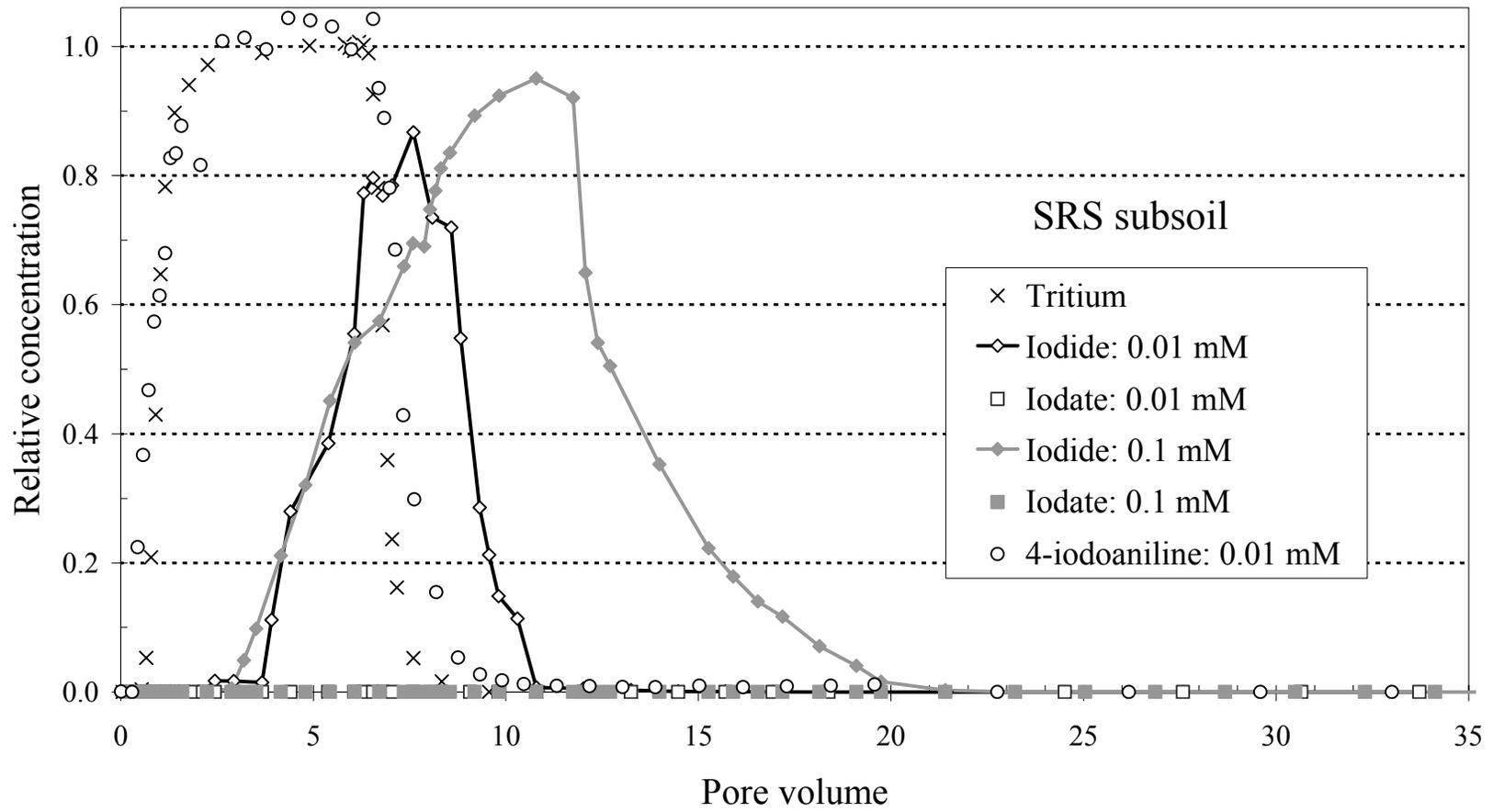


Figure 8

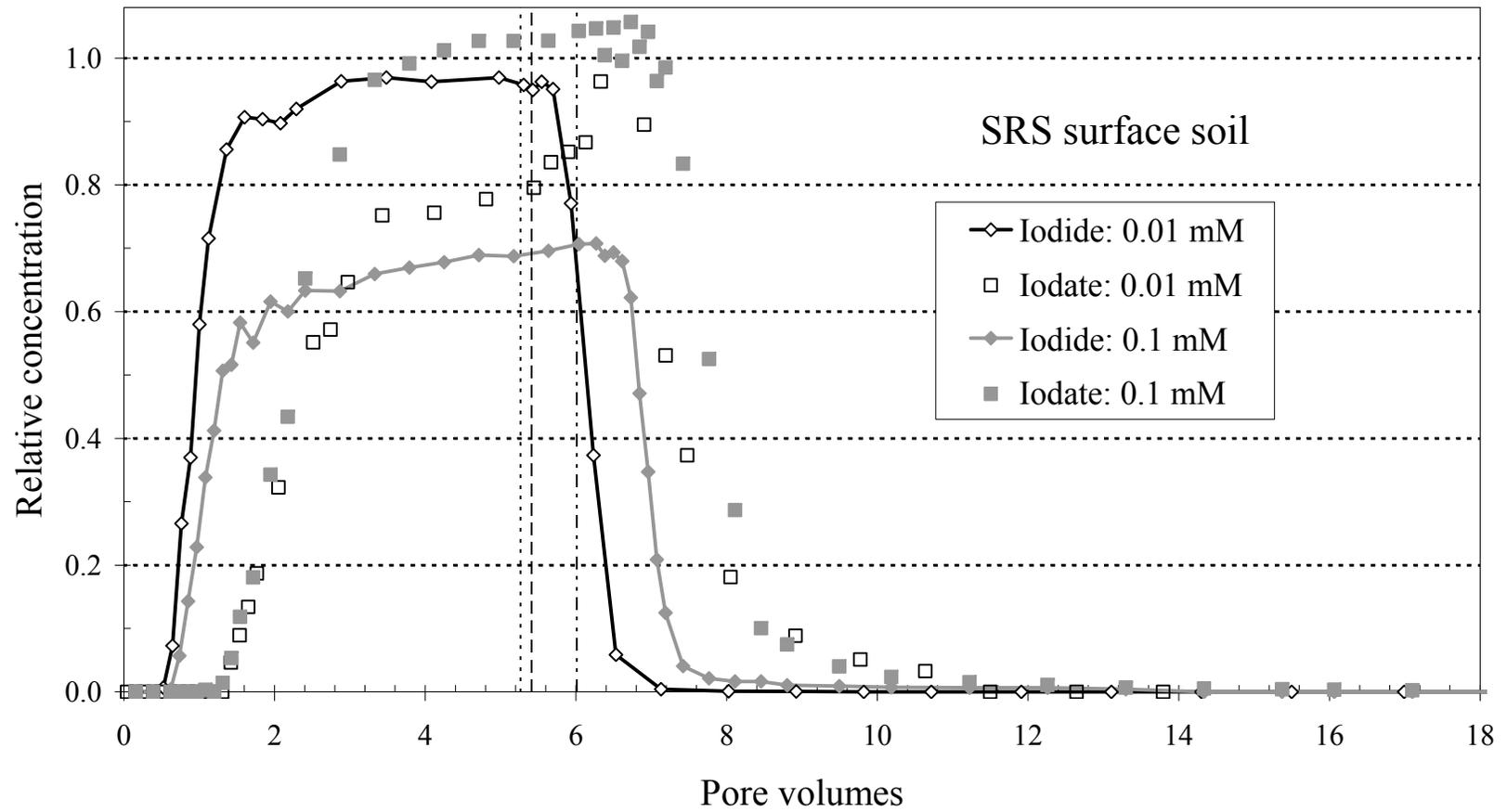


Figure 9

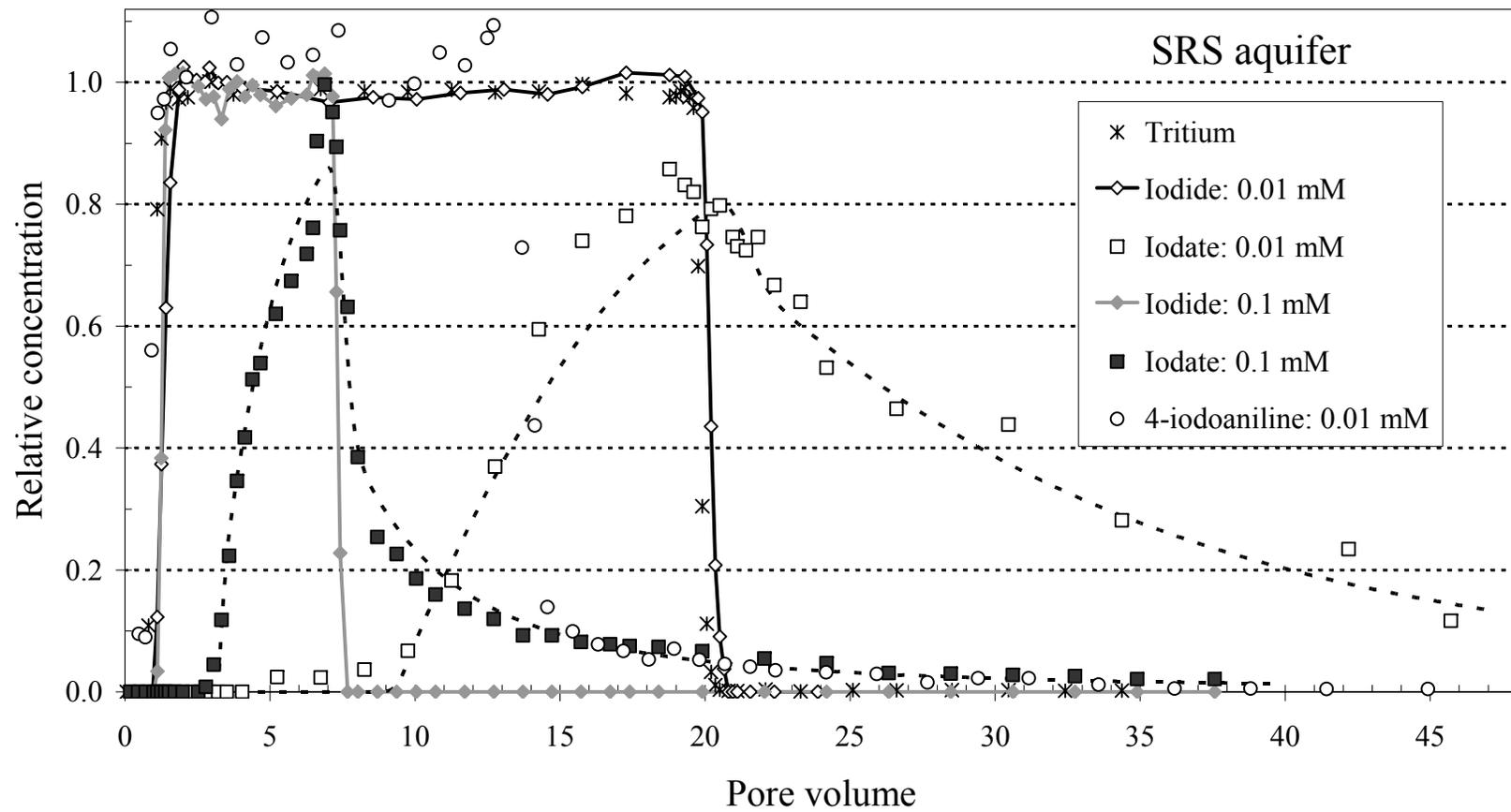


Figure 10

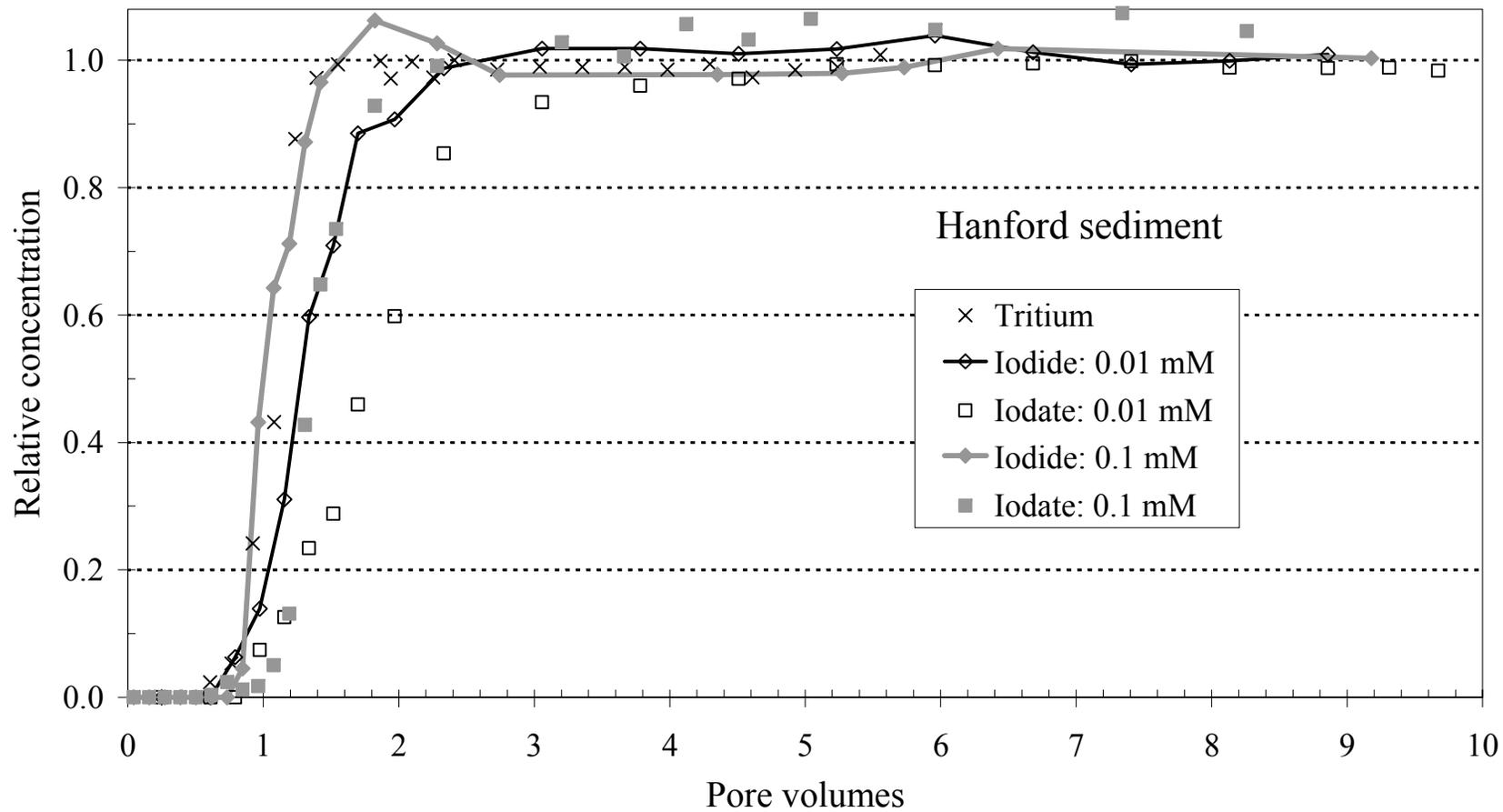


Figure 11

