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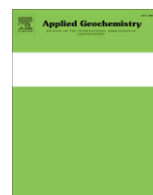
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## Sorption, degradation, and transport of methyl iodide and other iodine species in geologic media

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## ABSTRACT

Iodine is an important element in studies of human nutrition to combat I deficiency disorders, and in protection of the environment and human health from anthropogenic release of radioactive I. Biogeochemical cycling of I in the subsurface environment is complex, because it occurs in multiple oxidation states and as inorganic and organic species that may be volatile, hydrophilic and biophilic. Predicting the fate and transport of anthropogenic radioiodine deposited from the atmosphere or released into the subsurface requires knowledge of the sorption and degradation behavior of the various I species that may interact with soils and sediments. In this study, sorption, degradation, and transport behavior of I species (iodide, iodate, methyl iodide, and 4-iodoaniline) were examined in 12 geologic samples of differing physico-chemical characteristics, collected at numerous nuclear facilities in the USA. In particular, this work focuses on the sorption and degradation behavior of  $\text{CH}_3\text{I}$  in geologic media, for which few studies are available, even though it is recognized as an important gaseous form of I in the marine atmosphere, and as a major form released from nuclear fuel reprocessing facilities and during nuclear accidents. Results from complementary batch and column experiments show that different I species exhibit very different sorption and transport behavior in geologic media. Sorption of  $\text{I}^-$  is in general minimal, but a low concentration ( $5 \times 10^{-13} \text{ M}$ ) of radioactive  $^{125}\text{I}$  is found to be strongly sorbed onto samples with high organic matter. Sorption of  $\text{IO}_3^-$  is consistently greater than that of  $\text{I}^-$ , and sorption of 4-iodoaniline is generally strong and seems to be related to the amount of organic matter in the media. Methyl iodide is weakly sorbed onto 12 geologic samples with a distribution coefficient of about 1 mL/g, but its degradation varies greatly as a function of organic matter content, with a regression line of  $t_{1/2} = 0.084 \times \text{OM} + 0.088$  ( $R^2 = 0.898$ ,  $N = 6$ ) where  $t_{1/2}$  is the degradation half-life and OM is the organic matter content. These results will be useful in predicting the mobility of anthropogenic radioactive I deposited on a soil surface, and highlight the fact that it will exhibit different residence times according to its original chemical form and to the composition of host sediments.

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## 1. Introduction

Iodine is a trace element widely distributed in the atmosphere, lithosphere, hydrosphere and biosphere at varying concentrations (Hu and Moran, 2010). It is an essential micronutrient in mammals, necessary for the production of thyroid hormones and for the proper functioning of the thyroid gland. Iodine deficiencies can lead to severe metabolic disorders, including thyroid enlargement (goiter), hypothyroidism (underactive thyroid gland), hyperthyroidism (overactive thyroid gland), mental retardation in infants and children whose mothers are I-deficient during pregnancy, reproductive damage, and childhood mortality (Vitti et al., 2003).

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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. In addition to concern about I deficiency disorders, an uncontrolled release of radioactive I could constitute a direct threat to human populations because radioactive I is concentrated in the human thyroid (e.g., VanMiddlesworth et al., 2000). Following a nuclear accident (such as at Chernobyl and more recently at the Fukushima nuclear reactor in Japan) or an intentional radiological release,  $^{131}\text{I}$  is an acute contaminant because of its short half-life (8.02 days) and high specific activity. Following the earthquake and tsunami of March 11, 2011 and subsequent damage to the Fukushima reactor in Japan, trace levels of  $^{131}\text{I}$  were detected on April 7, 2011 in rainwater and milk samples in the state of Washington, USA and elsewhere in the western USA. In contrast,  $^{129}\text{I}$  has a long half-life (15.6 Ma), high-abundance fission yield, and presumed high mobility in the environment; it

has been recognized as one of the most important radionuclides for long-term health concerns.

The coexistence of various inorganic and organic I species, in different proportions, has been reported in various environments (cf., Hu et al., 2009). Organically-bound I can be a significant fraction of total I in aqueous systems and in the atmosphere. Dissolved organo-I compounds comprise up to 50% of total I in aqueous samples from estuaries, rivers and rain (Santschi and Schwehr, 2004; Steinberg et al., 2008a). In addition, CH<sub>3</sub>I is an important gaseous form of I in the marine atmosphere, and in releases from nuclear fuel reprocessing facilities and during nuclear accidents (Yoshida and Muramatsu, 1995; Baker et al., 2001).

In studies of I biogeochemical cycling, large uncertainties remain in assessing global emission fluxes of volatile I compounds (Davis et al., 1996; Moore and Groszko, 1999; Amachi, 2008). There is evidence that CH<sub>3</sub>I is produced by living organisms (phytoplankton, marine algae, marine bacteria, marine aggregates) in the ocean, and by some terrestrial sources (rice paddies, peatland, higher plants, fungi, bacteria) (Laturnus et al., 1998; Amachi et al., 2003; Fuse et al., 2003; Ban-nai et al., 2006; Amachi, 2008; Hughes et al., 2008; Brownell et al., 2010).

Methyl iodide can also be a significant component in radioactive I released from nuclear fuel reprocessing facilities, and during accidents at nuclear power plants (Collins et al., 2004; Aldahan et al., 2006). According to UNSCEAR (2000), the <sup>131</sup>I inventory in the reactor core in which the accident took place at Chernobyl was estimated to be  $3.2 \times 10^6$  TBq and the total <sup>131</sup>I released to the atmosphere over the course of the accident was about  $1.7 \times 10^6$  TBq. From 4 air samples collected at 14.5 m above the ground surface in Japan 10–23 days after the Chernobyl nuclear reactor accident, Noguchi and Murata (1988) reported the following proportions of airborne <sup>131</sup>I species during the Chernobyl accident:  $19 \pm 9\%$  particulate I (iodine attached to particulate matter of mean diameter of 0.8  $\mu$ m),  $5 \pm 2\%$  I<sub>2</sub>,  $6 \pm 3\%$  HIO and other nonI<sub>2</sub> inorganic I species, and  $70 \pm 11\%$  organic I species (e.g., CH<sub>3</sub>I). Other studies on species distribution of radioactive I in and around nuclear power plants, and of stable I in the environment, have also indicated the important role of organic I species (Guentay et al., 2005). Aldahan et al. (2006) reported that the main forms of I released into the environment from European reprocessing facilities are alkyl iodides, CH<sub>3</sub>I and iodides (e.g., HI) that transform into water-soluble molecules and/or IO<sub>3</sub><sup>−</sup>, which are subsequently adsorbed on and/or nucleate to form aerosols and return to Earth's surface as wet and dry fallout.

Fate and transport of CH<sub>3</sub>I in the terrestrial environment has been examined in the context of CH<sub>3</sub>I as a replacement for CH<sub>3</sub>Br as a soil fumigant (Gan and Yates, 1996; Gan et al., 1997; Zheng et al., 2003; Pelley, 2009). The fumigant CH<sub>3</sub>Br has been used extensively in California and other parts of the world to control plant pathogens such as nematodes, soil-borne diseases, and weeds in economically important crops such as strawberries and nursery stock (Zheng et al., 2003). Because of its stratospheric ozone depletion potential, production and import phase-out for CH<sub>3</sub>Br was implemented in the USA and other developed countries in 2005.

Methyl iodide does not damage the ozone layer, with its atmospheric lifetime of only 4–8 days, compared with 1.5–2 a (Gan et al., 1996) or 0.4–0.9 a (Zheng et al., 2003) reported for CH<sub>3</sub>Br. However, California (the largest potential market of the chemical) has identified it as a carcinogen, neurotoxin, and endocrine disruptor (Pelley, 2009). The US Environmental Protection Agency (USEPA) approved the use of CH<sub>3</sub>I as a soil fumigant in 2008. In February 2010, the California Department of Pesticide Regulation (CDPR) concluded that CH<sub>3</sub>I is “highly toxic”, but in December 2010, CDPR approved its usage as a pesticide, mandating additional controls for usage in California which are aimed at minimizing exposure for farm workers and guarding against unintentional releases (<http://www.cdpr.ca.gov/docs/risk/methyl iodide.htm>). Nonetheless, objections have been raised by environmentalists, researchers and farmers. As of now, the future of agricultural use of CH<sub>3</sub>I in California and the USA is uncertain. The main concerns stem from the high vapor pressure of CH<sub>3</sub>I, which can result in the emission of a significant proportion of the applied CH<sub>3</sub>I mass into ambient air. Release of CH<sub>3</sub>I to the atmosphere may lead to pollution of the environment and health issues for farm workers when adequate controls such as thick, continuous tarps are not properly utilized. Of secondary concern is the potential for a significant fraction of the applied CH<sub>3</sub>I to be leached into groundwater, either as CH<sub>3</sub>I or as a degradation product.

Major pathways of global I cycling include the volatilization of organic I compounds into the atmosphere, accumulation of I in living organisms, oxidation and reduction of inorganic I species, and sorption of I by soils and sediments (Amachi, 2008). Accurate assessment of global I cycling has to consider the speciation of I and disparate sorption and transport behavior for the different I species.

Here laboratory experiments are reported, with complementary batch and transport experiments, aimed at evaluation of the sorption, degradation, and transport of important I species (iodide, iodate, 4-iodoaniline, and methyl iodide in particular) in a variety of geologic media gathered at locations near some of the major nuclear operations in the USA. In particular, this work focuses on the sorption and degradation behavior of CH<sub>3</sub>I in geologic media, for which few studies are available. Batch sorption experiments with environmentally-low level concentrations of <sup>125</sup>I<sup>−</sup> were conducted to compare to the sorption results conducted at much higher I<sup>−</sup> concentrations, in order to evaluate the concentration effect on I sorption. The results of these experiments, aimed at understanding the fate and transport of different I species (methyl iodide, iodide, iodate, and organo-iodine) in a suite of geologic media with a variety of physico-chemical characteristics will provide the basis for qualitative and quantitative predictions of the mobility of I species in the near subsurface terrestrial environment.

## 2. Materials and methods

### 2.1. Materials

Soils and sediments were obtained from locations in the USA within or near several Department of Energy (DOE) complex sites (Table 1), including the following: Savannah River Site (SRS) in South Carolina; the Oak Ridge Reservation in Tennessee; the Hanford Site in Washington; the Idaho National Laboratory (INL) site in Idaho; the Nevada Test Site (NTS) in Nevada; a location (Owngate) in Santa Fe near Los Alamos National Laboratory, New Mexico; and two sites occupied by Lawrence Livermore National Laboratory (LLNL) in Livermore and Tracy, California. A sample of Wisconsin surface soil with a high amount of organic matter was also included in the experiment. Contamination with radionuclides, including <sup>129</sup>I, already is or may become an environmental problem at these DOE complex sites, especially at the Savannah River Site (Kaplan et al., 2011). These locations also represent a large range in geologic and climatologic conditions. For example, Savannah River Site (SRS) in South Carolina has a humid subtropical climate with annual rainfall of 91–112 cm, and geology representative of Atlantic Coastal Plain. In contrast, the Hanford Site in Washington 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, as well as two LLNL samples were collected at different depths, providing an opportunity to examine the sorption and transport of I species, in a vertical sense.

**Table 1**  
Sample characterization, with samples presented in order of increasing organic matter.<sup>a</sup>

| Sample                 | SRS aquifer | LLNL alluvium       | INL basalt                              | Hanford sediment                               | NTS alluvium                                    | SRS subsoil                              | Oak Ridge sediment                            | NTS tuff                          | LLNL aquifer         | Owngate soil | SRS surface soil | Wisconsin soil |
|------------------------|-------------|---------------------|-----------------------------------------|------------------------------------------------|-------------------------------------------------|------------------------------------------|-----------------------------------------------|-----------------------------------|----------------------|--------------|------------------|----------------|
| Description            | Aquifer     | 0.7 m below surface | Crushed basalt core 0.3 m below surface | Composite of core samples 9–12 m below surface | ~300 m below surface in the U-1a tunnel complex | Composite of sediment 12 m below surface | Composite of core samples 2–3 m below surface | Crushed tuff ~300 m below surface | 14.5 m below surface | Surface soil | Surface soil     | Surface soil   |
| Location               | Aiken, SC   | Livermore, CA       | Idaho Falls, ID                         | Richland, WA                                   | Mercury, NV                                     | Aiken, SC                                | Oak Ridge, TN                                 | Mercury, NV                       | Livermore, CA        | Santa Fe, NM | Aiken, SC        | Plover, WI     |
| pH                     | 5.60        | 7.10                | 7.46                                    | 7.48                                           | 7.53                                            | 4.20                                     | 4.50                                          | 7.80                              | 7.75                 | 7.50         | 3.84             | 5.52           |
| Organic matter         | 0.013       | 0.03                | 0.04                                    | 0.06                                           | 0.06                                            | 0.072                                    | 0.12                                          | 0.14                              | 0.17                 | 2.3          | 2.33             | 8.70           |
| Particle size          |             |                     |                                         |                                                |                                                 |                                          |                                               |                                   |                      |              |                  |                |
| Sand (%)               | 97.2        | 42.0                | 77.4                                    | 89.0                                           | 69.9                                            | 76.7                                     | 7.68                                          | 89.1                              | 64.8                 | 35.0         | 87.6             | 67.0           |
| Silt (%)               | 0.90        | 25.6                | 21.1                                    | 7.9                                            | 19.7                                            | 3.50                                     | 70.9                                          | 8.8                               | 22.3                 | 39.2         | 2.90             | 21.0           |
| Clay (%)               | 1.90        | 32.4                | 1.5                                     | 3.1                                            | 10.3                                            | 19.8                                     | 21.4                                          | 2.1                               | 12.9                 | 25.7         | 3.50             | 12.0           |
| CEC (meq/100 g)        | 0.06        | 26.3                | 1.67                                    | 7.37                                           | 11.8                                            | 1.78                                     | 9.41                                          | 4.54                              | 21.1                 | 15.1         | 1.29             | 14.1           |
| AEC (meq/100 g)        | 0.15        | 0.35                | 0.13                                    | 0.01                                           | 0.14                                            | 4.0                                      | 0.12                                          | 0.18                              | 0.024                | 0.01         | 0.27             | 0.01           |
| Iron-CBD (g Fe/kg)     | 7.30        | 9.78                | 3.12                                    | 3.26                                           | 7.68                                            | 15.9                                     | 1.08                                          | 1.48                              | 2.04                 | 3.82         | 2.50             | 10.1           |
| Iron-oxalate (g Fe/kg) | 0.04        | 0.94                | 12.9                                    | 0.94                                           | 0.08                                            | 0.20                                     | 0.18                                          | 0.12                              | 7.35                 | 0.21         | 0.32             | 5.86           |

<sup>a</sup> OM: organic matter; CEC: cation exchange capacity; AEC: anion exchange capacity; CBD: citrate–bicarbonate–dithionite; oxalate: ammonium oxalate; LLNL: Lawrence Livermore National Laboratory; NTS: Nevada Test Site; INL: Idaho National Laboratory; SRS: Savannah River Site.

The wide variety of sample types provided an opportunity to examine the influence of organic matter, clay mineralogy, soil pH, and texture on the sorption, degradation, and transport behavior of inorganic I ( $I^-$  and  $IO_3^-$ ) and organic I (methyl iodide and 4-iodoaniline). The 4-iodoaniline (chemical formula:  $IC_8H_4NH_2$ ) was used as a representative refractory organic I species. All properties of the solid materials presented in Table 1 were measured according to standard procedures. Briefly, sample pH was measured in a 1:1 soil/0.01 M  $CaCl_2$  suspension (Sparks et al., 1996). For particle size distribution analyses, soil aggregates were destructured and dispersed into discrete sizes and separation of particle sizes quantified by sieving and sedimentation (Dane and Topp, 2002). Soil organic matter was determined by the Walkley-Black method, where C is oxidized by the dichromate ion and the excess dichromate ion is then back-titrated with  $Fe^{2+}$  (Sparks et al., 1996). The cation and anion exchange capacities were quantified according to the un-buffered salt  $NH_4Cl$  saturation methods (Sparks et al., 1996). Both ammonium oxalate ( $NH_4-Ox$ ) and citrate-bicarbonate-dithionite (CBD) extractable Fe were determined (Sparks et al., 1996);  $NH_4-Ox$  extractable Fe contains crystalline Fe oxide minerals such as hematite, goethite and lepidocrocite, while CBD extraction targets noncrystalline Fe oxides, including ferrihydrite.

Solutions were prepared with 18 MΩ reagent water from a NANOpure Infinity Water Purification System (Barnstead International, Dubuque, IA). The tracer chemicals ( $KI$ ,  $KIO_3$ , methyl iodide, and 4-iodoaniline; all with purity >99%) used in the laboratory studies were purchased from Aldrich Chemical Co. (St. Louis, MO). All I solutions were prepared and stored in amber glass bottles to minimize photodecomposition or inter-conversion.

## 2.2. Batch sorption experiments

Batch tests, in accordance with ASTM method D4646-87 (1998), were conducted to investigate sorption of  $I^-$  and  $IO_3^-$  species in contact with geologic samples. A solution to solid ratio of 4:1 was employed instead of the 20:1 ratio specified in the ASTM method (a ratio of 20:1 is unrealistically high when compared to that commonly encountered under field conditions). For each sediment, triplicate blank treatments were conducted (adding only 5 mM  $CaCl_2$  as the electrolyte solution) and triplicate treatments of an I species ( $I^-$  or  $IO_3^-$ ) at different concentrations ( $1 \times 10^{-5}$  M for  $I^-$  and  $IO_3^-$ , as well as  $5 \times 10^{-13}$  M for  $^{125}I^-$ ), that are dictated by the detection limits of the different analytical methods. Duplicate control samples were also prepared in the same manner with an I species but no solid sample material to evaluate potential I concentration change during the batch test. After 24-h equilibration, the mixture was centrifuged at 4000g for 30 min and then filtered through 0.45 μm Supor membranes. The liquid samples were analyzed by ion chromatography for the concentration of  $I^-$  (amperometry detection) and for  $IO_3^-$  (conductivity detection) (Hu et al., 2005). Radioactive  $^{125}I$  was determined by gamma-spectrometry. Concentrations of I species observed in the controls indicated that they were not affected by interaction with the experimental apparatus or during sample processing.

Methyl iodide is relatively difficult to work with in the laboratory because of its high volatility. The following procedure was used to estimate sorption of  $CH_3I$  in different types of geologic samples. Soil (2 g) was weighed into 50-mL Teflon centrifuge tubes, 10 mL of 0.5 mM  $CaCl_2$  solution was added to each tube, and then 10 μL of 10 mM  $CH_3I$  solution ( $1 \times 10^{-7}$  M  $CH_3I$ ) in acetone was added. After spiking with  $CH_3I$ , the Teflon centrifuge tube was immediately capped and mixed at low speed on a mechanical shaker for 24 h. The sediment slurry was then centrifuged at 4000g for 20 min. A 1.0 mL aliquot of the separated aqueous phase was transferred into a 21-mL glass vial containing 5 mL of ethyl acetate and 3 g of dried  $Na_2SO_4$ . Sodium sulfate is commonly used as a



drying agent to absorb water in the sample during solvent extraction. The use of ethyl acetate was based on good  $\text{CH}_3\text{I}$  recoveries observed in preliminary experiments. The solvent selection also considered such factors as boiling points and potential toxicity of the solvent; ethyl acetate has no known acute toxicity to humans. The sample vial was stirred on a vortex mixer for about 2 min. The solvent phase was transferred into an autosampler vial to be analyzed by gas chromatography–electron capture detector (GC-ECD) in order to obtain the aqueous-phase concentration  $C_w$  ( $\text{mg L}^{-1}$ ).

The remaining sediment phase, along with the centrifuge tube, was weighed to determine the amount of solution remaining in the sediment. The sediment was then extracted with 10 mL of ethyl acetate by shaking for 2 h, and centrifuging at 4000g for 20 min and an aliquot of the sample extract was transferred into an autosampler vial and analyzed by GC-ECD. Using similar extraction procedures, Zheng et al. (2003) reported >95%  $\text{CH}_3\text{I}$  recovery for unamended soils. The sorbed concentration  $C_s$  ( $\text{mg kg}^{-1}$ ) was calculated from the measured aqueous and solid-phase concentrations. The sorption/distribution coefficient  $K_d$  ( $\text{L kg}^{-1}$ ) was calculated as the ratio of  $C_s$  over  $C_w$ ; note that sorption equilibrium is not assumed at the experimental duration of 24 h mixing.

### 2.3. Degradation experiments on methyl iodide

In order to examine degradation of  $\text{CH}_3\text{I}$  in the different types of geologic media, a procedure similar to that used by Zheng et al. (2003) was used. Soil samples (10 g) were weighed into 21-mL glass vials and the moisture content was adjusted to 10% and left over night before spiking with  $\text{CH}_3\text{I}$ . For degradation treatments, 10  $\mu\text{L}$  of 10 mM  $\text{CH}_3\text{I}$  solution in acetone was spiked into the vial. The spiked vials were immediately capped with Al seals and Teflon-lined septa, mixed, and incubated at room temperature ( $21 \pm 1^\circ\text{C}$ ). Triplicate vials were removed at 0, 3, 7, 15, 28, and 56 days after the treatment, and the samples were stored in a freezer at  $-22^\circ\text{C}$  to stop the degradation. To extract samples, vials were removed from the freezer, and 10 mL of ethyl acetate and 5 g of dried  $\text{Na}_2\text{SO}_4$  were added. The vial was immediately re-capped and thawed at room temperature. The soil samples were vigorously mixed on a mechanical shaker for 2 h. The solvent phase was transferred into an autosampler vial for analysis by gas chromatography by GC-ECD.

### 2.4. Column transport experiments

For column transport tests, either a glass column from Omnifit in Boonton, NJ (1.5-cm inner diameter, 10.0-cm long) or Alltech (Deerfield, IL) stainless steel column (2.1-cm inner diameter, 7.0-cm long) was incrementally packed with the air-dried sediment (<2 mm grain size) to obtain a uniform bulk density. The packed columns were first evacuated by pulling vacuum and then 5 mM  $\text{CaCl}_2$  was introduced to achieve full liquid saturation. There were no visible air pockets after the column had been saturated. Then approximately 100 column pore volumes of 5 mM  $\text{CaCl}_2$  electrolyte solution were slowly pumped for 2–3 days through the column prior to the transport study.

The methods employed for the column studies were similar to those used in previous experiments (e.g., Hu and Brusseau, 1996). A HPLC pump (Model 301, Alltech Associates, Inc., Deerfield, IL) was connected to the column, and a 3-way valve was placed in-line to facilitate switching between solutions with and without the tracer of interest. Column experiments involving transport of I species (iodide, iodate, or 4-iodoaniline) in the 5 mM  $\text{CaCl}_2$  electrolyte solution were conducted at concentrations of either  $1 \times 10^{-5}$  or  $1 \times 10^{-4}$  M. For 4-iodoaniline transport experiments, the solution was allowed to contact only glass or stainless steel to avoid poten-

tial interaction of organoiodine with plastics in the column system. In addition, a separate transport run of nonreactive  $^3\text{H}$  (activity 33 kBq/L) or  $\text{Br}^-$  was carried out to compare its transport behavior with the I species. Column effluent fractions were collected with an automated fraction collector (Retriever 500, ISCO Inc., Lincoln, NE) for analyses. Liquid scintillation and ion chromatography were used to measure the activity of  $^3\text{H}$  or concentration of  $\text{Br}^-$ , respectively, in the column effluent.

### 2.5. Analyses of iodine species

Analysis of  $\text{CH}_3\text{I}$  was carried out on an Agilent 6890 N GC (Agilent, Wilmington, DE) equipped with a microECD and a 7683 autosampler. Pulsed splitless injection was applied at 25 psi for 0.4 min and the total splitless time was 0.5 min. Separation was achieved on a RTX-624 capillary column (30 m  $\times$  0.53 mm i.d.  $\times$  3.0  $\mu\text{m}$  film thickness) at a flow rate of 4.0  $\text{mL min}^{-1}$  (He). The inlet temperature was  $210^\circ\text{C}$ , and detector temperature was  $260^\circ\text{C}$ . The oven temperature was initially set at  $45^\circ\text{C}$  (2.0 min), ramped to  $170^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$ , then to  $240^\circ\text{C}$  at  $40^\circ\text{C min}^{-1}$ , and finally heated at  $240^\circ\text{C}$  for 4.45 min. Calibration was with external standards of known  $\text{CH}_3\text{I}$  concentrations.

A Dionex Corp. (Sunnyvale, CA) ion chromatography (IC) DX-600 system was used to analyze  $\text{I}^-$  and  $\text{IO}_3^-$ , as well as other common anions, using a hydroxide gradient method developed by Hu and Moran (2005). 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, an IonPac AG17 guard column in conjunction with an IonPac AS17 analytical column, and an anion self-regenerating suppressor that operated at 248 mA in recycled-water mode was used. The guard and analytical columns, both maintained at  $35^\circ\text{C}$ , were 4-mm inner diameter, and 50-mm-long. An EG50 eluent generator with an EGC-KOH cartridge and a continuously regenerated anion trap column was employed 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  $\text{mL/min}$ .

To measure low (sub-ppb) concentrations of  $\text{I}^-$ , the ED50A electrochemical detector was used in pulsed amperometric mode, with a Ag working electrode and Ag/AgCl reference electrode, after separation using IonPac AG11 and IonPac AS11 columns (Hu et al., 2005). Iodide separation was achieved with 50 mM  $\text{HNO}_3$  eluent under an isocratic flow of 1.5  $\text{mL/min}$ . The method is fast (with a run time of less than 3 min) and sensitive (with a method detection limit of 0.6  $\mu\text{g/L}$  at a 25  $\mu\text{L}$  injection volume). A 25  $\mu\text{L}$  injection loop was used for both 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 Ar flow rates of 16, 1.0, and 0.9  $\text{L/min}$ , respectively, for plasma, auxiliary gas, and carrier gas flows. The column effluent sample was spiked with internal standard elements at 20  $\mu\text{g/L}$  for  $^{127}\text{I}$  analyses. A rinse solution of 10% methanol was used between samples to mitigate potential memory effects. For ICP-MS analysis of total I (in this study, introduced as 4-iodoaniline), several internal standard elements (Y-89, Rh-103, In-115, Tb-159, and Bi-209) were tested to examine potential matrix effects introduced by the effluent samples collected from column transport studies. Rhenium-103 consistently stood out as the best choice for all samples types, and was, therefore, used in the I data reduction.

### 3. Results and discussion

#### 3.1. Sorption of iodine species

Information on the sorption of I species was obtained through two approaches: batch sorption and column transport. In the column experiments, the retardation factor and mass recovery are calculated by moment analysis of the I breakthrough curve, with the size of the I pulse known from the experimental setup (Hu et al., 2005).

Most  $K_d$  values in the literature have been acquired through batch experiments performed under saturated conditions. For weakly sorbing solutes, batch sorption experiments can yield negative  $K_d$  values with a large variability, because the  $K_d$  value is calculated from the difference of two large numbers (initial and final aqueous concentration). This is evident in the case of  $I^-$  in several geologic samples, which have a negative  $K_d$  value with large variability (Table 2); anion exclusion is not likely because of measured low anion exchange capacities and positive  $K_d$  results from column work.

In all of the column transport runs,  $^3H$  exhibited ideal breakthrough with symmetrical behavior and negligible tailing and conservative (not retarded) transport with a retardation factor of about 1. Iodide sorption on to many types of geologic media has been reported to be extremely limited (e.g., Whitehead, 1974; Kaplan et al., 2000). It was likewise observed that very limited sorption of  $I^-$  occurred during transport in many soils and sediments (Table 2), and yet these values are all positive, which differs from the batch sorption results. Column tests are more appropriate than the batch tests to evaluate solute sorption with minimal interaction, while batch sorption is more applicable for strong sorbers, as these chemicals will not break through in column experiments within a reasonable experimental time (e.g.,  $I^-$  in ORNL sediment and SRS surface soil; shown in Table 2).

However, there was strongly retarded transport of  $I^-$ , compared to  $^3H$ , in the ORNL sediment, SRS surface soil, and SRS subsoil sample. These samples contained an appreciable amount of Fe and Al oxide minerals (Table 1), which possess positively charged surfaces and contribute to anion sorption, as confirmed from anion exchange capacity measurements. These samples also show appreciable sorption of other anionic species, such as  $Br^-$  (data not shown).

Distribution coefficients ( $K_d$  values) of  $I^-$  determined in laboratory experiments are relatively low ( $\sim 1$  mL/g), whereas  $K_d$  values of  $IO_3^-$  and organo-iodine are on the order of  $10^3$  mL/g, depending on sediment type and microbial biomass richness in the sediment (c.f., Schwehr et al., 2009). Microorganisms can strongly influence I sorption by affecting I speciation, including the formation of org-

ano-iodine (Schwehr et al., 2009). The disparate sorption behavior between  $I^-$  and  $IO_3^-$  was observed in the column experiments in all 12 soils and sediments examined in this work, which consistently showed greater sorption of  $IO_3^-$  than of  $I^-$ . This is consistent with previous studies that have shown that  $IO_3^-$  interacts more strongly than  $I^-$  with both clays and organic matter (c.f., Hu et al., 2009). Even in Hanford sediment, which has a very low anion exchange capacity, noticeable sorption of  $IO_3^-$  took place (Table 2).

Ideally, to evaluate sorption one would use a concentration that is comparable to real-world situations, i.e.  $10^{-8}$  M for stable I in the hydrosphere (Fuge and Johnson, 1986) and a few orders-of-magnitude lower for anthropogenic  $^{129}I$ , as observed at SRS (Kaplan et al., 2011; Li et al., 2011). However, for trace concentrations of  $I^-$ , usually introduced as radioactive  $^{125}I$  in laboratory experiments, in a system open to air, the  $I^-$  can be readily oxidized to  $IO_3^-$ , which complicates data interpretation, considering the different sorption behavior of  $I^-$  and  $IO_3^-$ . There are limited reports of sorption at low concentrations comparable to real-world situations. However, Kaplan et al. (2000) reported  $I^-$  sorption at a much lower ( $10^{-12}$  M) concentration for three subsurface sediments from the Hanford Site. A study by Schwehr et al. (2009) of SRS sediment using  $^{125}I^-$  tracer and stable  $I^-$  addition, found that the interactions between aqueous  $I^-$  and sediments were highly dependent on  $I^-$  concentrations added to sediment suspensions, contact time with the sediment, and organic C content, which resulted in an empirical  $K_d$  that was an inverse power function of the added  $I^-$  concentration.

In this work, the  $K_d$  values were measured for  $5 \times 10^{-13}$  M  $^{125}I^-$  in 12 geologic samples. For most of the samples,  $K_d$  values are similar to the values obtained from batch and column experiments using a high concentration of  $I^-$  (Table 2). The exception is observed for two surface soil samples (Owngate and Wisconsin soils, both with high organic matter) which have much higher  $K_d$  values at the lower ( $5 \times 10^{-13}$  M)  $I^-$  concentration. Organic matter, or associated high microbial activity, in these samples is the likely cause of the strong sorption at low initial  $I^-$  concentration. A linear correlation is evident between the  $K_d$  values for  $5 \times 10^{-13}$  M  $^{125}I^-$  and sample organic matter, with a regression line of  $K_d = 9.96 \times OM - 1.39$  ( $R^2 = 0.915$ ,  $N = 12$ ) (Fig. 1). There are two outliers – the ORNL sediment and the SRS surface soil, which have the lowest pH values of all samples except for the SRS subsoil. The regression line, not including these two samples, is  $K_d = 11.4 \times OM - 1.04$  ( $R^2 = 0.998$ ,  $N = 10$ ). Overall, this result highlights the close relationship (even for the Wisconsin soil with organic matter as high as 8.7%) between the organic matter and sorption of low-level  $I^-$ , consistent with the work of Schwehr et al. (2009).

Sorption of  $CH_3I$  onto soils is reported to be insignificant, with a small, but nonzero  $K_d$  value. Gan and Yates (1996) reported  $K_d$  values of 0.08 mL/g for Greenfield sandy loam, 0.12 mL/g for Corsetas

**Table 2**  
Measured sorption distribution coefficient ( $K_d$ , mL/g) for iodine species in different geologic samples.

| Sample           | Batch-sorption exp. (average $\pm$ standard deviation, $N = 3$ ) |                   |                           | Column transport exp. |                      |                           |
|------------------|------------------------------------------------------------------|-------------------|---------------------------|-----------------------|----------------------|---------------------------|
|                  | $5 \times 10^{-13}$ M $^{125}I^-$                                | $10^{-5}$ M $I^-$ | $10^{-7}$ M methyl iodide | $10^{-4}$ M $I^-$     | $10^{-4}$ M $IO_3^-$ | $10^{-5}$ M 4-iodoaniline |
| SRS aquifer      | $0.060 \pm 0.020$                                                | $-0.01 \pm 0.12$  | $0.80 \pm 0.11$           | 0.074                 | 1.64                 | -0.016                    |
| LLNL alluvium    | $0.036 \pm 0.020$                                                | $-0.34 \pm 0.09$  | $0.99 \pm 0.15$           | 0.049                 | 0.880                | 0.18                      |
| INL basalt       | $0.20 \pm 0.11$                                                  | $-0.09 \pm 0.04$  | $1.04 \pm 0.24$           | 0.011                 | 0.516                | 0.089                     |
| Hanford sediment | $0.097 \pm 0.015$                                                | $-0.11 \pm 0.36$  | $1.03 \pm 0.07$           | 0.012                 | 0.100                | 1.74                      |
| NTS alluvium     | $0.011 \pm 0.010$                                                | $-0.16 \pm 0.02$  | $0.86 \pm 0.21$           | 0.007                 | 0.139                | 0.324                     |
| SRS subsoil      | $1.01 \pm 0.086$                                                 | $1.46 \pm 0.20$   | $0.79 \pm 0.09$           | 1.61                  | 11.7                 | -0.011                    |
| ORNL sediment    | $12.0 \pm 0.93$                                                  | $9.99 \pm 0.44$   | $1.14 \pm 0.27$           | >34                   | >34                  | >216                      |
| NTS tuff         | $0.065 \pm 0.03$                                                 | $-0.03 \pm 0.08$  | $1.03 \pm 0.33$           | 0.068                 | 0.209                | NM                        |
| LLNL aquifer     | $0.17 \pm 0.031$                                                 | $-0.30 \pm 0.03$  | $0.95 \pm 0.16$           | 0.020                 | 13.0                 | NM                        |
| Owngate soil     | $20.8 \pm 1.60$                                                  | $0.41 \pm 0.12$   | $1.29 \pm 0.08$           | 0.019                 | 0.166                | NM                        |
| SRS surface soil | $3.78 \pm 0.17$                                                  | $2.20 \pm 0.29$   | $1.30 \pm 0.36$           | -0.003                | 0.400                | 7.55                      |
| Wisconsin soil   | $99.8 \pm 3.83$                                                  | $0.58 \pm 0.10$   | $1.62 \pm 0.23$           | 0.012                 | 0.619                | >31                       |

NM: not measured.

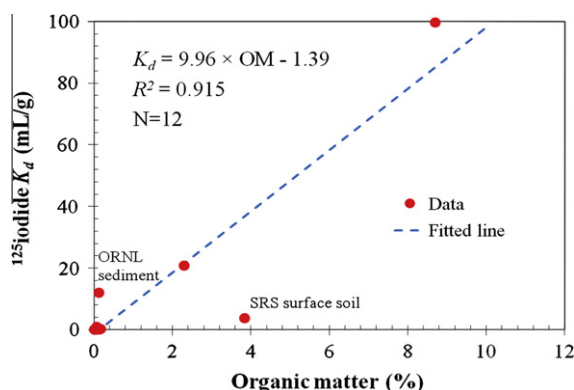


Fig. 1. Relationship between organic matter and sorption of  $^{125}\text{I}$ .

loamy sand, 0.13 mL/g for Linne clay loam, and 0.46 mL/g for potting mix (with a very high organic content of 9.6%). The results also show modest sorption in 12 geologic samples, with  $K_d$  values of about 1 mL/g for an applied  $\text{CH}_3\text{I}$  concentration of  $10^{-7}$  M (Table 2).

### 3.2. Degradation of methyl iodide

Methyl iodide can undergo degradation in sediments and soils. In moist soil,  $\text{CH}_3\text{I}$  was about twice as persistent as  $\text{CH}_3\text{Br}$ , and the persistence has been found to decrease with increasing soil organic content (Gan and Yates, 1996). Chemical reactions, likely nucleophilic substitutions on soil organic matter, were identified as the predominant degradation pathway for  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$ . In water,  $\text{CH}_3\text{I}$  degraded to  $\text{I}_2$  and  $\text{I}^-$  under 254-nm UV irradiation and dissipated rapidly ( $t_{1/2} = 26$  h) through volatilization and photohydrolysis under outdoor conditions (Gan and Yates, 1996).

Degradation of  $\text{CH}_3\text{I}$  in 6 samples was observed over a period of 56 days; examples are shown for SRS surface and sub-soils (Fig. 2). The degradation can be described by a first-order kinetic process; the results are presented in Table 3. The short phase lag was observed in several samples (including SRS subsoil in Fig. 2b) and may be attributable to microbial adaptation to  $\text{CH}_3\text{I}$  in the samples. A short lag phase is often observed for chemical degradation in soils, and it is related to the microbial reaction with the anthropogenic substance (e.g., Wiggins et al., 1987). Through mutation, gene expression activation and simple increases in the population of degraders, the degradation increased rapidly after the short acclimation period. In the calculation of half-lives, this period was excluded.

The half-life of  $\text{CH}_3\text{I}$  in two high organic matter soils (SRS surface soil and Wisconsin soil) is as short as 1 day, while the half-life is about 36 days in the NTS alluvium sample which has an organic matter content of only 0.06%. The half-life values are correlated with the organic matter content of tested samples, giving a regression line of  $t_{1/2} = 0.084 \times \text{OM} + 0.088$  ( $R^2 = 0.898$ ,  $N = 6$ ). For 3 vertical samples collected at the Savannah River site, the degradation half-lives of  $\text{CH}_3\text{I}$  are 1, 15 and 21 days for the surface soil, subsoil and aquifer samples, respectively. Considering the low sorption (or high mobility) of  $\text{CH}_3\text{I}$ , it will persist in deep sediments if it migrates quickly through the surface soil with minimal degradation as would be the case for low organic-matter soils. Disparate degradation and sorption behavior of three different I species, in three types of samples in a vertical cross-section from the Savannah River Site highlights the need to consider sediment properties when predicting the geochemical behavior and transport of I. In agricultural areas where  $\text{CH}_3\text{I}$  is proposed as a replacement for  $\text{CH}_3\text{Br}$ , soils are likely to be high in organic content, with a corresponding high rate of  $\text{CH}_3\text{I}$  degradation.

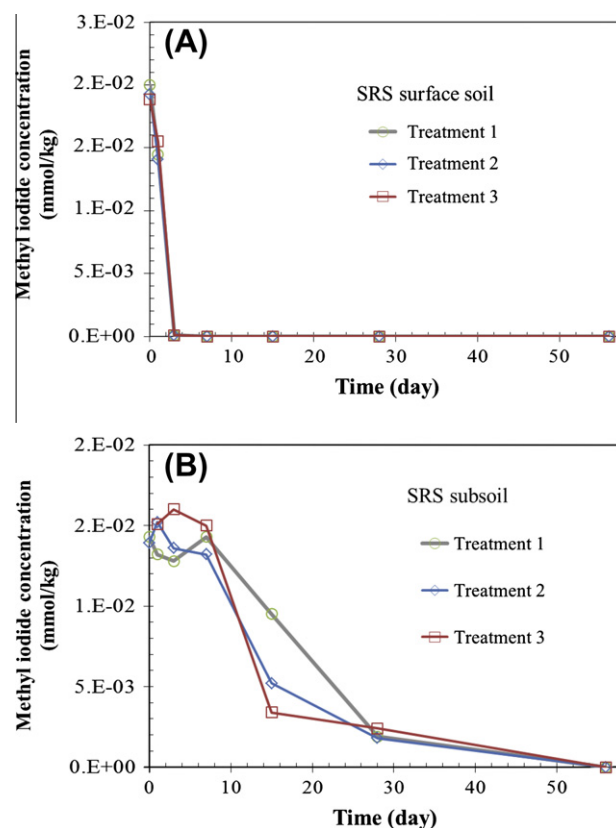


Fig. 2. Degradation kinetics of methyl iodide in (A) SRS surface soil, and (B) SRS subsoil. Triplicate degradation tests are presented.

Table 3

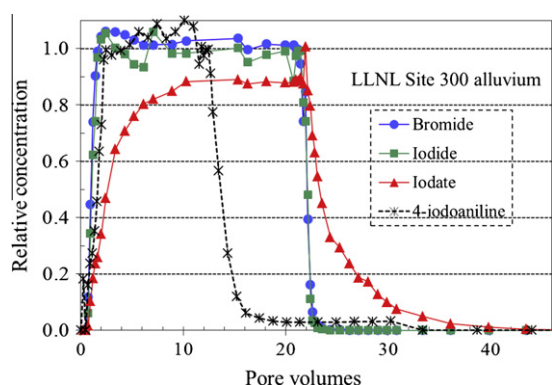
First-order rate constant  $k$  (1/day), half-life (day), and goodness of fit for the degradation of methyl iodide at an initial concentration of 0.01 mmol/kg.

| Sample           | $k$    | $t_{1/2}$ | $R^2$ |
|------------------|--------|-----------|-------|
| NTS alluvium     | 0.0193 | 35.9      | 0.91  |
| ORNL sediment    | 0.1151 | 6.02      | 0.72  |
| SRS surface soil | 0.6931 | 1.0       | 0.99  |
| SRS subsoil      | 0.0553 | 12.5      | 0.89  |
| SRS aquifer      | 0.0332 | 20.9      | 0.85  |
| Wisconsin        | 0.6931 | 1.0       | 0.99  |

### 3.3. Transport of iodine species

Column transport experiments were performed to evaluate the transport of  $\text{I}^-$ ,  $\text{IO}_3^-$  and 4-iodoaniline species in two of the geologic media. Representative breakthrough curves for I species, as well as nonsorbing  $\text{Br}^-$ , in the LLNL alluvium sample are shown in Fig. 3. The  $K_d$  values obtained from the breakthrough curve analyses are shown in Table 2, with sorption of  $\text{IO}_3^-$  greater than that of  $\text{I}^-$  and 4-iodoaniline (due to the low organic matter of this alluvium sample). Compared to  $\text{I}^-$  and  $\text{IO}_3^-$ , studies on transport of organoiodine compounds are much scarcer, given the challenges associated with the analysis of various organoiodine compounds, many of which are volatile. The authors used 4-iodoaniline as a representative nonvolatile organoiodine species, and found that the transport of 4-iodoaniline is different from that of the inorganic forms,  $\text{I}^-$  and  $\text{IO}_3^-$ , and is likely related to the amount of organic matter in the sample. This observation is consistent with the hydrophobicity of organoiodine and its affinity for hydrophobic organic matter. For example, in the Wisconsin soil with a high organic matter content of 8.7%, the effluent mass recovery of 4-iodoaniline is very low





**Fig. 3.** Breakthrough curves of bromide and iodine species in a column homogeneously packed with LLNL site 300 alluvium. The input pulse for bromide, iodide, and iodate is 20.3 column pore volumes and 11.4 pore volumes for 4-iodoaniline.

(44%), with the remainder of the applied I probably irreversibly retained in the organic matter (Hu et al., 2009). The very low recovery (6%) of 4-iodoaniline in ORNL sediment is not readily explained, as this sample has only a moderate concentration of organic matter.

In SRS surface soil with 2.33% organic matter, transport of 4-iodoaniline is retarded by more than 20 times compared to  $I^-$ , with a  $K_d$  value of 7.5 mL/g. In contrast, 4-iodoaniline migrates without retardation, similar to  $Br^-$  and  $^3H$  in the SRS subsoil, while  $IO_3^-$  and  $I^-$  are significantly retarded because of the strong anion exchange capacity of this sample. This is also true for the SRS aquifer material, though the magnitude of sorption for  $IO_3^-$  and  $I^-$  is less than for SRS subsoil. Such disparate transport behavior for different I species should be considered when studying the behavior of I because inorganic I could be fixed onto macromolecular humic substances (Tikhomirov et al., 1980; Rädlinger and Heumann, 2000; Steinberg et al., 2008b), and this fixation changes the physicochemical characteristics and associated behavior of I.

#### 4. Conclusions

Redox-sensitive I occurs as multiple species (inorganic and organic) in the environment, each with varying volatile, hydrophilic and biophilic characteristics. This work examines the sorption, transport, and degradation of several I species in 12 geologic media. In particular, the experiments address sorption and degradation of  $CH_3I$  in soils and sediments, which has not been extensively documented in prior studies. Different I species exhibit very different sorption and transport behavior in subsurface media, making prediction of I transport in field settings challenging. Sorption of  $IO_3^-$  is consistently greater than that of  $I^-$ , while transport of organo-iodine is quite limited because of its strong interaction with organic matter. Methyl iodide is weakly sorbed onto the 12 geologic samples tested, but its degradation varies greatly as a function of organic matter in the samples, from a degradation half-life of 35.9 days in a sediment sample with <0.1% organic matter to 1 day in a soil with >2% organic matter. Consequently, anthropogenic radioactive I will have different residence times as the different species migrate through the various sediment types, and this should be considered when modeling transport at the field scale and in attempting to understand the processes affecting biogeochemical cycling of I in the environment.

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