1 **Radioiodine sorption/desorption and speciation transformation by subsurface sediments**
2 **from the Hanford Site**

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4 Chen Xu^{a*}, Daniel I. Kaplan^b, Saijin Zhang^a, Matthew Athon^a, Yi-Fang Ho^a, Hsiu-Ping Li^a, Chris
5 M. Yeager^c, Kathleen A. Schwehr^a, Russell Grandbois^a, Dawn Wellman^d, Peter H. Santschi^a

6
7 ^aLaboratory for Environmental and Oceanographic Research, Department of Marine Sciences,
8 Texas A&M University, Building 3029, Galveston, Texas 77551

9 ^b Savannah River National Laboratory, Aiken, SC 29808

10 ^c 29808 Los Alamos National Laboratory, Los Alamos, NM 87545

11 ^d Pacific Northwest National Laboratory, Richland, WA 99354

12 *Corresponding author: xuchen66@tamu.edu (C. Xu);

13 Tel: +1-409-740-4530, Fax: +1-409-740-4787

ABSTRACT (443 words)

During the last few decades, considerable research efforts have been extended to identify more effective remediation treatment technologies to lower the ^{129}I concentrations to below federal drinking water standards at the Hanford Site (Richland, USA). Few studies have taken iodate into consideration, though recently iodate, instead of iodide, was identified as the major species in the groundwater of 200-West Area within the Hanford Site. The objective of this study was thus to quantify and understand aqueous radioiodine species transformations and uptake by three sediments collected from the semi-arid, carbonate-rich environment of the Hanford subsurface. All three sediments reduced iodate (IO_3^-) to iodide (I^-), but the loamy-sand sediment reduced more IO_3^- (100% reduced within 7 days) than the two sand-textured sediments (~20% reduced after 28 days). No dissolved organo-iodine species were observed in any of these studies. Iodate uptake K_d values ($[\text{I}_{\text{solid}}]/[\text{I}_{\text{aq}}]$; 0.8 to 7.6 L/kg) were consistently and appreciably greater than iodide K_d values (0 to 5.6 L/kg). Furthermore, desorption K_d values (11.9 to 29.8 L/kg) for both iodate and iodide were consistently and appreciably greater than uptake K_d values (0 to 7.6 L/kg). Major fractions of iodine associated with the sediments were unexpectedly strongly bound, such that only 0.4 to 6.6 % of the total sedimentary iodine could be exchanged from the surface with KCl solution, and 0 to 1.2% was associated with Fe or Mn oxides (weak $\text{NH}_2\text{HCl}/\text{HNO}_3$ extractable fraction). Iodine incorporated into calcite accounted for 2.9 to 39.4% of the total sedimentary iodine, whereas organic carbon (OC) is likely responsible for the residual iodine (57.1 to 90.6%) in sediments. The OC, even at low concentrations, appeared to be controlling iodine binding to the sediments, as it was found that the greater the OC concentrations in the sediments, the greater the values of uptake K_d , desorption K_d , and the greater residual iodine concentrations (non-exchangeable, non-calcite-incorporated and non-Mn, Fe-oxide associated). This finding is of particular interest because it suggests that even very low OC concentrations, <0.2%, may have an impact on iodine geochemistry. The findings that these sediments can readily reduce IO_3^- and that IO_3^- sorbs to a greater extent than I^- , sheds light into earlier unexplained Hanford field data that demonstrated increases in groundwater $^{127}\text{I}^- / ^{127}\text{IO}_3^-$ ratios and a decrease groundwater $^{129}\text{IO}_3^-$ concentrations along a transect away from the point sources, where iodine was primarily introduced as IO_3^- . While a majority of the radioiodine does not bind to these alkaline sediments, there is likely a second smaller iodine fraction in the Hanford subsurface that is strongly bound, presumably to the sediment OC (and carbonate) phases. This

second fraction may have an impact on establishing remediation goals and performance assessment calculations.

1. Introduction

The Hanford Site in southeastern Washington State contains the largest inventory of nuclear waste stored in the Western Hemisphere (Gephart, 2010). This highly radioactive and complex waste was generated between the 1940s and the early 1990s as part of the nation's defense activities, including production and irradiation of fuel assemblies, chemical separation of nuclear materials, and storage of waste materials (Fritz and Patton, 2006). During past operations at the Hanford Site, waste water was discharged directly to the ground, resulting in the present-day formation of several plumes of radionuclides, including ^{129}I , ^3H , ^{99}Tc , and ^{90}Sr . ^{129}I is a key risk driver at several U.S. Department of Energy sites, such as the Hanford and Savannah River Sites (SRS). Its risk stems from its long half-life (16 M years), high bioaccumulation factor (90% of all the body's iodine concentrated in the thyroid), high inventory (e.g., $\sim 1.6 \times 10^{12}$ Bq ^{129}I at the Hanford Site, which is the largest inventory in the US), and high perceived mobility. Currently, ^{129}I groundwater plumes with concentrations exceeding drinking water standards encompass >50 km² in the 200-West Areas of the Hanford Site (Duncan et al., 2008). Although groundwater on the Hanford Site is not a source for public drinking water, there is still concern that ^{129}I contaminated groundwater may flow into the Columbia River, which is just 5 km from the leading edge of the ^{129}I plume (Hartman et al., 2003).

Major iodine species in aquatic systems include iodide (I^-), iodate (IO_3^-), and organo-I. Based on thermodynamic calculations using Hanford Site groundwater pH and redox (Kaplan et al. 2014), it was previously assumed that I^- was the dominant species, thus, almost all studies to date have focused on I^- uptake to Hanford Site subsurface sediments (Kaplan and Serne, 2000; Kaplan et al., 2000; Um et al., 2004). In addition, it has been traditionally assumed that very low organic carbon (OC) concentration in subsurface sediment (<0.2 wt-%), including those at the Hanford Site, have little influence on iodine speciation and sorption (Serne, 2007). Only a few studies (e.g., Hu et al., 2005) have investigated the potential migration of iodine species other than I^- through the Hanford Site sediments. However, due to detection limitations, experimental iodine concentrations (10^{-4} – 10^{-5} M) that were used were orders of magnitude higher than environmental levels (10^{-7} M – 10^{-8} M for ^{127}I , 10^{-9} – 10^{-10} M for ^{129}I). Non-linear sorption isotherms were observed for sediments containing high natural organic matter (NOM) contents, when amended iodine concentrations exceeded 10^{-5} M, (Emerson et al., 2013; Schwehr et al.,

2009). Therefore, one has to be cautious when using elevated concentrations in the laboratory to interpret iodine uptake behavior at environmental levels due to limited binding sites available in the sediment (Xu et al., 2013; Xu et al., 2011a; Xu et al., 2012).

In contrast to this iodide-centric paradigm, $^{127}\text{IO}_3^-$ and $^{129}\text{IO}_3^-$ were recently identified as the dominant stable and radioiodine species (45-84%) in groundwater collected from 200-West Area of the Hanford Site, followed by organo-I (15-40%) and minor amounts of I^- (Zhang et al., 2013). These findings bring new challenges to the determination of credible geochemical parameters, including K_d values, for use in understanding and predicting the transport and fate of ^{129}I through subsurface sediments of the Hanford Site. Previous K_d values of ^{129}I were primarily based on the assumption that I^- was the only species present in the Hanford Site's alkaline and carbonate-rich groundwater system. Therefore, the objectives of this study were to 1) identify and quantify the key processes controlling I^- and IO_3^- uptake to three representative Hanford Site subsurface sediments collected from the vadose, upper saturated and deeper saturated zones; and 2) assess groundwater iodine speciation transformations in the presence of sediments maintained under different experimental conditions (open-air vs. air-sealed). An air-sealed with limited headspace condition was employed often in other iodine-sediment interaction studies (e.g., Kaplan et al., 2000; Um et al., 2004) to mimic the Hanford Site underground anaerobic conditions. In this study we also applied an open-air and agitated condition, as an effort to replenish O_2 and mimic the possible aerobic conditions in Hanford groundwater-sediment systems (e.g., groundwater recharge with aerobic recycled water, mixing with river water, infiltrating banks and riverbed sediments, etc.). Particular attention was directed at evaluating the indigenous stable iodine speciation in the sediment and groundwater, quantifying groundwater iodine speciation transformations once it came into contact with the three Hanford sediments, and evaluating the extent of iodine sediment uptake, iodate reduction, iodide oxidation, and the formation of organo-iodine species. In-depth studies were conducted with the sediments that varied greatly in regard to texture, carbonate and OC concentrations, but had similar fine-fraction mineralogy and pH.

2. Materials and methods

2.1. Groundwater and sediment sampling

Groundwater and subsurface sediments were collected from the 200-West Area on the Hanford Site in eastern Washington, adjacent or within a ^{129}I plume. Between the 1940s and early 1990s, liquid waste, primarily generated during plutonium separation and uranium recovery operations, was disposed directly to the ground (Gephart, 2010). The contaminants of health concern in the plume emanating from these disposal cribs and trenches include ^{14}C , carbon-tetrachloride, uranium, nitrate, chromium, ^{129}I , ^{99}Tc , and ^3H (DOE, 2012).

Groundwater was collected from well 299-W11-88, which is located about 1.3 km from the primarily contaminant source, disposal crib 216-T-26 (which received 11,000,000 L of liquid waste containing about 59 Bq/L ^{129}I) (Corbin et al., 2005) (Table 1). This was the same groundwater studied in Zhang et al. (2013). Groundwater was recovered with a “Mega Typhoon” pump (Proactive Pumps, Trenton, New Jersey). The groundwater was stored frozen at $-20\text{ }^{\circ}\text{C}$. Sediment samples were collected from two boreholes that had been archived during the 1990s: wells 299-W15-226 and 299-W15-765. The sediment samples were from three stratigraphic layers: vadose zone (sediment H1; 30 – 41 m depth, Cold Creek Formation), upper saturated zone (sediment H2; 102-113 m depth, Ringold Formation Middle unit), and deeper saturated zone (sediment H3; 136 – 142 m depth, a transition zone from Ringold Formation Middle unit to Ringold Lower Mud) (Table 2).

2.2. Groundwater and sediment characterization

The three sediment samples were characterized using standard methods (Sparks, 1996). Oven-dried ($60\text{ }^{\circ}\text{C}$) sediment was homogenized and the $<2\text{-mm}$ sieved fraction was used for subsequent characterization (Mudroch and Azcue, 1995). E_h and pH were measured on 1:1 sediment:water slurries using an OAKTON 510 pH/mV/ $^{\circ}\text{C}$ meter. Sediment texture was determined by a combination of sieves (for sand and silt fractions) and the hydrometer method (for the $<2\text{ }\mu\text{m}$ clay fraction). Surface area was determined by the BET method using N_2 gas. Total carbon contents were measured using a Perkin Elmer CHNS 2400 analyzer and organic carbon content was determined after a direct acidification step (Ryba and Burgess, 2002), both of which had errors well within 5% with triplicate samples. Inorganic carbon was then calculated as the difference between total carbon and organic carbon contents; the propagated error associated

with this technique was usually less than <5% for triplicates. The mineralogy of the <53 μm fraction was determined by X-ray diffraction (XRD; (Moore and Reynolds, 1989). XRD was conducted on Mg-, K-, and ethylene glycol-saturated samples. The K-saturated samples were analyzed after air-drying and again after heating for 1 hr at 550 °C. Scans were processed with JADE[®] XRD pattern processing software. Semi quantification of mineral phases in the sediment samples were determined by the whole pattern fitting technique provided by JADE[®] XRD pattern processing software. Cation exchange capacity was measured by the Mehlich 1 method, which extracts 5 g sediment with 20 mL of a dilute hydrochloric acid/sulfuric acid solution for 5 minutes. Desorbed cations were measured by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) (Sparks, 1996). Metals were extracted by dithionite citrate buffer, which provides a measure of metals existing as coatings on the mineral surface (Sparks, 1996).

The groundwater sample was analyzed for dissolved organic carbon (DOC) with a Shimadzu 5000 Analyzer and for pH and redox potentials (ORP) using an OAKTON 510 pH/mV/°C meter. Groundwater cations were measured using standard ICP-AES methods and groundwater anions by standard ion chromatography methods.

2.3. Iodine analyses

2.3.1. Stable iodine (¹²⁷I) speciation analysis by GC-MS

Determination of aqueous I^- and IO_3^- followed the procedure described by Zhang et al. (2010). Briefly, each sample was sequentially analyzed three times to determine I^- , total inorganic iodine (I^- and IO_3^-), and total iodine (I^- , IO_3^- , and organo-I). For the I^- analysis, I^- was oxidized by 2-iodosobenzoate to I_2 , and then N,N-dimethylaniline was added to bind the I_2 to form 4-iodo-dimethylaniline. The resulting derivative was extracted by cyclohexane and measured using a Finnigan Trace GC and Polaris Q EI-MS from Thermo Scientific (Austin, TX). Using a second subsample, total inorganic iodine was measured by converting IO_3^- to I^- by adding sodium meta-bisulfite. The solution I^- was measured using the same derivatization method used to measure I^- concentrations in the first measurement. In the third subsample, total iodine concentrations were determined after the aqueous solution was catalytically combusted using the method described by Zhang et al. (2010). Again, the resulting I^- was detected following

the derivatization method used for the I^- and total inorganic iodine subsamples. This method has a detection limit of $0.04 \mu\text{g/L } ^{127}\text{I}^-$, $0.14 \mu\text{g/L } ^{127}\text{IO}_3^-$, and $0.35 \mu\text{g/L organo-}^{127}\text{I}$.

2.3.2. Radioiodine speciation analysis by liquid scintillation counting

Because ^{125}I has a high specific activity ($6.3 \times 10^{14} \text{ Bq/g}$), it is very difficult for the mass spectrometer to detect it without using high levels of radioactivity (when the total added activity is only $1.2 \times 10^6 \text{ Bq}$ (section 2.4)). In order to track the distribution and transformation of the added tracer $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$, the same derivatization method (Section 2.3.1) was thus applied but the cyclohexane extract was measured by a Beckman Coulter LS6500 Liquid Scintillation Counter (LSC; Indianapolis, IN) (Xu et al., 2011a). The significant advantage of this method is that the total ^{125}I concentration can be counted directly with the LSC and thus the time-consuming combustion step (i.e., the third analyses in the stable iodine method) is not necessary for calculating organo- ^{125}I .

^{129}I speciation was conducted on the groundwater sample collected from the 200-West Area of the Hanford Site. The sample speciation protocol was used as described above in Section 2.3.1. The method had detection limits of $0.01 \mu\text{g/L}$ (i.e., $0.07 \text{ Bq } ^{129}\text{I/L}$) for $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$ and $0.03 \mu\text{g/L}$ (i.e., $0.19 \text{ Bq } ^{129}\text{I/L}$) for organo- ^{129}I .

2.3.3. Sediment exchangeable, carbonate-bound, Mn, Fe-oxide associated, residual and total iodine determination

A sequential extraction was adopted and modified from Hu et al. (2005), Kaplan et al. (2000), Yamaguchi et al. (2010), Miller et al. (1986) and Tessier et al. (1979) to obtain naturally-occurring ^{127}I in fractions assigned as 1) exchangeable, extracted with 0.005 N KCl and then 0.1 N KCl solution, 2) carbonate, extracted with $0.44 \text{ N acetic acid}$ in 0.1 N KCl , 3) Mn-, Fe-oxide associated, extracted first with $0.01 \text{ N NH}_2\text{HCl}$ in 0.1 N HNO_3 at room temperature and then with $0.04 \text{ N NH}_2\text{HCl}$ in 0.1 N HNO_3 at 96°C , and 4) residual fractions in the sediments (Fig. 1).

After each extraction step, the slurry was centrifuged at low-speed ($\sim 3200 \times g$) to separate the aqueous phase with the extracted iodine from the sediment and the supernatant was filtered through a sterile disposable vacuum filter ($0.45 \mu\text{m}$) (Corning, USA) to ensure the removal of fine particles. Total iodine content of the initial sediment (without any extraction) was measured by catalytically combusting and converting all the iodine in the sediment into inorganic iodine

species that were then detected by a GC-MS derivatization method (Zhang et al., 2010). While I^- and IO_3^- in each extracted fraction was measured by the GC-MS derivatization method described above (section 2.3.1), total iodine in each individual extractant was measured by an inductively coupled plasma mass spectrometer (ICP-MS) Thermo X series II, equipped with a Xt cone and SC4 DX autosample with PC³ spray chamber kit. Thus, residual iodine was calculated based on a mass balance by subtracting iodine in the three extraction from the total sedimentary iodine.

2.4. I^- and IO_3^- uptake/transformation in sediment suspension experiments

Ten g homogenized, sieved (< 2-mm) and dry sediment was mixed with groundwater (40 mL) to create a groundwater:sediment ratio of 4:1. All treatments were performed in triplicates and permitted to equilibrate on an orbital shaker, in the dark, and at room temperature (20 ± 2 °C). A 10 μ L aliquot of carrier free $Na^{125}I$ or $Na^{125}IO_3^-$ (concentration of stock solution: 1.5×10^{-8} M or 1.2×10^9 Bq/L), was added to each treatment. Though no additional buffer was added, pH drifts during the experiments were self-maintained within 0.5 of their original pH level.

For each treatment, particle-water distribution coefficients or partitioning coefficients were determined (uptake K_d (L/kg), Eq.1):

$$K_d = \frac{A_{>0.45\mu m}}{A_{<0.45\mu m} \times C}, \quad (1)$$

where $A_{>0.45\mu m}$ (Bq) is the total ^{125}I activity in the $>0.45 \mu m$ particulate phase, $A_{<0.45\mu m}$ is the total ^{125}I activity in the dissolved phase ($< 0.45 \mu m$) and C is the sediment concentration (0.25 g/mL). $A_{<0.45\mu m}$ was determined by liquid scintillation analysis, whereas $A_{>0.45\mu m}$ was calculated by subtracting $A_{<0.45\mu m}$ from the total added activity. ^{125}I associated with colloids in the $< 0.45 \mu m$ fraction was negligible (see discussion in section 3.2). All values were decay-corrected. Note that the uptake K_d shown in Eq.1 represents the K_d of a suite of iodine species, which is quite different from a species specific- K_d , that is a I^- or IO_3^- K_d value. While we know the iodine species added to the experiments, we also know that they commonly undergo reduction, oxidation, and iodination transformations once they come in contact with sediments (Schwehr et al., 2009; Xu et al., 2011a).

2.4.1. Air-sealed Uptake Study

Uptake and species transformations of inorganic iodine were monitored for samples that were in the presence of the three sediments and in sediment-free groundwater samples. The three sediment samples were amended with either: 1) a final $^{125}\text{I}^-$ activity of 3×10^7 Bq/L (3.8×10^{-10} M), or 2) a final $^{125}\text{IO}_3^-$ activity of 3×10^7 Bq/L (3.8×10^{-10} M), which is close to the average chemical concentration of ^{129}I (8×10^{-10} M) in the Hanford groundwater (Zhang et al., 2013). These sediment slurries in 50 mL polypropylene centrifuge tubes, contained minimal headspace and were placed on an orbital shaker at 120 rpm for 3, 7, 14, 21, and 28 days. Sediment-free control samples amended with $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ were also included in the experiment and sampled in triplicates at each contact time interval. These sediment-free controls provided information about sediment-independent iodine species transformation, loss of the added $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ tracer to the atmosphere, and $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ tracer sorption to the reactions vessels during the experiment (discussed in more detail below). Usually the loss of aqueous $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ by sorption to filters and reaction and separation vessels was $< 5\%$. This minor loss has been taken into consideration for uptake K_d or desorption K_d' calculation, and was not regarded as either particulate ($> 0.45 \mu\text{m}$) or dissolved ($< 0.45 \mu\text{m}$) fractions. Phase separation was achieved by low-speed ($\sim 3200 \times g$) centrifugation and supernatant filtration, using a sterile disposable vacuum filter ($0.45 \mu\text{m}$) (Corning, USA). The resulting filtrate was further subjected to ultrafiltration through an Amicon Ultra-15 centrifugal unit with a cut-off of 3 kDa, calibrated previously using polystyrene sulfonate standards (Polysciences, Inc.; Warrington, PA) with molecular weights of 1.6, 4.3 and 8 kDa (Xu et al., 2011b).

2.4.2. Open-air Uptake Study

The intent of this treatment was to create conditions that were moderately more aerobic than those in the Air-sealed Uptake K_d Experiment described in Section 2.4.1. Greater contact with the ambient air was promoted in these experiments by adding holes to the caps of the reaction vessels. Additionally, instead of using 50-mL centrifuge tubes, 500-mL Teflon beakers were used as reaction vessels to hold the 10g sediment/40mL groundwater suspensions. These larger reaction vessels resulted in a greater air-suspension interface (the sediment suspension was < 1 cm deep in the 500mL beaker). The beakers were placed for 28 days on an orbital shaker at 120 rpm. The treatments were sampled and processed in a similar manner as for the Air-sealed

Uptake K_d Experiment (Section 2.4.1) to determine uptake of $^{125}\text{I}^-$ and $^{125}\text{IO}_3^-$ by the sediment, as well as the speciation in the aqueous phase (Section 2.3).

2.4.3 Desorption Study

After the 28-day contact period of the Air-sealed Uptake Study, the radioiodine-laden sediments were used for the Desorption Study. The moist sediments (10 g dry weight) were re-suspended in 40 mL Hanford groundwater amended with 0.1 M KCl to assess sorption reversibility (Kaplan et al., 2000; Yamaguchi et al., 2010). Elevated concentrations of Cl^- were selected as an extraction solution because it was anticipated that it would readily exchange with I^- and IO_3^- . KCl solution was also added to the sediment-free control samples (in triplicates) to monitor the release of radioiodide or radioiodate from the sample container walls and provide information needed for mass balance calculations. It is noteworthy that the Hanford groundwater also included trace amounts of ^{127}I (0.5 $\mu\text{g/L}$) and fairly high $^{127}\text{IO}_3^-$ (22.7 $\mu\text{g/L}$) concentrations that, in addition to the amended KCl, promoted radioiodine desorption from the sediments (Zhang et al., 2013). The desorption experiment was carried out for two weeks under the conditions described for the Air-sealed Experiment, after which the desorption K_d' values (L/kg) were determined, using equation 2:

$$K_d' = \frac{A'_{>0.45\mu\text{m}}}{A'_{<0.45\mu\text{m}} \times C}, \quad (2)$$

where $A'_{>0.45\mu\text{m}}$ (Bq) is the residual ^{125}I activity in the particulate phase ($>0.45\mu\text{m}$), $A'_{<0.45\mu\text{m}}$ is the ^{125}I activity in the desorbing solution ($<0.45\mu\text{m}$), and C is the sediment concentration (0.25 kg/L).

3. Results and discussion

3.1 Speciation of naturally-occurring iodine in groundwater and sediment

One of the key objectives of this study was to provide speciation information of the naturally-occurring iodine on the solid phase. This is important because it provides insight into

the long-term behavior of ^{129}I in the system that may not be obvious from a short-term laboratory study. Also of interest was to study the naturally-occurring iodine at ambient concentrations, i.e., at $\mu\text{g/L}$ for groundwater and $\mu\text{g/g}$ for sediments. It has been shown repeatedly that when iodine concentrations are elevated to mg/L or percent levels to ease analytical detection, that the iodine speciation changes significantly, especially in regard to underestimating the percentage of organo-I present and in maintaining proper OC and iodine molar ratio at ambient levels (Schwehr et al., 2009).

The chemistry of the groundwater recovered from the ^{129}I plume in the 200-West Area suggests that it was moderately impacted by site operations (Table 1) (DOE, 2012). While most parameter levels were about what would be expected for non-impacted groundwater, such as pH, turbidity, and specific conductance, other parameters, notably nitrate and ^{129}I concentrations, were well above background levels (DOE, 2012). The high nitrate concentrations resulted from site operations involving the direct ground disposal of nitric acid into unlined trenches and cribs (Gephart, 2010). Iodine-129 concentrations were 0.15 Bq/L (4.1 pCi/L), which is above the regulatory maximum contaminant level (MCL) of 0.037 Bq/L (1 pCi/L) (Table 1). Stable iodine, ^{127}I , concentration in this groundwater sample was $9.33\text{ }\mu\text{g/L}$, which consisted of 1.8% I^- , 75.9% IO_3^- , and 22.3% organo-I. These percentages are consistent with previous aqueous I speciation measurements showing that the vast majority of the groundwater iodine at the Hanford Site existed as IO_3^- (Zhang et al., 2013).

The three subsurface sediments were selected to provide a wide range of properties expected in the vadose zone and aquifer of the 200-West Area (Table 2). However, the three sediments had a relatively narrow range of pH values, 7.96 to 8.89, and similar mineralogy in the fine size fraction ($<53\mu\text{m}$). Important differences were that sediment H1 had a loamy-sand texture and a relatively high OC level of 0.12%. Conversely, sediments H2 had a sandy texture and a low OC concentration of only 0.04%. Sediment H3, also a sandy texture, had a relatively high OC concentration of 0.15% (all errors well within 5%). The 1:1 laboratory-measured E_h of the sediments increased with sampling depth: 71 mV for H1, 90 mV for H2, and 125 mV for H3. Given that the sediments were stored in the presence of atmospheric O_2 and once air-dried at 60°C , the measured E_h values do not represent *in-situ* conditions. Instead, they represent the E_h values during the experiment.

Because the sediments were collected from boreholes just outside the ^{129}I -contaminant plume, the sediment iodine speciation had to be conducted with naturally occurring stable ^{127}I instead of ^{129}I (Table 3). Total ^{127}I was greatest in the loamy sand sediment, H1 ($4.75 \pm 0.06 \mu\text{g/g } ^{127}\text{I}$), and was lowest in the sandy sediment with lowest OC concentrations, sediment H2 ($0.40 \pm 0.00 \mu\text{g/g } ^{127}\text{I}$). Only a small percentage of the total ^{127}I in the sediment was exchangeable (or mobile), but the range of exchangeable ^{127}I varied largely: 0.4% (sediment H3), 2.3% (sediment H1) and 6.6% (sediment H2) (Table 3 and Fig. 2). Previous research (Shimamoto et al., 2011; Xu et al., 2011a; Yamaguchi et al., 2010) reported that 0.005 M or 0.1 M KCl also extracted very small fractions of the total sediment iodine and proposed that the majority of the sediment iodine was trapped in intragranular spaces or organically bound (Hu et al., 2005). More importantly, IO_3^- was the main species in the exchangeable fraction (80 to 100% of the extracted iodine). Speciation analysis with the GC-MS derivatization method was not successful for other fractions, due to the presence of acid (e.g., 0.44 N acetic acid, 0.1 N nitric acid) or reductant (0.04 N NH_2HCl) in the solvent. It is consistent with recent findings by Zhang et al. (2013) that IO_3^- , instead of I^- , is the main species present in the groundwater of Hanford Site 200-West Area. As a matter of fact, a significant fraction (39.4% for H1, 2.9% for H2, and 35.9% for H3) of the total sedimentary iodine was associated with the carbonate fraction, likely as IO_3^- substituting $(\text{CO}_3)^{2-}$ ion in the calcite structure due to the fact that the Ca-O distance in $\text{Ca}(\text{IO}_3)_2$ is similar to that in calcite (Lu et al., 2010; Zhang et al., 2013). Mn-, Fe-oxide bound iodine was a very minor fraction for H1 (1.2%) and negligible for the other two sediments. Generally, organo-iodine compounds are quite stable, as the C-I bond can only be broken by strong nucleophiles (e.g., dissolved sulfides or thiosulfates). Additionally, replacement of iodine in the C-I only occurs in the presence of stronger electrophiles or in the abiotic conditions, thus, little release of organo-iodine compounds should be expected with the extraction of 0.44 M HOAc. The stability of organo-iodine compounds is also supported in other studies (Carlsen et al., 1992; Moulin et al., 2001; Schlegel et al., 2006; Yamaguchi et al., 2010). We did not evaluate the efficiency of carbonate extraction (i.e., if all the carbonate associated iodine was mostly extracted with 0.44 M HOAc). Regardless, the following extraction targeting Mn-, Fe- oxide associated iodine, which applied 0.1 M HNO_3 together with heat treatment (96 °C for 6 hrs), did not release significant amounts of iodine into the aqueous phase. The Mn-, Fe-oxide extraction step actually uses “harsher” conditions (more acidic, with heat and reductant), compared to the carbonate

extraction. This also indirectly confirms that carbonate extraction is efficient in extracting carbonate associated iodine and non-destructive to organo-iodine components. One has to be still cautious that this could be operationally biased, as one type of solvent is not necessarily efficient enough to extract all iodine in the targeted fraction, or one type of solvent could be extracting more than the targeted fraction (Miller et al., 1986; Tessier et al., 1979). Nevertheless, the residual iodine (57.1% of the total iodine for H1, 90.6% for H2 and 63.7% for H3) was presumably mainly associated with organic matter due to the formation of strong C-I bonds (Xu et al., 2013; Xu et al., 2011a; Xu et al., 2011b; Xu et al., 2012), as operationally defined by the above sequential extraction methods.

3.2 Kinetics of $^{125}\text{I}^-$ and $^{125}\text{IO}_3^-$ Uptake

A novel aspect of this study is that added ^{125}I was not only in I^- form (Kaplan et al., 2000; Um et al., 2004), but was also added as IO_3^- to more closely reflect iodine uptake under Hanford subsurface conditions. This is important, because IO_3^- , as previously discussed, is the dominant species in unconfined Hanford groundwater (Table 1) (Zhang et al., 2013).

After only three days under air-sealed experimental conditions, ~45% of the added ^{125}I was taken up by sediment H1, but uptake then decreased to 7% by day 28 (Fig. 3a). The large initial $^{125}\text{I}^-$ uptake was not observed for sediments H2 and H3. The cause for this difference is not known, but may be attributed to the vadose zone sediment, H1, requiring more time to come to steady state with the added groundwater than the two sediments collected from below the water table, H2 and H3. Vadose zone sediments could be expected to include more evaporates than aquifer sediments; evaporates would quickly or slowly enter into the aqueous phase, depending on their composition. Uptake of $^{125}\text{I}^-$ by sediment H2 decreased to almost 0% after 20 days. Uptake of $^{125}\text{I}^-$ by sediment H3, the sediment with the greatest OC, increased with time and reached ~54% of total added $^{125}\text{I}^-$ by day 28.

Uptake of $^{125}\text{IO}_3^-$ by sediments H2 and H3, the two sand-textured sediments, showed little change during the 28-day equilibration period (Fig. 3b). As was the case with the $^{125}\text{I}^-$ additions (Fig. 3a), $^{125}\text{IO}_3^-$ uptake by H1 was initially high (day 3), but then decreased and levelled off by day 28. While strikingly different uptake kinetic patterns were observed between the iodine species and sediment samples, two conclusions may be made. First, it appears that 28 days is

sufficient to reach steady state; this was true in five of the six kinetic experiments (Fig. 3). Secondly, a ranking of the sediments for total iodine uptake, irrespective of iodine species added was: H3 > H1 > H2. This ranking is consistent with the ranking of these sediments for OC content (Table 2).

In these experiments, significant $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ partitioning into the colloidal fraction (3 kDa-0.45 μm) was not detected (data not shown). In contrast, we reported previously that suspensions of a Savannah River Site (SRS) surface sediment with high organic carbon content (24%-wt) contained significant colloidal fractions (3 kDa – 0.45 μm) that retained 6% of the amended $^{127}\text{I}^-$ and 3% of the amended $^{127}\text{IO}_3^-$ (Xu et al., 2011a). However, another SRS aquifer sediment with extremely low organic carbon (0.01%-wt) contained no detectable $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ in the colloidal fraction (Xu et al., 2011a). Together, these results suggest that colloid facilitated transport of radioiodine could be more prevalent in organic rich sediments, such as the wetland area of the SRS, and less important in sediments of arid environments with low organic carbon content, such as the Hanford Site.

3.3. Speciation changes of amended radioiodine and naturally-present iodine in groundwater

3.3.1. ^{125}I speciation

In the Air-sealed Uptake Study, $^{125}\text{I}^-$ was the only aqueous species detected in the three sediment suspensions amended with $^{125}\text{I}^-$, indicating that no appreciable IO_3^- or organo-I (data not shown) was stable in the aqueous phase (Fig. 4a, 4c, 4e). However, when the loamy sand, H1, suspensions were amended with $^{125}\text{IO}_3^-$, the percentage of $^{125}\text{IO}_3^-$ decreased along with concomitant increases in $^{125}\text{I}^-$ (Fig. 4b). By day 3, 55% of the total aqueous ^{125}I (< 0.45 μm) was $^{125}\text{I}^-$ and by day 7, 100% had been reduced to $^{125}\text{I}^-$. The strong reduction capacity of Hanford sediments has previously been demonstrated with respect to $\text{Tc}^{\text{VII}}\text{O}_4^-$ reduction to Tc^{+4} (Fredrickson et al., 2004), $\text{U}^{\text{VI}}\text{O}_2^{2+}$ to U^{4+} (Zachara et al., 2007a), $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ to Cr^{3+} (Ginder-Vogel et al., 2005), $\text{Pu}^{\text{V}}\text{O}_2^{2+}$ to Pu^{4+} (Zachara et al., 2007b). The reductant in these sediments is primarily from the Fe^{2+} found in the structure of illite and to a smaller extent iron oxides (Dong et al., 2003). Iodate reduction was also observed, but to a smaller extent, in the two sand-textured sediments, H2 and H3 (Fig. 4d, 4f). In the H2 slurries amended with $^{125}\text{IO}_3^-$, the $^{125}\text{I}^-$ fraction increased from 5% at day 3 to 17% at day 14 and then stayed relatively constant through to day

28. In the H3 slurries amended with $^{125}\text{IO}_3^-$, the $^{125}\text{I}^-$ fraction increased from 5% at day 3 to 23% at day 21 and reached equilibrium afterwards (Fig. 4d, 4f). Organo- ^{125}I formation was not detected in the aqueous fractions in any of these slurries. Based on this small number of samples, it appears that the reductant originated primarily from the fine minerals (and associated bacteria), and to a lesser extent from the organic matter; the sediment with a loamy sand texture, H1, promoted reduction, whereas the sediment with the greatest OC concentrations, H3, exhibited much less reduction.

3.3.2. ^{127}I speciation

Temporal changes of naturally-present $^{127}\text{I}^-$ and $^{127}\text{IO}_3^-$ concentrations in the aqueous phases of the Air-sealed Uptake Study are shown in Fig. 5. In order to assess the influence of sediments on groundwater iodine speciation, the change in iodine speciation (ΔI) was calculated by subtracting the $^{127}\text{I}^-$ or $^{127}\text{IO}_3^-$ concentrations in the groundwater controls (i.e., groundwater without sediment as described in Table 1) from those in the aqueous phase of the sediment slurry, using equation 3:

$$\Delta I = I_{aq-slurry} - I_{aq} \quad (\text{Eq. 3})$$

where $I_{aq-slurry}$ is the iodine species concentrations in the aqueous phase of the slurry and I_{aq} is the iodine species concentrations in the groundwater alone. I_{aq} was measured in triplicate sediment-free control samples that were carried through the experiment along with the sediment slurries. The slurries and the sediment-free controls were sampled at 3, 7, 14, 21, and 28 days. Therefore ΔI values provide a measure of the impact of the sediment on groundwater iodine speciation, and were only useful in showing the relative variations of aqueous iodine speciation in the groundwater upon contacting different sediment types. A positive $^{127}\text{I}^-$ or $^{127}\text{IO}_3^-$ ΔI value represents an increase in the species concentration in the groundwater after it was put in contact with the sediment. As such, an increased ΔI value could result from a species: 1) transforming from other species after coming into contact with the sediment, e.g., through reduction, or 2) desorbing from the sediment and entering the aqueous phase. Theoretically, sediments H1, H2, and H3 could contribute their exchangeable fraction (Table 3) to the aqueous phase, which would be 27.5 $\mu\text{g/L}$, 7.5 $\mu\text{g/L}$ and 2.5 $\mu\text{g/L}$ ^{127}I , respectively.

The aqueous phase of the sediment H1-groundwater slurries contained the greatest increase in $^{127}\text{I}^-$ concentrations, followed by H2 and then H3 slurries (Fig. 5a). The slightly positive ΔI values for the two sandy sediments, H2 and H3, indicate that a small amount of I^- desorption or IO_3^- reduction took place. When sediments were added to the groundwater, aqueous $^{127}\text{IO}_3^-$ concentrations decreased, i.e., ΔI for $^{127}\text{IO}_3^-$ became negative (Fig. 5b). These results with naturally occurring $^{127}\text{IO}_3^-$ are consistent with those of the $^{125}\text{IO}_3^-$ -amended study where greater IO_3^- than I^- sorbed to the sediments (Fig 3a) and IO_3^- reduction was observed in all three sediment (Fig. 4b, 4d, 4f). For sediment H1, the increase of I^- and the concomitant decrease in IO_3^- concentrations, indicates that the negative ΔI for $^{127}\text{IO}_3^-$ values can be attributed largely to reduction.

In the Open-air Uptake Study (Fig. 6a and 6b, respectively), the aqueous phases of H1 and H2 sediment slurries amended with $^{125}\text{I}^-$ were exclusively comprised of $^{125}\text{I}^-$ at the end of the experimental period, similar to the results for H1 and H2 sediment slurries amended with $^{125}\text{I}^-$ observed in the Air-sealed Uptake Study. There was some oxidation of $^{125}\text{I}^-$ to $^{125}\text{IO}_3^-$ in the aqueous phase of H3 sediment slurries amended with $^{125}\text{I}^-$ over this period (Fig. 6a). When H1 sediment slurries were amended with $^{125}\text{IO}_3^-$, the majority of the aqueous $^{125}\text{IO}_3^-$ (~96.5%) had been reduced to $^{125}\text{I}^-$. In contrast, in the H2 and H3 sediment slurries amended with $^{125}\text{IO}_3^-$, a much smaller fraction of aqueous $^{125}\text{IO}_3^-$ (6% and 12% for H2 and H3, respectively) was reduced to $^{125}\text{I}^-$ over the 28 day incubation period. Overall, a slightly greater reduction of $^{125}\text{IO}_3^-$ to $^{125}\text{I}^-$ was observed in the air-sealed environment than that in the open-air environments (Fig. 4b, 4d, 4f vs. 6a).

^{127}I speciation in the aqueous phase of the open-air groundwater-sediment slurries at day 28 is shown in Fig. 6b. There was less net $^{127}\text{I}^-$ gain in the open-air H1 groundwater-sediment slurries than that in air-sealed H1 incubation (Fig. 5a vs. Fig. 6b). The H1 groundwater-sediment systems exhibited relatively large net gains of $^{127}\text{I}^-$ under both conditions (Fig. 5a and 6b), compared to the other two sediments, which can be attributed to 1) its higher reducing capacity and thus higher conversion of $^{127}\text{IO}_3^-$ to $^{127}\text{I}^-$ in groundwater upon contacting the sediment, and 2) its higher concentration of exchangeable I and thus more release of sediment-bound $^{127}\text{I}^-$.

Because pH variations were less than 0.5 in all groundwater-sediment slurry experiments (Table 4), other factors, such as changes in redox potential (E_h), abundance of reductants in the

sediments, and the presence of organic matter, are possible causes of the observed ^{125}I and ^{127}I speciation changes.

The average E_h value of the Air-sealed Uptake Study ($E_h = 137 \pm 8$ mV) was slightly lower than that in the Open-air Uptake Study ($E_h = 144 \pm 13$ mV), however these averaged values were not significantly different. Significant ($P \leq 0.05$, $n = 3$) differences in the E_h values were not noted until comparisons were made between the E_h of the individual sediments. The E_h of sediment H2 was 145 ± 3 mV and 155 ± 2 mV in the air-sealed and open-air studies, respectively. Similarly, the E_h of sediment H3 was 137 ± 2 mV and 148 ± 0 mV in the air-sealed and open-air studies, respectively. The E_h values of sediment H1 were not significantly different, 128 ± 4 mV and 130 ± 1 mV in the air-sealed and open-air studies, respectively. Adopting the average reduction capacity of 5.2 ± 0.5 nmol IO_3^- /g for Hanford sediments reported by Hu et al. (2005), 10 g sediments used in the groundwater-sediment slurry experiments would contain a total reduction capacity for ~ 52 nmol IO_3^- . The groundwater used in this study contained $7.08 \mu\text{g/L}$ (40 nM) of ^{127}I as IO_3^- , resulting in only ~ 1.6 nmol IO_3^- in the 40 mL slurry, which is > 32 times less mol equivalents than those IO_3^- -reducing agents existed in the 10 g of Hanford sediment (52 nmol- IO_3^- equivalents/ 10 g). X-ray diffraction analyses of the three sediments revealed that the primary mineral phase in the $< 53 \mu\text{m}$ fraction was illite (Table 2), which, as noted earlier, contains structural Fe (II) that can promote reducing conditions (Dong et al., 2003). Moreover, E_h value of groundwater was higher than those of all three sediments measured by 1:1 (sediment-to-distilled water) ratio method (Table 1 and 2). Therefore, the regulation of aqueous iodine speciation in these systems appears to be a redox competition between the relatively oxidizing groundwater, which originated from a plume on the Hanford Site that contained oxidizing nitric acid (Zhang et al., 2013), and the sediments with substantial amounts of microzonal reducing agents (Table 2). Consistent with the ranking of E_h values of the three sediments ($\text{H1} < \text{H2} < \text{H3}$), the vadose zone sediment (H1) showed the highest reducing capacity and thus acted as a ^{127}I source under all incubation conditions (Fig. 5- 6), and as a significant $^{127}\text{IO}_3^-$ sink only under air-sealed conditions. The upper saturated sediment (H2) was a weak ^{127}I source under all incubation conditions, whereas the deeper saturated sediment (H3) was a significant $^{127}\text{IO}_3^-$ sink. Actually, Zhang et al. (2013) observed that the groundwater $^{127}\text{I}^- / ^{127}\text{IO}_3^-$ ratios increased, while $^{129}\text{IO}_3^-$ concentrations dramatically decreased, along a transect away from the contaminant source terms in 200-West Area. These field observations are consistent with: 1) greater IO_3^- than I^-

sediment uptake, and, 2) the tendency for aqueous IO_3^- (from source waters) to be reduced to I^- by these subsurface sediments. What remains unclear is why the system appears to remain in disequilibrium between the added aqueous IO_3^- and the tendency for the aquifer sediment to reduce IO_3^- to I^- . An alternative explanation is that in our batch experiment, we conduct it as a slurry, i.e., sediment is agitated. That brings more surface sites into contact with the water, which would normally be more shielded in a groundwater aquifer.

3.4. ^{125}I uptake K_d under both air-sealed and open-air equilibrating conditions and a comparison with desorption K_d values under air-sealed condition

Three studies were conducted to measure iodine K_d values under different conditions: Air-sealed Uptake Study, Open-air Uptake study, and Air-sealed Desorption study. The air-sealed uptake study equilibrated the slurries in sealed reaction vessels with limited headspace placed on the lab bench. The Open-air Uptake Study equilibrated the suspension in reaction vessels with holes placed in the caps and in a large diameter vessel that maximized the air-suspension interface. The Air-sealed Desorption study measured desorption of iodine in the presence of 0.1 M KCl from the samples used in the Air-Sealed Uptake study. The intent of the first two studies was to measure iodine uptake under slightly different redox conditions (Table 4), as opposed to end member conditions that may be created by conducting the equilibration in air or a glove box containing a N_2 or H_2 atmosphere.

Iodate K_d values were consistently greater than iodide K_d values (Table 4; the “*” indicate significant ($P \leq 0.05$, Student’s T-test) differences between IO_3^- and I^- K_d values within a study). This finding has previously been attributed to: 1) IO_3^- compared to I^- preferably reacts with organic matter abiotically to form immobile organo-I compounds (Shetaya et al., 2012; Xu et al., 2011a), and 2) IO_3^- with a harder base nature, compared to I^- , favoring hard-hard interactions with the hard acid sites present on the sedimentary mineral surface (Kaplan et al., 2000).

The K_d values for the open-air uptake study were consistently greater ($P \leq 0.05$, Duncan’s Multiple Range Test), and as a whole >2x greater, than those measured under the more reducing conditions of the Air-sealed Uptake Study (Table 4). A comparison of the uptake and desorption K_d values from the Air-sealed Uptake study indicate that the desorption K_d ’ values were >8x greater (Table 4). The minimal desorption of sediment iodine indicates that anion exchange is

likely not the dominant form of iodine binding to the sediment. This finding has been previously reported in Hanford sediments (Kaplan et al., 2000; Um et al., 2004). Sediment H1 exhibited partial release of sorbed $^{125}\text{I}^-$ when placed in a 0.1 M KCl groundwater solution (Table 4 and Fig. 7a). No iodine desorption was noted in sediment H2 due to negligible $^{125}\text{I}^-$ uptake under these experimental conditions. H3 sediments exhibited no detectable $^{125}\text{I}^-$ desorption. All three sediments exhibited partial desorption of $^{125}\text{IO}_3^-$ (Fig. 7b). As was observed in the other studies, IO_3^- reduction was noted in the desorbed iodine from all three sediments (Fig. 7d). Iodide oxidation and organo-I formation were not noted (Fig. 7c).

A ranking of the three sediments by their uptake K_d or desorption K_d' values, irrespective of added iodine species or experimental conditions was $\text{H3} > \text{H1} > \text{H2}$. This ranking coincides with the ranking of sediment OC concentrations and the dithionite citrate buffer (DCB) extractable Fe (a measure of surface iron, including iron oxide coatings and nanoparticles) (Table 2). This is not surprising given the extraordinary strong correlation between DCB-Fe and OC because of the strong bond formed between these two sediment constituents and the tendency for iron in sediments to preserve organic matter (Lalonde et al., 2012). But between these two sediment constituents, it is more likely that OC, and not iron, is responsible for the iodine uptake in these studies. Goethite and nanoparticulate Fe, the dominant Fe oxides in these sediments (Dong et al., 2003), bind decreasing amounts of iodine as the pH increases, and negligible amounts as the pH approaches neutral and basic pH systems (Kaplan et al., 2000). Conversely, at the pH of these studies, pH 7.6, natural organic matter continues to bind iodine strongly (Steinberg et al., 2008a; Steinberg et al., 2008b; Xu et al., 2011a). The observation that the iodine was strongly bound to the sediments, that $\leq 7\%$ could be exchangeable with KCl and $< 2\%$ was associated in the Mn-, Fe-oxide (Table 3 and Fig. 2), is also more characteristic of iodination (covalent bond with OC), than it is of complexation with iron oxides.

Positive correlations were also found between specific surface area (Table 2) and uptake K_d or desorption K_d' values (Table 4). Such correlations are even stronger than those between OC and uptake K_d or desorption K_d' . Extensive studies have reported that organic matter, instead of the specific surface area, should play the major role in controlling the sorption of iodine species onto sediment (e.g., Li et al. (2014), Takata et al. (2013), Shimamoto (2011), Steinberg et al. (2008a), Steinberg et al. (2008b), Schwehr et al. (2009); Xu et al (2011a, b, 2012, 2013); Yamaguchi et al. (2010); Zhang et al. (2011)). It is expected that for sediments with a limited

range of OC that a higher specific surface area will promote higher radionuclide sorption due to more available reactive sites (Rogers and Meijer, 1993). In other studies with different types of sediments, especially those with a wide range of OC, sorption K_d did not correlate well with specific surface area, and in some cases an inverse relationship between sorption K_d and surface area were noted (Emerson et al., 2014; Miller et al., 2012). Specific organic moieties, i.e., aromatic components, appear to have even higher correlations than the bulk OC, with iodine uptake K_d or desorption K_d' (Xu et al., 2011a; Xu et al., 2011b). However, identifying the specific organic matter moieties responsible for iodine uptake in this system is outside the scope of the present study. As noted above, sedimentary OC has been reported to be a radioiodine sink in the organic-rich vadose zone and wetlands of the SRS (4-24% OC) (Kaplan et al., 2011; Schwehr et al., 2009; Shetaya et al., 2012; Xu et al., 2011b; Zhang et al., 2011) and in regions containing moderate OC concentrations (Dai et al., 2009; Dai et al., 2004; Shimamoto et al., 2011; Yamaguchi et al., 2010), but the impact of low concentrations of OC (<0.2%-wt) has not been established.

Equally important from a modeling perspective was the poor correlation between the iodine uptake and the concentrations of fine particles (the sum of silt and clay contents, Table 2). Reactive transport modelling is often based on the selection of geochemical parameters, including K_d values, in part on fine particle concentrations in the geological strata. The greatest iodine uptake took place in sediment H3, which contained only 1.5% fines, whereas significantly lower K_d or K_d' values were measured for sediment H1, which contained 22.2% fines (Table 2). Additional research with a larger number of low OC sediments is needed to confirm this finding.

4. Conclusions

An in-depth evaluation of the reactions that occur between iodine and three Hanford subsurface sediments were conducted. Additionally, the speciation and solid phase partitioning of indigenous ^{127}I was characterized in these samples, providing insight into the long-term fate that may be expected for radioactive ^{129}I . These experiments identify two important geochemical processes that influenced iodine behavior in this environment: 1) long-term iodine is mainly associated with carbonate fraction as IO_3^- and organo-iodine fraction in the sediments; and 2) freshly introduced IO_3^- to a sediment/groundwater system readily reduces to I^- . As early as 7

days, 100% of the added aqueous IO_3^- had converted to I^- when put in contact with the loamy-sand sediment, sediment H1. Even the two sand-textured sediments, with less than 2% clay and silt, could promote the reduction of 17-23% of the added IO_3^- . Furthermore, unlike other redox-sensitive radionuclides and metals, including U, Tc, Pu, and Cr, where the reduced form is immobile, the reduced species of iodine, I^- , sorbs appreciably less than the oxidized species IO_3^- . Previous work has attributed the reductant in these soils to Fe(II) present in the illite clays and iron-oxyhydroxides. For this reason, the greatest amount of iodine reduction occurred in the sediment with the greatest fraction of fines (sediment H1).

There were two observations that lead to the conclusion that sediment OC was important for binding aqueous iodine in this system: 1) I^- and IO_3^- uptake K_d and desorption K_d values increased with OC concentrations, and 2) appreciable amount of sedimentary iodine (57.1 to 90.6% of the total sedimentary iodine) was not extracted by the three sequential extractions targeting exchangeable, carbonate and Mn-, Fe-oxide associated fractions. The remaining iodine likely existed as organo-iodine, which forms strong bonds through iodination (covalent bond between iodine and OC, Xu et al., 2012, 2013). Minimal iodine uptake would be expected by surface complexation to iron oxyhydroxide surfaces at pH 7.6, the pH of these systems; similarly, at this pH, a greater readily exchangeable fraction would be expected if the iodine was bound directly to illitic clay (Kaplan et al., 2000). Finally, together these two processes help explain earlier results demonstrating an increase in field groundwater $^{127}\text{I}^- / ^{127}\text{IO}_3^-$ ratios, and $^{129}\text{IO}_3^-$ concentrations dramatically decreasing, along a transect away from the contaminant source terms in the 200-West Area (Zhang et al., 2013). At the study site, the iodine was primarily introduced in the cribs and tanks as IO_3^- in a nitrate rich, heat-treated waste stream. The changes in field $^{127}\text{I}^- / ^{127}\text{IO}_3^-$ ratios and $^{129}\text{IO}_3^-$ concentrations are consistent with: 1) greater IO_3^- than I^- sediment uptake, and 2) the tendency for aqueous IO_3^- to be reduced to I^- by these subsurface sediments.

Finally, the geochemical behavior of IO_3^- in an alkaline, carbonate-rich subsurface environment has not previously been studied. Such environments are common in western United States and Europe. Previous reports have emphasized I^- geochemistry because of the expected dominance of this species based on thermodynamic considerations (Kaplan et al., 2014). Contrary to this expectation, IO_3^- has been shown to account for a significant fraction of the aqueous species in a wide range of natural conditions: about 25% of the total ^{129}I exists as IO_3^- in the semi-tropical, pH 5.5, Savannah River Site groundwater (Otosaka et al., 2011), and 85% of

the total ^{129}I exists as IO_3^- at the semi-arid, pH 7.6, Hanford Site groundwater (Zhang et al., 2013). The two iodine species (I^- and IO_3^-) had unique geochemical behavior, including differences in uptake and redox chemistry. Iodate not only binds more strongly, but, unlike iodide, can be incorporated in newly-formed calcium carbonate phases (Zhang et al., 2013). A broader and perhaps less in-depth study that includes more sediment samples might be warranted to validate the proposed mechanisms put forth here to explain iodine speciation transformation and uptake measured. While a majority of the radioiodine does not bind to these alkaline sediments, there is very likely a second smaller iodine fraction in the Hanford subsurface that is strongly bound, presumably to the sediment OC (and carbonate phases). This second fraction may have an impact on establishing remediation goals and performance assessment calculations.

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Table 1**Properties of groundwater used in the experiment.**

¹²⁹ I, Bq/L	0.15
¹²⁷ I, (µg/L)	9.33
¹²⁷ I ⁻ (%)	1.8
¹²⁷ IO ₃ ⁻ (%)	75.9
¹²⁷ Organo-I (%)	22.3
pH	7.99
dissolved organic carbon (DOC) (µM)	15.6
Turbidity (NTU)	1.28
Temperature (°C)	20.3
Specific conductance (µS/cm)	463
Alkalinity (µg/L)	120000
Sulfate (µg/L)	27900
Nitrate (µg/L)	86300
Nitrite (µg/L)	131
Chloride (µg/L)	8180
Ca (µg/L)	47400
Na (µg/L)	14800
Mg (µg/L)	17000
K (µg/L)	5330
Fe (µg/L)	38
Mn (µg/L)	6
Eh (mV)	154

Table 2

Sediment description and properties.

Property	Units	Sediment H1	H2	H3
Subsurface location		Vadose zone	Upper saturated zone	Deeper saturated zone
Depth	m	30.5-41.1	102.1-112.8	123.4-141.7
Sand/silt/clay	wt-%	77.7/21.7/0.5	99.6/0.4/0.003	98.5/0.4/1.1
Surface area	m ² /g	12.4	5.6	46.8
pH ^a		8.89	8.58	7.96
E _h (S.H.E.) ^a	mV	70.9	90.3	124.7
OC	(wt-%)	0.12	0.04	0.15
Inorganic C	(wt-%)	0.92	0.01	0.18
Extractable Fe ^b	(mg/g)	3.46±1.13	1.59±0.65	4.22±1.48
Extractable Al ^b	(mg/g)	0.39±0.12	0.15±0.07	0.62±0.23
Mineralogy ^c		Illite >> smectite >> kaolinite >chlorite	Illite >> smectite >> kaolinite = chlorite	Illite >> smectite >> kaolinite >chlorite

^a Measured in a 1:1 sediment:water suspension.^b Metals were extracted by dithionite citrate buffer (Jackson et al., 1986)^c Based on XRD of Mg, K, and ethylene glycol saturated samples. Samples were analyzed after air drying and again after heating for 1 hr at 550 °C (Moore and Reynolds, 1989). Scans were processed with JADE[®] XRD pattern processing software. Semi quantification of mineral phases in the sediment samples were determined by the whole pattern fitting technique provided by JADE[®] XRD pattern processing software.

619 **Table 3**

620 Speciation of the sediment-bound ion-exchangeable inorganic iodine

621

	Total sedimentary iodine	exchangeable			Carbonate	Mn-, Fe- oxide associated	residual
	($\mu\text{g/g}$)	($\mu\text{g/g}$)	* IO_3^- (%)	* I^- (%)	($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)
H1	4.75±0.06	0.11	83.87	16.13	1.87	0.06	2.71
H2	0.40±0.00	0.03	80.14	19.86	0.01	0.00	0.36
H3	1.85±0.35	0.01	100.00	0.00	0.66	0.00	1.18

622 * IO_3^- and I^- species were measured by a GC-MS derivatization method (Zhang et al., 2010), whereas others were measured by ICP-MS.

623

624 **Table 4**625 Uptake K_d values (eq. 1) and desorption K_d' values (eq. 2) for iodine added as Γ^- and IO_3^- (units = L/kg).

Sediment		Air-sealed Uptake Study ($E_h = 137 \pm 8$ mV, pH = 7.64 ± 0.15)		Open-air Uptake Study ($E_h = 144 \pm 13$ mV, pH = 7.58 ± 0.22)		Air-sealed Desorption Study ($E_h = 142 \pm 7$ mV, pH = 7.61 ± 0.12)	
		Γ^- Amendment	IO_3^- Amendment	Γ^- Amendment	IO_3^- Amendment	Γ^- Amendment	IO_3^- Amendment
H1	Kd	0.08 ± 0.00	$1.78 \pm 0.38^*$	0.78 ± 0.17	$3.91 \pm 0.27^*$	11.90 ± 1.16	$21.94 \pm 2.98^*$
	pH	7.82 ± 0.06		7.82 ± 0.02		7.71 ± 0.15	
	Eh	127.9 ± 4^a		130.2 ± 1.2		130.8 ± 0.3	
H2	Kd	no detectable uptake	0.83 ± 0.10	0.30 ± 0.21	$1.99 \pm 0.01^*$	no detectable uptake	12.30 ± 5.38
	pH	7.53 ± 0.07		7.38 ± 0.04		7.53 ± 0.01	
	Eh	145.1 ± 2.6		155.3 ± 2.1		146.9 ± 0.6	
H3	Kd	3.38 ± 0.13	$3.94 \pm 0.17^*$	5.64 ± 0.05	$7.56 \pm 0.19^*$	no desorption	29.77 ± 4.53
	pH	7.63 ± 0.05		7.51 ± 0.00		7.57 ± 0.08	
	Eh	137.2 ± 1.5		148.4 ± 0.0		144.4 ± 4.6	

* is used to identify significant ($P \leq 0.05$; $n = 2$ or 3) difference between Γ^- and IO_3^- K_d values within an experiment according to Student's T-test. No statistics were conducted using K_d values from below detection limit measurements.

^a E_h values are calculated on four duplicates: two from the Γ^- amendment and the other two from the IO_3^- amendment, assuming the trace amount of $^{125}\text{I}^-$ or $^{125}\text{IO}_3^-$ would not seriously cause different redox variations in the groundwater-sediment slurries.

Figure Captions

Figure 1. Flow scheme for sequential extraction of exchangeable, carbonate, Mn-, Fe-oxide associated and residual iodine in sediments.

Figure 2. Naturally-occurring ^{127}I distribution of the three sediments.

Figure 3. Percent total ^{125}I uptake by sediments when added as: a) $^{125}\text{I}^-$ and b) $^{125}\text{IO}_3^-$. Percentage of ^{125}I uptake by sediment was calculated by subtracting the total aqueous ^{125}I ($< 0.45\ \mu\text{m}$) concentration from the total initial added ^{125}I and then dividing by the total added ^{125}I (the total added ^{125}I activity for each treatment was $3 \times 10^7\ \text{Bq/L}$ ($3.8 \times 10^{-10}\ \text{M}$)). Values represent the means and errors associated with three replicates. H1, H2 and H3 are three subsurface sediments collected in vadose, upper saturated and deeper saturated zones, respectively. They represent loamy-sand texture with relatively high organic carbon (OC, 0.12%), sandy texture with relatively low OC (0.04%) and sandy texture with relatively high OC (0.15%), respectively.

Figure 4. Time-series observations of aqueous ^{125}I ($< 0.45\ \mu\text{m}$) speciation of the air-sealed uptake study, where: a) sediment H1 was amended with $^{125}\text{I}^-$; b) sediment H1 was amended with $^{125}\text{IO}_3^-$; c) sediment H2 was amended with $^{125}\text{I}^-$; d) sediment H2 was amended with $^{125}\text{IO}_3^-$; e) sediment H3 was amended with $^{125}\text{I}^-$; and f) sediment H3 was amended with $^{125}\text{IO}_3^-$. Values represent the mean and error associated with three replicates. Organo-iodine concentrations were below detection limit in all experiments.

Figure 5. Temporal concentration changes of naturally occurring aqueous: a) $^{127}\text{I}^-$ and b) $^{127}\text{IO}_3^-$ after Hanford groundwater is put in contact with three sediments in air-sealed reaction vessels (Eq. 3). A positive value indicates the “gain” of I^- or IO_3^- in the aqueous phase with respect to their respective concentrations in a sediment-free groundwater; whereas a negative value indicates the loss of I^- or IO_3^- with respect to the sediment-free groundwater. Values represent the mean and error associated with three replicates. No iodine was added to these systems.

Figure 6. a) aqueous ^{125}I speciation (% of the total ^{125}I in the $< 0.45\ \mu\text{m}$ fraction); b) aqueous ^{127}I speciation in the Open-air Uptake Study.

Figure 7. Percent of total ^{125}I desorbed from sediments amended with: a) $^{125}\text{I}^-$ or b) $^{125}\text{IO}_3^-$. The three sediments were equilibrated with ^{125}I in air-sealed reaction vessels for four weeks and then solutions were changed to 0.1 M KCl-amended natural groundwater. Total ^{125}I desorption were measured in the 0.1 M KCl solution after two weeks. Values represent the mean and error associated with three replicates. Aqueous ^{125}I speciation in the 0.1 M KCl solution used to promote desorption, in the c) $^{125}\text{I}^-$ amended sediment; d) $^{125}\text{IO}_3^-$ amended sediment, which was previously conducted in the air-sealed condition.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig.5

Fig. 6

Fig.7

References:

- Carlsen, L., Lassen, P., Christiansen, J.V., Warwick, P., Hall, A., Randall, A., 1992. RADIO-LABELING OF HUMIC AND FULVIC MATERIALS FOR USE IN ENVIRONMENTAL-STUDIES. *Radiochim. Acta* 58-9, 371-376.
- Corbin, R.A., Simpson, B.C., Anderson, M.J., Danielson, W.F., Field, J.G., Jones, T.E., Kincaid, C.T., 2005. Hanford Soil Inventory Model, Revision 1. RPP-26744, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.
- Dai, J.L., Zhang, M., Hu, Q.H., Huang, Y.Z., Wang, R.Q., Zhu, Y.G., 2009. Adsorption and desorption of iodine by various Chinese soils: II. Iodide and iodate. *Geoderma* 153, 130-135.
- Dai, J.L., Zhang, M., Zhu, Y.G., 2004. Adsorption and desorption of iodine by various Chinese soils - I. Iodate. *Environment International* 30, 525-530.
- DOE, 2012. "Proposed plan for remediation of the 200-UP-1 groundwater operable unit," Rep. No. DOE/RL-2010-05, Rev. 0.
- Dong, H., Kukkadapu, R.K., Fredrickson, J.K., Zachara, J.M., Kennedy, D.W., Kostandarithes, H.M., 2003. Microbial reduction of structural Fe(III) in illite and goethite. *Environmental Science & Technology* 37, 1268-1276.
- Duncan, J.P., Poston, T.M., Dirkes, R.L., 2008. Summary of the Hanford Site Environmental Report for Calendar Year 2008, PNNL-18427-SUM.
- Emerson, H.P., Xu, C., Ho, Y.-F., Zhang, S., Schwehr, K.A., Lilley, M.S., Kaplan, D.I., Santschi, P.H., Powell, B.A., 2014. Geochemical controls of iodine uptake and transport in Savannah River Site subsurface sediments. *Applied Geochemistry* 45, 105-113.
- Fredrickson, J.K., Zachara, J.M., Kennedy, D.W., Kukkadapu, R.K., McKinley, J.P., Heald, S.M., Liu, C., Plymale, A.E., 2004. Reduction of TcO₄⁻ by sediment-associated biogenic Fe(II). *Geochimica Et Cosmochimica Acta* 68, 3171-3187.

- 43 Fritz, B.G., Patton, G.W., 2006. Monitoring iodine-129 in air and milk samples collected
44 near the Hanford Site: an investigation of historical iodine monitoring data. *Journal*
45 *of Environmental Radioactivity* 86, 64-77.
- 46 Gephart, R.E., 2010. A short history of waste management at the Hanford Site. *Physics*
47 *and Chemistry of the Earth, Parts A/B/C* 35, 298-306.
- 48 Ginder-Vogel, M., Borch, T., Mayes, M.A., Jardine, P.M., Fendorf, S., 2005. Chromate
49 reduction and retention processes within arid subsurface environments. *Environ. Sci.*
50 *& Technol* 39, 7833-7839.
- 51 Hartman, M.J., Morasch, L.F., Webber, W.D., 2003. Summary of Hanford Site
52 Groundwater Monitoring for Fiscal Year 2002, PNNL-14187-SUM.
- 53 Hu, Q.H., Zhao, P.H., Moran, J.E., Seaman, J.C., 2005. Sorption and transport of iodine
54 species in sediments from the Savannah River and Hanford Sites. *Journal of*
55 *Contaminant Hydrology* 78, 185-205.
- 56 Jackson, M.L., Lim, C.H., Zelazny, L.W., 1986. Oxides, hydroxides, and aluminosilicates,
57 in: Klute, A. (Ed.), *Methods of soil analysis. Part 1* 2nd ed. *Agonomy Monograph* 9.
58 ASA and SSSA, Madison, WI, pp. 101-150.
- 59 Kaplan, D.I., Denham, M.E., Zhang, S., Yeager, C., Xu, C., Schwehr, K.A., Li, H.P., Ho,
60 Y.F., Wellman, D., Santschi, P.H., 2013. Radioiodine biogeochemistry and prevalence
61 in groundwater *Critical Review of Environmental Science and Technology* accepted;
62 DOI 10.1080/10643389.2013.828273.
- 63 Kaplan, D.I., Roberts, K.A., Schwehr, K.A., Lilley, M.S., Brinkmeyer, R., Denham, M.E.,
64 Diprete, D., Li, H.P., Powell, B.A., Xu, C., Yeager, C.M., Zhang, S.J., Santschi, P.H.,
65 2011. Evaluation of a radioiodine plume increasing in concentration at the Savannah
66 River Site. *Environmental Science & Technology* 45, 489-495.
- 67 Kaplan, D.I., Serne, R.J., 2000. *Geochemical Data Package for the Hanford Immobilized*
68 *Low-Activity Tank Waste Performance Assessment (ILAW PA)*, PNNL-13037, Rev.1,
69 Pacific Northwest National Laboratory.

- 70 Kaplan, D.I., Serne, R.J., Parker, K.E., Kutnyakov, I.V., 2000. Iodide sorption to
 71 subsurface sediments and illitic minerals. *Environmental Science & Technology* 34,
 72 399-405.
- 73 Lalonde, K., Mucci, A., Ouellet, A., Gelinas, Y., 2012. Preservation of organic matter in
 74 sediments promoted by iron. *Nature* 483, 198-200.
- 75 Li, J.X., Wang, Y.X., Guo, W., Xie, X.J., Zhang, L.P., Liu, Y.Q., Kong, S.Q., 2014. Iodine
 76 mobilization in groundwater system at Datong basin, China: Evidence from
 77 hydrochemistry and fluorescence characteristics. *Science of the Total Environment*
 78 468, 738-745.
- 79 Lu, Z., Jenkyns, H.C., Rickaby, R.E.M., 2010. Iodine to calcium ratios in marine
 80 carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology* 38, 1107-
 81 1110.
- 82 Miller, A., Kruichiak, J., Tellez, H., Wang, Y., 2012. Iodide Sorption to Clays and the
 83 Relationship to Surface Charge and Clay Texture WM2012 Conference, Phoenix,
 84 Arizona, USA.
- 85 Miller, W.P., Martens, D.C., Zelazny, L.W., 1986. Effect of Sequence in Extraction of
 86 Trace Metals from Soils1. *Soil Sci. Soc. Am. J.* 50, 598-601.
- 87 Moore, D.M., Reynolds, R.C., 1989. X-Ray Diffraction and the Identification and
 88 Analysis of Clay Minerals. Oxford University Press.
- 89 Moulin, V., Reiller, P., Amekraz, B., Moulin, C., 2001. Direct characterization of iodine
 90 covalently bound to fulvic acids by electrospray mass spectrometry. *Rapid*
 91 *Communications in Mass Spectrometry* 15, 2488-2496.
- 92 Mudroch, A., Azcue, J.M., 1995. Manual of aquatic sediment sampling. CRC Press, Inc.
- 93 Ootosaka, S., Schwehr, K.A., Kaplan, D.I., Roberts, K.A., Zhang, S.J., Xu, C., Li, H.P., Ho,
 94 Y.F., Brinkmeyer, R., Yeager, C.M., Santschi, P.H., 2011. Factors controlling mobility

- 95 of I-127 and I-129 species in an acidic groundwater plume at the Savannah River Site.
96 Science of the Total Environment 409, 3857-3865.
- 97 Rogers, P.S.Z., Meijer, A., 1993. Dependence of radionuclide sorption on sample
98 grinding surface area, and water composition. American Society of Civil Engineers,
99 345 East 47th Street, New York, NY 10017-2398 (United States).
- 100 Ryba, S.A., Burgess, R.M., 2002. Effects of sample preparation on the measurement of
101 organic carbon, hydrogen, nitrogen, sulfur, and oxygen concentrations in marine
102 sediments. Chemosphere 48, 139-147.
- 103 Schlegel, M.L., Reiller, P., Mercier-Bion, F., Barré, N., Moulin, V., 2006. Molecular
104 environment of iodine in naturally iodinated humic substances: Insight from X-ray
105 absorption spectroscopy. Geochimica Et Cosmochimica Acta 70, 5536-5551.
- 106 Schwehr, K.A., Santschi, P.H., Kaplan, D.I., Yeager, C.M., Brinkmeyer, R., 2009. Organo-
107 Iodine Formation in Soils and Aquifer Sediments at Ambient Concentrations.
108 Environmental Science & Technology 43, 7258-7264.
- 109 Serne, R.J., 2007. Kd Values for Agricultural and Surface Soils for Use in Hanford Site
110 Farm, Residential, and River Shoreline Scenarios, PNNL-16531, Pacific Northwest
111 National Laboratory.
- 112 Shetaya, W.H., Young, S.D., Watts, M.J., Ander, E.L., Bailey, E.H., 2012. Iodine
113 dynamics in soils. Geochimica Et Cosmochimica Acta 77, 457-473.
- 114 Shimamoto, Y.S., Takahashi, Y., Terada, Y., 2011. Formation of Organic Iodine Supplied
115 as Iodide in a Soil-Water System in Chiba, Japan. Environmental Science &
116 Technology 45, 2086-2092.
- 117 Sparks, D.L., 1996. Methods of Soil Analysis, Part 3 - Chemical Methods. Madison, WI,
118 Soil Science Society of America, Inc.

- 119 Steinberg, S.M., Kimble, G.M., Schmett, G.T., Emerson, D.W., Turner, M.F., Rudin, M.,
120 2008a. Abiotic reaction of iodate with sphagnum peat and other natural organic
121 matter. *J. Radioanal. Nucl. Chem.* 277, 185-191.
- 122 Steinberg, S.M., Schmett, G.T., Kimble, G., Emerson, D.W., Turner, M.F., Rudin, M.,
123 2008b. Immobilization of fission iodine by reaction with insoluble natural organic
124 matter. *J. Radioanal. Nucl. Chem.* 277, 175-183.
- 125 Takata, H., Zheng, J., Tagami, K., Aono, T., Fujita, K., Yamasaki, S., Tsuchiya, N.,
126 Uchida, S., 2013. Distribution coefficients (K_d) of stable iodine in estuarine and
127 coastal regions, Japan, and their relationship to salinity and organic carbon in
128 sediments. *Environ Monit Assess* 185, 3645-3658.
- 129 Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the
130 speciation of particulate trace metals. *Analytical Chemistry* 51, 844-851.
- 131 Um, W., Serne, R.J., Krupka, K.M., 2004. Linearity and reversibility of iodide adsorption
132 on sediments from Hanford, Washington under water saturated conditions. *Water*
133 *Research* 38, 2009-2016.
- 134 Xu, C., Chen, H., Sugiyama, Y., Zhang, S., Li, H.-P., Ho, Y.-F., Chuang, C.-y., Schwehr,
135 K.A., Kaplan, D.I., Yeager, C., Roberts, K.A., Hatcher, P.G., Santschi, P.H., 2013.
136 Novel molecular-level evidence of iodine binding to natural organic matter from
137 Fourier transform ion cyclotron resonance mass spectrometry. *Science of the Total*
138 *Environment* 449, 244-252.
- 139 Xu, C., Miller, E.J., Zhang, S.J., Li, H.P., Ho, Y.F., Schwehr, K.A., Kaplan, D.I., Otosaka,
140 S., Roberts, K.A., Brinkmeyer, R., Yeager, C.M., Santschi, P.H., 2011a. Sequestration
141 and Remobilization of Radioiodine (I-129) by Soil Organic Matter and Possible
142 Consequences of the Remedial Action at Savannah River Site. *Environmental*
143 *Science & Technology* 45, 9975-9983.

- 144 Xu, C., Zhang, S., Ho, Y.-F., Miller, E.J., Roberts, K.A., Li, H.-P., Schwehr, K.A., Otosaka,
145 S., Kaplan, D.I., Brinkmeyer, R., Yeager, C.M., Santschi, P.H., 2011b. Is soil natural
146 organic matter a sink or source for mobile radioiodine (^{129}I) at the Savannah River
147 Site? *Geochimica et Cosmochimica Acta* 75, 5716-5735.
- 148 Xu, C., Zhong, J.Y., Hatcher, P.G., Zhang, S.J., Li, H.P., Ho, Y.F., Schwehr, K.A., Kaplan,
149 D.I., Roberts, K.A., Brinkmeyer, R., Yeager, C.M., Santschi, P.H., 2012. Molecular
150 environment of stable iodine and radioiodine (I-129) in natural organic matter:
151 Evidence inferred from NMR and binding experiments at environmentally relevant
152 concentrations. *Geochimica Et Cosmochimica Acta* 97, 166-182.
- 153 Yamaguchi, N., Nakano, M., Takamatsu, R., Tanida, H., 2010. Inorganic iodine
154 incorporation into soil organic matter: evidence from iodine K-edge X-ray
155 absorption near-edge structure. *Journal of Environmental Radioactivity* 101, 451-457.
- 156 Zachara, J., Brown, C., Christensen, J., Davis, J.A., Dresel, E., Liu, C., Kelly, S., McKinley,
157 J., Serne, J., Um, W., 2007a. A site-wide perspective on uranium geochemistry at the
158 Hanford Site., Pacific Northwest National Laboratory, Richland, WA.
- 159 Zachara, J.M., Serne, J., Freshley, M., Mann, F., Anderson, F., Wood, M., Jones, T., Myers,
160 D., 2007b. Geochemical processes controlling migration of tank wastes in Hanford's
161 vadose zone. *Vadose Zone J.* 6, 985-1003.
- 162 Zhang, S., Du, J., Xu, C., Schwehr, K.A., Ho, Y.F., Li, H.P., Roberts, K.A., Kaplan, D.I.,
163 Brinkmeyer, R., Yeager, C.M., Chang, H.S., Santschi, P.H., 2011. Concentration-
164 Dependent Mobility, Retardation, and Speciation of Iodine in Surface Sediment from
165 the Savannah River Site. *Environmental Science & Technology* 45, 5543-5549.
- 166 Zhang, S., Schwehr, K.A., Ho, Y.F., Xu, C., Roberts, K.A., Kaplan, D.I., Brinkmeyer, R.,
167 Yeager, C.M., Santschi, P.H., 2010. A Novel Approach for the Simultaneous
168 Determination of Iodide, Iodate and Organo-Iodide for I-127 and I-129 in
169 Environmental Samples Using Gas Chromatography-Mass Spectrometry.
170 *Environmental Science & Technology* 44, 9042-9048.

- 171 Zhang, S., Xu, C., Creeley, D., Ho, Y.-F., Li, H.-P., Grandbois, R., Schwehr, K.A., Kaplan,
172 D.I., Yeager, C.M., Wellman, D., Santschi, P.H., 2013. Iodine-129 and Iodine-127
173 Speciation in Groundwater at the Hanford Site, U.S.: Iodate Incorporation into
174 Calcite. *Environmental Science & Technology* 47, 9635-9642.