Laboratory report on iodine (^{129}I and ^{127}I) speciation, transformation and mobility in Hanford groundwater, suspended particles and sediments

P. H. Santschi[a], C. Xu[a], S. Zhang[a], Y. -F. Ho[a], H.-P. Li[a], K. A. Schwehr[a], D. I. Kaplan[b]

[a] Texas A&M University, Galveston, TX 77551
[b] Savannah River National Laboratory, Aiken, SC 29808

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Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

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EXECUTIVE SUMMARY

The Hanford Site in eastern Washington produced plutonium for several decades and in the process generated billions of gallons of radioactive waste. Included in this complex mixture of waste was 50 Ci of iodine-129 (^{129}I). Iodine-129's high abundance, due to its high fission yield, and extreme toxicity result in iodine-129 becoming a key risk driver at many Department of Energy (DOE) sites. The mobility of radioiodine in arid environments, such as the Hanford Site, depends largely on its chemical speciation and is also greatly affected by many other environmental factors, especially natural sediment organic matter (SOM). Groundwater radioiodine speciation has not been measured in arid regions with major plumes or large disposed ^{129}I inventories, including the Hanford Site, Idaho National Laboratory, and Nevada Test Site. In this study, stable iodine-127 and radioiodine-129 speciation, pH, and dissolved organic carbon (DOC) of groundwater samples collected from seven wells located in the 200-West Area of the Hanford site were investigated. The most striking finding was that iodate (IO_3^-) was the most abundant species. Unexpectedly, iodide (I^-), which was likely the form of iodine in the source materials and the expected dominant groundwater species based on thermodynamic considerations, only accounted for 1-2% of the total iodine concentration. It is likely that the relatively high pH and the low abundance of sedimentary organic matter (SOM) that is present at the site slowed down or even inhibited the reduction of iodate, as SOM abiotically reduce iodate into iodide (Xu et al., 2011a).

Moreover, a study on the kinetics of iodide and iodate uptake and aqueous speciation transformation by three representative subsurface Hanford sediments was performed over a period of about one month. This study was carried out by using iodide-125 or iodate-125 at the ambient iodine-127concentration found at the site. Iodate K_d values were on average 89% greater than iodide K_d values, and the K_d values for both species tended to increase with the amount of organic carbon (OC) present in the sediment. It is especially noteworthy that this trend existed at the very low OC concentrations that naturally exist in the Hanford sediments. Iodine and OC can form essentially irreversible covalent bonds, thereby providing a yet unstudied ^{129}I retardation reaction at the Hanford Site. In addition to the transformation of iodine species, the sediment collected from the vadose zone also released stable iodide into the aqueous phase. It was found that the three sediments all took up the ambient iodate from the groundwater and slowly transformed it into iodide under the laboratory conditions, likely dependent on the abundance of reducing agents such as organic matter and Fe^{2+}. Therefore two competitive iodine processes were identified, the tendency for the sediment to reduce iodate to iodide, and the groundwater chemistry to maintain the iodine as iodate, presumably it is largely the result of natural pH and dissolved O_2/Eh levels.

Suspended carbonate (and silica) particles collected from Hanford groundwater contained elevated amounts of iodine (142 ± 8 µg/g iodine), consisting mainly of iodate (>99%). Iodate was likely incorporated into the carbonate structure during calcite precipitation upon degasing of CO_2 as the groundwater samples were removed from the subsurface. This concentration of groundwater iodate in precipitated carbonate has implication to long-term fate and transport of ^{129}I and on active in-situ ^{129}I groundwater remediation. This study provides some of the first groundwater radioiodine speciation studies conducted in arid environments and provides much needed mechanistic descriptions to permit making informed decisions about low-cost/high intellectual input remediation options, such as monitored natural attenuation, or long-term stewardship of nuclear waste disposal sites.

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DOC	Dissolved organic carbon
I^-	Iodide
IO_3^-	Iodate
K_d	Partitioning coefficient
K_d'	Desorption partitioning coefficient
OC	Organic carbon
SRNL	Savannah River National Laboratory
TOC	Total organic carbon

1.0 Introduction

^{129}I has been recognized as a high risk radionuclide in groundwater at most low-level and high-level radionuclide disposal sites, including locations at Hanford, Savannah River (SRS) and Idaho (Denham et al., 2009). This high risk stems mainly from its long half-life (16 M years), relatively high mobility, and the large inventory at these sites. Furthermore, iodine has biophilic properties, which permit it to highly concentrated in human thyroids. Some of these factors have contributed to ^{129}I having the lowest permissible maximum contaminant level (MCL) of 1 pCi/L in groundwater among all radionuclides.

The Hanford Site, located in southeastern Washington State along the Columbia River, was established by the U.S. Department of Energy as the home of nine previous nuclear reactors built beginning in 1943. These reactors were responsible for producing plutonium needed for the development of atomic weapons for the Manhattan Project during World War II and throughout the Cold War. The reactors at this site produced plutonium from 1944 to 1987, but are currently no longer used for this purpose. During this forty-three year period billions of gallons of liquid nuclear waste and millions of tons of solid waste were produced from the plutonium production. Today, the Hanford site is the most contaminated nuclear waste site in the U.S. and is the focal point of extensive environmental cleanup projects. The Hanford Site is located in an arid environment with an average annual precipitation of only 16 cm/yr. The stratigraphy at the site consists of bedded alluvial plain sediments with sand and gravels. Its surface groundwater has an average pH of ~7.7 and an aqueous chemistry that is dominated by carbonate (and hydroxide), which are in equilibrium with calcite (Zachara et al., 2007b). The dominant cation is calcium and its ionic strength is of the order of 50 mM. Its fine-grained clay is dominated by 2:1 minerals, such as smectites, micas and vermiculites, and its total carbonate concentration is generally of the order of 2% $CaCO_2$. Sediment particles commonly have carbonate and Fe-oxide coatings (Zachara et al., 2007b).

A key factor that determines the mobility of iodine in the environment is its chemical speciation. In terrestrial systems, iodine exists mainly as iodide (I^-), iodate (IO_3^-) and organo-iodine (OI), of which the inter-conversion is primarily dependent on a number of factors, e.g., redox potential, pH, the presence of organic matter and/or iron and manganese oxide, as well as microbial enzymatic activity (Denham et al., 2009). The classic Eh-pH stability diagram (Fuge, 1986) (Figure 1) shows iodide extends almost over the entire pH and Eh range of water in the natural environment, thus it is commonly assumed to be the dominant species in the terrestrial water, especially in the less oxygenated deep groundwater or aquifer. However, recent field studies of the SRS groundwater indicate significant amounts of iodate and organo-iodine, accounting for comparable or even higher proportion of the total iodine in the aqueous phase (Kaplan et al., 2011; Otosaka et al., 2011b; Xu et al., 2011a; Zhang et al., 2011; Zhang et al., 2010), which could also be true for the Hanford site. It is important to note that the Hanford formation has 200-2000 mg kg^{-1} carbon (0.02-0.2wt- % organic carbon (OC)), which is about seven to eight orders-of-magnitude greater in molar concentration than the greatest plume concentrations of 20 pCi/L ^{129}I (MCL = 1 pCi/L = 6x10^{-6} ppm) (Kaplan et al., 2012). However, it is not known whether the low OC concentration in the Hanford subsurface would be sufficient to significantly influence the sorption and retardation of ^{129}I.
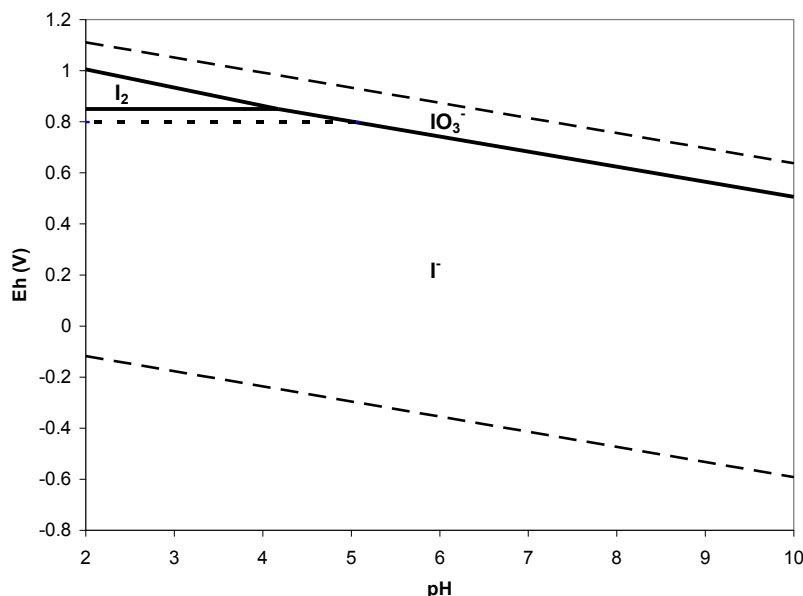
Figure 1. Eh-pH diagram of aqueous iodine speciation; solid line = total iodine concentration of 1 µg/L, a typical groundwater concentration, dotted line = total iodine concentration of 58 µg/L, a typical concentration; dashed lines are stability limits of water (note that organo-iodine species are not included in these calculations).

The overall objectives of this study were to conduct laboratory studies to provide information that could be used to generate a species-based, biogeochemical [129]I conceptual model for the Hanford Site. The specific objectives were to determine: 1) the [127]I and [129]I speciation (iodide, iodate and organo-iodine) in the groundwater and explore the key factors that might affect the speciation; 2) the role of sediments, collected from different depths (vadose zone vs. saturated zone) and of different composition (silt vs. sand), in sequestering radioiodine, by assessing how the newly-introduced inorganic iodine partitions among the particulate (sediment, > 0.45 µm), colloidal (3 kDa- 0.45 µm) and truly dissolved phases (<3 kDa); 3) iodine species transformation in the dissolved phases in the soil-water system and the re-mobilization of radioiodine during surface runoff, groundwater exfiltration/infiltration, storm-induced events. A newly-developed GC-MS technique (Zhang et al., 2010) was used to simultaneously measure [127]I and [129]I speciation in the groundwater. For the latter two objectives, our approach was to use ^{125}I as the analogue of [129]I, dosed at the average chemical concentration of [129]I, which was obtained from the first objective. The GC-MS technique (Zhang et al., 2010) and a liquid scintillation counting method (Xu et al., 2011a) was combined to simultaneously measure [127]I and ^{125}I in both aqueous and solid phases, which allowed us to compare the behavior of both isotopes in the same experiment. The intent of this research is to provide data that would provide input for making remediation decisions related to the >50 km² [129]I plumes in the Hanford Central Plateau region.

2.0 Materials and methods

2.1 Iodine speciation analysis by GC-MS

Determination of iodide, iodate, and organo-iodine of both iodine isotopes (^{127}I and ^{129}I) followed the method of Zhang et al. (2010). Using this analytical method, the detection limits of iodide-127, iodate-127, and organo-iodine-127 were 0.34 nM, 1.11 nM, and 2.75 nM, respectively, whereas the detection limits for both iodide-129 and iodate-129 was 0.08 nM (i.e., 2 pCi ^{129}I/L). The detection limit for organo-iodine-129 was 0.2 nM (i.e., 5pCi ^{129}I/L). In this study, all data were reported based on duplicate or triplicate measurements. Error for iodine speciation analysis was usually less than 5%. In addition, the error for elemental analysis (C,H,N) for acidified samples (to measure the organic elements) was usually less than 15%, whereas that for unacidified samples (to measure total elements) was usually less than 5%.

2.1.1 *Equipment.*

GC-MS instrumentation consisted of an autosampler AS3000, Finnigan Trace GC and Polaris Q EI-MS from Thermo. A TR-5MS capillary column (30m×0.25 mm id, 0.25 μm) was used for separation. The injector temperature was 220 °C and 2 μL sample injections were made in the splitless mode. For each sample run, the oven temperature was held at 90°C for 3 minutes and then increased to 220°C at a rate of 30 °C/min. The GC transfer line was set at 280 °C. The MS ion source temperature was set to 250°C. All the mass spectra were collected in full scan mode. Thermo Xcalibur^{TM} software was used for data acquisition and processing. Quantification of ^{127}I and ^{129}I was based on the different mass of their respective derivatives in the mass spectrum (247 for ^{127}I and 249 for ^{129}I), which were used as the "screening filter" to distinguish their respective responses in the gas chromatograms.

2.1.2 *Reagents and Standard Solutions*

Sodium 2-iodosobenzoate reagent was prepared by mixing 200 mg of free benzoic acid (Alfa Aesar, U.S.) with 3.8 mL of 0.2 M sodium hydroxide on a Touch Mixer (model 231, Fisher Scientific) and diluted to 50 mL with ultrapure water. The solution was filtered through a 0.45 μm polycarbonate membrane. This solution is stable for at least 4 months when stored at ambient temperature. N,N-dimethylaniline solution was prepared by diluting 20 μL of N,N-dimethylaniline to 10 mL with methanol. Phosphate buffer (pH 6.5) was prepared by dissolving 10 g each of $NaH_2PO_4 \cdot H_2O$ and $Na_2HPO_4 \cdot 7H_2O$ in 250 mL of ultrapure water. Fresh solutions of 0.01 M of $Na_2S_2O_5$ were prepared daily by dissolving 0.019 g of sodium metabisulfite (Fisher Scientific) in 10 mL of ultrapure water. An internal standard stock solution was prepared by dissolving 25 mg of 2,4,6-tribromoaniline in 50 mL of methanol. The working internal standard solution was prepared by adding 50 μL of the stock solution to 10 mL methanol. To prepare an iodide stock solution (1000 mg/L), 65.4 mg of potassium iodide was dissolved in 50 mL of ultrapure water. An iodate stock solution (1000 mg I- eq/L) was prepared by dissolving 84 mg of potassium iodate in 50 mL of ultrapure water. Both the iodide and iodate stock solutions were stored in glass vials at 4 °C in light-proof containers and were stable for one week.

2.1.3 *Determination of Iodide in Aqueous Samples*

A 5 ml aliquot of sample or iodide standard solution was mixed with 0.5 mL of 1% acetic acid and 1 ml of phosphate buffer in a culture tube (16×150mm). Internal standard (50 μL), N,N-dimethylaniline solution (50 μL), and 2-iodosobenzoate solution (0.4 mL) were then added to each tube and shaken on a Touch Mixer for 1 minute. Next, cyclohexane (0.5 mL) was added to the tubes and shaken on a Touch Mixer for 20 seconds. The top cyclohexane layer was removed and placed into an auto sampler vial for GC-MS analysis.

2.1.4 *Determination of Iodate in Aqueous Samples*

A 5 mL aliquot of sample or standard was mixed in a culture tube (16×150mm) with 50 µL of 1M HCl and 100 µl of 0.01 M sodium meta-bisulfite. This solution was reacted at room temperature for 30 minutes. Next, 1 mL of phosphate buffer was added and mixed. Internal standard (50 µL), N,N-dimethylaniline solution (50 µL), and 2-iodosobenzoate solution (1.0 mL) were added, and the solution was shaken on a Touch Mixer for 1 minute. The solutions were then extracted with cyclohexane for GC-MS analysis, as described in the previous section. Iodate concentrations were then calculated by difference using the iodide concentrations before and after $Na_2S_2O_5$ treatment.

2.1.5 *Determination of Organo-iodine in Groundwater*

The organo-iodine concentration was determined by calculating the difference between total iodine and total inorganic iodine. Total iodine concentration was determined by combustion of aqueous samples. Aqueous sample (2.0 mL) was mixed with 100 mg of vanadium pentoxide (vanadium pentoxide acts as a catalyst for the rapid combustion of environmental samples) in a porcelain combustion boat. The boat with the sample was placed into a quartz combustion tube and subjected to combustion on a tube furnace (Lindberg/Blue M Mini-Mite, Thermo Scientific). The temperature of the furnace was programmed as follows: the temperature was ramped up from room temperature to 200°C over 1 minute and held for 8 minutes. After that, the temperature of the furnace was again increased to 900°C over 10 minutes and then held steady for an additional 10 minutes. Oxygen was used as a carrier gas during the combustion at a flow rate of 200-250 mL/minute. A glass tube containing 1 mL of ultrapure water was used as a receiver. The carrier was directed into the receiver by connecting glass tubing with the tapered end of the quartz combustion. After combustion, the furnace was cooled down to 700°C and then the receiver containing the water was moved to a nitrogen stream and was blown for additional 30 minutes at the same rate of oxygen. Then the glass tubing and the tapered end of the combustion tube were rinsed twice with 0.75 mL and 0.5 mL of ultrapure water, respectively. The rinses were combined with the receiving solution (~6 mL final volume) and subjected to the iodate quantification as described above.

2.1.6 *Determination of Total Iodine in Sediment*

The procedure for the determination of total iodine in aqueous samples can be applied to the measurement of total iodine in sediments by appropriate modifications of the temperature program. A 5-mg aliquot of dry soil was mixed with 100 mg vanadium pentoxide and combusted. The combustion temperature was increased to 300°C over the course of 1 minute and then held constant for 3 minutes. After that, the temperature of the furnace was increased to 850°C over a 10 minute period and then held steady for an additional 5 minutes. The rate of oxygen was reduced to 100 mL/minute. Additionally, a glass tube containing 2 mL of ultrapure water was used as a receiver.

2.2 <u>Iodate-125 preparation from iodide-125</u>

Carrier-free ^{125}I was purchased in the form of NaI from MP Biomedical, USA. $^{125}IO_3^-$ was prepared from ^{125}I by combustion and oxidation of $Na^{125}I$. 0.5 mL of Milli-Q water and 5 µL of $Na^{125}I$ (45 µCi) was mixed with 100 mg V_2O_5 and combusted with a programmed procedure (Zhang et al., 2010). Oxygen flow was adjusted to 100 mL/min to ensure the well-oxidation of iodide. Still, the conversion was only 50% (i.e., I^-:IO_3^-=1:1). Thus a Strata X_A 33u polymeric strong anion exchange column (Phenomenex, USA, Cat #: 8B-S123-EBJ) was used to separate I^- from IO_3^-. The column was first conditioned with 2 mL methanol and then 2 mL Milli-Q water. After combustion and rinsing, 2 mL of the solution was loaded on the column and then eluted with 20 mM ammonium acetate. No I^- was detected in the eluate according to the speciation analysis. The purpose of using combustion method instead of other chemical conversion is to minimize the interference from other chemicals during iodine uptake experiment.

2.3 Sampling of Groundwater

Eighteen 1 L groundwater samples collected from seven wells of the Hanford Site were shipped from Pacific Northwest National Laboratory (PNNL) in April 2012 and store at -4°C before analysis. The seven wells were 299-W14-11, 299-W14-13, 299-W14-15, 299-W11-43, 299-W11-88, 699-36-70B, 699-38-70B, respectively (Figure 2).
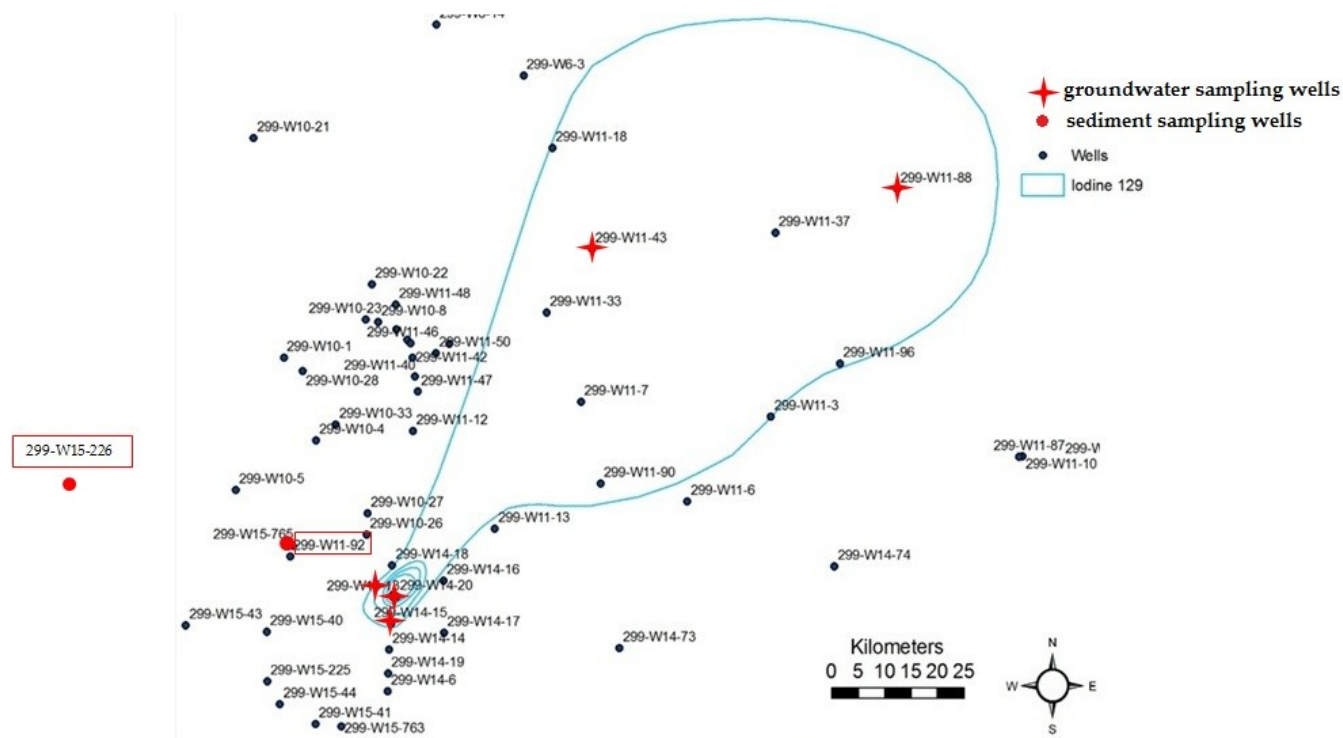
Figure 2. Sampling map for groundwater and sediments at the 200-West Area on the Hanford Site. (Two wells, 699-36-70B and 699-38-70B are not shown in this map.

2.4 Iodide and iodate (ad)sorption/desorption study: Air-sealed environment

The three Hanford sediments were sampled from wells 299-W11-92 and 299-W15-226, and named "H1, H2 and H3" for convenience (Figure 2). These three sediments were collected at different depths and horizons, thus providing an opportunity to examine the influence of organic matter, clay mineralogy and texture on sorption and transport behavior of iodine species.

> **H1**: This sample is a composite of fine-grained sediments, mostly silt, from the vadose zone of two different wells (30-38 m from well 299-W11-92 and 38- 41 m from well 299-W15-226). There may be some natural calcium carbonate cementation in the sediment.
> **H2**: Sand from two different depths of the saturated zone within one well (102-113 m depth from well 299-W11-92)

H3: Composite of silt and clay from the saturated zone of two wells (136-142 m depth from well 299-W11-92 and 123-128 m depth from well 299-W15-226).

Oven-dried (60 °C), 2-mm sieved sediment was mixed with Hanford groundwater at a realistic solid to water ratio of 1:4 (Hu et al., 2005). Uptake and transformation of inorganic iodine was monitored in three treatments for each sediment: 1) control (without any iodine addition), 2) an initial $^{125}I^-$ activity of 3×10^7 Bq/L, 3) an initial $^{125}IO_3^-$ activity of 3×10^7 Bq/L. Carrier free $^{125}I^-$ and $^{125}IO_3^-$, as analogues for ^{129}I, was added to each reaction vessel. A series of 40 mL sediment slurries were gently shaken with an orbital shaker at ~120 rpm in 50 mL centrifuge tubes containing minimal headspace. Sampling of duplicate tubes for each treatment occurred after 3, 7, 14, 21, and 28 days. Particles were allowed to settle by low-speed (~3200 g) centrifugation and the supernatant was immediately filtered by using sterile disposable vacuum filter/storage systems (Corning, USA). The filtrate (< 0.45 µm) was ultrafiltered through an Amicon Ultra-15 centrifugal device with a cut-off of 3 kDa.

Sediments from the 21 and 28 day uptake experiments were used in the desorption K_d studies. It was assumed that iodide or iodate uptake onto these triplicated sediment systems had reached equilibrium. The 21-day sediment samples were re-suspended in 5 mL 0.1 M KI prepared in Hanford groundwater. The 28-day sediment samples were re-suspended with 5 mL 0.1 M KCl in Hanford groundwater. KI or KCl solution was also added to the control sample tubes (groundwater amended with $^{125}I^-$ and $^{125}IO_3^-$ without any sediments) to monitor if any iodide or iodate sorbed to the sample container walls. All desorption experiments were carried out for two weeks.

2.5 Iodide and iodate (ad)sorption/desorption studies: Open-air environment

10 g of Hanford sediments were mixed with 40 mL groundwater to reach a solid: water ratio of 1:4, in a 500 mL Teflon beaker. Uptake and transformation of inorganic iodine was observed in three treatments for each sediment: 1) control (without any iodine addition), 2) an initial $^{125}I^-$ activity of 3×10^7 Bq/L, 3) an initial $^{125}IO_3^-$ activity of 3×10^7 Bq/L. The beaker was capped with holes on top to allow the air to contact the sediment slurry. As opposed to the previous K_d experiment, which was performed with closed 50 mL centrifuge tubes, the sediment-water slurry in the open-air experiment was quite shallow (~ 1 cm depth), therefore it was less likely that any anoxic conditions could have developed during the experimental time frame. The beakers were placed on an orbital shaker at room temperature for 22 days. Samples were processed the same way as described in the previous section to determine the $^{125}I^-$ and $^{125}IO_3^-$ uptake by the sediment as well as the speciation in the aqueous phase.

2.6 Determination of iodine speciation by liquid scintillation counting

The permeate (< 3 kDa) fraction was analyzed for iodide, iodate, and organo-iodine speciation. The derivation method was the same as that described by Zhang et al. (2010). Basically, iodide was oxidized by 2-iodosobenzoate to iodine (I_2), which was then subsequently iodinated with N,N-dimethylaniline to become 4-iodo-dimethylaniline. The resulting derivative was extracted by cyclohexane and then detected by liquid scintillation counting for ^{125}I activity (Xu et al., 2011a). Iodate was converted to iodide first by sodium meta-bisulfite, followed by the same reaction as iodide and calculated as the difference between total inorganic iodine and iodide. Organo-iodine was calculated as the difference between total iodine (measured by the ^{125}I counting of the bulk solution) and total inorganic iodine.

Iodine uptake into the >3 kDa fraction was detected by liquid scintillation counting for total activity, while the iodine uptake into the >0.45 μm was calculated by difference from the mass balance (i.e., total added iodine minus iodine in the other two fractions).

2.7 <u>Characterization of Hanford suspended particles and sediments</u>

Groundwater was filtered through pre-weighed polycarbonate filter (0.2 μm). Suspended particles captured by the filter were dried at 50 °C and weighed. The total C, H, and N contents of sediments and suspended particles were determined with a Perkin Elmer CHNS 2400 analyzer. Acetanilide (71.09% C, 6.71% H, 10.36% N) was used as an analytical standard. In order to measure the organic carbon (OC) content, samples were weighed in a silver capsule and acidified directly with 200 μL 1 N HCl to remove inorganic C and then transferred to a 60 °C oven to remove the acid. This was repeated again to insure complete inorganic C removal. The whole sample tray was allowed to stay in the 60 °C oven overnight to eliminate the acid completely. Inorganic carbon was calculated as the difference between total carbon and organic carbon (Xu et al., 2011b).

For silica contents of the three groundwater suspended particles, 5-10 mg of samples were weighed into Teflon tube and 4.5 mL of TMAH (10%) was added. The digestion mixture was heated at 95 °C for over 12 hours (Hauptkorn et al., 2001). SiO_2 standard was also digested the same time as the samples and measured for silicate to see the recovery rate of the procedure. It turned out that recovery rate was approximately 100%. Silicate contents of the digested samples were measured with a colorimetric method (Parsons et al., 1984; Strickland and Parsons, 1972).

The operational definition of sediment inorganic iodine was to extract a re-suspension of 2 g sediment particles with 10 ml 0.005 M KCl solution and shake on an orbital shaker at 180 rpm for one hour (Hu et al., 2007). The sediments were then separated from the aqueous phase by centrifugation. An additional extraction of 0.1 M KCl solution was performed with the residual sediment, to determine if any more ion-exchangeable iodide or iodate was released.

3.0 Results and Discussion

3.1 <u>Iodine speciation of groundwater at the Hanford site</u>

At the Hanford site where the pH is 7.6~7.9 and dissolved organic carbon (DOC) is 15~63 μM, iodate was found to be the most abundant stable iodine species in groundwater followed by organo-iodine, except in the groundwater from well 299-W11-88 where no organo-iodine was detected and DOC was 15.6 μM (Table 1).. Iodide only accounted for 1-2% of the total iodine (Table 1). For [129]I, only iodate was detected, iodide and organo-iodine concentrations were so low that they were below the detection limits of the methods. The ratio of $^{129}IO_3/^{127}IO_3$ was in the order of 0.001-0.006, which is 10 times less than that for the SRS site groundwater (Otosaka et al., 2011a), partly due to the higher $^{127}IO_3^-$ concentrations at Hanford.

Despite the fact that the environmental factors influencing the iodine speciation have not been identified, the relatively high pH values and low sediment organic matter content in Hanford Site would be expected to slow down or even inhibit the reduction of iodate by organic matter (Xu et al., 2011a), and thus might account for the dominance of iodate in the Hanford site groundwater.

In addition, the total ^{127}I concentration of the Hanford site groundwater decreased significantly with increasing distance from the disposal cribs (Figure 2 and Table 1), suggesting that dilution and/or absorption have taken place as the groundwater moves along the flow path.

Table 1. Iodine speciation of the Hanford Site groundwater.

	Approx. Distance (m)	DOC μM	pH	I-127						I-129		
				Iodide nM	Iodate nM	Organo-I nM	Iodide %	Iodate %	Organo-I %	Iodide pCi/L	Iodate pCi/L	Organo-I pCi/L
299-W14-11	20	50.2	7.7	14.6	706.6	65.7	1.9	89.8	8.3	<DL [a]	31.6	<DL
299-W14-13	20	63.0	7.7	12.2	481.2	83.5	2.1	83.5	14.4	<DL	35.6	<DL
299-W14-15	70	25.5	7.9	11.6	347.3	150.9	2.3	68.1	29.6	<DL	<DL	<DL
299-W11-43	720	37.2	7.6	1.8	134.9	31.0	1.1	80.5	18.4	<DL	<DL	<DL
299-W11-88	1150	15.6	7.8	1.7	140.8	0.0	1.2	98.5	0.0	<DL	6.6	<DL
699-38-70B	2300	35.3	7.8	10.8	66.3	29.1	10.2	61.9	27.9	<DL	6.9	<DL
699-36-70B	2700	21.5	7.8	2.4	76.5	12.5	2.6	84.1	13.2	<DL	12.6	<DL

[a] DL: Detection limit, DL for Organo-127 was 2.75 nM, for I^--129 and IO_3^--129 was 2 pCi/L, and for Organo-I-129 was 5 pCi/L.

3.2 <u>Characteristics of three representative sediments in the iodine K_d experiment</u>

The characterization of both groundwater and sediments used in this experiment are listed in Table 2 and Table 3, respectively. Groundwater consisted predominantly of iodate (94%) and minor amounts of iodide and organo-iodine, suggesting that the redox potential of the groundwater at the Hanford site would be expected to be over 700 mV, in order to keep iodate to be the dominant species at slightly alkaline conditions (Figure 1). Such an extraordinarily high redox potential is unlikely, and likely reflects the fact that Figure 1 does not accurately describe the Hanford subsurface system because it does not include organic matter, microbial activity, and/or the system is not in equilibrium (Kaplan et al., 2012).

Table 2. Groundwater used for sediment groundwater resuspension experiment (groundwater was collected from well 299-W11-88 and 299-W14-11 and mixed in a ratio of 2:1).

	DOC µM	pH	$^{127}I^-$ (µg/L)	$^{127}IO_3^-$ (µg/L)	O-$^{127}I^-$ (µg/L)	$^{127}I^-$ (%)	$^{127}IO_3^-$ (%)	O-^{127}I (%)
Groundwater	25.2	7.7	0.76	41.7	1.8	1.7	94.1	4.1

OI = organo-iodine

The sediment collected from the deepest saturated zone in this study (H3) and the one from the vadose zone contained ten times higher organic carbon than the one from intermediate depth of the saturated zone (H2) (Table 3). This can also be explained by their different sediment textures: H1 and H3 consisted of silt and clay, whereas H2 consisted of sand. The release of mobile organic carbon into the aqueous phase during the iodine K_d experiment reached equilibrium on day 3: sediment H1 had the highest dissolved organic carbon (DOC; which can be thought of as the mobile OC fraction), followed by sediment H3. Sediment H2 did not release significant amounts of mobile OC. Total iodine contents of the three sediments followed the same order as that of DOC.

The properties of these sediments are largely representative of those from borehole W10-35 located in the Central Plateau of the Hanford Site (see Appendix A). Of 21 sediments from this borehole, the pH averaged 9.1 ± 0.5 and the organic carbon ranged from 0.053 to 0.549 % of the silt+clay sediment fraction, with an average of 0.210 ± 0.134%. The organic carbon concentrations reported in Table 3 are on the lower end of this scale because they were measured on the <2 mm sediment fraction (and not the <0.053 mm fraction as presented in Appendix A) and the lower specific surface area may contain less organic carbon binding sites on a mass basis.

Table 3. Sediment characteristics used for sediment groundwater resuspension experiments.

Sedi-ment	OC (%)	Inorganic C (%)	DOC* (μM)	Total iodine (μg/g)	Gravel/sand/silt/ clay (%)	pH	Composition	Location	Depth (m)
H1	0.12	0.92	284±33	4.75±0.06	8.0/71.6/20.0/0.50	8.61	Silt & Clay, fine-grained, mostly silt, maybe some natural calcium carbonate cementation (299-W11-92 and 299-W15-226)	Vadose zone	30.5-41.1
H2	0.04	0.01	0	0.40±0.39	30.0/69.8/0.3/0.002	8.51	Sand from two depths of a single well (299-W11-92)	Vadose zone	102.1-112.8
H3	0.15	0.18	94±17	1.85±0.35	28/72.1/0.3/0.78	7.90	Silt & Clay from two different wells (299-W11-92 and 299-W15-226)	Saturated zone	123.4-141.7

DOC* means the total organic carbon released from the sediment to the aqueous phase (<0.45 μm) during the sediment groundwater resuspension experiment, after it reached equilibrium on day 21.

Inorganic iodine accounted for only 1.34% of the total iodine in sediment H1, 10.06% in sediment H2 and 0.17% in sediment H3 (Table 4). The remaining iodine was organically bound or iodine trapped in intragranular positions (i.e., could not be extracted with 0.1 M KCl). Iodide and iodate were both present in comparative proportions of the total inorganic iodine species (Table 4).

Table 4. Speciation of the sediment bound iodine.

Sediment	Inorganic iodine (µg/g)				Total iodine	Total ion-exchangeable inorgnic iodine in total iodine (%)
	1st extraction with 0.005 M KCl		2nd extraction with 0.1 M KCl			
	iodide	iodate	iodide	iodate	(µg/g)	
H1	0.009	0.015	0.006	0.024	4.75±0.06	1.34
H2	0.014	0.008	0.002	0.001	0.40±0.00	10.06
H3	<DL	<DL	0.003	<DL	1.85±0.35	0.17

DL: detection limit.

3.3 Characteristics of three representative groundwater suspended particles

It was discovered while filtering the groundwater samples that there were suspended solids that were very fine and appeared homogeneous in size and color (Table 5). The particles were mostly soluble in 1 N HCl and partially dissolved in 55% NaOH solution. Our hypothesis is that these suspended particles consisted of carbonate and silica, based on the carbon and silica analysis and considering the geological characteristics of Hanford site (Table 5). The carbonate particles could have formed from degassing of CO_2 upon collection of the groundwater supersaturated with CO_2. The concentrations of these suspended particles were >100 mg/L (Table 5). Analytical work of characterizing these particles is still on-going. Calcite formation in groundwater samples recovered from the Hanford subsurface has previously been reported (Zachara et al., 2007a).

Total iodine content analysis indicated that these particles were greatly enriched in iodine (142 ±8 µg/g), about 30 times greater than sediment H1, which had the highest total iodine content of all the sediments that were tested (Table 3 and Table 5). In order to learn what compounds in the suspended particles were responsible for iodine uptake, parallel extractions of the suspended particles with 0.005 M KCl, 1 N HCl and 55% NaOH were performed, by re-suspending ~10 mg of the particles with 500 µL of each solution overnight on a vortexer. Speciation analysis showed that the 1 N HCl extracted the most iodine, which is exclusively composed of iodate (Table 5). However, the three parallel extractable fractions only accounted for 42% of the total iodine of the suspended particles. The unextracted fraction may be the result of the formation of volatile species after adding 1 N HCl, as significant amounts of CO_2 were formed which could have 'purged' other volatiles out of the solution at such low pH (Figure 1). This will require further study.

Table 5. Inorganic carbon, organic carbon and total iodine contents of the three representative groundwater suspended particles as well as the parallel extraction and iodine analysis of one suspended particle collected from Well 299-W11-88.

	Well ID	Conc. (mg/L)	Inorganic carbon (%, wt)	Organic carbon (%, wt)	Total iodine (µg/g)	SiO$_2$	Estimated CaCO$_3$ based on inorganic carbon value
S1	299-W11-88	126.0	6.38±0.25	0.26±0.04	142±8	50.5	53.1
S2	299-W11-43	150.8	7.71±0.14	0.13±0.03	n.d.	15.8	64.3
S3	299-W14-13	116.3	6.52±0.26	0.17±0.03	n.d.	34.4	54.3
	Total iodine	0.005 M KCl extraction		1 N HCl	55% NaOH		
µg/g	142±8	1.64		48.1	8.0		
%	100	1		35	6		

n.d.: not determined.

The high iodine concentration in the particles is likely not the result of iodine sorption because calcite has low sorption for iodide in Hanford Site conditions (K_d $_=$~0.2 – 0.3 mL/g) (Kaplan et al., 2000). However, the abundant iodate present in the ambient groundwater could have become incorporated into the carbonate structure during calcite precipitation, as iodate is found to be enriched in calcites (Lu et al., 2010). Other supporting evidence from this study is that iodate was the major (>99%) species found in the 1 N HCl digestible fraction of the suspended particles (Table 5). Iodine enrichment in these carbonate particles has implications in regard to: 1) the long-term fate and transport of [129]I in the Hanford subsurface, and 2) a potential strategy for in-situ immobilization of [129]I.

3.4 <u>Iodide and iodate uptake studies: Air-sealed environment</u>

A relatively small amount of amended iodide-125 or iodate-125 partitioned onto the colloidal phase, as iodine-125 activity in the colloidal fraction (0.45 µm- 3 kDa) was close to that in the control group (data not shown for brevity). This finding is in contrast to what we reported for a Savannah River Site (SRS) surface sediment with high organic carbon (24%-wt), which resulted in 6% and 3% of the total added I$^-$ or IO$_3^-$ at ambient concentration (0.1 µM) partitioning into the colloidal fraction (3kDa - 0.45 µm), respectively (Xu et al., 2011b). However, it is in agreement with another SRS aquifer sediment with extremely low OC (0.01%-wt), as no [125]I$^-$ or [125]IO$_3^-$ was found in the colloidal fraction. This indicates the colloidal transport of radioiodine might be more critical in organic rich vegetation covered regions such as the wetland area of the SRS, whereas it might be less important in arid environments with a low vegetation cover such as the Hanford site.

Because iodide and iodate undergo speciation transformation after they are first introduced into a sediment suspension (discussed below in relation to Figure 7), it is not correct to think of the measured K_d values after 28 days as a species-specific K_d value; that is, we are not strictly measuring an iodide or a iodate K_d. Instead, we are measuring a K_d value of a distribution of iodine species when iodide or iodate are amended to the sediment. For each species (iodide or iodate), a ranking of the sediments by their respective K_d values was: H3> H1> H2 (Figure 3), which correlates with the organic carbon contents (H3:

0.15%; H1: 0.12%; H2: 0.01%). This correlation is not surprising given the large amount of literature showing great iodine sorption capacity for sediment organic matter (Schwehr et al., 2009; Xu et al., 2011a; Xu et al., 2011b; Xu et al., 2012, in press; Yamaguchi et al., 2010; Zhang et al., 2011). What is novel is that it was not known if differences at these low organic carbon concentrations would influence iodine sorption. This suggests that sediment organic matter likely plays a role in sequestering iodide or iodate.
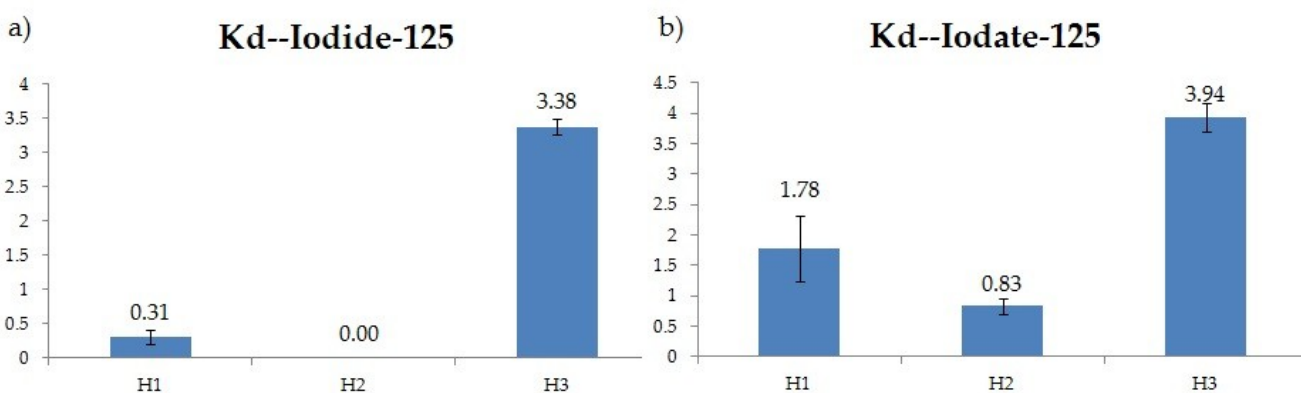
Figure 3. Partitioning coefficient (K_d; units = mL/g) of iodine when a) iodide and b) iodate are added to three Hanford sediments after 28 days in air-sealed and agitated environments (error bars are calculated from duplicate samples).

The K_d values for the iodate amended systems were significantly higher than those of iodide (Figure 3), indicating that iodate is more retarded compared to iodide. Iodate is commonly reported to exhibit higher sorption onto the mineral surfaces than iodide because of the harder base nature of IO_3^-, as compared to I^-, which would favor hard-hard interactions with the hard acid sites on the mineral surfaces (Hu et al., 2005; Kaplan et al., 2000; Xu et al., 2011a; Zhang et al., 2011).

Kinetics studies of iodide uptake by the three sediments showed that uptake of iodide by sediment H1 was large at the beginning (45% of total added iodide, day 3) (Figure 4a), but decreased sharply after 28 days to 7%. Uptake of iodide by sediment H2 gradually decreased to 0% at the end of this experiment. Uptake of iodide by sediment H3 increased with time, and more slowly after day 14 and reached ~54% of total added iodide at day 28.

Uptake of iodate by sediments H2 and H3 increased slowly with time (Figure 4b), whereas uptake of iodate by H1 decreased dramatically from day 3 to day 7 and then stayed fairly constant afterwards.
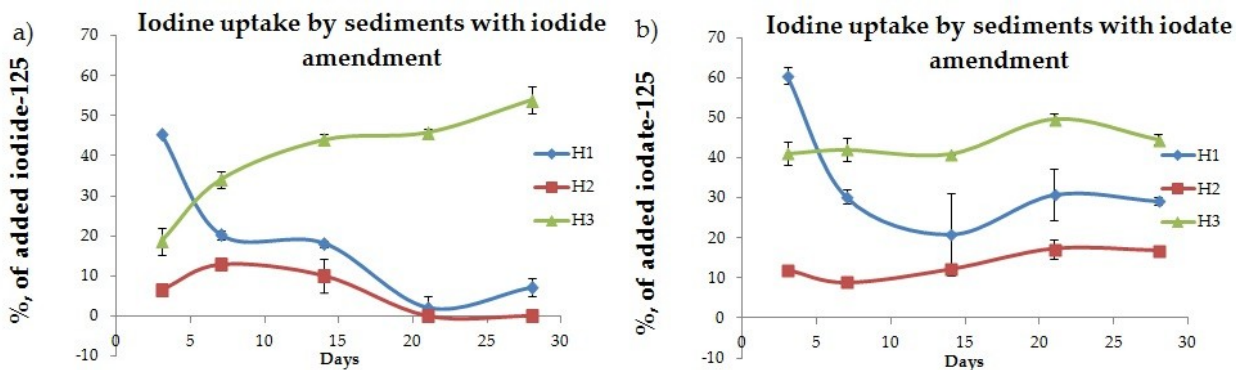
Figure 4. Percent of iodine-125 on sediments H1, H2, and H3 when amended with a) Iodide-125 or b) iodate-125. Error bars are calculated from duplicate samples.

3.5 Iodide and iodate desorption studies: Air-sealed environment

There was no significant desorption of iodide-125 or iodate-125 from the three sediments, when 0.1 M KI in natural groundwater was used as the desorbing solution. The uptake of iodide-125 by sediment H2 was almost zero (Figure 4), therefore it was not possible to collect desorption from this sediment when iodide-125 was amended. For iodide-125 amended sediment suspensions, only sediment H1 showed partial desorption, indicating that iodide-125 uptake by H3 might be all in the intragranular positions of the sediment and thus not easily accessible by the Cl^- ion (Figure 5a). This also suggests that uptake of iodide-125 by H1 is partially reversible whereas it was irreversible for H3 sediment. Lack of iodine desorption in the presence of 0.1 M KI may also indicate iodine binding to sediment organic carbon.

All three sediments show desorption of iodate-125, when 0.1 M KCl in natural groundwater was used as the desorbing solution, but the desorption K_d (we used K_d' to denote it) values were much higher than their corresponding uptake- K_d values (Figure 5b). This suggests that iodate-125 uptake by the three sediments is only partially reversible.
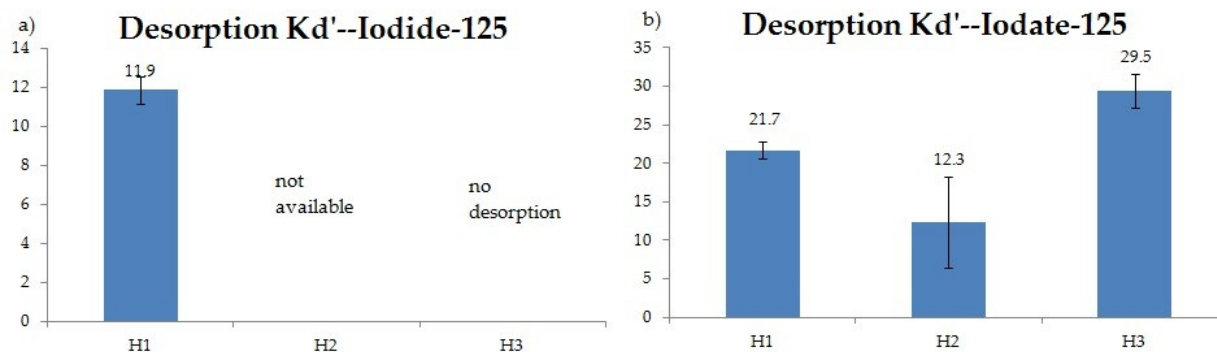
Figure 5. Desorption iodine partitioning coefficients (K_d'; units = mL/g) after two weeks of contact with 0.1 M KCl in natural groundwater when the sediments suspensions were originally amended with a) iodide and b) iodate (error bars were calculated based on duplicate samples).

Speciation analysis of the desorbing solution suggests that iodide was the major species of the desorbing solution when iodide-125 or iodate-125 was amended to H1 (Figure 6). This agrees with the results from the uptake experiment, in which H1 showed the highest reducing capacity and converted all amended iodate into iodide in the aqueous phase within the experimental period. Sediment H2 and H3 showed some reducing capacity, though the released iodine was still mainly composed of iodate (28% of iodide and 72% of iodate for sediment H2, 20% of iodide and 80% of iodate for sediment H3).
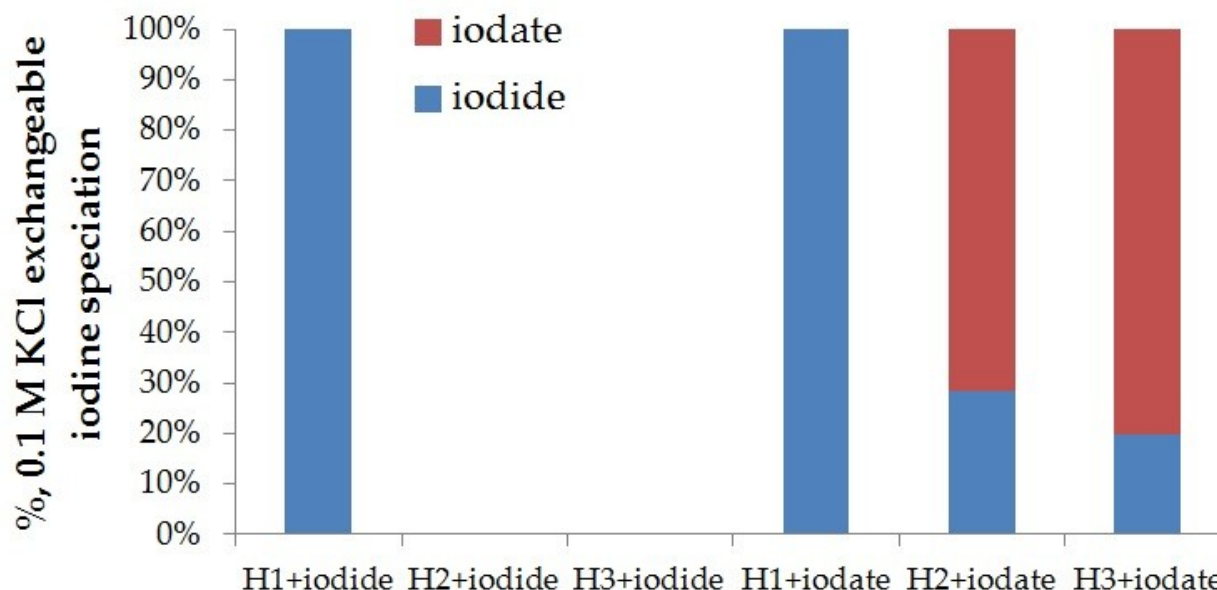
Figure 6. Speciation analysis of the desorbing solution (0.1 M KCl in natural groundwater) in contact with H1, H2, and H3 sediments when amended originally with either iodide-125 or iodate-125. All species were normalized to total iodine in the aqueous phase.

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3.6 Spiked iodine-125 speciation in the aqueous phase

Iodide-125 was the dominant species in the aqueous phase of the resuspension solution of H1 sediment amended by either iodide-125 or iodate-125, indicating that H1 sediment had some reducing capacity (Figure 7).

Iodide-125 was the dominant species in the aqueous phase of resuspension solution of H2 sediment amended by iodide-125. About 28% of the aqueous phase iodine was present as iodide when the H2 sediment was amended with iodate-125, suggesting that the H2 sediment had some reducing capacity but not as much as the H1 sediment. A similar trend was found with the H3 sediment. Therefore, the three sediments have some reducing capacity but no oxidizing capacity.

As groundwater used in this study had been filtered through 0.2 μm membranes and all the reaction vessels were sterile, it is unlikely that bacteria from groundwater or other sources, except the sediments are present in the experimental systems. Biomass of the three wet sediments measured by DAPI stain suggests that H1, H2 and H3 contains $(12.3 \pm 1.5) \times 10^8$, $(4.9 \pm 1.4) \times 10^8$ and $(9.4 \pm 1.3) \times 10^8$ cells/g soil, respectively. Then the sediments were oven-dried at 60 °C for several days before experiments. Though the presence of microbes can contribute to IO_3^- reduction, conversion of IO_3^- to I^- is more likely mediated by abiotic reductions with some reducing agents present in the sediment such as structural iron (Fe) (Hu et al., 2005). Furthermore, one has to consider a 'disturbance' or 'slurry' effect in a batch experiment with the aim to determine the iodine K_d values in a homogeneous mixture, in which sediments and water are mixed more vigorously than what really occurs under natural conditions, thus exposing surface sites that are not exposed under natural conditions.
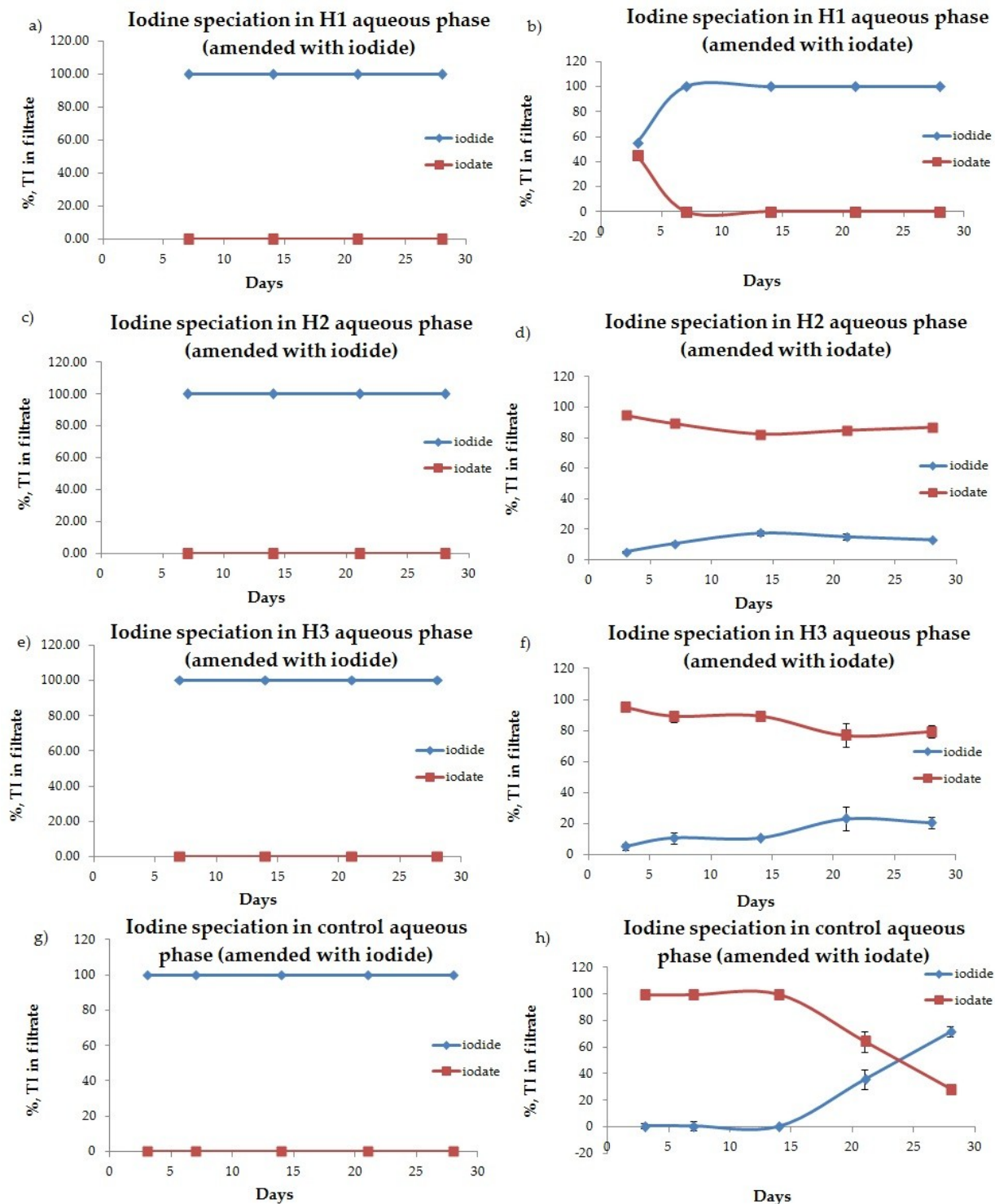
Figure 7. Time-series observation of spiked iodine-125 speciation in the aqueous phase (<0.45 μm) of sediment groundwater resuspension experiments of a) H1 sediment amended with iodide-125; b) H1 sediment amended with iodate-125; c) H2 sediment amended with iodide-125; d) H2 sediment amended with iodate-125; e) H3 sediment amended with iodide-125; f) H3 sediment amended with iodate-125; g) no-solids control amended with iodide-125; and h) no-solids control amended with iodate-125. (TI: total iodine)

3.7 <u>Stable iodine (^{127}I) speciation in the aqueous phase of the sediment groundwater resuspension experiment</u>

During the sediment-groundwater resuspension experiment, H1 sediment released the highest amount of iodide among the three sediments (H1> H2 > H3) (Figure 8). The three sediments did not release any significant amount of iodate; instead, they took up iodate-127 that was originally present in the natural groundwater (Figure 8). The gain of iodide and loss of iodate may be explained by: 1) release of iodide from the sediments, which was originally sorbed through anion exchange; 2) conversion of ambient iodate in the natural groundwater into iodide by the resuspended sediment. For the H1 sediment, it is very likely that the release of iodide from the sediment accounted for a major part of iodide present in the resulting aqueous phase of sediment groundwater resuspension, due to the fact that the measured value (119 µg/L) was much higher than the original ambient iodate present in the natural groundwater (42 µg/L).
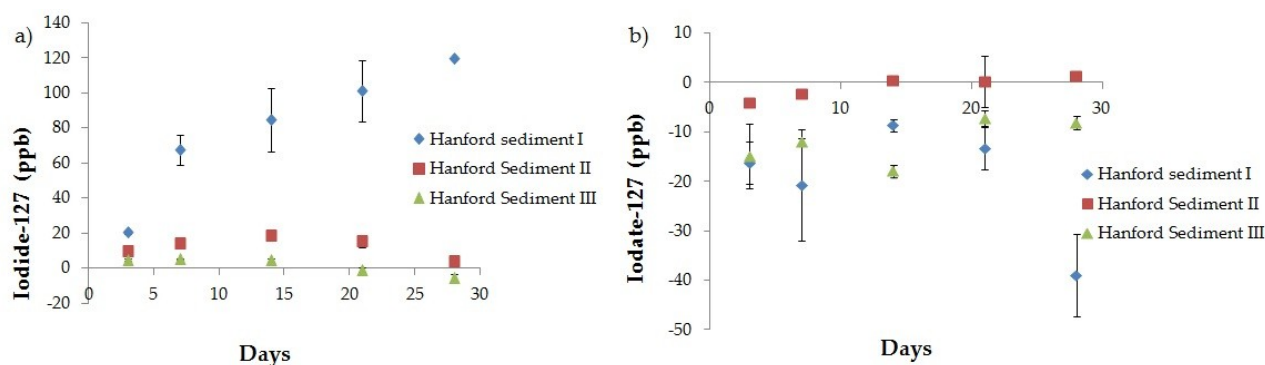

Figure 8. a) Iodide-127 and b) iodate-127 variation in the aqueous phase of a sediment groundwater resuspension experiment with respect to the iodide-127 or iodate-127 concentrations in the no-solids control group. No-solids control aqueous concentrations were subtracted from the sediment suspension aqueous iodine concentrations. A positive value indicates that iodide or iodate was released to the aqueous phase of the sample group, whereas negative value indicate iodide was lost from the aqueous phase of the sample group (error bars were calculated based on duplicate samples).

3.8 <u>Iodide and iodate (ad)sorption studies: Open-air environment</u>

In order to investigate if the transformation of iodate into iodide by the three Hanford sediments is caused by anoxic environment formed in the closed container during the one month K_d experiment and/or a 'slurry effect' (i.e., reducing agents of the sediments were more thoroughly exposed to the groundwater, due to agitation during the K_d experiment which is not usually expected in the subsurface static environment), iodide and iodate uptake by the three Hanford sediments were carried out in open-air, agitated conditions.

It was found that the iodide uptake partitioning coefficients (K_ds) increased by 1.24 to 2.62 times under the more oxic conditions, compared to those under air-sealed conditions, while the iodate uptake partitioning coefficients (K_ds) increased by 10% to 3.5 times. It is likely that under open-air conditions, in which oxygen is plentiful, less iodate is converted to iodide and thus, iodate is more stable. Iodate generally had a higher uptake K_d value than iodide (Figure 3, Figure 5, and Figure 9), except in the case

of H3 under oxic conditions. Therefore, a higher K_d value is expected under oxic conditions than that under air-sealed conditions. Iodine speciation analysis and data interpretation is still going on to confirm this.
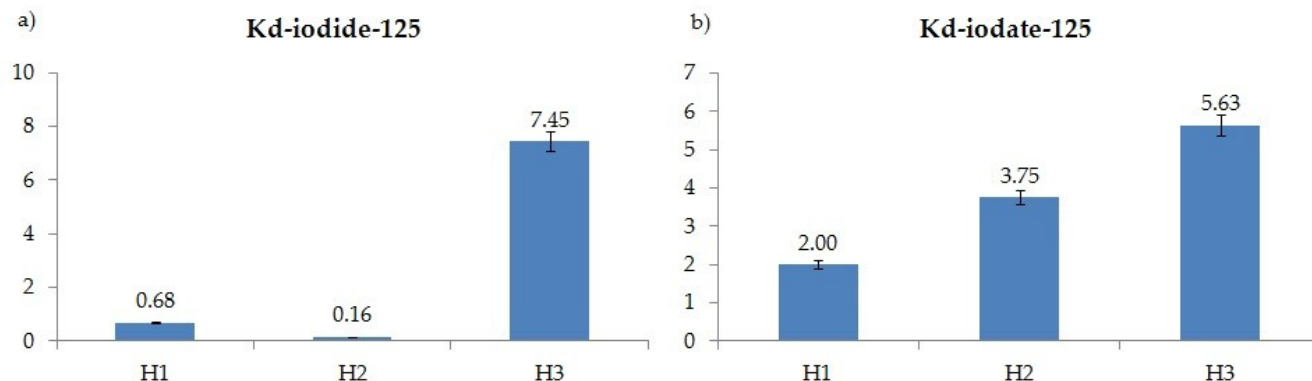

Figure 9. Partitioning coefficient (K_d; units = mL/g) of a) iodide and b) iodate for three Hanford sediments at equilibrium (day 22, error bars are calculated from two duplicates and less than 5%) under open-air and agitated conditions.

Speciation analysis using liquid scintillation counter for iodine activity suggests that the Hanford groundwater (well ID#: 299-W11-88) has some oxidizing capacity, as 15% and 9% of the total iodine-125 was identified as iodate in the aqueous phases of H1 and H3 groups amended with iodide, respectively, after 22 days incubation under open-air condition (Figure 10). It is likely that the observed transformation of iodide to iodate result from the competing reactions of the oxidizing processes in the groundwater (derived presumably from the dissolved O_2) and the reducing capacity of the sediments (derived presumably from ferrous iron). In the iodate-125 amended treatments, ~97%, 6% and 12% of total iodate-125 left in the aqueous phase of the H1, H2 and H3 sediment suspensions was converted to iodide-125 (Figure 10), respectively, by the reducing agents present in the sediments. It also demonstrates that the reduction of iodate into iodide during the K_d experiment was not totally caused by sealed-air condition, but could be partially ascribed to 'slurry' effects in batch experiments, in which iodate is accessible to more reducing sites of the sediments than it is in the real static environment. These results demonstrate that K_d experiments as commonly conducted indicate 'potential' rather than 'actual' (i.e., in-situ) K_d values influenced by surface sites that are normally less accessible to sorbent reactions.

The stable iodine speciation in the aqueous phase, after the subtraction of iodide or iodate present in the no-solids control group, describes the gain and loss of iodide or iodate species, due to the interaction between the sediment and groundwater. The original groundwater was mainly composed of iodate, but was then dominated by iodide after shaking with H1 sediment for 22 days, similar to the case under the sealed-air condition at the close time-point (21st day,

Table **6**). The relatively high amounts of iodide present in the aqueous phase of H1 sediment-groundwater slurry was likely contributed by 1) the reduction of iodate that was originally present in the groundwater and 2) the release from the sediment. The latter was inferred from the fact that the total inorganic iodine in the aqueous phase of H1 sediment-groundwater slurry was about four times higher than that in the control group. In contrast, the reducing capability of H1 sediment under the sealed-air condition was a little bit higher than that in the open-air condition (

Table **6**). Moreover, the release of total inorganic iodine (the sum of control-subtracted iodate and iodide) from the sediments into the groundwater was 'suppressed' under open-air condition, in the case of H2 and H3. This is consistent with the comparison of K_d values, which was calculated based on iodine-125 activity data (Figure 3 vs. Figure 9).
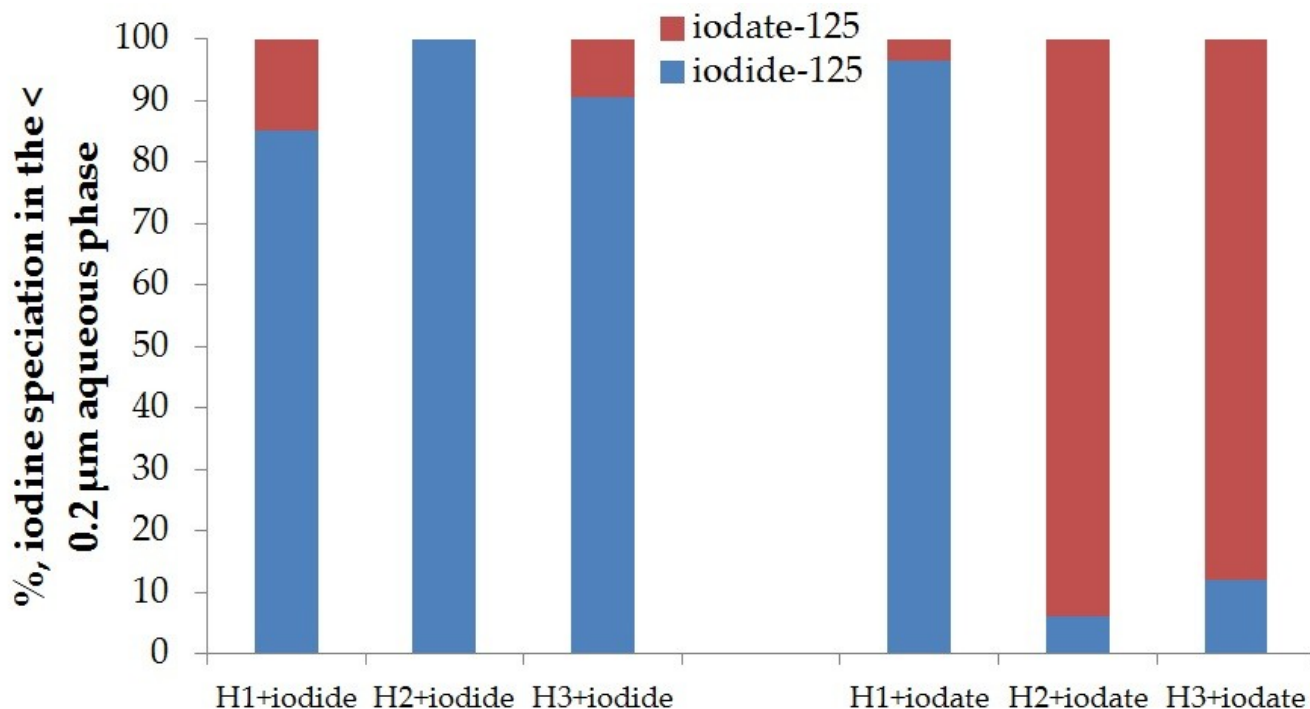
Figure 10. Speciation analysis of iodine-125 in the aqueous phase of sediment-groundwater slurries amended with either iodide-125 or iodate-125 after 22 days of equilibration. All species were normalized to total iodine-125 in the aqueous phase.

Table 6. Stable iodine speciation of the aqueous phase (µg/L) of three sediment-groundwater slurries under a sealed-air condition at day 21st and an open-air condition at day 22nd.

	Seal-air condition	Open-air condition
Iodide concentration (µg/L)		
H1	101.0	85.4
H2	15.3	6.9
H3	-1.0	2.9
Iodate concentration (µg/L)		
H1	-13.2	4.8
H2	0.2	0.0
H3	-7.1	-20.7

4.0 Conclusions

Iodine speciation for [127]I at the Hanford Site is predominantly iodate followed by organo-iodine. Iodide only accounted for 1-2% of total iodine. Unlike at SRS, colloidal transport of radioiodine was not an important pathway at the Hanford site, where mobile iodine was mostly present as iodate in the truly dissolved phase (<3 kDa). Uptake of iodide or iodate by three Hanford sediments suggest organic matter might be a controlling factor in the sequestration of iodide or iodate, as elevated uptake of iodide or iodate was observed with sediments with higher OC content, compared to the one with ten times lower OC content. However, iodate exhibited higher sorption, compared to that of iodide, for all sediments evaluated. Speciation analysis indicated that the three sediments had the ability to reduce iodate-125 to iodide-125, yet at different rates. Moreover, iodide was also released from the sediments into the aqueous phase during batch experiments.

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6.0 Appendix A: Particle size distribution and organic carbon concentrations in the clay+silt size fraction from Borehole W10-35

Table 7. Particle size distribution and organic carbon concentrations in the clay+silt size fraction from Borehole W10-35

Borehole	Depth interval (ft)	Total % in <53um fraction C	N	S	pH	Gravel wt-%	Sand wt-%	Silt/Clay wt-%	Clay wt-%
W10-35	250-255	0.377	0.007	<0.001	8.37	92	7.7	0.4	
W10-35	260-265	0.255	0.008	<0.001	8.69	79	20.3	0.7	
W10-35	270-275	0.287	0.011	<0.001	7.58	75	24.3	0.4	
W10-35	280-285	0.255	0.004	<0.001	8.8	54	44.5	1.2	
W10-35	290-295	0.135	0.010	0.0020	8.72	65	33.9	1.3	
W10-35	300-305	0.264	0.008	<0.001	9.09	61	38.1	0.7	
W10-35	310-315	0.113	0.007	0.0024	8.65	64	35.7	0.2	
W10-35	320-325	0.080	0.004	0.0017	8.83	67	32.8	0.5	
W10-35	330-335	0.103	0.007	0.0022	9	68	32.2	0.3	
W10-35	340-345	0.302	0.008	0.0077	9.39	68	31.9	0.1	
W10-35	350-355	0.549	0.009	0.0108	9.58	72	28.1	0.2	
W10-35	360-365				9.57	64	35.6	0.0	
W10-35	370-375	0.093	0.010	0.0012	9.46	46	53.6	0.5	
W10-35	380-385	0.133	0.011	0.0011	9.6	50	50.3	0.2	
W10-35	395-400	0.373	0.021	0.0118	9.53	75	25.2	0.1	
W10-35	405-410				9.41	78	21.5	0.0	
W10-35	415-420	0.197	0.008	0.0028	9.4	72	27.4	0.2	
W10-35	440-445				9.75	84	16.3	0.0	
W10-35	453-458	0.053	0.015	0.0046	9.47	59	36.2	5.2	
W10-35	468-473	0.072	0.009	0.0033	9.11	0	76.8	23.1	
W10-35	473-478	0.136	0.009	<0.001	9.53	2	79.8	18.2	
						Gravel	Sand	Silt	Clay
H1	105-130 125-130	1.617	0.011	0.0013	8.61	8	71.6	20.0	0.50
H2	335-340 350-370	0.290	0.010	<0.001	8.51	30	69.8	0.3	0.002
H3	445-465 405-420	0.388	0.022	<0.001	7.9	28	72.1	0.3	0.78

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Texas A&M University, Ocean and Coastal Studies Building, 200 Seawolf Parkway, Galveston, TX 77553

Y. F. Ho
H. P. Li
P. H. Santschi
K. A. Schwehr
C. Xu
S. Zhang