Cause of a Multi-species Radioiodine Plume that is Increasing in Concentration

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Abstract

Field and laboratory studies were carried out to understand the cause for steady increases in ^{129}I concentrations emanating from radiological seepage basins located on the Savannah River Site. The basins were closed in 1988 by adding limestone and blast furnace slag and then capping with a RCRA low permeability engineered cover. Groundwater ^{129}I concentrations in a well near the seepage basin in 1993 were 200 pCi L^{-1} and are presently between 400 and 1000 pCi L^{-1}. Iodine speciation in the plume was not uniform. Near the source, the iodine was comprised of 86% iodide, 2% iodate, and 12% organo-iodine (total activity = 178 pCi L^{-1}). Whereas, groundwater iodine speciation 365 m down stream (25 m up stream from a wetland) was 0% iodide, 93% iodate, and 7% organo iodine. Batch desorption studies demonstrated that high concentrations of ^{129}I could be incrementally desorbed from an archived seepage basin sediment sample by raising the pH. Batch sorption studies showed that iodate, IO_3^-, sorbed more strongly than iodide, I^-, to a subsurface clayey sediment, but equally well as iodide to a subsurface sandy sediment and a wetland sediment. Placing an organic-rich wetland sediment, but not nearby mineral sediments, under reducing (or microaerobic) conditions resulted in a large decrease in iodide K_d values (from 73 to 10 mL g^{-1}) and iodate K_d values (from 80 to 7 mL g^{-1}). Between pH and reduction-oxidation potential, it appears that pH seems to have a stronger influence on iodide and iodate sorption to mineral sediment. This may not be true for sediments containing higher concentrations of organic matter, such as the 7.6% organic matter sediment used in this study. First order calculations based on desorption studies with seepage basin sediments indicate that the modest increase of 0.7 pH units detected in the study site groundwater over the last 17 years since closure of the seepage basin may be sufficient to produce the observed increased groundwater ^{129}I concentrations. Groundwater monitoring of the plume at the F-Area seepage basin has shown that the migration of many of the high risk radionuclides originally present at this complex site has been attenuated. However, ^{129}I continues to leave the source at a rate that may have been exacerbated by the initial remediation efforts. This study underscores the importance of identifying the appropriate in situ stabilization technologies for all contaminants present at a source term, especially if their geochemical behaviors differ.

Introduction

^{129}I is typically either the top or among the top three risk drivers at radiological waste disposal sites in the United States [1-3]. The risk stems largely from ^{129}I having large inventories, large perceived mobility in the subsurface environment, high toxicity, a high bioaccumulation factor (90% of all the body's iodine concentrates in the thyroid), and an extremely long half-life (16M yr). To illustrate how these properties can magnify the risk of ^{129}I, ^{129}I at the Savannah River Site (SRS), South Carolina accounted for only a very small portion of the total radioactivity released from the site, approximately 0.00002%, yet it comprised 13% of the offsite population dose, a six order of magnitude increase of risk compared to the other released radionuclides [4]. Another indication of the risk posed by ^{129}I is its very low Maximum Contaminant Level, MCL, in groundwater, which is set at 1 pCi/L, the lowest of all radionuclides in the Federal Register [5]. By way of comparison, the MCL for ^{137}Cs is 200 pCi/L, ^{239}Pu is 15 pCi/L, and ^{99}Tc is 900 pCi/L.

Based on thermodynamic considerations, iodine should exist in the terrestrial environment almost exclusively as iodide, and only under extremely oxidizing conditions should iodate, IO_3^-, exist and only under high total iodine concentrations should I_3^- exist [6-8] (Figure 1). Neal and Truesdale [9] observed that there was little sorption of iodide by ferric hydroxide or kaolinite, whereas iodate sorbed strongly to ferric hydroxide. Oshida et al. [10] concluded that the difference was that iodide sorption was likely purely electrostatic attraction, while iodate was chemically adsorbed or exchanged by the mineral allophane or sesquioxides. Nishimaki et al. [11] observed the same behavior of iodide versus iodate sorption, with the iodate sorption showing a two-step mechanism - an initial rapid equilibrium sorption, followed by slow non-equilibrium sorption. The single strongest natural complexant of iodine is dissolved organic carbon [12,13]. All studies of sorption in soils that contain organic matter (OM) indicate that the OM is a primary control on sorption of iodine [6,8]. Whitehead [14] showed this by demonstrating that sorption in untreated soils was greater than in soils that were treated to destroy OM. This can be attributed to the soft Lewis base nature of iodine. In lysimeter studies of four soils with organic contents ranging from 0.2 to 6.8%, Sheppard and Thibault [15] measured K_d values that were two orders of magnitude higher in the organic-rich soils relative to the organic-poor soils. Similar results were shown in comparative studies by Yoshida et al. [10], Bird and Schwartz [16], Sheppard et al. [17], and Yoshida et al. [18]. Kaplan [19] compared iodide sorption in two soils that had similar grain-size, mineralogy, and pH values, but had very different organic carbon contents, <200 versus 1395 mg kg^{-1}. Sorption was substantially higher in the organic-rich soil as a function of pH.

In-situ site remediation is generally complicated by the presence of multiple contaminants, each having a unique set of parameters governing its geochemical behavior. The selection of a remediation strategy, being chemistry specific, becomes increasingly difficult with increasing numbers of contaminants present because conditions that may be immobilizing for one contaminant may be mobilizing for another contaminant. For example, apatite ($(Ca_{10}(PO_4)_6(OH,F)_2)$) has been successfully used as a soil amendment to immobilize certain metals and radionuclides, but unintentionally can promote the mobilization of other metals [20-22]. In one study at the Savannah River Site, SRS, the addition of apatite reduced the aqueous porewater concentrations in the targeted Hg, Pb, and U, but enhanced the pore water concentrations of As, Se, and Th [23]. The phosphate in the apatite promoted precipitation of the cation contaminants and anion exchange of the anion contaminants. The Th, existed primarily as an organic complex and as such, it behaved as an anion complex. Elsewhere, apatite, and more generally phosphate fertilizers, have caused porewater As and U concentrations to increase due to either phosphate exchange for sorbed arsenate or the release of As and U directly from the phosphate amendment [24,25]. In another example, zero-valent iron permeable barriers are commonly used to reductively degrade chlorinated hydrocarbons, such as dichloroethelene. Under some environmental conditions, the degradation products from this technology result in the formation of a more hazardous product, vinyl chloride, than the original contaminant [26].

F-Area at the SRS was a separations facility for the production of radionuclides required for nuclear weapons. Radionuclides were extracted from irradiated materials at F-Area and waste generated from this process was disposed between 1955 and 1988 in an acidic (pH 1.5 to 4) aqueous form to three Seepage Basins ([27]; Figure 2). There were dozens of radionuclides disposed in these basins, of which ^{241}Am, ^{90}Sr, $^{235/238}$U, $^{239/240}$Pu and tritium posed the greatest risk at the time of closure. The 22,000 m^2 basins were closed in 1988 by adding limestone and blast furnace slag to the unlined basin bottom and then covering with a RCRA (Resource Conservation and Recovery Act) low permeability engineered barrier to reduce groundwater infiltration. Blast furnace slag is a waste product from the smelting industry and is mostly silica with inclusions of iron sulfides that act as a strong reductant to convert such mobile species as Pu(V/VI) and Tc(VII) and U(VI) to their less mobile reduce species, Pu(IV), Tc(IV), and U(VI), respectively. The limestone was added to: 1) promote the precipitation of trivalent, tetravalent, petavalent, and hexavalent metals, such as Ce, Cm, Am, Pu and U, and 2) increase the cation exchange capacity of the sediment and sludge in the seepage basins and the sediment in the plume flow path.

Since 1988, groundwater monitoring data has indicated that essentially all the radionuclide and metal concentrations in the F-Area plume are decreasing, except ^{129}I [27] (the basins received ~2 Ci ^{129}I (7x10^{10} Bq; [28]). The overall objective of this study was to understand why groundwater ^{129}I concentrations are increasing near the F-Area seepage basins. The hypothesis was that groundwater ^{129}I concentrations were increasing because they were being desorbed from the F-Area seepage basin sediment as a result of increasing basin pH levels. It is possible that the limestone and slag basin treatments contributed to the pH increase, promoting anionic desorption from the pH-dependent charge sediment. Studies were established to evaluate whether the slag promoted the conversion of iodine from the more strongly sorbing form, iodate (IO_3^-) to the more reduced form of iodine, iodide (I^-). The specific objectives of this study were to: 1) conduct ^{129}I desorption and (ad)sorption tests as a function of pH with a contaminated seepage basin sediment, 2) conduct iodide and iodate sorption tests to vadose zone and wetland sediments under oxidized and reducing conditions, and 3) measure groundwater ^{129}I speciation in F-Area under ambient conditions.

Materials and Methods

Field Sampling. The three wells sampled in this study, wells FSB-95DR, FSB-110D (FSB-130D for iodine speciation), and FSB-79, fall along a transect of increasing distance away from the seepage basins, 10 m, 220 m and 375 m down stream from the seepage basin, respectively (Figure 2). Each of these wells is screen in the upper aquifer. They were sampled approximately quarterly between 1990 through 2010 as part of the site wide groundwater monitoring program for a full suite of constituents, of which the ^{129}I and pH data was extracted from the data base and reported here. Samples for groundwater ^{129}I speciation were collected in August 2009 from wells FSB-95DR, FSB-130D, and FSB-79. We originally had attempted to sample well FSB-

110D, the subject of a great deal of historical data, but the well was not available at the time of sampling. Well FSB-130D is located 60 m from FSB-110D and is screen in the same aquifer (Figure 2).

Four sediments were collected for this study, three non-contaminated sediments and one contaminated sediment from the bottom of the seepage basin (Table 1). The characterization of the sediments will be described in the Results and Discussion section. Three non-contaminated sediments were collected for conducting iodide and iodate sorption studies under oxidizing and reducing conditions: Subsurface Sandy, Subsurface Clayey, and Four-Mile Branch Wetland. Two of the sediments were from the vadose zone, both from the Tobacco formation, and were selected to represent end members in terms of iodine sorption geochemistry. The wetland sediment was collected from a stream adjacent to F-Area, Four Mile Branch (Figure 2). The O-horizon was removed and the mineral horizon was used for this study. The wetland sediment was maintained moist at all times due to the relatively high organic matter, 7.9 wt-%. The contaminated sediment was collected from the seepage basin bottom in 1987 prior to closure and prior to adding the limestone and slag. This sample was used in an ^{129}I desorption experiment and a separate ^{125}I (ad)sorption experiment described below. The sediment sample was air dried and stored in the dark at room temperature.

Groundwater Iodine Speciation. Iodide, IO_3^-, and organo-iodine species were determined by the methods described in Schwehr and Santschi [29] and modified in Zhang et al. [30]. Briefly, I^- was measured directly by high performance liquid chromatography (HPLC). Total inorganic iodine (TII), a measure of the major iodine inorganic species in water (I^- and IO_3^-), was determined by measuring aqueous I^- after acidification and reduction of the sample with HCl and $NaHSO_3$. Total iodine (TI), a measure of the major inorganic and organic iodine (OI) species, was measured by dehydrohalogenating the liquid or solid sample, as described in Schwehr and Santschi [29]. These three measured values (I^-, TII, and TI) were then used to estimate DOI (DOI = TI – TII) and IO_3^- (IO_3^- = TII – I^-).

Dehydrohalogenation is achieved by base hydrolysis coupled with ethanol addition and heat to break the covalent iodine bonds between iodine and aromatic carbon molecules. Solutions of L-thyroxine ($C_{15}H_{11}I_4NO_4$), a persistent form of DOI, and of NIST SRM 2709 San Joaquin soil were used as DOI standards. Immediately, prior to the DOI decomposition of each set of samples, a fresh stock solution was made and diluted to an equivalence of 0.125 μM I^- for thyroxine, and both 0.1 and 1.0 μM I^- for the San Joaquin soil. The standards were then run as controls with each sample set. The relative standard deviation (RSD) for the recovery of the I^- equivalence in these standards was ≤5%. Concentrations determined using this methodology were tested against samples that had been analyzed using ICP-MS and were within 6% RSD [29]. The I^- and TII were analyzed by HPLC using standard additions. Each aqueous phase sample was measured in duplicate or triplicate and with at least two different I^- standard concentrations added to the sample solution as part of the standard addition analysis. The freshly prepared I^- standards used in the standard additions were also used in calibration regression curves for comparison; they were within 3% RSD for 0.02 μM (~2.5 ppb) for 1 standard deviation or 95% confidence level (CL) [29]. The propagated error for IO_3^- was <5%, and for DOI <7%. The HPLC method was validated using certified reference materials and independent measurements by ICP-MS and voltammetry [29]. The limit of detection (LOD) of the HPLC method is 0.2 ppb (~0.001 μM), so all measured I^- concentrations in this study are above the LOD. Additional analytical error estimates are provided as footnotes to the data tables.

Additional Analytical Analyses. Sediments were characterized for: pH in a 1:1 water-sediment slurry; particle-size distribution by the sieve and hydrometer method; and free Fe by the dithionite-citrate buffer method [31]. Organic matter was determined by the weight-loss-on-ignition method conducted at 360°C for 2 h [32]. Mineralogy was determined by X-ray diffraction analyses of the <2-μm fraction that was separated by sedimentation. X-ray diffraction was conducted on samples that were subjected to three sequential heat treatments (for mineral identification purposes): 16-h at 25°C, 16-h at 65°C, and then 16-h at 300°C. BET surface area was determined on a Micromeritics (Norcross, GA) surface area analyzer.

Laboratory Batch (Ad)sorption and Desorption Experiments: Four batch sorption/ desorption experiments were conducted: 1) desorption versus pH using contaminated F-Area seepage basin sediment, 2) $^{125}I^-$ (ad)sorption versus pH, 3) iodide and iodate sorption under oxidizing conditions, and 4) iodide and iodate sorption under reducing conditions.

The desorption experiment was conducted with original seepage basin sediment that had been archived in a room-temperature dried state. This sediment, as mentioned above, was collected before limestone or slag was added to the seepage basins. The sediment at the start of the experiment contained 14.62 pCi g^{-1} ^{129}I (Table 1) and for analytical reasons, a large sediment to groundwater ratio was required for the experiments: 100 g: 70 mL uncontaminated groundwater. Duplicate suspension were adjusted to pH 3, 4, 4.8 (background, not adjusted), 6, 7, 8, and 9 using a slow moving platform shaker. The sediments were pH adjusted every other day for two weeks then two to three times a week for two weeks by adding 0.01 N HNO_3 or 0.01 NaOH. By the fourth week, the pH of the suspensions remained relatively constant, suggesting the systems were approaching steady state. After an additional week, the solids were permitted to settle, and the liquids were passed through a 0.1-μm filter and analyzed for ^{129}I by standard radiological techniques using LOAX HPGe gamma spectroscopy and neutron activation analysis.

The $^{125}I^-$ (ad)sorption as a function of pH experiment was also conducted with original seepage basin sediment. ^{125}I is a short lived isotope ($t_{1/2}$=59 days), that does not exist in these sediments. A ratio of 1 g sediment to15 mL liquid (67 g L^{-1} sediment) was established and the pH was varied between 4.6 and 7.8 by adding varying volumes of 0.005 M HCl, 0.01 M NaOH, 0.02 M NaCl and distilled water. The ionic strength for all solutions, irrespective of pH, was held constant at 0.02M. After the sediment suspension was generated, the pH was monitored until a steady state (<0.1 pH unit change over a one week period) was achieved while mixing on a platform shaker. After reaching the desired pH steady state, an $^{125}I^-$ spike (100 μL; 4.5 pCi L^{-1} in 0.01 M NaOH carrier) was introduced in each suspension, including three no-sediment controls. The pH-equilibrated-sediment suspensions were further equilibrated with the $^{125}I^-$ for one week, and then liquids were separated from solids by first settling and then passing the liquids through a 0.1-μm filter. The liquids were analyzed for total ^{125}I by gamma analysis. Data was presented as ^{125}I K_d ($K_d = I_{solids}/I_{aq}$), whereby the K_d values were calculated by assuming that all ^{125}I lost from the aqueous phase had partitioned into the sediment. No solid controls included with the samples and previous studies have demonstrated between 97 and 104% mass balance [33].

Another batch study was conducted to compare iodide and iodate under oxidizing conditions using three sediments, the Subsurface Clayey, the Subsurface Sandy, and the Four-Mile Branch Wetland sediments. The study was conducted with sediment concentrations of 25 g L^{-1} in 0.01 M NaCl and 0.1, 0.5 or 1 mg L^{-1} ^{127}I, as iodide stock from High Purity Standards (Charleston, SC), or iodate, from KIO_3. The suspensions were mixed end-over-end at 8 rpm and aliquots were removed for iodine analysis at 1, 4, and 8 day intervals. All systems were prepared in triplicate yielding a total of nine samples for each sediment. For the iodide and iodate comparison experiment, the stock concentration was re-checked every time samples were run on the ICP-MS. The pH for this experiment was not adjusted, instead it was permitted to drift to that of the suspension. The pH values were generally the same or slightly lower than that of the 1:1 sediment: water pH reported in Table 1. The notable exception were the wetland sediments which had average pH values of 4.69 ± 0.07 (n=18) and 5.54 ± 0.04 (n=15) under oxidizing and reducing conditions, respectively. A similar pH drift was not observed for the clayey and sandy sediment suspensions so the change in pH appears to be due to a physical/chemical change in the wetland sediment. After equilibration, the sediments were permitted to settle and then the liquids were passed through a 0.10-μm nylon filter. The iodide versus iodate under reducing condition study was identical to that conducted in oxidizing conditions except it was conducted in an anaerobic glovebox maintained under a 2% $H_2(g)$/ 98% $N_2(g)$ atmosphere. Analysis for both studies was conducted with a Thermo Scientific X Series 2 inductively coupled plasma – mass spectrometer (ICP-MS). All samples were diluted 10x in a basic "trap" solution (0.5 mM $NaSO_3$, 1% tetramethylamonium hydroxide, and 1% CFA-C (Spectrasol, Inc.)) for ICP-MS analysis with ^{95}Mo, ^{115}In, and ^{187}Re used for internal standards. K_d values were report and calculated as described above.

Results and Discussion

Groundwater Iodine Concentrations and Speciation at the Study Site. Two points to keep in mind while discussing groundwater ^{129}I are, 1) the MCL level of ^{129}I is 1 pCi L^{-1}, which is an extremely low concentration, and 2) site closure of the F-Area seepage basins was in 1988. In the well closest to the F-Area seepage basins, FSB-95DR, groundwater ^{129}I concentrations have generally increased since 1993 to 2010. In 1993, ^{129}I concentrations were ~ 200 pCi L^{-1} and in 2010 they were measured between 500 and 700 pCi L^{-1} (Figure 3). During this same period, the pH has slightly, but steadily increased from pH 3.1 to 3.8. In well FSB-110D, about 220 m down gradient from the seepage basins, the ^{129}I concentrations in the early 1990's was frequently between 200 and 300 pCi L^{-1} with numerous spurious large spike concentrations. After July 1999 through present day, the concentrations decreased to <100 pCi L^{-1}. ^{129}I concentration in the well furthest from the seepage basins (375 m downgradient), FSB-79, has been rather steady at about 50 pCi L^{-1}, except for what appears to be an ^{129}I pulse that came through between 1993 and 2000. The pH in this well was 3.1 in 1990 and was steadily increasing through 2004. The sharp increase in 2004 reflects remediation actions imposed by a subsurface base-injection project that was initiated up gradient of this well [3] (Figure 2). Increased ^{129}I concentrations in groundwater, such as observed at well FSB-95DR, have not been noted at well FSB-110D, some 210 m downgradient. Groundwater flow rates in this aquifer are about 0.15 m day^{-1} [3] and as such, unretarded travel time between the two wells would be about 4 years. The ^{129}I presently being released from the seepage basin may be retarded by the aquifer.

^{129}I speciation was measured on FSB-95DR and FSB-79 (Figure 2). At the time of sampling, well FSB-110D was not suitable for sampling, so a nearby well, FSB-130D was sampled but this latter well's groundwater had insufficient ^{129}I concentrations to complete iodine speciation. Groundwater sampled from well FSB-95DR near the seepage basin, which contained of 177.95 pCi L^{-1} ^{129}I, was largely composed of iodide, yet it contained surprisingly large amounts of organo-iodine species (12.7%). The nature of the organic moieties is not known and it is not known whether the organic species was of natural or of anthropogenic origin. The iodine speciation, in well FSB-79, some 375 m from the seepage basins and approximately 10 m from the wetland edge, was entirely different from that of well FSB-95DR. It consisted of no detectable iodide, 93.4% of iodate, and 6.6% organo-iodine. Supporting these findings, Schwehr et al. [34] also measured iodate and organo iodine in groundwater samples from this aquifer. The cause for the difference in iodine speciation between these wells, or more specifically between groundwater chemistries, is the subject of on going research and is beyond the scope of this manuscript. However, Li et al. [35] has reported iodide oxidation by microbial enrichment cultures containing sediment from the wetlands of F-Area, some 40 m from well FSB-79. As Figure 1 indicates, the presence of iodate is not expected in these samples based on thermodynamic considerations and organo-iodine was not even considered due to the unavailability of thermodynamic data. Therefore, the data presented in Figure 1 is of limited value given the contradictory results we observed by evaluating iodine speciation in F-Area field samples. There could be several causes for this inconsistency, including, but not limited to, that the system may not be in equilibrium, poor thermodynamic data, and not all the constituents are included in the calculations, e.g., organo-iodine [30,34-37].

Laboratory Batch (Ad)Sorption and Desorption Experiments. The ^{129}I desorption experiment was conducted by pH adjustment of the ^{129}I-contaminated basin sediment and measuring aqueous ^{129}I. At the completion of this desorption step, a second desorption step was conducted with pH-adjusted 0.1 mM KCl. Properties of the sediment are presented in Table 1. The sediment had been in dried archive storage at room temperature for 22 years. The implications of the long term storage on the experimental results are not known, but what little microbial activity that may have been originally present was inevitably significantly reduced during the storage period. The importance of sediment microflora on iodine biogeochemistry has been well documented [8,34,38-40]. This sediment is highly disturbed and contained secondary iron-containing precipitates, or sludge, as suggested by the high CDB extractable Fe and the high silt and clay content. The basin received large volumes of strong acids and intermittent volumes of strong bases over the 33 years when it was in service. X-ray diffraction analysis showed the presence of all typical subsurface sediment mineral phases found on the Savannah River Site and no new secondary phases. The pH of the F-Area seepage basin sediment, 4.4, was higher than expected based on groundwater pH values (~3.0) measured near the time that the core was removed from the subsurface. The pH of uncontaminated groundwater in this area is ~5 - 6.5.

Aqueous ^{129}I concentrations released from the contaminated sediments increased as the pH of the suspension increased (Figure 4). Below pH 4 in the groundwater system, no aqueous ^{129}I was detected. Above pH 4, for every increase in pH, the ^{129}I concentration increased by about 800 pCi L^{-1}. In the KCl system, where anion exchange was promoted, a somewhat fixed release of ^{129}I of ~3200 pCi L^{-1} was obtained at pH levels ≥4.6. One reason that the KCl treatment concentrations are less than those of the groundwater treatment is because they were done sequentially after the groundwater treatments. Also, the concentrations of the KCl treatments indicate that that a significant amount of the easily exchangeable ^{129}I existed in these sediments. Together, this data set shows that ^{129}I sorption to the seepage basin sediment is very strongly dependent to pH and that a small fraction of the ^{129}I pool is weakly anion exchangeable.

The $^{125}I^-$ (ad)sorption experiments conducted with the seepage basin sediment also demonstrated a very strong pH dependency, consistent with the desorption data (Figure 4). The sorption is expressed in terms of the distribution coefficient ($K_d = I^-_{solids}/I^-_{aq}$) of I^- and the magnitude of these K_d values is much higher than –that commonly measured in oxidized SRS undisturbed subsurface sediments at pH 5 to 6.5, which tend to be between 0.2 and 10 mL g^{-1}

[19,34,41]. These K_d values are also much larger than the K_d values calculated from the desorption data above. Between pH 4.4 through pH 9, the calculated K_d decreases in the desorption data from 2.6 to 1.0 mL g^{-1}. This difference between the two experiments may be attributed to the solids-to-liquids ratio, where larger ratios tend to lower measured K_d values [42]. In the desorption experiment, the ratio expressed as a concentration was 1428 g L^{-1} sediment, whereas in the (ad)sorption study the ratio was 66.7 g L^{-1} sediment, a 21 fold difference. These sediment concentrations were originally selected to optimize sorption conditions or analytical considerations. Given that the solid-to-liquid ratio of the desorption study more closely approximates nature and that desorption and not (ad)sorption is the phenomenon of interest, these lower K_d values of 1.0 to 2.6 mL g^{-1} are more likely to reflect the magnitude of desorption.

Sorption of iodide and iodate to the subsurface and wetland sediments were measured under oxidizing and reducing conditions (Table 2). The names of the sediments are descriptive of their properties. Subsurface clayey sediment has a sandy loam texture and no detectable organic matter (Table 1). Subsurface sandy sediment has a sandy texture and no organic matter and the wetland sediment has a loamy sand texture and 7.9 wt-% organic matter. This study was originally set up as a kinetic study looking at sorption at 1, 4, and 8 days. Changes in sorption were observed over time for the wetland sediments but there was no apparent difference between iodide or iodate sorption to the clayey or sandy sediments after 1, 4 or 8 days. To remain consistent, the data below are discussed for the partitioning reached after 8 days for all sediments. There were no statistical differences as a function of total iodine concentration (0.1, 0.5, or 1.0 mg L^{-1}), so the triplicate results from each initial concentration were combined to produce one mean, typically of nine observations (Table 2). The observation made by other researchers [9-11] that iodate sorbs more strongly than iodide is supported in Oxidized/Clayey Sediment and Reduced/Clayey Sediment data (see the capital letter following the means in /Table 2). Comparison of oxidizing and reducing conditions indicates that there were no significant differences between these treatments in the Subsurface Sandy and Subsurface Clayey sediments (Table 2.) However, there was a large (~10 fold) difference in the K_d value measured under fully aerobic versus anaerobic (or microaerobic) conditions (<0.5 mg L^{-1}) for both iodide and iodate. Specifically, the oxidized iodide K_d values decreased by 86% when repeated under microaerobic conditions. Similarly, the iodate K_d values decreased by 92%. Although it is supportive of the findings of [16,39,43-48], who reported decreased iodine sorption under reducing conditions, one cause we can likely rule out for this biogeochemical behavior is iodate reduction to iodide because both iodide and iodate treatments showed similar reduced K_d values under reducing conditions. The cause for this substantial decrease in apparent K_d values is presently under investigation but is likely attributed to the slight difference in pH between the oxidizing (average pH 4.69) and reducing (average pH 5.55) systems. This is consistent with the desorption data shown in Figure 4. It is clear that once the sediments are under more reduced conditions, the iron mineralogy, organic matter chemistry, and/or the iodine speciation is altered in a manner that leads to a significant decrease in iodine sorption. One possible outcome of iodine speciation in sediments is the formation of volatile methylated iodine species. However, oxidized and microaerobic controls had good mass balance. There was about 100% mass balance under oxidizing condition and 95% under reducing condition for the eight-day equilibration samples [33].

The addition of limestone, slag, and the low permeable RCRA barrier has been very effective at reducing the spread of numerous contaminants in the F-Area Seepage Basin [27]. For example, since 1990, tritium and uranium groundwater concentrations emanating from the seepage basins have significantly decreased. Tritium concentrations have significant decreased because of the low permeability RCRA cap, groundwater dilution, and radiological decay ($t_{1/2}$=13 yr). Uranium concentrations have significantly decreased presumably because of the RCRA cap, dilution, increased pH in the seepage basin sediments, which promoted uranium surface complexation, and decreased oxidation-reduction potential, promoting the reduction of U(VI) to U(IV), which in turn leads to in situ precipitation. However, the very chemical conditions conducive to immobilizing uranium and other cations, such as high cationic exchange capacity (surface hydroxylation) and lower oxidation-reduction potential tend to promote iodine mobility. In this study, it was observed that when the pH of the seepage basin sediment was increased, the aqueous ^{129}I increased on average by 800 pCi L^{-1}. Adding 0.1 mM KCl after the equilibrium experiment did not further promote ^{129}I exchange, suggesting that very little readily exchangeable ^{129}I remained on the sediment surfaces (Figure 4). Both (ad)sorption and desorption experiments demonstrated a strong pH dependency of iodine partitioning to the sediment. These results confirm that the interaction between anions and soil and sediment particles of the southeastern United States is strongly pH dependent [19,49-51].

Based on the findings in this study, it appears that limestone had a greater influence on ^{129}I sorption and desorption to the seepage basin sediments than did the redox status. Redox status is probably a contributing factor, but not likely as important a mechanism responsible for the release of ^{129}I from these sediments. In support of this conclusion, we demonstrated that the iodide and iodate K_d values for the mineral surfaces of these sediments were largely unaffected when O_2 concentrations were lowered from atmospheric values to <0.5 mg L^{-1} (Table 2). This suggests that if all else was equal (i.e., discounting secondary reactions such as reactions with iron or sulfide chemistry), that the slag's influence on Eh would not be sufficient to produce quantitative changes to iodine K_d values.

The substantial increases in groundwater ^{129}I concentrations near the seepage basins are consistent with first order calculations using the seepage basin desorption data and the groundwater pH changes (Figure 4). Groundwater pH in the well closest to the seepage basins, well FSB-95DR, increased by about 0.7 units between 1993 (pH 3.1) and 2010 (pH 3.8) (Figure 3). Using the desorption data (Figure 4), this pH change corresponds to a ^{129}I concentration change of 933 pCi L^{-1} (approximately 8000 pCi L^{-1} over a pH range of 6 units; 1333 pCi L^{-1} per pH unit). Figure 3 shows a 200 to 800 pCi L^{-1} increase. This aqueous concentration is certainly consistent with the groundwater field data presented in Figure 3, given that the field data includes such processes as dilution, dispersion, and other geochemical processes. Therefore, the seemingly small pH changes of less than one pH unit may potentially result in the corresponding 100% to 500% increases in groundwater ^{129}I concentrations reported in well FSB-95DR.

The F-Area closure program clearly attenuated mobilization of many of the radionuclides originally present at this complex site with dozens of different high risk contaminants [27]. However, ^{129}I continues to leave the source at a rate that may have been exacerbated by the initial remediation efforts. This study underscores the importance of identifying the appropriate in situ stabilization technologies for all contaminants present at a source term, especially if their geochemical behaviors differ from one another.

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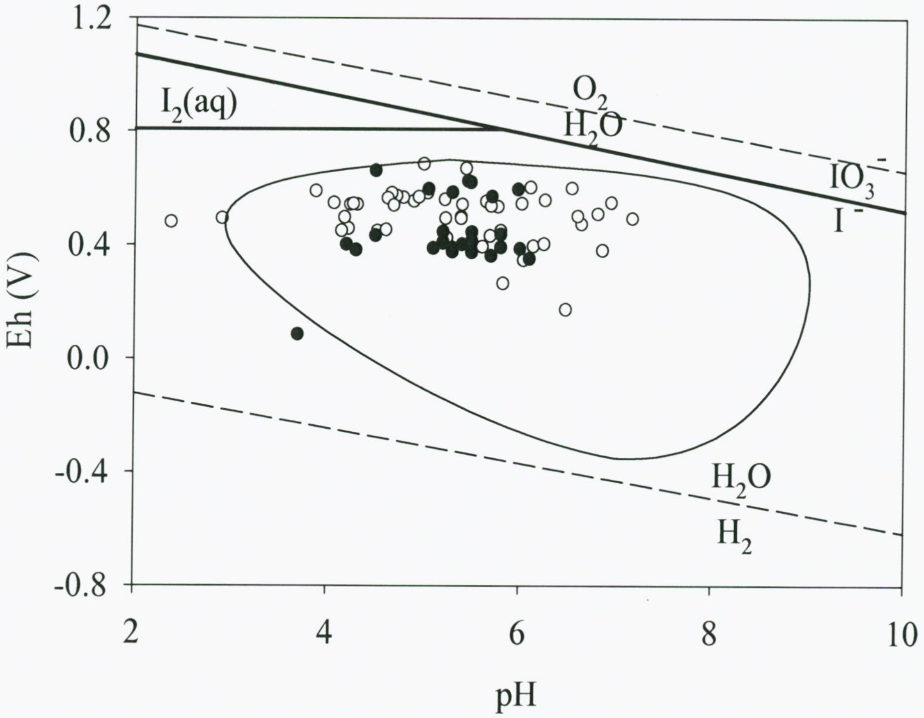
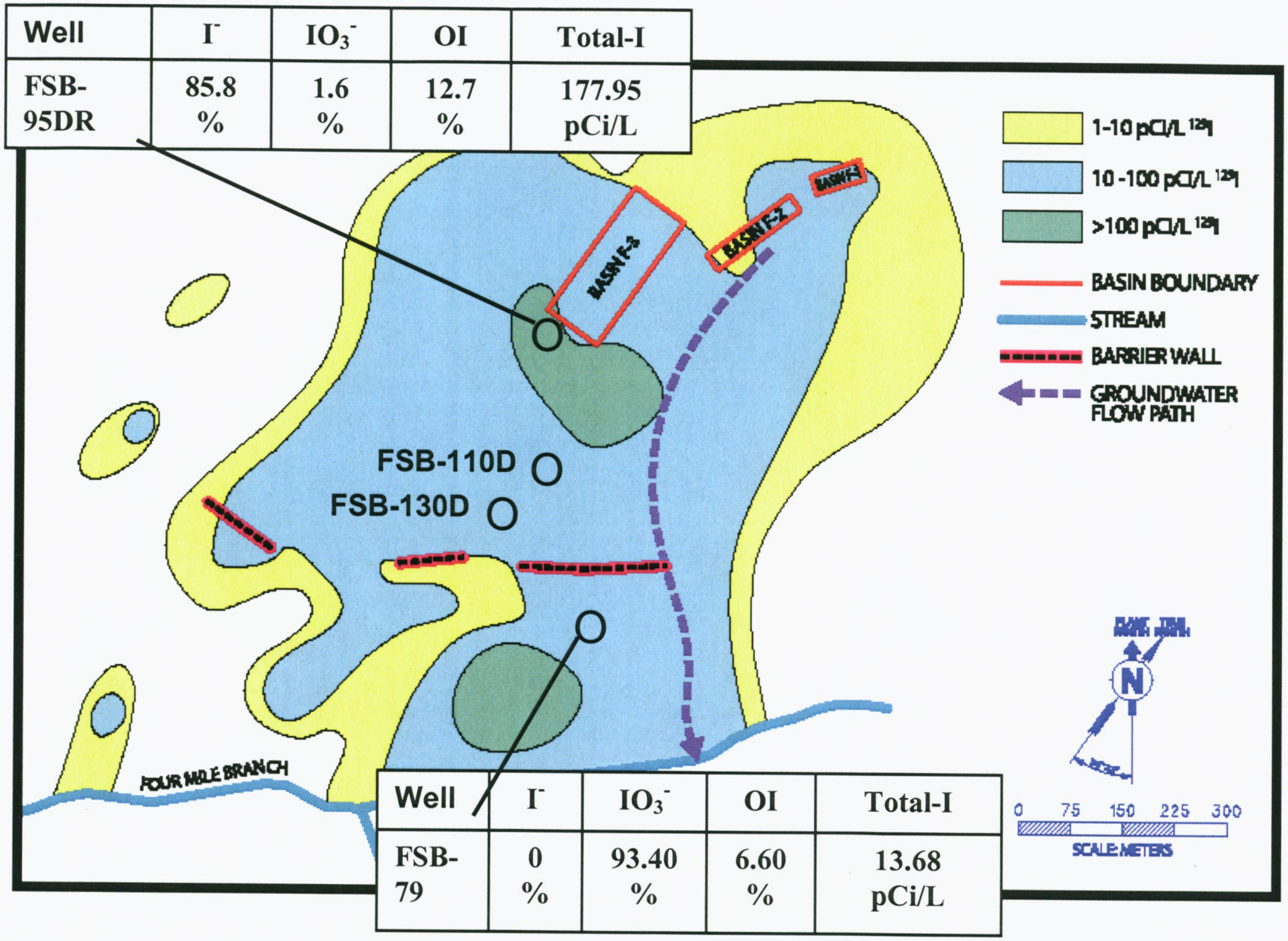


FIGURE 1. Filled circles represent pH-Eh values from a wetland on the Savannah River Site and the open circles represent an upper aquifer in E-Area, adjacent to F-Area, on the SRS. Inscribed area was adopted from Baas-Becking et al. (1960) and is representative of most sediments. Lines representing O_2/H_2O and the H_2/H_2O couples provide limits of oxidation-reduction potentials in aqueous systems (calculated using Geochemist's Workbench®, Bethke 2005; organo-iodine was not considered in these calculations).



Well	I^-	IO_3^-	OI	Total-I
FSB-95DR	85.8 %	1.6 %	12.7 %	177.95 pCi/L

Well	I^-	IO_3^-	OI	Total-I
FSB-79	0 %	93.40 %	6.60 %	13.68 pCi/L

FIGURE 2. F-Area ^{129}I plume originating from F-Area Seepage Basins and moving towards Four-Mile Branch. Iodine speciation was successfully determined at two locations, well FSB-95DR, and FSB-79 but the ^{129}I concentrations were too low in well FSB-130D to complete full iodine speciation.

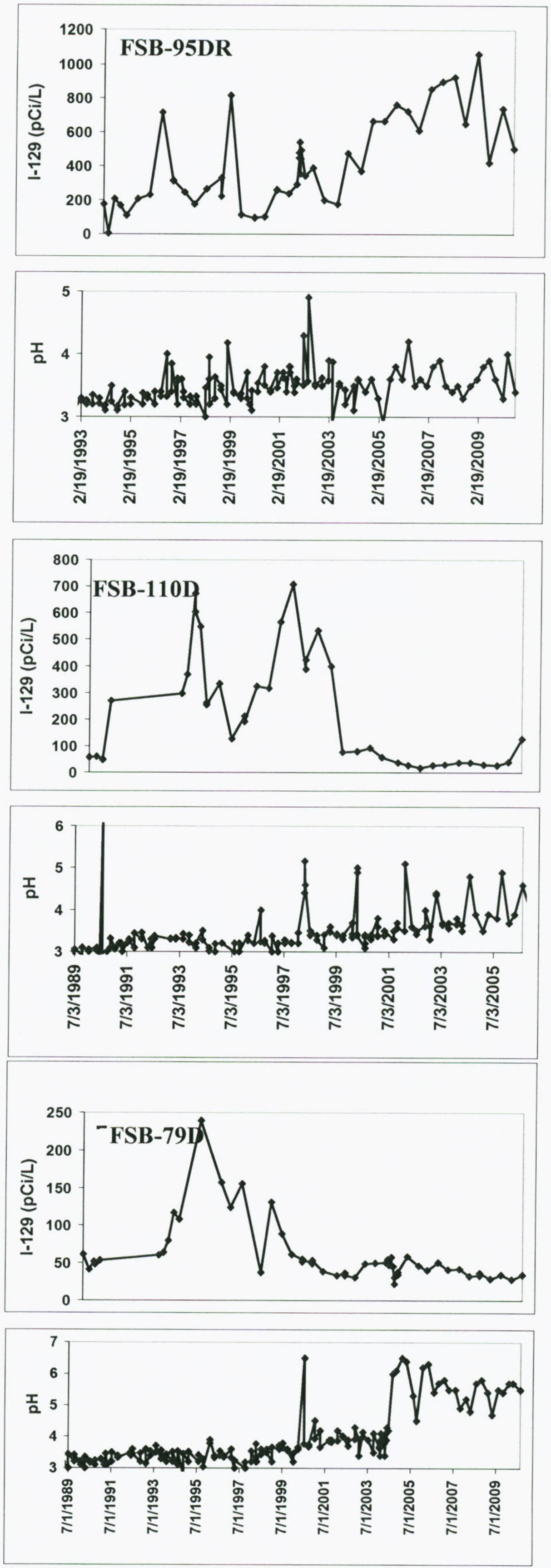


FIGURE 3. Groundwater ^{129}I and pH in three well in F-Area between 1989 and 2010. Well locations are identified in Figure 2.

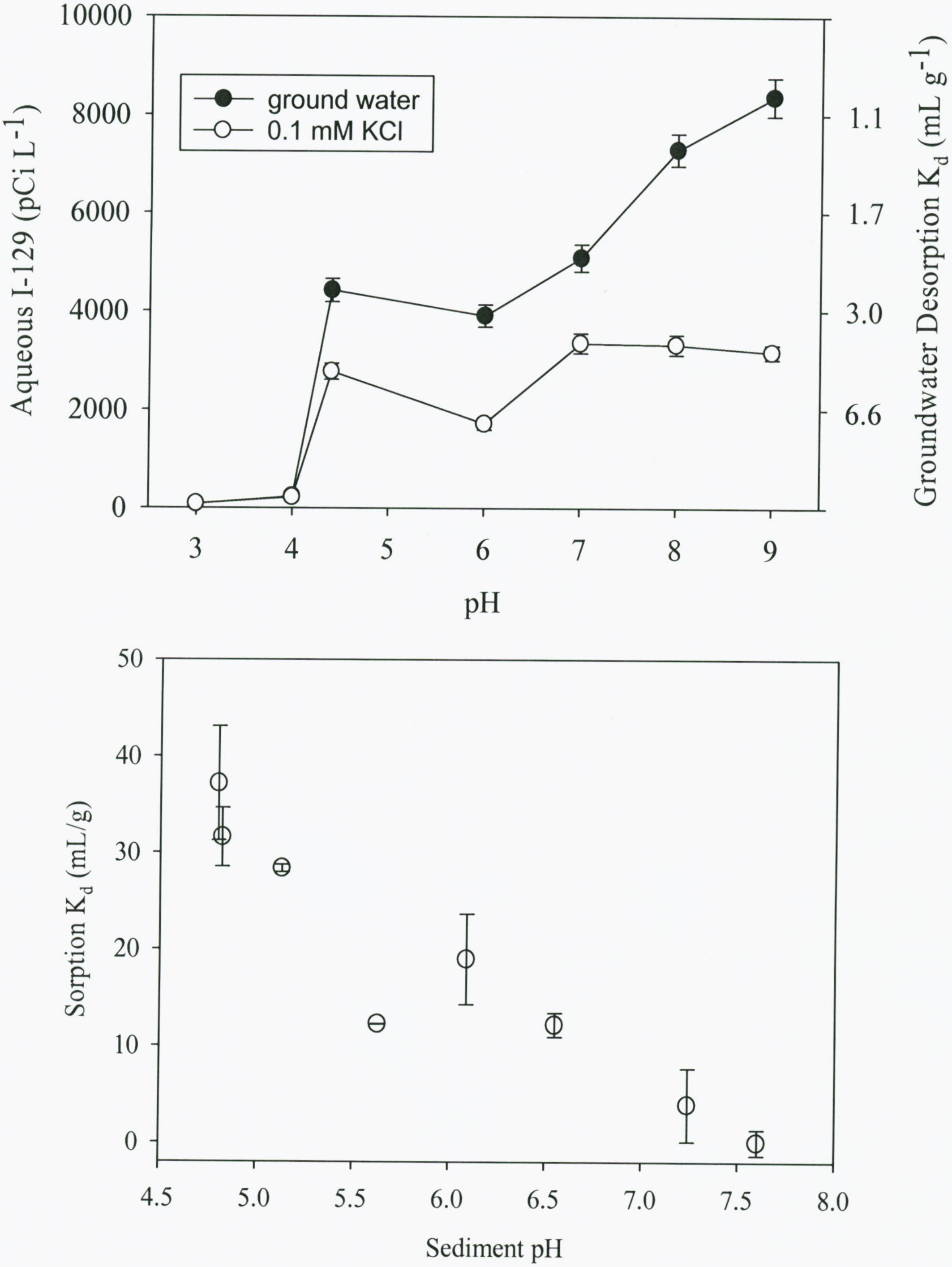


FIGURE 4. (Top) ^{129}I Desorption from F-Area Seepage Basin Sediment as a Function of pH (conducted in duplicate, contaminated sediment contained 14.6 pCi g^{-1} ^{129}I, 100 g/ 70 mL pH-adjusted groundwater, followed by 70 mL of pH adjusted 0.1mM KCl was added to sediment, original sediment pH = 4.4, three month pH sediment adjustment period, one week desorption period, sediment contaminated with ^{129}I between 1955 and 1988). Groundwater Desorption K_d Scale is non-linear. (Bottom) ^{125}I Adsorption to F-Area Seepage Basin Sediment as a Function of pH (Triplicate, 1g:15mL; pH adjustment with NaOH and HCl, constant ionic strength = 0.02 M; sediment pH equilibration of three months ^{125}I equilibration period of one week; ^{125}I addition = 0.03 pCi L^{-1} ^{125}I^{-}).

TABLE 1. Sediment Characterization

parameter	Subsurface Clayey Sediment	Subsurface Sandy Sediment	Four Mile Branch Wetland Sediment	F-Area Seepage Basin Sediment
sand / silt / clay (wt%)	57.9 / 40.6 / 1.6	97 / 2.9 / 0.2	85.5 / 11.7 / 2.8	77.2 / 15.5 / 7.3
textural classification	sandy loam	sand	loamy sand	loamy sand
pH	4.55	5.1	4.1	4.4
OM[a] (wt-%)	<0.05	<0.05	7.9	<0.05
CEC (cmol kg^{-1})	1.09 ± 0.31	BD[b]		
AEC (cmol kg^{-1})	1.58 ± 0.61	0.06 ±0.19		
BET surface area (m^2 g^{-1})	15.31	1.27	3.76	22.21
CDB extrac. Fe (mg g^{-1})	15.26	7.06	2.24	27.44
^{129}I (pCi g^{-1})	0	0	0	14.62
Mineralogy	kaolinite, goethite, hematite	kaolinite, goethite, muscovite/14Å	kaolinite, goethite, quartz, hematite, muscovite/14Å	kaolinite, goethite, quartz, hematite

[a] OM = organic matter, CEC = cation exchange capacity, AEC = anion exchange capacity, CDB = citrate dithionate, buffer

[b] BD = below detection

TABLE 2. Iodide and Iodate Distribution Coefficients ($K_d = I_{solids}/I_{aq}$) Measured Under Oxidizing and Reducing Conditions[a]

Soil	Iodide		Iodate	
	Oxidizing[b]	Reducing	Oxidizing	Reducing
Sandy	5.93 ± 3.44 Ab[c]	8.09 ± 3.68 Aa	5.95 ± 1.60 Ac	Not Measured
Clayey	8.04 ± 7.21Bb	3.78 ± 3.00 Bb	41.4 ± 4.99 Ab	45.3 ± 7.19 Aa
Wetland	72.5 ± 23.4 Aa	9.79 ± 2.69 Ba	80.3 ± 27.7 Aa	6.82 ± 2.72 Bb

[a] K_d values for data collected after eight days of equilibration, data from one and four days not included in this data set. There were no meaningful statistical differences as a function of time, so the duplicate or triplicate results from each treatment were combined to produce one mean, typically of nine observations. Equilibrium K_d values represent averages and standard deviations of seven to nine samples. Suspensions were allowed to reach natural pH levels of the sediment suspension, pH 5.3 – 6.3. Spike was <1000 ppb, 25g L^{-1} in 0.01 M NaCl. In all cases, the background iodine concentration due to desorption of native iodine from the sediments was measured and subtracted out of the measured iodine concentration for samples to which iodide or iodate had been amended.

[b] Oxidizing experiments were conducted on the lab bench and reducing experiments were conducted in a glovebox that was maintained at <0.5 mg L^{-1} O_2 throughout experiment.

[c] Means followed by the same CAPITAL LETTER within a ROW and means followed by the same small letter within a column are not significantly different according to Duncan's Multiple Range Test (p ≤0.05; JMP 8, Cary NC).