



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



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ABSTRACT

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

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1. Introduction

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

Major iodine species in aquatic systems include iodide (I^-), iodate (IO_3^-), and organo-I. Based on thermodynamic calculations using Hanford Site groundwater pH and redox (Kaplan et al., 2013), it was previously assumed that I^- was the dominant species, thus, almost all studies to date have focused on I^- uptake to Hanford Site subsurface sediments (Kaplan and Serne, 2000; Kaplan et al., 2000; Um et al., 2004). In addition, it has been traditionally assumed that very low organic carbon (OC) concentration in subsurface sediment (<0.2 wt-%), including those at the Hanford Site, have little influence on iodine speciation and sorption (Serne, 2007). Only a few studies (e.g., Hu et al., 2005) have investigated the potential migration of iodine species other than I^- through the Hanford Site sediments. However, due to detection limitations, experimental iodine concentrations (10^{-4} – 10^{-5} M) that were used were orders of magnitude higher than environmental levels (10^{-7} M– 10^{-8} M for ^{127}I , 10^{-9} – 10^{-10} M for ^{129}I). Non-linear sorption isotherms were observed for sediments containing high natural organic matter (NOM) contents, when amended iodine concentrations exceeded 10^{-5} M, (Emerson et al., 2014; Schwehr et al., 2009). Therefore, one has to be cautious when using elevated concentrations in the laboratory to interpret iodine uptake behavior at environmental levels due to limited binding sites available in the sediment (Xu et al., 2013, 2011a, 2012).

In contrast to this iodide-centric paradigm, $^{127}\text{IO}_3^-$ and $^{129}\text{IO}_3^-$ were recently identified as the dominant stable and radioiodine species (45–84%) in groundwater collected from 200-West Area of the Hanford Site, followed by organo-I (15–40%) and minor amounts of I^- (Zhang et al., 2013). These findings bring new challenges to the determination of credible geochemical parameters, including K_d values, for use in understanding and predicting the transport and fate of ^{129}I through subsurface sediments of the Hanford Site. Previous K_d values of ^{129}I were primarily based on the assumption that I^- was the only species present in the Hanford Site's alkaline and carbonate-rich groundwater system. Therefore, the objectives of this study were to 1) identify and quantify the key processes controlling I^- and IO_3^- uptake to three representative Hanford Site subsurface sediments collected from the vadose, upper saturated and deeper saturated zones; and 2) assess groundwater iodine speciation transformations in the presence of sediments maintained under different experimental conditions

(open-air vs. air-sealed). An air-sealed with limited headspace condition was employed often in other iodine-sediment interaction studies (e.g., Kaplan et al., 2000; Um et al., 2004) to mimic the Hanford Site underground anaerobic conditions. In this study we also applied an open-air and agitated condition, as an effort to replenish O_2 and mimic the possible aerobic conditions in Hanford groundwater-sediment systems (e.g., groundwater recharge with aerobic recycled water, mixing with river water, infiltrating banks and riverbed sediments, etc.). Particular attention was directed at evaluating the indigenous stable iodine speciation in the sediment and groundwater, quantifying groundwater iodine speciation transformations once it came into contact with the three Hanford sediments, and evaluating the extent of iodine sediment uptake, iodate reduction, iodide oxidation, and the formation of organo-iodine species. In-depth studies were conducted with the sediments that varied greatly in regard to texture, carbonate and OC concentrations, but had similar fine-fraction mineralogy and pH.

2. Materials and methods

2.1. Groundwater and sediment sampling

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

Groundwater was collected from well 299-W11-88, which is located about 1.3 km from the primarily contaminant source, disposal crib 216-T-26 (which received 11,000,000 L of liquid waste containing about 59 Bq/L ^{129}I) (Corbin et al., 2005) (Table 1). This was the same groundwater studied in Zhang et al. (2013). Groundwater was recovered with a "Mega Typhoon" pump (Pro-active Pumps, Trenton, New Jersey). The groundwater was stored frozen at -20 °C. Sediment samples were collected from two boreholes that had been archived during the 1990s: wells 299-W15-226 and 299-W15-765. The sediment samples were from three stratigraphic layers: vadose zone (sediment H1; 30–41 m

Table 1
Properties of groundwater used in the experiment.

^{129}I , Bq/L	0.15
^{127}I , (μg/L)	9.33
$^{127}\text{I}^-$ (%)	1.8
$^{127}\text{IO}_3^-$ (%)	75.9
$^{127}\text{Organo-I}$ (%)	22.3
pH	7.99
dissolved organic carbon (DOC) (μM)	15.6
Turbidity (NTU)	1.28
Temperature (°C)	20.3
Specific conductance (μS/cm)	463
Alkalinity (μg/L)	120,000
Sulfate (μg/L)	27,900
Nitrate (μg/L)	86,300
Nitrite (μg/L)	131
Chloride (μg/L)	8180
Ca (μg/L)	47,400
Na (μg/L)	14,800
Mg (μg/L)	17,000
K (μg/L)	5330
Fe (μg/L)	38
Mn (μg/L)	6
Eh (mV)	154

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