



Speciation of iodine isotopes inside and outside of a contaminant plume at the Savannah River Site



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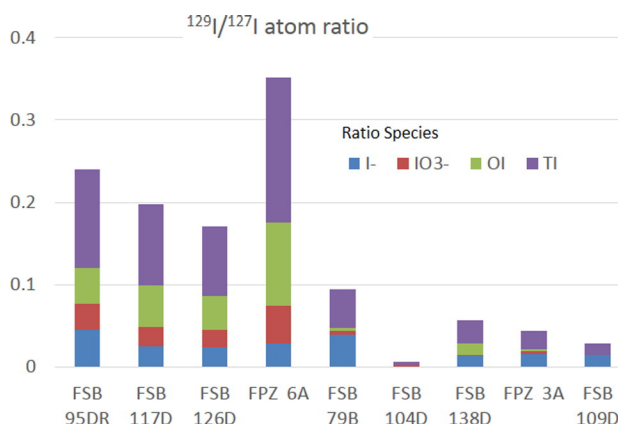
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HIGHLIGHTS

- Total ^{129}I in a plume impacted aquifer ranged from >1.7 to 0.001 Bq/L (1 Bq/L = 10^{-13} M).
- For $^{129}\text{I}/^{127}\text{I}$, % of organo-I ranges from 0 to 82.4% and averages 36.8%.
- $^{129}\text{I}/^{127}\text{I}$ ratio range showed a variability in source within the plume.
- $^{129}\text{I}/^{127}\text{I}$ ratio between low level plume and US rivers identified a 2nd plume source.
- $^{129}\text{I}/^{127}\text{I}$ ratios and species distribution proportional to pH with $[\text{I}^-] \gg [\text{IO}_3^-] = [\text{OI}]$

GRAPHICAL ABSTRACT



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ABSTRACT

A primary obstacle in understanding the fate and transport of the toxic radionuclide ^{129}I (a thyroid seeker) is an accurate method to distinguish it from the stable isotope, ^{127}I , and to quantify the various species at environmentally relevant concentrations ($\sim 10^{-8}$ M). A pH-dependent solvent extraction and combustion method was paired with accelerator mass spectrometry (AMS) to measure ambient levels of $^{129}\text{I}/^{127}\text{I}$ isotope ratios and iodine speciation (iodide (I^-), iodate (IO_3^-), and organo-I (OI)) in aquatic systems. The method exhibited an overall uncertainty of 10% or less for I^- and IO_3^- , and less than 30% for OI species concentrations and enabled ^{129}I measurements as low as 0.001 Bq/L (1 Bq/L = 10^{-13} M). The method was used to analyze groundwater from the Savannah River Site (SRS), South Carolina, USA, along a pH, redox potential (Eh), and organic carbon gradient ($8\text{--}60$ μM DOC). The data confirmed that the $^{129}\text{I}/^{127}\text{I}$ ratios and species distribution were strongly pH dependent and varied in a systematic manner from the strongly acidic source. While ^{129}I speciation in plume samples containing total I concentrations >1.7 Bq/L was similar whether measured by AMS or GC-MS ($[\text{I}^-] \gg [\text{IO}_3^-] = [\text{OI}]$), AMS enabled ^{129}I speciation measurements at much lower concentrations than what was possible with GC-MS. AMS analyses demonstrated that groundwater samples minimally

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impacted by the plume were still orders of magnitude higher than ambient ^{129}I concentrations typically found elsewhere in the USA groundwaters and rivers. This is likely due to past atmospheric releases of volatile ^{129}I species by SRS nuclear reprocessing facilities near the study site. Furthermore, the results confirmed the existence of ^{129}I not only as I^- , but also as OI and IO_3^- species.

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1. Introduction

Radioiodine (^{129}I ; half-life = $(1.57 \pm 0.04) \times 10^7$ a, (Emery et al., 1972)) is naturally produced by cosmic ray bombardment of ^{130}Te and atmospheric xenon isotopes, as well as spontaneous nuclear fission of primordial uranium in the earth's crust. However, most ^{129}I in the surface environment originates from nuclear fuel reprocessing plant emissions and nuclear weapon testing. These sources have increased the concentration of ^{129}I in aquatic systems by as much as three orders of magnitude above natural levels ($\sim 7.5 \times 10^{-11}$ Bq/L) and raised the natural isotopic ratio as much as 5 orders of magnitude above the natural ratio ($^{129}\text{I}/^{127}\text{I} = 1.5 \times 10^{-12}$) in the last few decades (Santschi and Schwehr, 2004; Snyder and Fehn, 2004; Hou et al., 2008). Hou and Hou (2012) have provided a review of sources and concentrations of ^{129}I and $^{129}\text{I}/\text{I}$ ratio values in the environment. The Fukushima Daiichi Nuclear Power Plant accident reportedly introduced ~ 1.2 kg of ^{129}I into the environment (Hou et al., 2013), and the Chernobyl accident introduced ~ 1.3 – 6 kg of ^{129}I into the environment. However, ^{129}I releases from these well-known nuclear incidents are relatively small compared to the amount released into the environment from ongoing nuclear fuel reprocessing in France and England, where approximately 5600 and 255 kg of ^{129}I have been released into the ocean and atmosphere, respectively, through 2008 (Hou and Hou, 2012).

In this study, we develop more insight as to how the ^{129}I contamination at the nuclear separation facility at the US Department of Energy Savannah River Site (SRS) F-Area fits into the global picture. It is our intent to demonstrate that management of the radionuclide waste at this facility should be an ongoing consideration. Past operations at the SRS F-Area nuclear separation facility resulted in the release of multiple radionuclides into the environment, including ^3H , ^{129}I , ^{90}Sr , ^{239}Pu , ^{235}U , and ^{238}U (Savannah River Nuclear Solutions, 2008). Unlined seepage basins associated with the facility routinely received acidic (average $\text{pH} = 2.3$), radionuclide-contaminated wastewaters between 1955 and 1988 (Kaplan et al., 2011; Savannah River Nuclear Solutions, 2008). The seepage basins were closed in 1988 by removing the bottom layer of highly contaminated sediment, and adding limestone and blast furnace slag (a sulfide based by-product recovered from iron ore processing) to immobilize heavy metals (including Hg, Pb, Cd, Cr, and As) and multi-valent radionuclides (e.g., ^{241}Am , $^{141\&144}\text{Ce}$, ^{244}Cm , $^{238\&239}\text{Pu}$, ^{90}Sr and $^{235\&238}\text{U}$). The basins were capped in 1991 with a low permeability engineered barrier system to reduce downward migration of radionuclides into the groundwater. In addition, since 2005, a base-injection/funnel-and-gate remediation program was established 300–500 m down gradient from the primary seepage basin. These remediation efforts have led to the effective immobilization of most radionuclides and heavy metal contaminants (Dai et al., 2002). However, the rising pH of the groundwater over the last 19 years due to the remedial base injection and the basin closure with limestone has been shown to be partially responsible for the remobilization of ^{129}I from the seepage basins and aquifer sediments, resulting in groundwater concentrations increasing from 7.4 to 37 Bq/L ^{129}I (the Environmental Protection Agency's (EPA) maximum contaminant level (MCL) is 0.037 Bq/L (1 pCi/L)) (Kaplan et al., 2011).

In aquatic systems iodine occurs in three chemical forms – iodide (I^-), iodate (IO_3^-) and organo-iodine (OI) – whose proportions vary as a function of biogeochemical properties in the aquatic system, including pH, redox state (Eh), dissolved organic carbon (DOC)

concentrations, and microbial processes (Hou et al., 2008; Schwehr et al., 2005a,b; Lehto et al., 2012; Xu et al., 2011a,b; Kaplan et al., in press). The ^{129}I speciation and concentrations in groundwater from the SRS F-Area were found to vary as a function of: 1) proximity to the source term (the seepage basins), 2) pH, 3) Eh, and 4) proximity to the high-organic matter wetland that receives the ^{129}I plume (Otosaka et al., 2011).

Most importantly, ^{129}I partitioning to the aquifer solid phase was found to be influenced by I concentration (Schwehr et al., 2009; Zhang et al., 2010, 2011), pH (Kaplan et al., in press), redox potential (Emerson et al., accepted for publication), sediment organic matter (SOM) concentrations (Xu et al., 2011a,b), and microbial activity (Li et al., 2012). These studies have consistently demonstrated the necessity of studying I biogeochemistry at environmentally relevant concentrations (10s to 100s of Bq/L) to avoid experimental artifacts associated with I speciation, partitioning to sediments, and complexation with naturally occurring aqueous and solid phase organic carbon (Schwehr et al., 2009; Xu et al., 2011a,b; Zhang et al., 2011).

In our previous studies of SRS groundwater, ^{129}I and ^{127}I speciation was determined by a gas chromatography–mass spectrometry (GC–MS) method (Zhang et al., 2010). This method is very useful because it only requires small sample volumes (~ 5 mL), and it is relatively fast, simple, and inexpensive. Additionally, both isotopes can be measured simultaneously. This GC–MS method has been used to simultaneously measure ^{129}I and ^{127}I speciation and isotopic ratios in groundwater collected from the ^{129}I -contaminated F-Area plume (Otosaka et al., 2011). However, although Zhang et al. (2010) report a detection limit of 0.08 Bq/L, it is difficult to measure complete ^{129}I speciation at levels below 0.5 Bq/L, such as that found in groundwater outside of the ^{129}I plume. As a consequence, little is known about ^{129}I species outside or along the boundaries of plumes, where contamination levels are relatively low.

Since the 1980s, accelerator mass spectrometry (AMS) has been recognized as the most reliable analytical method for ^{129}I and has been used for measurements of natural-levels of ^{129}I in environmental samples (e.g., Fabryka-Martin et al., 1985; Schink et al., 1995; Santschi et al., 1996; Moran et al., 1999; Schwehr et al., 2005a,b; Suzuki et al., 2009). Detection limits of AMS are orders of magnitude lower than those of GC–MS and lower than those of radiochemical neutron activation analysis (RNAA) (Szidat et al., 2000) and inductively coupled plasma-mass spectrometry (ICP-MS) (Hou et al., 2008; Muramatsu et al., 2008). Even though analysis of ^{129}I species in aquatic samples has been performed using AMS, existing speciation separation techniques are complicated, employing ion exchange chromatographic resins and dehydrohalogenation of OI, and typically require solvent extractions (e.g., Schwehr et al., 2005a,b).

In this study, we used the GC–MS method of Zhang et al. (2010) to analyze ^{129}I concentration and speciation levels within the SRS F-Area plume, and AMS to determine ^{129}I concentration and speciation where I concentrations are near or below the detection limits of the GC–MS. The I species were determined by AMS after selective extraction into an organic phase controlled by pH^- and oxidant strength, similar to the method of Hou et al. (2009), with the exception that their treatment of total I (TI) and OI is different.

The hypothesis of this study was that the distribution of iodine species would remain largely similar at 10^{-9} – 10^{-11} M (GC–MS detectable levels) and $< 10^{-12}$ M (AMS detectable levels) because key

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