STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Insights into the sorption and release mechanisms of Iodine-129 at Savannah River Site

DOE-FIU SCIENCE & TECHNOLOGY
WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

December 16, 2022

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Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0005213

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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2022, a DOE Fellow intern, Phuong Pham, spent 10 weeks doing a summer internship at Savannah River National Laboratory under the supervision and guidance of Hansell Gonzalez-Raymat. The intern's project was initiated on June 6, 2022, and continued through August 12, 2022, with the objective of gaining a better understanding of the dominant attenuation and release mechanisms for ^{129}I in the wetlands.

Iodine-129 (^{129}I), a long-lived fission product and one of the major constituents of concern at the Savannah River Site (SRS), migrates through the vadose zone into the saturated zone due to its mobility. The elevated concentrations of radioiodine, mostly as ^{129}I with multiple anionic species (i.e., iodide (I^-), iodate (IO_3^-), and organo-iodide), were detected in the groundwater of the SRS F-Area wetlands. The wetland's complex and diverse physical and biogeochemical processes are mainly responsible for retaining these contaminants. However, these areas are sensitive to changing boundary and geochemical conditions. If water levels fluctuate, organic-bound contaminants can be released. Likewise, pH and redox changes may result in contaminant releases as well. The goal of this study is to understand the factors that contribute to the attenuation and release of iodine (iodide and iodate) occurring at the F-area wetlands. To accomplish this goal, the first task was to provide a literature review to identify the main mechanisms that cause the attenuation and release of iodine in the environment and build a conceptual model for iodine specific to the F-Area wetland conditions. The second task was to investigate the sorption of iodine species on the wetland soil collected at different depth intervals from an uncontaminated area of the F-Area wetlands. Batch experiments were performed under oxic environments and varying pH to investigate the degree of binding or association of iodine with the mineral and organic fractions in the F-area wetland soils. The potential findings of this study will improve the conceptual model of the F-Area and provide an understanding of the natural attenuation processes occurring at the wetlands that will help in the development of enhanced attenuation strategies as well as assessing whether remedial actions have undesirable collateral consequences. The outcome of these studies will help to better understand the dominant attenuation mechanisms for ^{129}I in the wetlands, the strength of the attenuation, and what conditions would influence it.

1. INTRODUCTION

Exposure to long-lived radioactive iodine-129 (^{129}I) has a negative impact on public health, water quality, and ecosystems. Once released into the environment via the operation of low-level nuclear waste disposal facilities and occasional nuclear accidents like Chernobyl and Fukushima (Suzuki et al. 2013; Kaplan, Denham, et al. 2014), ^{129}I poses a serious chemical and radiological threats to human and living organisms due to its long half-life of 16 million years and bioconcentration, which causes it to accumulate in the food chain (Kaplan, Denham, et al. 2014).

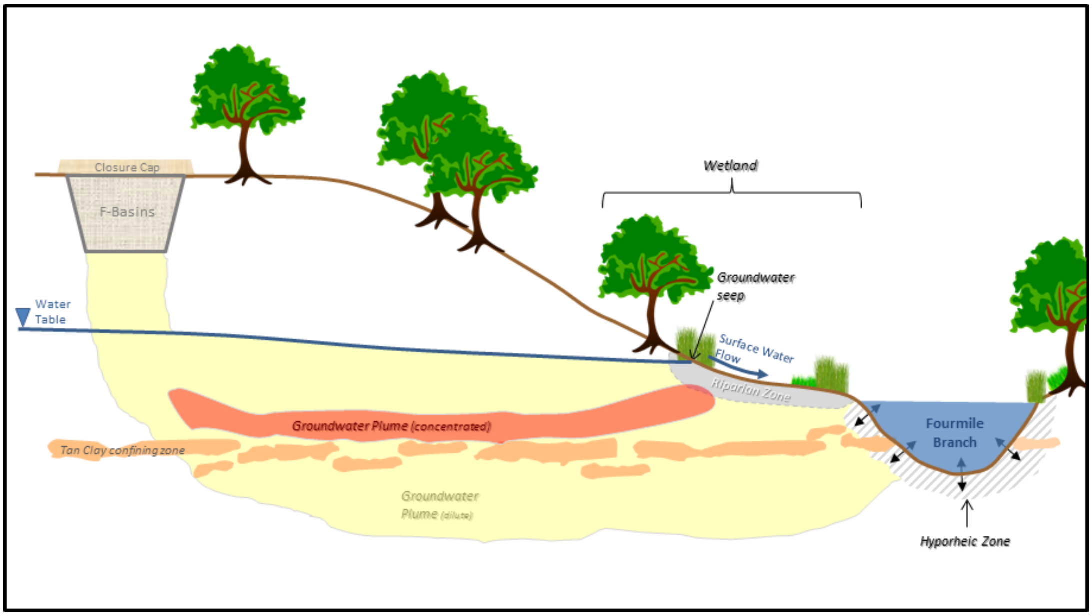

Figure 1. Conceptual model of F-Area groundwater plume.

The Savannah River Site (SRS) is a nuclear separation facility built in the 1950's to refine nuclear materials for nuclear weapons. The F-Area Seepage Basins, located within the General Separation Area of the SRS consisted of three unlined basins. These basins received low-level radioactive wastewater originating from the reprocessing of uranium slugs and irradiated fuel in the F-Area Separation Facility. A large amount of ^{129}I and other radionuclides migrated to the vadose zone and contaminated the groundwater, where it was transported to the wetlands associated with a local stream, Fourmile Branch, shown in Figure 1 (Zhang et al. 2014; Kaplan, Zhang, et al. 2014; Kaplan, Denham, et al. 2014). In the past, wetlands at the F-Area have been an important sink for ^{129}I and other contaminants, but changes in biogeochemical conditions could cause the release of these contaminants into the surrounding areas (Neeway et al. 2019; Santschi et al. 2017; Emerson et al. 2014; Chang et al. 2014; Kaplan, Zhang, et al. 2014; Zhang et al. 2011; Xu et al. 2011).

2. RESEARCH DESCRIPTION

Materials:

Potassium iodide (KI), potassium iodate (KIO_3), and sodium chloride (NaCl) salt were obtained from Fisher Scientific. Nanopure water, resistivity~18.0 MΩ·cm^{-1} at 25 °C, was used for preparing standards and samples unless indicated.

Wetland soils were collected at an uncontaminated area along the Fourmile Branch seepline that has not been affected by site operations. Vertical soil profile sampling was performed using a Geoprobe (model 6620DT) for deeper samples (≥ 5 feet) and a hand auger for shallower samples (0 – 2 feet). Soil samples were collected from the soil cores at ~six-inch-long for the first 2 feet of soil core and then ~one-foot-long for the remaining soil core as shown in Figure 2.

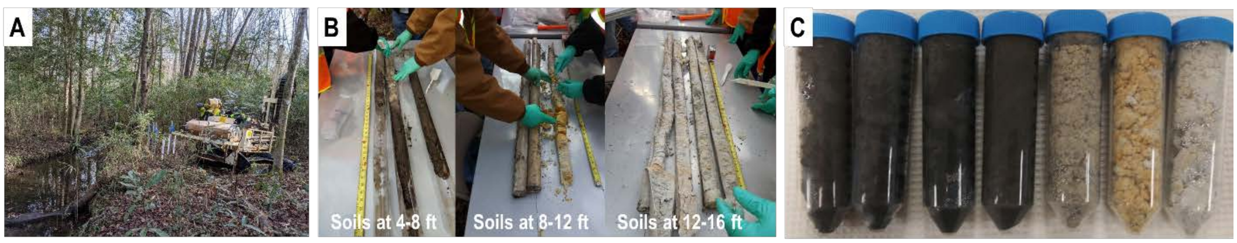

Figure 2. (a) Soil Sampling at background area; (b) collecting soil cores; and (c) sorting soil samples into different depth intervals.

Adsorption experiments:

Stock solutions of 1000 mg/L of iodide and iodate were prepared by dissolving an appropriate amount of potassium iodide and potassium iodate in nanopure water (>18MΩ). Working solutions of iodide and iodate were prepared by diluting the stock solutions to final concentration of 10 mg/L. A background solution (0.01M NaCl) was also prepared in a similar way by dissolving an appropriate amount of sodium chloride in nanopure water (>18MΩ). Batch sorption studies were conducted to quantify the attenuation and release of iodide/iodate on soils collected at different depth interval in background solution (I = 0.01M NaCl). The 0.0135 g of sacrificial triplicate wetland soil samples were equilibrated with 0.01 M NaCl solution for a week prior to the adsorption study. The samples were spiked with working iodide/iodate solutions (10 mg/L) in the 15 mL centrifuge vials to reach the final concentration of ~ 100 µg/L. The initial adsorption studies were conducted at room temperature and at pH range from 4 to 8 by adjusting the pH with 0.1 M HCl and 0.1 M NaOH. Two set of triplicate sacrificial soil samples were suspended in 0.01 M NaCl at pH 4-8 in order to examine the release of iodine into aqueous phase during the sorption study. A set of control iodide and iodate solution in the absence of soil in 0.01 M NaCl at different pH values were prepared to identify any sorption of iodine on the vial's wall during the adsorption period. The samples were placed on the incubator shaker for one week at the agitation rate of 100 rpm. The triplicate sacrificial samples were then collected and centrifuged at 2700 rpm for 30 minutes to separate the solid from the liquid phase. The supernatants were mixed with 0.1% TMAH and analyzed by the ICP-MS for total iodine.

3. RESULTS AND ANALYSIS

Iodine Conceptual Model for the F-Area Wetlands

A conceptual model of the attenuation and release of iodine-129 was created to give insight into the mechanisms controlling the processes. There are several factors that could contribute to the attenuation/release of ^{129}I such as the changes in water level, soil/water temperature, microbial activity, redox potential, organic matter, and pH of the environment. The influences of primary productivity and redox conditions on the attenuation/release of contaminants were discussed below.

As the temperature rises, microbial activities may contribute to the biotransformation of iodine into other species, affecting iodine attenuation and release in the wetland. Microorganisms and higher plants can influence iodine mobility and speciation in the wetland by transforming iodide to the volatile methyl-iodide (Amachi et al. 2003; Bagwell et al. 2019; SAINI, ATTIEH, and HANSON 1995). The bacteria can also accumulate iodine, according to Li et al. 2011, iodide accumulation was probably caused by electrophilic substitution of cellular organic molecules. The covalently bonded iodide in the cells may eventually go by cell lysis processes to the organic-iodine pool, despite the low buildup. Furthermore, microbial exo-enzymatic iodide oxidizing activity and organic acids produced by microbes significantly contribute to organo-iodine formation (Li, Brinkmeyer, et al. 2012; Li, Yeager, et al. 2012). Denham and Amidon (2016) observed that during periods of high rainfall ^{129}I concentrations tend to increase. The increase in surface water and groundwater flow during the rainy periods might have released the bounded ^{129}I into the environment [3]. Their observations are consistent with a study conducted by Xu et al. (2011) of the speciation of ^{129}I in F-Area wetland soils. Soil flooding in wetlands leads to a chain of physical, chemical, and biological reactions being initiated leading to lower redox potential (E_h) in soil. The limited supply of oxygen within the soil profile is depleted rapidly by plant roots, microbes, and soil reductants. Hence, various facultative and obligate anaerobic microorganisms use oxidized compounds (NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}) as electron acceptors for respiration, thus converting them to reduced forms (Pezeshki and DeLaune 2012; Xue et al. 2022). This process could trigger the reductive dissolution of iodine-bearing iron oxyhydroxides in sediments under reducing environment (high water level period). Additionally, the degradation of labile dissolved organic matter could promote the transformation of Fe minerals in aquifer sediments and release of iodine into groundwater (Li et al. 2020). A recent study by Xue et al., shows that the release of iodine may be associated with the degradation of high molecular weight (HMW) organic compounds in organic rich sediments (Xue et al. 2022).

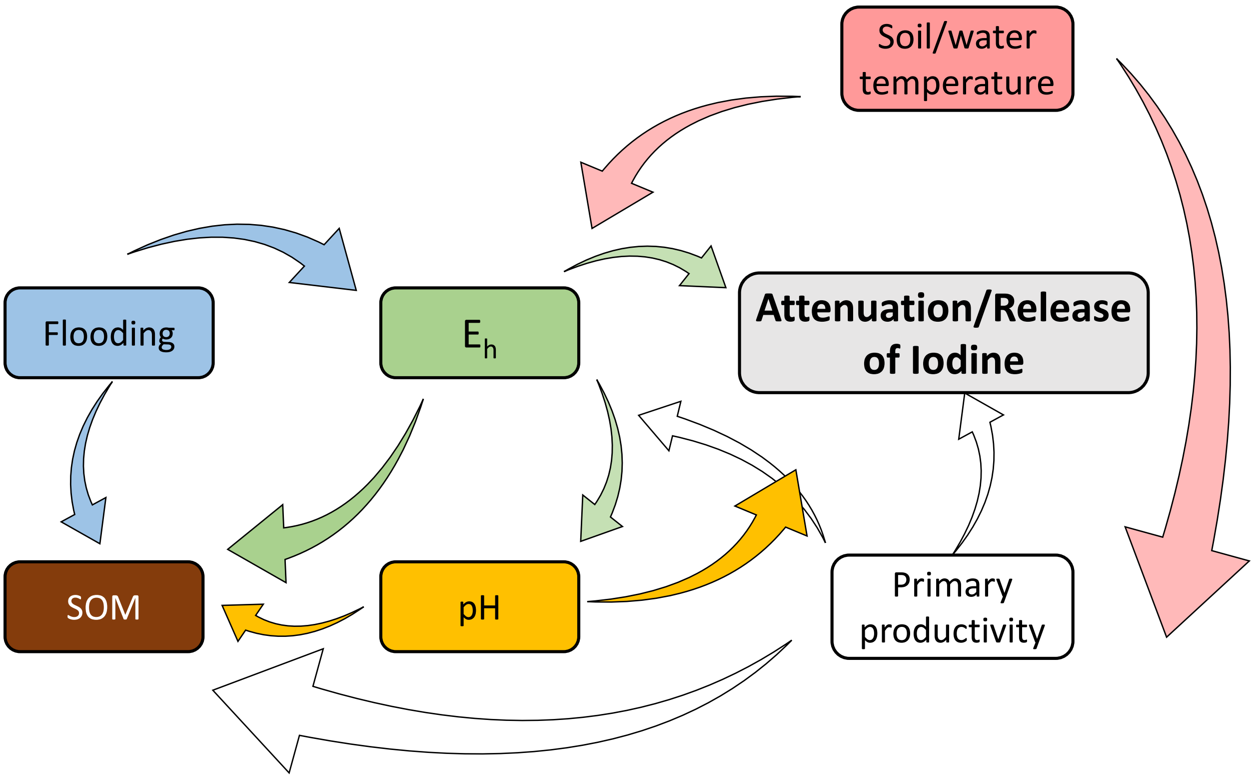

Figure 3. Conceptual model of the attenuation and release of ^{129}I at the Fourmile Branch wetland

Adsorption experiments:

Adsorption studies of iodide and iodate on wetland soils at different depth intervals were performed during this summer internship. Based on the recent field results conducted by Savannah River National Laboratory, the following depth intervals were chosen for the batch experiments: 5-6 feet and 13-14 feet, presenting the transition zone and the aquifer layer of Fourmile Branch wetland. The results from the sorption experiment indicate that there is minimal or no sorption of either iodide or iodate at different pH values for the soils at depth 5-6 and 13-14 feet within a week of the adsorption time.

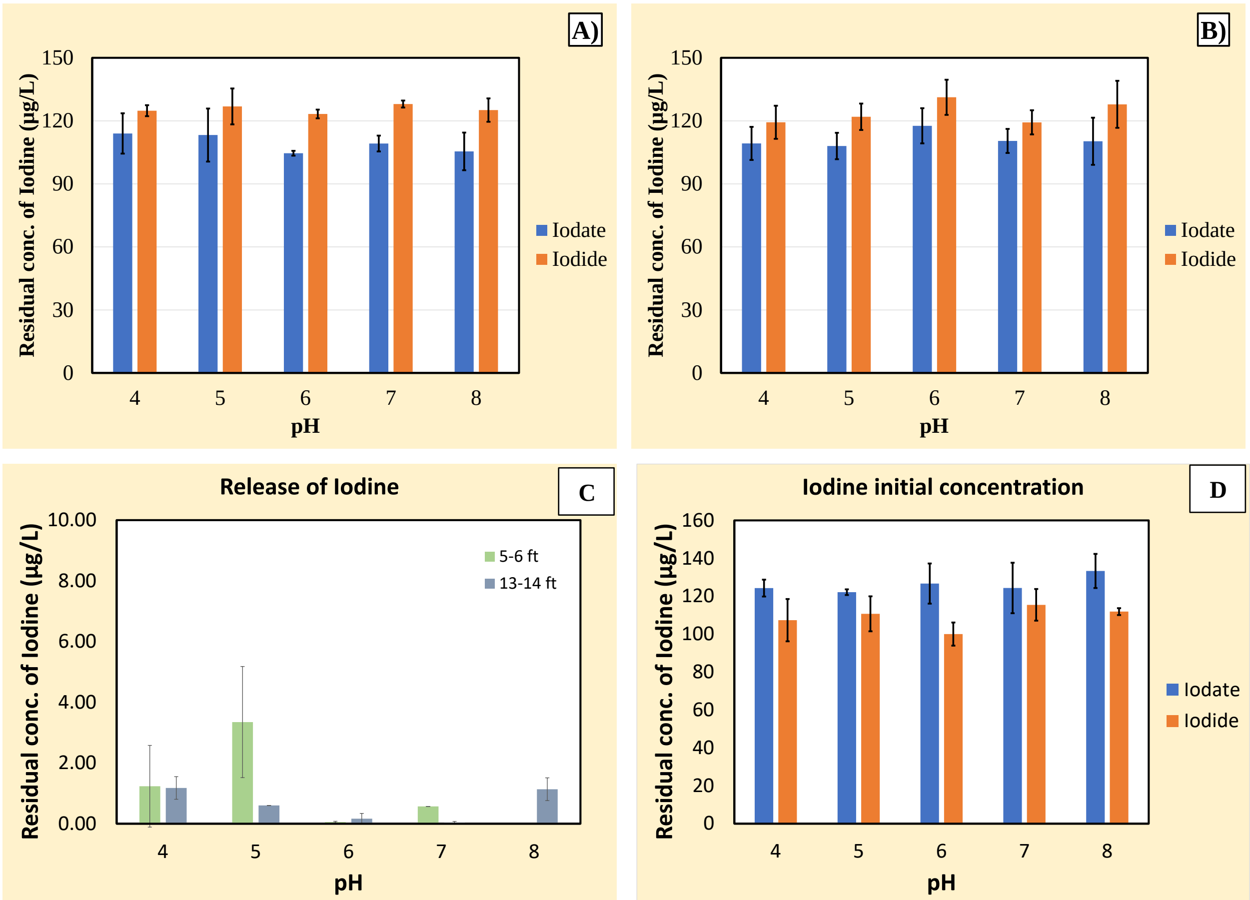

Figure 4: Residual concentration of iodide and iodate in solution after a week of sorption onto SRS wetland's soils at a) 5-6 feet, b) 13-14 feet depth intervals c) release of iodine from the soil and d) initial concentration of iodine spiked in the samples

4. CONCLUSION

The Fourmile Branch wetland presents a unique natural environment to study the long-term biogeochemistry of radionuclides under natural environmental conditions. From our observed results, the sorption and release of ^{129}I are not dictated by the pH of the environment for 5-6 ft and 13-14 ft soils. The sorption of ^{129}I (and other radionuclides) might be influenced by redox conditions, organic content and microbial community composition at different soil depth intervals. To further understand the mechanisms controlling the attenuation and release of ^{129}I at the Savannah River Site's wetland, further studies are needed.

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