

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Sorption of Iodine Species on SRS Wetland Soils

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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TABLE OF CONTENTS

TABLE OF CONTENTS.....	iii
LIST OF FIGURES	iv
LIST OF TABLES	iv
EXECUTIVE SUMMARY	5
1. INTRODUCTION	6
2. RESEARCH DESCRIPTION.....	8
3. RESULTS AND ANALYSIS.....	9
4. CONCLUSION.....	11
5. REFERENCES	12

LIST OF FIGURES

Figure 1. Conceptual model of F-Area groundwater plume.	6
Figure 2. (a) Soil Sampling at background area; (b) collecting soil cores; and (c) sorting soil samples into different depth intervals.	7
Figure 3. Sorption experiments of iodide and iodate on the soils at pH 4.5 and 7.	8
Figure 4. Preliminary adsorption kinetic of iodide/iodate on wetland soils at pH 4.5.	9

LIST OF TABLES

Table 1. Parameters of Soil at 5 Different Depth Intervals. Data received from SRNL	10
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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 2021, 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 May 24, 2021, and continued through July 30, 2021, with the objective of gaining a better understanding of the dominant attenuation mechanisms for ^{129}I in the wetlands, the strength of the attenuation, and what conditions would influence it.

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. Recently, the elevated levels 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. 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 sorption and release of iodine species on the wetland soil was investigated using soils collected from the 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 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 ¹⁻², ^{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 ².

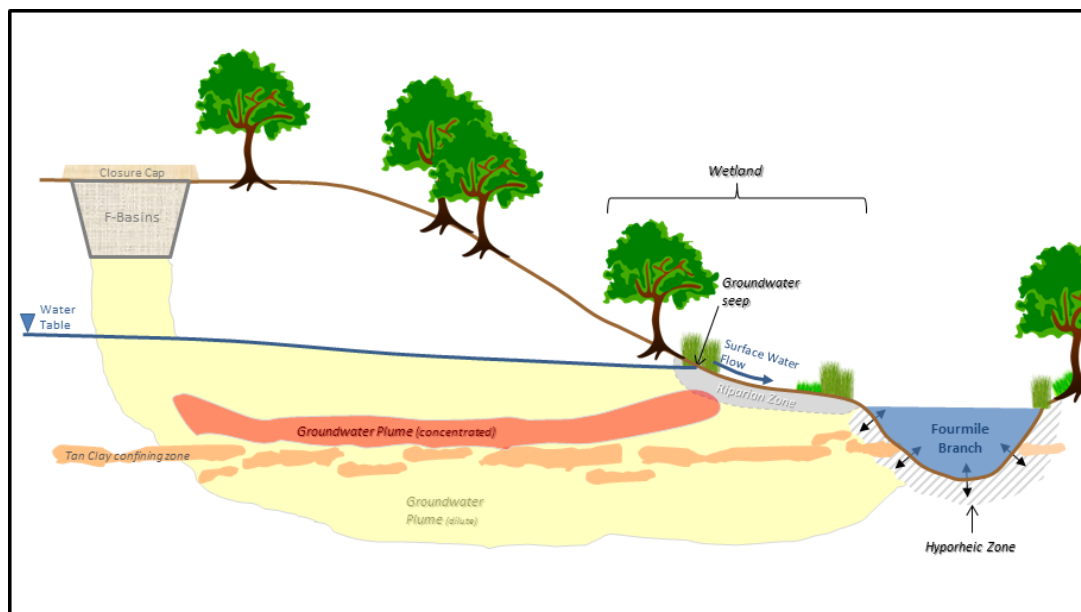


Figure 1. Conceptual model of F-Area groundwater plume.

The Savannah River Site (SRS) is a nuclear separation facility built in the 1950s 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 1²⁻⁴. 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 ⁴⁻¹⁰. Denham and Amidon ¹¹ found that during periods of high rainfall ^{129}I concentrations tend to increase, while tritium does not increase but at times instead decreases. The increase in surface water and groundwater flow during the rainy periods might have released the bounded ^{129}I into the environment ³. Their results are consistent with a study conducted by Xu, et al. ¹⁰ of the speciation of ^{129}I in F-Area wetland soils. The biogeochemical conditions such as variations in microbial activity, redox conditions, soil temperature, soil moisture, and pH, may cause the seasonal release of organically bound ^{129}I from wetland soils.

In this study, wetland soils were collected at an uncontaminated area along the Fourmile Branch seep line 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. In the present study, the sorption of iodide and iodate on soils at different depth intervals was investigated to better understand the dominant attenuation mechanisms for ^{129}I in the wetlands, the strength of the attenuation, and what conditions would influence it.

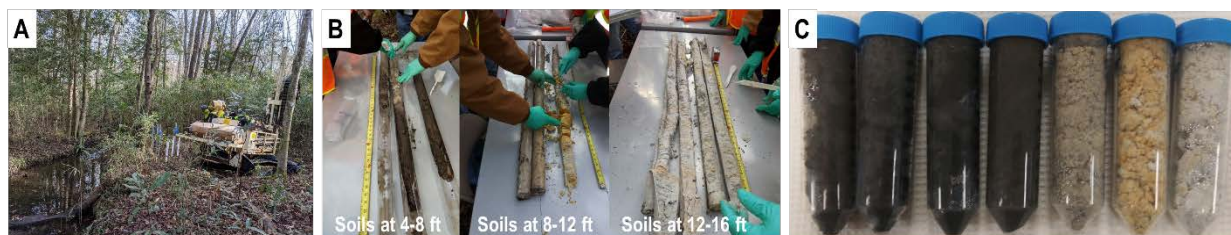


Figure 2. (a) Soil Sampling at background area; (b) collecting soil cores; and (c) sorting soil samples into different depth intervals.

2. RESEARCH DESCRIPTION

Materials:

Potassium iodide, potassium iodate, and sodium chloride salt were obtained from Fisher Scientific. The wetland soils were collected at an uncontaminated location near the Fourmile Branch stream at the Savannah River Site. Nanopure water, resistivity~18.0 M Ω ·cm⁻¹ at 25 °C, was used for preparing standards and samples unless indicated.

Preliminary adsorption experiments:

Preliminary adsorption experiments of iodide and iodate on wetland soils at pH 4.5 were conducted to determine the required amount of soil and contact time needed for the experiments. Triplicate background soils (100 g/L) were equilibrated with nanopure water for a week. The pH of suspension samples was adjusted with 0.1 M HCl and 0.1 M NaOH to reach a pH of 4.5. The samples were spiked with stock iodide/iodate to reach a final concentration of 100 μ g/L. The samples were shaken at 100 rpm on a platform shaker for a total of 20 days. Aliquots from the samples were collected at specific time intervals and analyzed for iodine residuals using the ICP-MS.

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 (>18M Ω). A background solution (0.01M NaCl) was also prepared in a similar way by dissolving an appropriate amount of sodium chloride in nanopure water (>18M Ω). Batch sorption studies were conducted to quantify the sorption of iodide/iodate and determine changes in iodine speciation when iodine is in contact with wetland soil suspension in background solution ($I = 0.01$ M NaCl). The 0.35 g of wetland soil samples were equilibrated with 0.01 M NaCl solution for a week prior to the adsorption study. The samples were spiked with iodide/iodate solutions in the 15 mL centrifuge vials to reach the final concentration of 200 μ g/L as shown in Figure 3. The initial adsorption studies were conducted at room temperature and at solution pH of 4.5 ± 0.1 and 7.0 ± 0.1 . The samples were placed on the incubator shaker for a total of 11 weeks at the agitation rate of 100 rpm. The samples were collected at specific time intervals and centrifuged at 2700 rpm for 30 minutes to separate the solid from the liquid phase. The liquid phase was analyzed using GC-MS.



Figure 3. Sorption experiments of iodide and iodate on the soils at pH 4.5 and 7.

3. RESULTS AND ANALYSIS

Preliminary adsorption experiments:

Data from the ICP-MS showed that the adsorption of iodide on wetland soils increased with time and reached adsorption equilibrium within 1 day with > 90 % of iodide adsorbed from the initial concentration of 100 $\mu\text{g/L}$ (Figure 4). Meanwhile, the adsorption rate of iodate was slower, and equilibrium was achieved after 5 days with > 90% of iodate adsorbed by the soils. Based on these preliminary results, it was decided to slow down the kinetics of iodide and iodate by using less soil (25 g/L) and increasing the initial concentration of iodide/iodate to 200 $\mu\text{g/L}$ to better observe the adsorption kinetics.

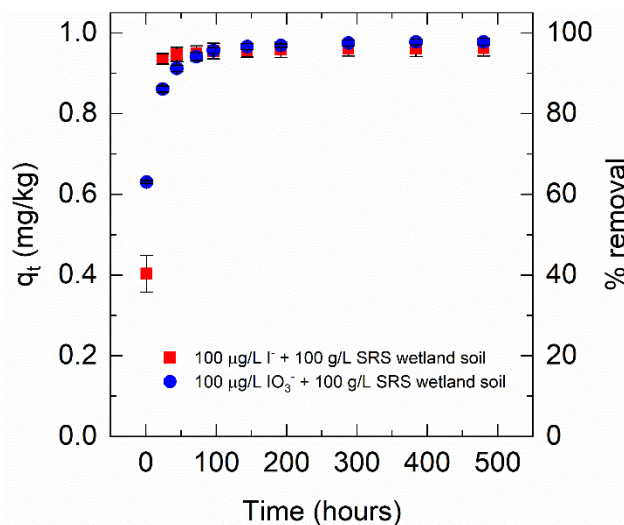
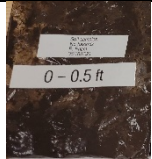
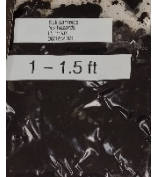

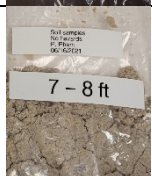



Figure 4. Preliminary adsorption kinetic of iodide/iodate on wetland soils at pH 4.5.

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: 0-0.5 feet, 1-1.5 feet, 5-6 feet, 7-8 feet, and 13-14 feet, presenting the organic layer, intermediate layer, and the aquifer layer as shown in Table 1. The 1-week, 3-week, 7-week, 9-week, and 11-week adsorption samples were initiated. The pH of these samples was adjusted periodically to keep the solutions' pH at 4.5 and 7, however, due to the buffering capacity of soils, the final pHs of the soil samples were ~ 4.2 and 6.5, respectively. The 1-week and 3-week samples have been retrieved from the shaker. The samples were then centrifuged at 2700 rpm for 30 min to separate the solid phase from the aqueous phase. The aqueous solutions were transferred into new vials and kept in the refrigerator until further analysis for iodine speciation. Sample analysis is being done by SRNL.

Table 1. Parameters of Soil at 5 Different Depth Intervals. Data received from SRNL

Soil depth interval (ft)		pH	Total Organic Carbon (mg/kg)	Aluminum (mg/kg)	Iron (mg/kg)
0 – 0.5		4.79	25300	7130	8940
1 – 1.5		4.81	119000	5310	1340
5 – 6		5.05	41700	4310	215
7 – 8		5.43	720	2210	230
13 – 14		5.49	350	2920	180

4. CONCLUSION

The Fourmile Branch wetland presents a unique natural environment to study the long-term biogeochemistry of radionuclides under natural environmental conditions. 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. Sample and data analyses are still ongoing, but preliminary conclusions suggest that iodine species were strongly adsorbed by wetland topsoil.

5. REFERENCES

1. Suzuki, T.; Ootosaka, S.; Kuwabara, J.; Kawamura, H.; Kobayashi, T., Iodine-129 concentration in seawater near Fukushima before and after the accident at the Fukushima Daiichi Nuclear Power Plant. *Biogeosciences* **2013**, *10* (6), 3839-3847.
2. Kaplan, D. I.; Denham, M. E.; Zhang, S.; Yeager, C.; Xu, C.; Schwehr, K. A.; Li, H. P.; Ho, Y. F.; Wellman, D.; Santschi, P. H., Radioiodine Biogeochemistry and Prevalence in Groundwater. *Critical Reviews in Environmental Science and Technology* **2014**, *44* (20), 2287-2335.
3. Zhang, S.; Ho, Y.-F.; Creeley, D.; Roberts, K. A.; Xu, C.; Li, H.-P.; Schwehr, K. A.; Kaplan, D. I.; Yeager, C. M.; Santschi, P. H., Temporal Variation of Iodine Concentration and Speciation (127I and 129I) in Wetland Groundwater from the Savannah River Site, USA. *Environmental Science & Technology* **2014**, *48* (19), 11218-11226.
4. Kaplan, D. I.; Zhang, S.; Roberts, K. A.; Schwehr, K.; Xu, C.; Creeley, D.; Ho, Y.-F.; Li, H.-P.; Yeager, C. M.; Santschi, P. H., Radioiodine concentrated in a wetland. *Journal of Environmental Radioactivity* **2014**, *131*, 57-61.
5. Neeway, J. J.; Kaplan, D. I.; Bagwell, C. E.; Rockhold, M. L.; Szecsody, J. E.; Truex, M. J.; Qafoku, N. P., A review of the behavior of radioiodine in the subsurface at two DOE sites. *Science of The Total Environment* **2019**, *691*, 466-475.
6. Santschi, P. H.; Xu, C.; Zhang, S.; Schwehr, K. A.; Grandbois, R.; Kaplan, D. I.; Yeager, C. M., Iodine and plutonium association with natural organic matter: A review of recent advances. *Applied Geochemistry* **2017**, *85*, 121-127.
7. Emerson, H. P.; Xu, C.; Ho, Y.-F.; Zhang, S.; Schwehr, K. A.; Lilley, M.; Kaplan, D. I.; Santschi, P. H.; Powell, B. A., Geochemical controls of iodine uptake and transport in Savannah River Site subsurface sediments. *Applied Geochemistry* **2014**, *45*, 105-113.
8. Chang, H.-s.; Xu, C.; Schwehr, K. A.; Zhang, S.; Kaplan, D. I.; Seaman, J. C.; Yeager, C.; Santschi, P. H., Model of radioiodine speciation and partitioning in organic-rich and organic-poor soils from the Savannah River Site. *Journal of Environmental Chemical Engineering* **2014**, *2* (3), 1321-1330.
9. Zhang, S.; Du, J.; Xu, C.; Schwehr, K. A.; Ho, Y. F.; Li, H. P.; Roberts, K. A.; Kaplan, D. I.; Brinkmeyer, R.; Yeager, C. M.; Chang, H.-s.; Santschi, P. H., Concentration-Dependent Mobility, Retardation, and Speciation of Iodine in Surface Sediment from the Savannah River Site. *Environmental Science & Technology* **2011**, *45* (13), 5543-5549.
10. Xu, C.; Zhang, S.; Ho, Y.-F.; Miller, E. J.; Roberts, K. A.; Li, H.-P.; Schwehr, K. A.; Ootosaka, S.; Kaplan, D. I.; Brinkmeyer, R.; Yeager, C. M.; Santschi, P. H., Is soil natural organic matter a sink or source for mobile radioiodine (129I) at the Savannah River Site? *Geochimica et Cosmochimica Acta* **2011**, *75* (19), 5716-5735.
11. Denham, M. E.; Amidon, M. B. *Analysis of concentration versus time trends for selected contaminants in groundwater and wetland surface water associated with the F-Area and H-Area Seepage Basins* SRNL-STI-2016-00558; Savannah River National Laboratory: Aiken, SC, 2016.