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**EFFECTS OF SEASONAL VARIABILITY ON THE MOBILITY OF ^{137}CS IN AN
ABANDONED REACTOR COOLING POND**

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Earth Sciences

by
Jessica Wheeler
May 2021

Accepted by:
Dr. Brian Powell, Committee Chair
Dr. Nicole Martinez
Dr. Daniel Kaplan

Abstract

Studies of radionuclide concentrations in Pond B, an 82 hectare abandoned reactor cooling pond at the Savannah River Site in Aiken, South Carolina, have shown the accumulation of cesium-137 (^{137}Cs) in the surface layers of sediments sampled from random locations within the pond. Pond B received discharged cooling water containing radionuclides from R reactor at the Savannah River Plant from 1961 until 1964, at which point the reactor ceased operation. Cesium-137, one of the fission-products released, has a significant tendency to sorb onto sediments available in aquatic ecosystems. Prior studies have demonstrated that Cs concentrations decrease in abundance with increased distance from the point of entry. Previous work has shown that thermal stratification of Pond B from April to October results in hypolimnion anoxia, which in turn leads to the release of ^{137}Cs from bottom sediments into the water column. This suggests that seasonal variability in environmental conditions influences ^{137}Cs mobility. The current work seeks to (1) build upon these previous studies to determine if historical observations have endured for a time period on the order of one half-life of ^{137}Cs and (2) further elucidate the mechanisms effecting ^{137}Cs mobility in the bottom sediments of Pond B. In this study, concentrations of ^{137}Cs were measured in water samples and sediment cores sampled from the pond's inlet stream as well as the open water near the outlet stream of Pond B in an effort to characterize the mobility of ^{137}Cs , as the most recent, prior data was collected over 20 years ago. Results from the inlet stream cores indicate a pattern of preferential accumulation in the top layers of the sediment cores with an activity of approximately 16.0 Bq g^{-1} , with decreasing concentrations to $<0.1 \text{ Bq g}^{-1}$ as depth increases to 12.6 cm. Increased concentrations of ^{137}Cs sampled from an area closest to the outlet stream demonstrate the radionuclide's tendency to

adhere to sediment focusing processes (Pinder et al. 1995). Organic matter percentages at this location ranged from ~8 – 43% and were significantly higher than inlet stream percentages of <5%, suggesting that ^{137}Cs may accumulate in organic matter rich zones. Along with characterizing ^{137}Cs concentrations in the pond, laboratory experiments were conducted to obtain a ^{137}Cs K_f value of 45 L kg^{-1} and a diffusion rate of $1.51 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. This evidence suggests that ^{137}Cs distribution and concentrations have remained relatively unchanged since the 1980s and only fluctuate between the sediment-water interface as a response to seasonal variations in the pond.

Dedication

To Mom and Dad for their love and support. And to Chris for having more faith in me than I had in myself.

Acknowledgements

I would like to thank Dr. Brian Powell. His unfailing leadership, expertise, and encouragement allowed me to achieve more than I thought was possible. Thank you to Dr. Fanny Coutelot for her constant guidance in the field and lab. Thank you to my committee members, Dr. Nicole Martinez and Dr. Dan Kaplan for their wisdom, support, and advice in regard to this thesis.

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1. Introduction

Over the past few decades, there have been numerous studies devoted to understanding radionuclide migration and behavior in contaminated aqueous systems. A prominent radionuclide investigated in these studies has been ^{137}Cs , a product of neutron-induced fission reactions of ^{235}U (Carlton et al. 1992). ^{137}Cs is of particular concern due to four important properties: 1) its relatively long half-life ($t_{1/2} = 30$ years); 2) its association with a majority of environmental radionuclide releases; 3) its ability to cause extensive damage to soft tissues if accumulated in the body or biota; and 4) its high biological availability due to similarities with potassium (Evans et al. 1983). Cesium has the ability to strongly adsorb to clay sediments due to its greater charge density compared to other hydrated cations containing radii of similar size (Denham, 1999). Therefore, Cs mobility in an environment is mainly controlled by its sorption to sediments (Alberts et al. 1979).

The southeastern U.S. coastal plain contains highly weathered, sandy soils that result in lower Cs sequestration and thus increased resuspension and mobility of ^{137}Cs as well as biological accumulation (Evans et al. 1983; Whicker et al. 2007). Studies of radionuclide concentrations in Pond B, an 82 hectare abandoned reactor cooling pond at the Savannah River Site in Aiken, South Carolina, have shown the accumulation of ^{137}Cs in the surface layers of silicate minerals in sediments sampled from random locations within the pond (Kim et al. 2005; Pinder III et al. 1995; Whicker et al. 1990). Kaolinite, a 1:1 phyllosilicate clay, contains sites on the outer layers readily available for Cs to sorb onto, as seen in Figure 1 (Wang et al. 2017). Clays possessing a 2:1 ratio, being another predominant phyllosilicate mineral in SRS soils, allow ion exchange to occur in

interlayers of the minerals and are readily available for Cs sorption (Alberts et al. 1987; Wampler et al. 2012).

Distribution of radionuclides in soils across a water reservoir is generally controlled by the distance from its location of release, as well as *sediment focusing*, a process involving the resuspension of radionuclides due to natural occurrences and effects of slopes on the transportation of sediments (Pinder III et al. 1995). As the soil becomes more weathered, Cs is more readily able to desorb from the exposed layers in the clay mineralogy and as a result, become mobilized in the water column (Onodera et al. 2017). Also, past studies have indicated that the presence of ^{137}Cs can be positively correlated with organic matter due to the high cationic exchange capacity (Ahmad et al. 2019; Kudelsky et al. 1996; Takahashi et al. 2017; Yu et al. 2012).

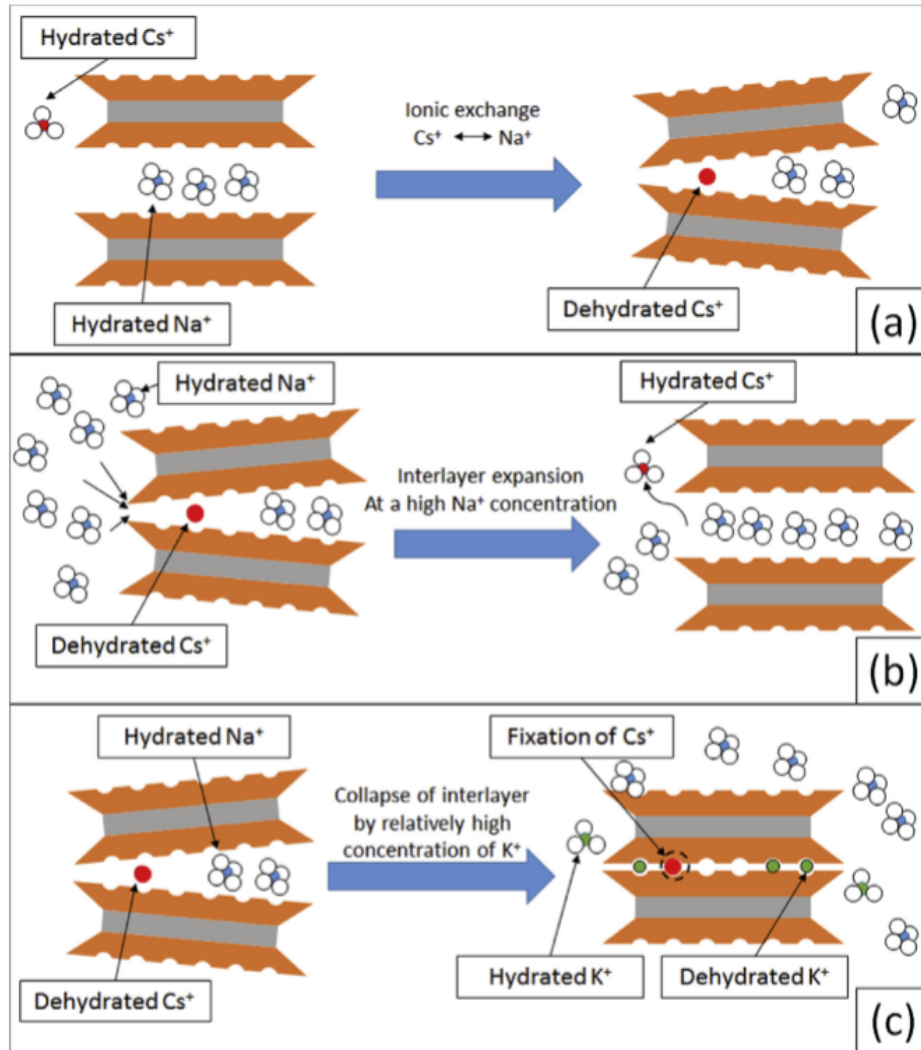


Figure 1. Conceptual model for mechanism of (a) Cs adsorption, (b) Cs desorption, and (c) inhibition of Cs⁺ desorption by K⁺ (Onodera et al. 2017).

From 1961-1964, R Reactor at the Savannah River Site released 5.7×10^{12} Bq of ^{137}Cs as well as other radionuclides into the environment (Evans et al. 1983; Mohler et al. 1997; Pinder III et al. 1995; Whicker et al. 1990). The fraction of ^{137}Cs that reached Pond B is unknown, however, as contaminants were diverted between Pond B and Pond C. Since the shutdown of R Reactor in 1964, Pond B has remained relatively undisturbed. The water level is controlled by runoff,

precipitation/evaporation, groundwater percolation, and an outlet stream (Mohler et al. 1997). The waters of Pond B, typical of natural freshwater systems in the eastern coastal plains, have become relatively acidic and nutrient poor, resulting in a system supporting high concentration factors for ^{137}Cs (Brisbin et al. 1986). Concentration factors are defined as the ratio of the ^{137}Cs concentration in the organism to the concentration in the surrounding water (Ishii et al. 2020). Past studies have shown a thermal gradient to form in the summer months due to an anoxic hypolimnion (Figure 2), resulting in an increase in major ions in this anoxic zone (Alberts et al. 1985; Evans et al. 1983; Jeong et al. 2018; Whicker et al. 1990). The thermal stratification of Pond B causes the release and potential mobility of ^{137}Cs from April to October as observed in Figure 3 (Alberts et al. 1987). Similar studies have attributed this phenomenon to the displacement of ^{137}Cs via NH_4^+ ions produced by anerobic activities in the anoxic hypolimnion (Evans et al. 1983). The release of ^{137}Cs into the water column during the summer months thus plays an important role in ^{137}Cs bioavailability.

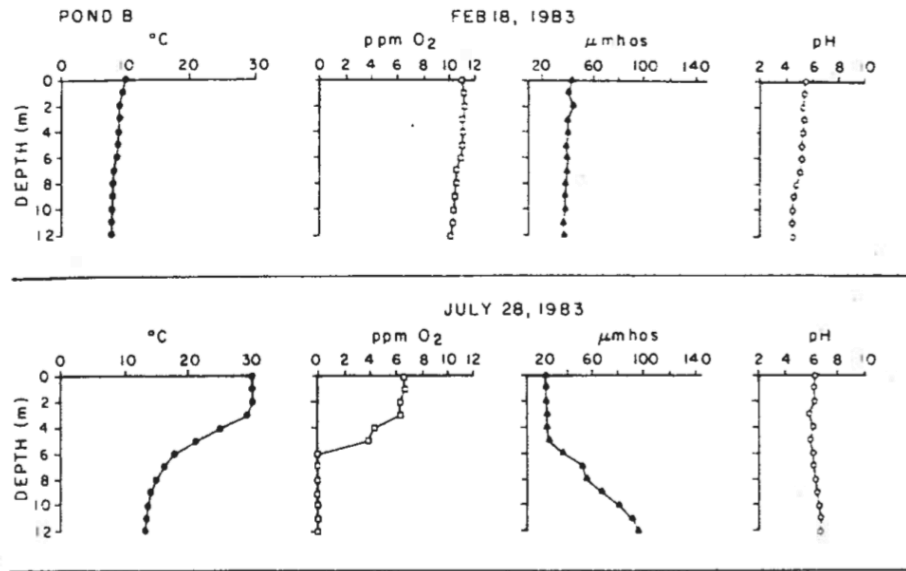


Figure 2. Depth profiles of temperature, dissolved oxygen, conductivity, and pH at the Pond B "Dam" site for Feb. 18, 1983 and July 28, 1983 (Alberts et al. 1987).

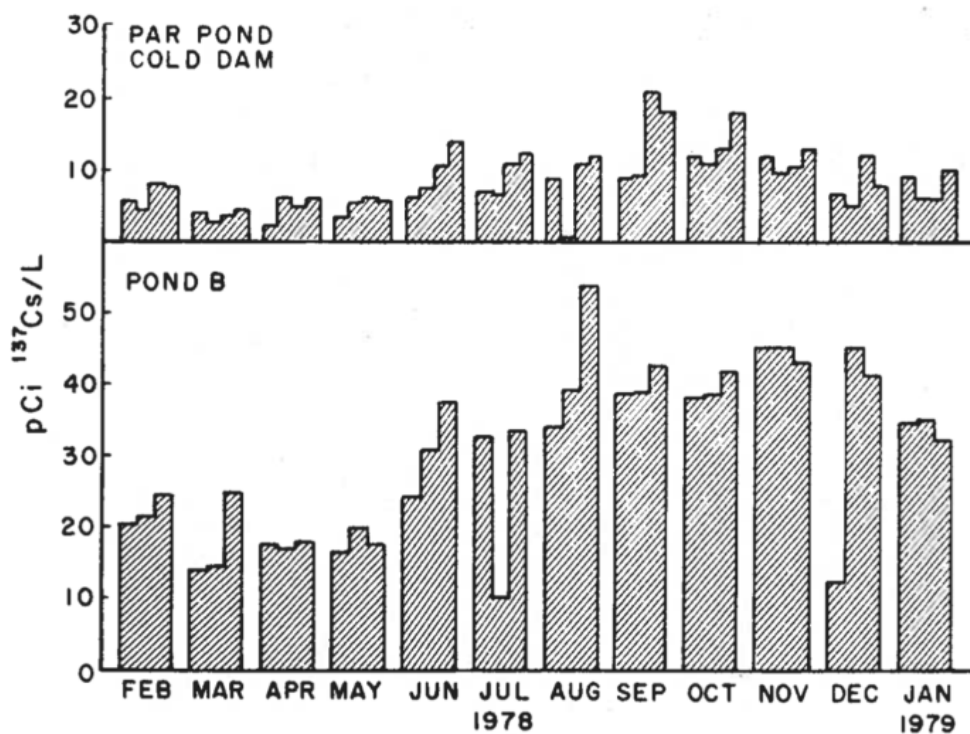


Figure 3. Seasonal dissolved concentrations of ^{137}Cs (pCi L $^{-1}$) at various depths in Par Pond (0, 5, 10, 15 m) and Pond B (0, 4, 8 m) during 1978 (Alberts et al. 1979).

2. Project Overview

The purpose of this project is to achieve a greater understanding of the fate and transport of ^{137}Cs in a freshwater pond located at the Savannah River Site. Field methods, including the collection of water samples and sediment cores, allowed a greater understanding of seasonal variations of ^{137}Cs in the reservoir (Figure 4). Sediment cores were sampled from locations Inlet 1, Inlet 2, Inlet 3, Pond 1 and Pond 5 with pore water sampled from Inlets 2 and 3. The ^{137}Cs concentration profile in the cores were determined as well as relevant water quality parameters in water samples such as pH, oxidation-reduction potential (ORP), major and minor element concentrations, and radionuclide concentrations. Results from the various methods assisted with

the development of a model used to predict Cs migration and bioavailability in the pond system and can be further utilized to make responsible decisions regarding public and environmental health.

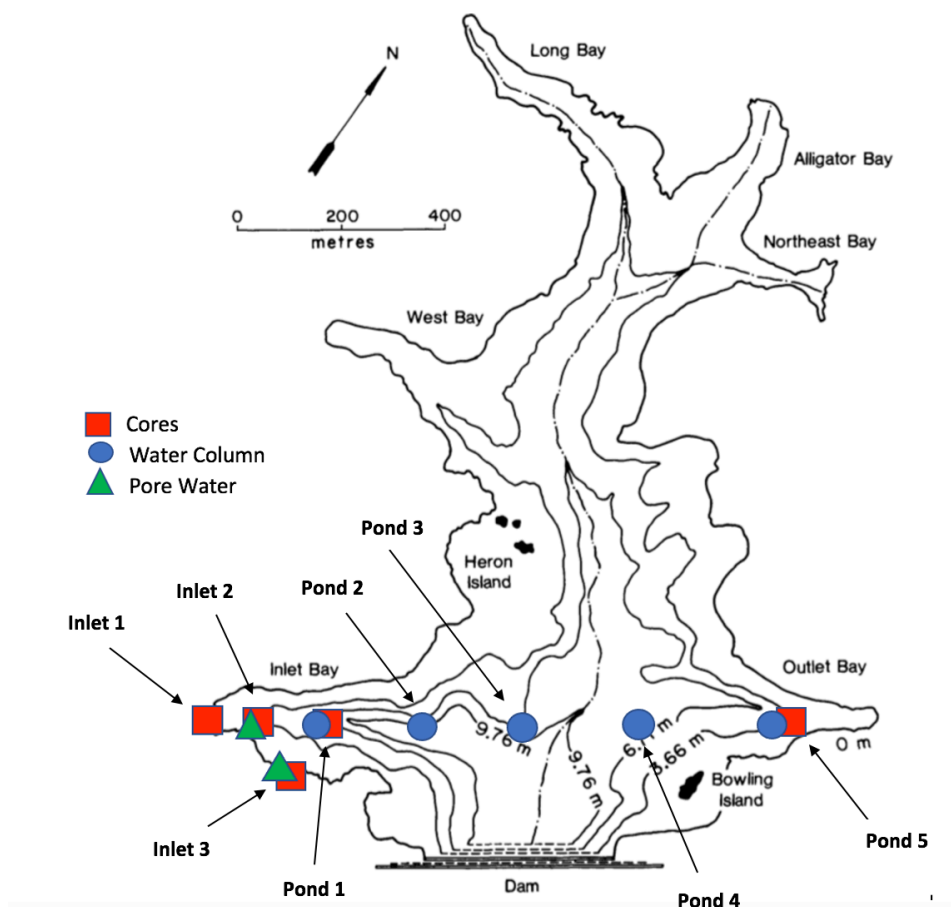


Figure 4. Diagram of Pond B with sample names and locations.

Research Objectives

Hypotheses for each type of water (i.e. the epilimnion, hypolimnion, and sediment volumes), are described in Figure 5. Objectives were designed to provide data to test those hypotheses and serve as the foundation of this paper.

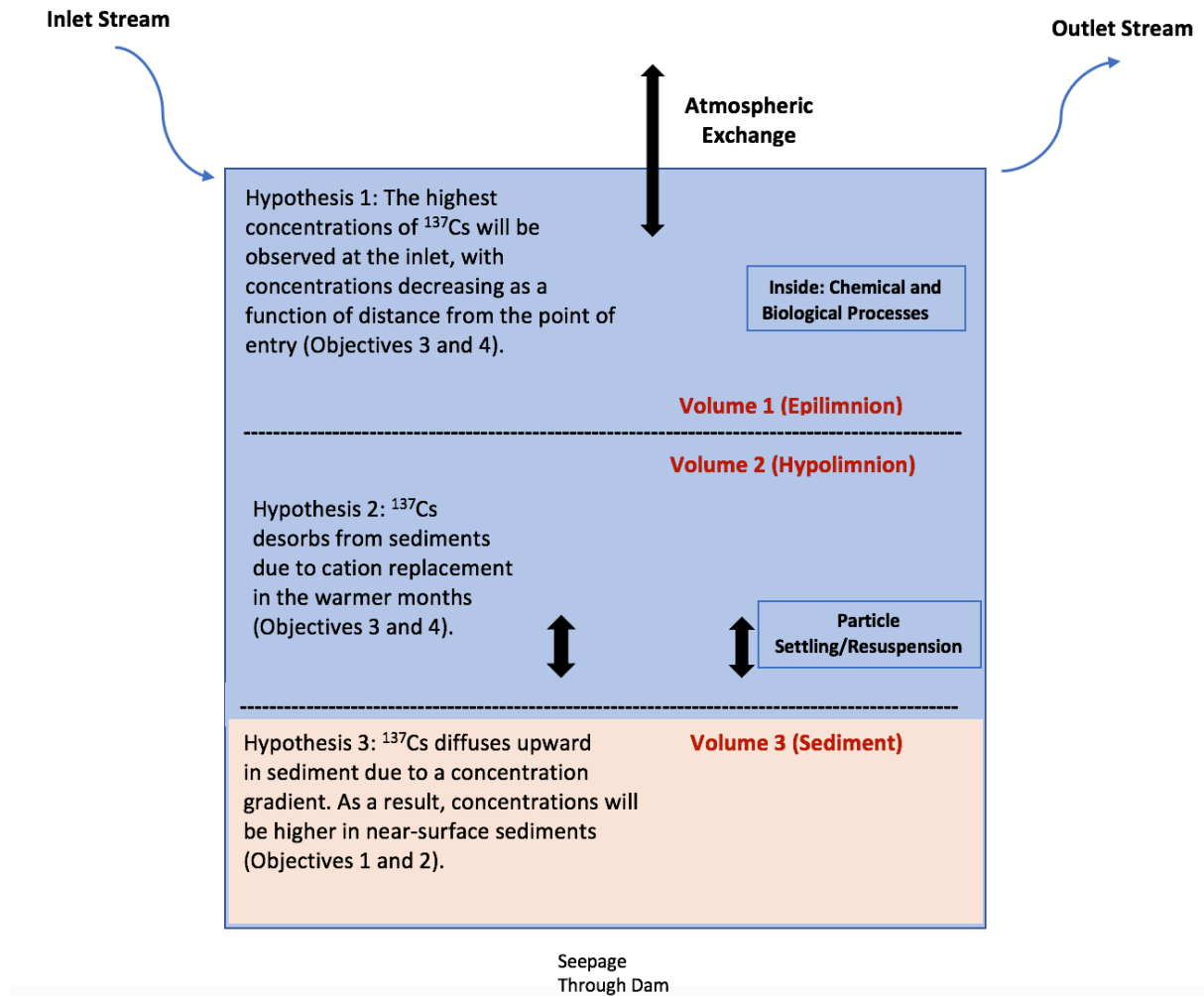


Figure 5. Mass-balance model of Pond B including all possible parameters controlling ^{137}Cs mobility.

Objective 1: Cores sampled from locations Pond 1 and 5 were analyzed for ^{137}Cs concentrations using a high purity germanium (HPGe, Ortec) detector (Bq/g).

Objective 1.1: Cores sampled from the inlet stream were analyzed to determine sediment concentrations of ^{137}Cs (Bq/g).

Objective 1.2: A Cs adsorption experiment was performed to calculate the K_f and retardation factor of ^{137}Cs .

Objective 1.3: Quantify the diffusion rate by spiking a modeled sediment core with ^{137}Cs and measuring the activity using a 1D Bismuth Germanium Oxide (BGO) detector.

Objective 1.4: Diffusion is less likely in the open pond. The study assessed whether this causes ^{137}Cs to be buried deeper into the sediments of the open pond.

Objective 2: Determine whether seasonal geochemical fluctuations affect ^{137}Cs concentrations in the water column.

Objective 2.1: ^{137}Cs concentrations in the water column were determined using a HPGe detector. This data was compared to Alberts et al. 1979.

Objective 2.2: Compare ^{137}Cs profiles in the water column to previous data. Determine whether the result signify water mixing as the dominant mechanism controlling ^{137}Cs .

Objective 2.3: Observe whether ^{137}Cs concentrations in the water column correlate with the seasonal cycling of trace metals.

Objective 2.4: Informed by the inlet stream data, it was determined whether geochemical fluctuations are more significant in shallow water compared to the bottom of the open pond.

Objective 3: A mass-balance model was used to help predict mechanisms controlling Cs migration.

Objective 4: Mineralogical characterization of Pond B sediments was performed using x-ray diffraction and total element analysis.

3. Materials and Methods

Water Collection and Data

Regular monitoring of water column temperature, pH, dissolved oxygen, and ORP (E_H), is essential to understanding the behavior of Cs in the environment as air temperature changes throughout the year. These data were collected from Pond B each month beginning in June 2019 and ending in December 2020, with the exception of a select, few months due to weather and COVID-19. This data was collected by dropping a data-logging sonde (YSI, In-situ Systems) every half of a meter in the water column in 5 different locations between the inlet and outlet streams of the pond each month (Figure 4). Ion concentrations of the water column were also measured in June 2019 and March 2020 to compare the chemical composition of the water in various seasons. To determine these measurements, 1 L water samples were collected every meter in depth at each of the 5 locations, and ion concentrations were measured using inductively coupled plasma mass spectrometry (Thermo X-Series II). Along with the chemical variations in the water column, ^{137}Cs concentrations were measured by collaborators at Lawrence Livermore National Laboratory (LLNL) using the 1 L water samples and concentrations were reported in Bq L^{-1} . These water samples were measured using HPGe detectors in an ultra-low level counting facility.

Sediment Cores

Measurements of ^{137}Cs concentrations in Pond B were conducted for cores sampled at the inlet stream in July of 2019, as well as cores sampled from locations Pond 1 and 5 in October of 2020. Cores were collected using a 2" diameter x 24" aluminum sediment corer containing plastic tubes pushed into sediments at the bottom of the stream or pond and subsequently

removed. Following sampling, plastic tubes were removed from the aluminum casing and kept in an upright position during transportation to Clemson University where they were frozen. When removing inlet stream sediment cores from the tubes, a rubber stopper was used to gently push sediment out one end, and a paint scraper was used to slice the resulting core in 1 cm segments. Cores from Pond 1 and 5 were extracted using an electric saw to cut through the plastic tubing, and a paint scraper was used to slice cores into segments. The extraction method used for each case was based on the need to keep each core intact until segmented. Samples were weighed before and after drying at 45°C to determine water content (as % water) and bulk density (g mL^{-1}) of the sediment. Cesium-137 concentrations from the resulting dried samples were determined using a HPGe detector, with 5 g of each of the 57 samples counted for 86400 seconds. Counts were corrected for background and counting efficiency, the latter of which was determined using ^{152}Eu and ^{137}Cs standards. Activities of ^{137}Cs in the cores are reported as Bq g^{-1} . Results were compared to previous data published by Whicker et al. (1990), and Pinder et al. (1995).

Major and minor ions in the sediment cores were measured using ICP-MS after acid digestion of the sediments. Briefly, an aliquot of dried sediment was ashed at 550°C in order to determine total organic carbon (TOC) and completely digested in a Teflon bomb in a microwave oven (CEM Mars5 microwave digester) based on EPA method 3052 using ultrapure HF and HNO_3 (Method 3052, 1996). Following digestion, the acids were evaporated to near-dryness and the residues were recovered in 2% HNO_3 prior to analysis using ICP-MS. Elemental analyses of solutions were performed using calibration solutions prepared with the same matrix as the samples (2% HNO_3) and internal standards ^{45}Sc , ^{115}In , and ^{209}Bi . Blanks were always below 5% of the sample concentrations.

1D Diffusion Experiment

Sediment sampled from Inlet 2 (see Figure 4) was used to determine the upward diffusion rate of ^{137}Cs . The sediment was sifted using a Fisher Scientific Company sifter with an opening of 840 microns, such that only silt and clay particles were packed into a 10 mm diameter Omnifit EZ Chromatography column. After each cm of sediment was packed into the column, the column was gently tapped onto a countertop to remove air pockets and the upper layer was disturbed to allow mixing with the next addition of sediment. To allow full saturation and opportunity for the soil to equilibrate, 1 L of DI water was slowly flushed through the column for 2 days using a Masterflex pump. Once equilibrated, the column was positioned upside down and the inlet housing was removed. Then a 0.5 mL of a $5.55 \times 10^4 \text{ Bq mL}^{-1}$ ^{137}Cs stock solution was spiked to the bottom of the column. The inlet housing was replaced and column was then placed upright in a vertically moving motor, and a BGO detector was used to measure activities in 1 cm increments across the column while maintaining a 6-hour count time. Increments were subsequently adjusted to 0.16 cm (6 hour count time) to facilitate a higher spatial resolution measurement of diffusion. The BGO detector was calibrated using a ^{137}Cs stock solution with a 10 minute count time for various δ length spacings (Figure 6). It was determined from this calibration that a δ length spacing of 1.6 mm resulted in optimal counting conditions. The equation used for this calibration is as follows:

$$b = \delta \left(1 + \frac{2(L_3 - L_1)}{L_1} \right)$$

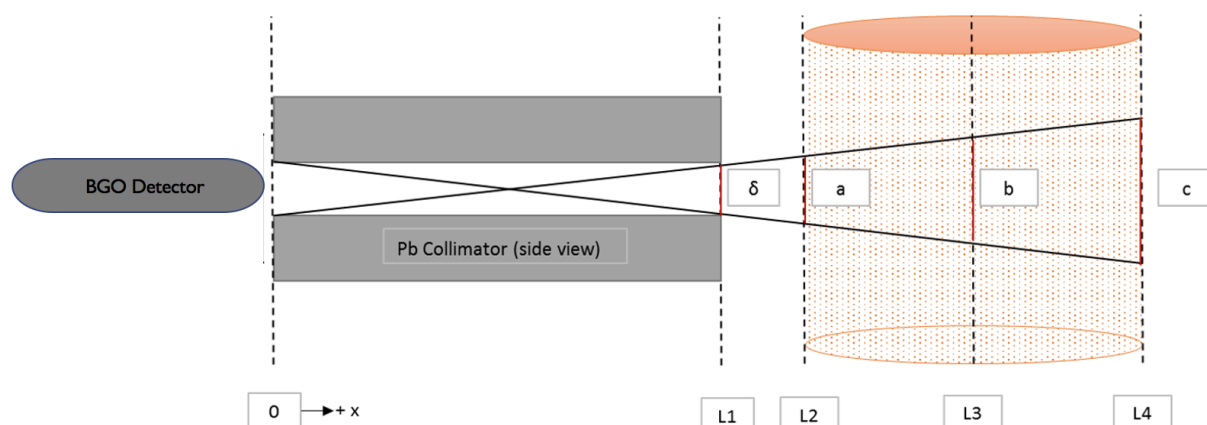


Figure 6. BGO detector setup showing the parameters defining the spatial resolution. Parameter b determines the spatial resolution of data. Parameter δ was adjusted to increase the efficiency of the detector (Figure adapted from Erdmann et al. 2018).

Batch Sorption Experiment

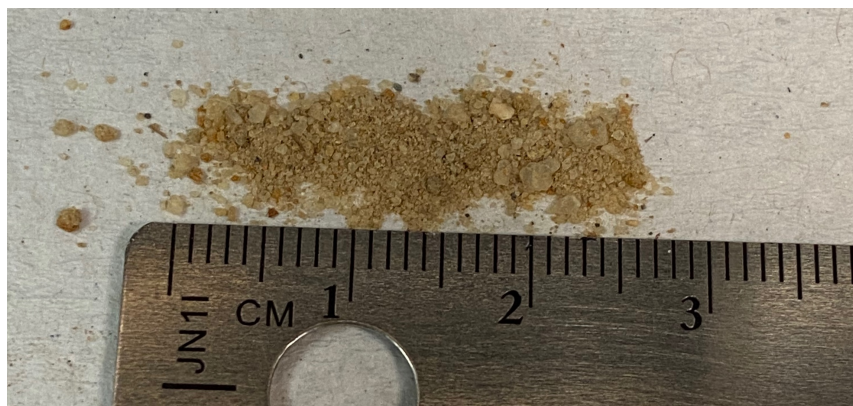
To better understand the adsorption of ^{137}Cs to clay particles located in Pond B, a batch sorption experiment was conducted using sediments from Inlet 2. Batch sorption experiments were performed using 0.5 g of Inlet 2 sediment in 2 mL polypropylene centrifuge tubes containing a background electrolyte solution of 0.01 M NaCl. An initial spike of ^{133}Cs solution ranging from 1.0×10^{-6} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$ were added to 14 sediment samples containing 4 duplicate samples, to reach cesium concentrations specific to each sample. Target ^{137}Cs concentrations ranging from 1.0×10^{-8} to $5.0 \times 10^{-4} \text{ mol L}^{-1}$ were added to the varying 10 samples to demonstrate an isotherm that increases with the amount of Cs sorbed with an increase in Cs in the aqueous phase. Samples were allowed to equilibrate on a rotating sample holder for 5 days. Sampling involved pipetting 1.5 mL of the aqueous solution from each sample into 2 mL centrifuge tubes. Tubes were placed

into a centrifuge for 20 minutes at 8000 rpm. A 1 mL sample was collected from the supernatant and pipetted into liquid scintillation vials with 5 mL of Optiphase Hisafe 3 solution. Samples were counted with a liquid scintillation detector (Tricarb TR2900 A/B) for 60 minutes each. Calibration of the liquid scintillation detector was used using both a blank and stock sample containing no soil. The blank sample contained 5 mL of Optiphase Hisafe 3 and 0.5 mL of DI water. The stock sample contained 5 mL of Optiphase Hisafe 3 as well as 0.5 mL of a $0.79 \text{ Bq mL}^{-1} \text{ }^{137}\text{Cs}$ stock solution.

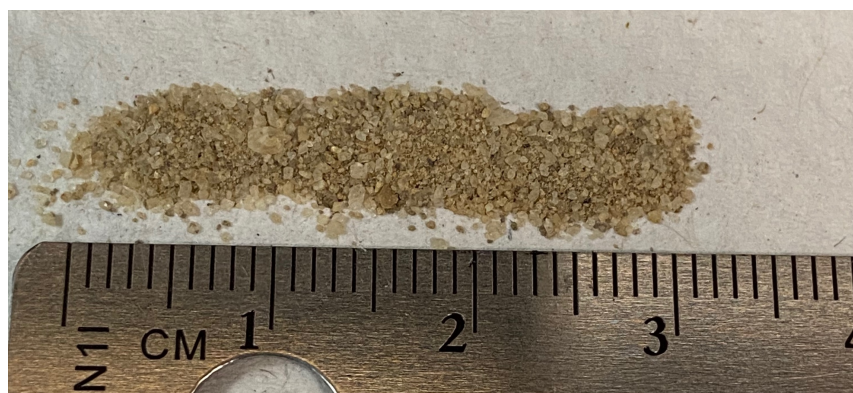
XRD Analysis

Sediment from various horizons in Inlet cores 1, 2, and 3 were analyzed using Rigaku Software Analysis – Miniflex 600 XRD equipment to characterize the mineralogical composition of Pond B soils. Samples for analysis were selected based on varying color and grain size of soils (Figure 7). Sediments from each sample were finely ground and dispersed onto glass slides. Each sample was counted using the XRD equipment for 25 minutes.

A



B



C



Figure 7. Color and grain size of the sediment used for XRD analysis where A) Inlet Core 1 at core depth of 6 cm; B) Inlet Core 2 at core depth of 2 cm; C) Inlet Core 3 at core depth of 2 cm.

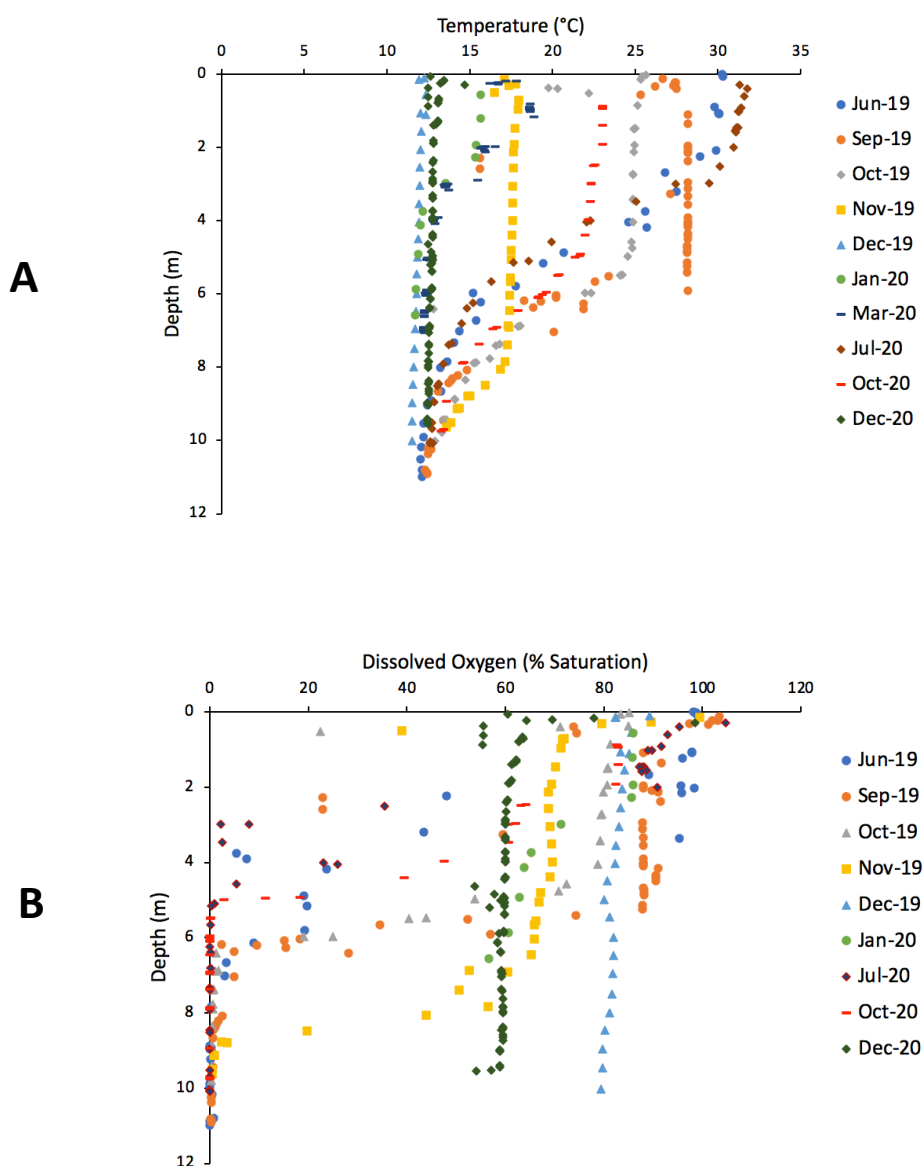
4. Results

Water Chemistry

CTD (Conductivity, Temperature, and Depth) data collected from each of the 5 locations between the inlet and outlet streams of Pond B demonstrate a well-defined thermocline that forms in late spring and continues until October. As shown in Figure 8A, consecutive months from November to March have a homogenous temperature profile through the water column at Pond 3, with temperatures between 10 to 15°C. Summer months, including June and September, have warmer temperatures near 30°C that decrease at a depth of 4 to 6 m in the water column to temperatures of <20°C. A similar trend can be seen with dissolved oxygen in Figure 8B, as summer months reach 0% saturation around 6 m in depth, while winter months remain much more homogenous at 80% saturation at this depth. The pH of the water column also demonstrates seasonal variations as observed in Figure 8C. December appears to be the only month with a uniform pH of <6, while all other months have surface pH values of >6 that decrease to a depth of 6 m, and then increase back to pH >6 at the bottom of the water column. The redox potential, using a Standard Hydrogen Electrode (SHE), of the water column also demonstrates a more homogenous profile during the winter months at values between 300 to 500 mV while summer months decrease from ~100 mV to <-200 mV (Figure 8D).

Total organic carbon at Pond 3 is shown in Figure 9 and demonstrates seasonal variations much like the parameters in Figure 8. For the warmer months, organic carbon is in greater concentrations at the top of the water column as compared to the bottom. There also appears to be a sudden decrease followed by an increase in organic carbon at a depth of ~3 m in the pond. As discussed, warmer months observe a thermocline at a depth of ~4 m in the pond. This shift

may be a result of an increase in metabolites released due to anaerobic metabolism that occurs near the thermocline of the water. The absence of organic carbon directly above the thermocline could also cause a potential decrease in acidity as seen in Figure 8C. For the colder month of October, the upper and lower regions of the water are well-mixed and allows potential settling of organic particles to the bottom of the pond where they have the ability to accumulate in higher concentrations.



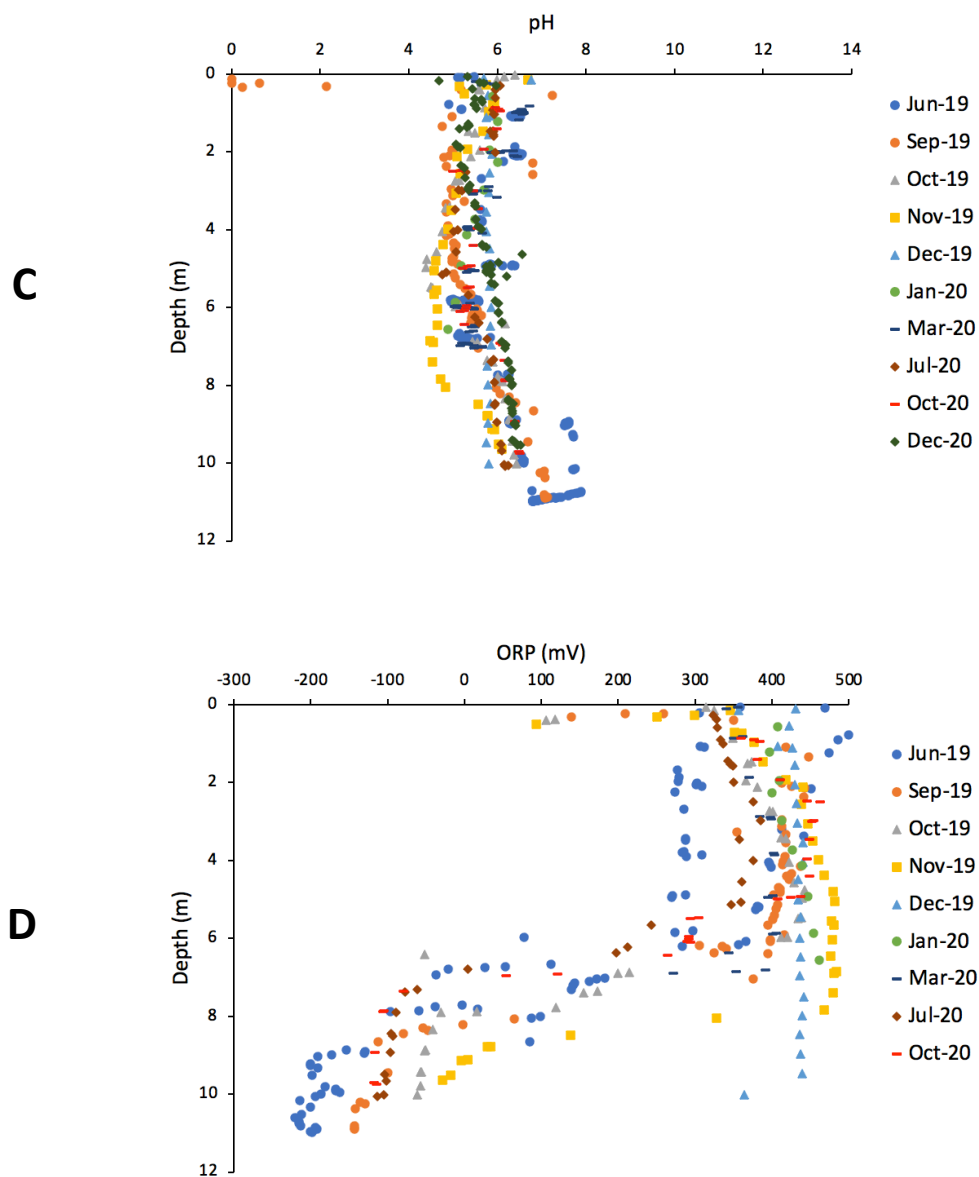


Figure 8A. Temperature profile in the water column at Pond 3 in Pond B during various months. **Figure 8B.** Dissolved oxygen profile in the water column at Pond 3 in Pond B during various months. **Figure 8C.** pH profile in the water column at Pond 3 in Pond B during various months. **Figure 8D.** ORP using SHE profile in the water column at Pond 3 in Pond B during various months.

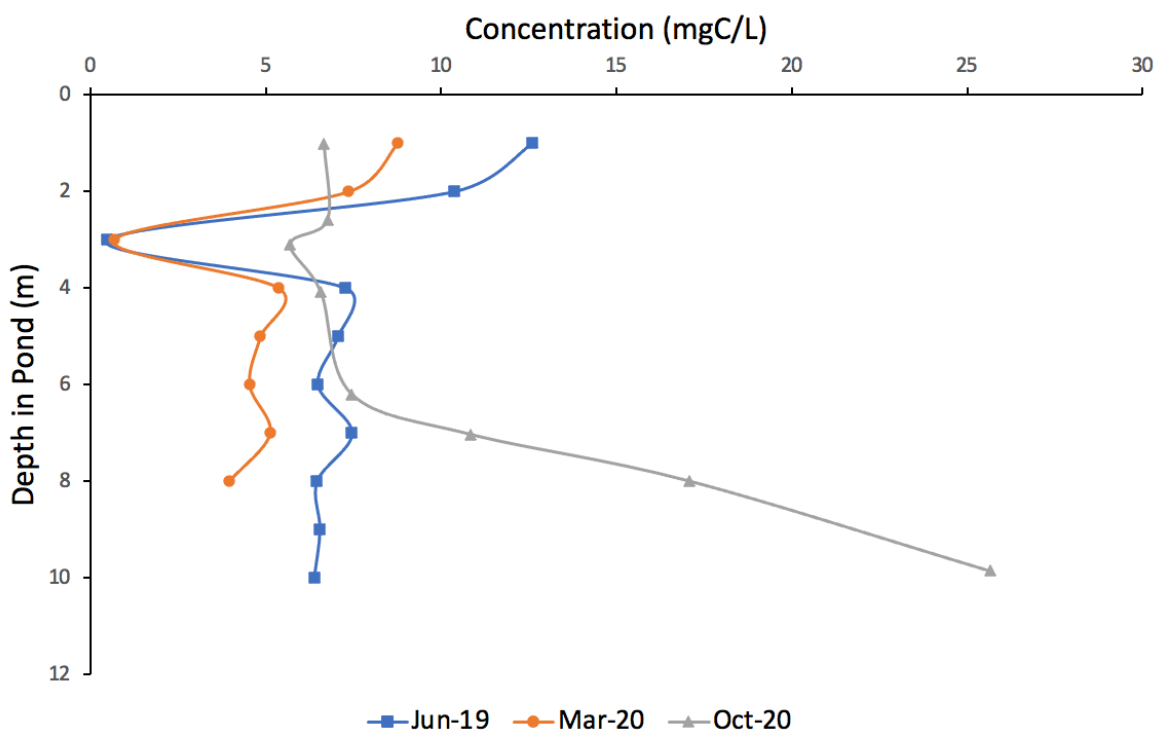


Figure 9. Total organic carbon profiles in the water column for the months of June 2019, March 2020, and October 2020 at Pond 3.

Total ^{137}Cs concentrations in 1 L samples from the pond showed varying concentrations with a change in depth in the pond (Figure 10). For reference, the Maximum Contaminant Level for ^{137}Cs in drinking water is 7.4 Bq L^{-1} (Rattray & Wehnke, 2003). For the month of March, locations Pond 4 and 5 contained the highest concentrations of ^{137}Cs out of all of the locations near the sediment-water interface (0.45 Bq L^{-1} and 0.30 Bq L^{-1} , respectively). Pond 1 (0.26 Bq L^{-1}), being closest to the inlet stream also contained higher concentrations than seen at Pond 2 (0.20 Bq L^{-1}) and 3 (0.17 Bq L^{-1}) but was still lower than Pond 4 and 5. In general, while ^{137}Cs concentrations varied with respect to depth, all locations had generally similar concentrations at

the bottom of the pond as compared to the surface water. However, changes in water temperature did not have as large of an impact on ^{137}Cs concentrations in the water column as anticipated. At Pond 1 and 2, March concentrations were generally greater than June concentrations in the epilimnion region of the pond. However in the hypolimnion region at all locations, June concentrations were generally greater than March concentrations. When comparing this data to data collected from the pond in 1978, results are similar (Figure 3). Trends show fairly homogenous concentrations with respect to depth in the pond with slightly greater concentrations in the summer months as compared to winter months.

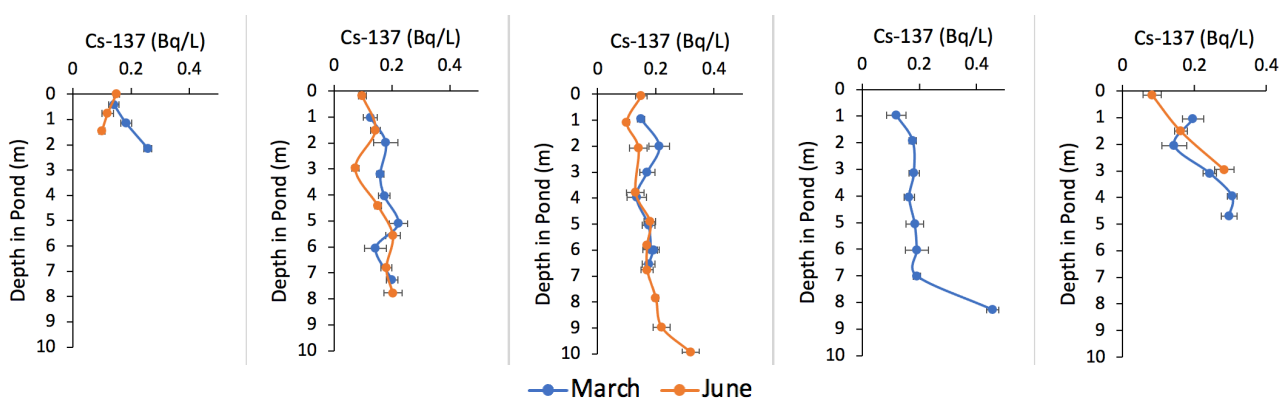


Figure 10. Total ^{137}Cs concentrations in the pond sampled during the month of March and June. From left to right: Pond 1, Pond 2, Pond 3, Pond 4, Pond 5.

Sediment Cores

In general, sediment cores sampled from the inlet stream showed the highest ^{137}Cs concentrations in the surface sediment, with decreasing activity as sediment depth increased (Figure 11). Inlet Core 1, located furthest upstream from the pond, provided a small increase in concentration from $\sim 16 \text{ Bq/g}$ at the sediment-water interface to $\sim 18 \text{ Bq g}^{-1}$ at a depth of 1.6 cm

in the core, prior to decreasing to $<1 \text{ Bq g}^{-1}$ at a depth of 5.6 cm from the surface (i.e., top of the core). Inlet Core 2, sampled in closer proximity to the pond, exhibited a surface sediment activity of $\sim 11 \text{ Bq g}^{-1}$ decreasing to $<1 \text{ Bq g}^{-1}$ at a depth of 3.5 cm, while Inlet Core 3, sampled closest to the open body of the pond, had a surface sediment concentration of $<1 \text{ Bq g}^{-1}$. These profiles closely resembled profiles published by Whicker et al. (1990), wherein sediment cores were randomly sampled throughout the pond. Data from historical papers were decay corrected for comparison to current data and graphed on Figure 11. Cores sampled from Pond 1 in the open water of Pond B demonstrated greater variability in ^{137}Cs activities throughout the column. At Pond 1, surface sediment activity (0.34 Bq g^{-1}) was observed to decrease to 0.21 Bq g^{-1} at a depth of 5 cm, then increasing to $>1 \text{ Bq g}^{-1}$ at a depth of 13 cm. Two surface sediment samples taken from Pond 3 showed ^{137}Cs concentrations of 0.10 Bq g^{-1} and 0.18 Bq g^{-1} . Finally, a surface sediment sample from Pond 4 resulted in a concentration of 0.92 Bq g^{-1} (Figure 12).

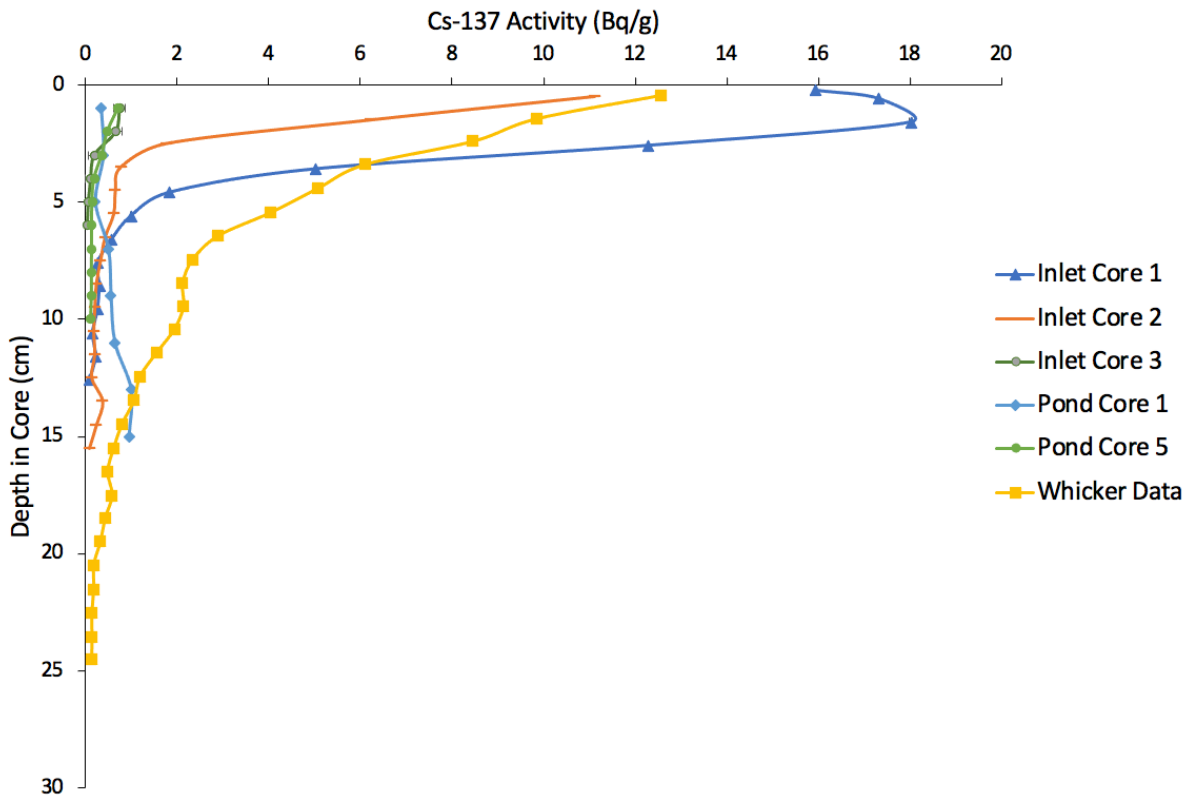


Figure 11. Sediment core ^{137}Cs profiles sampled from the inlet stream and Pond 1 and 5 of Pond B. Error bars are within markers.

Organic matter percentages resulting from cores sampled from Inlet 3 and Pond 5 demonstrate the high abundance of organic matter near the outlet stream (Figure 13). While the inlet stream contained homogenous percentages throughout the soil core, percentages for location Pond 5 were greatly higher and more varied as a function of depth in the core.

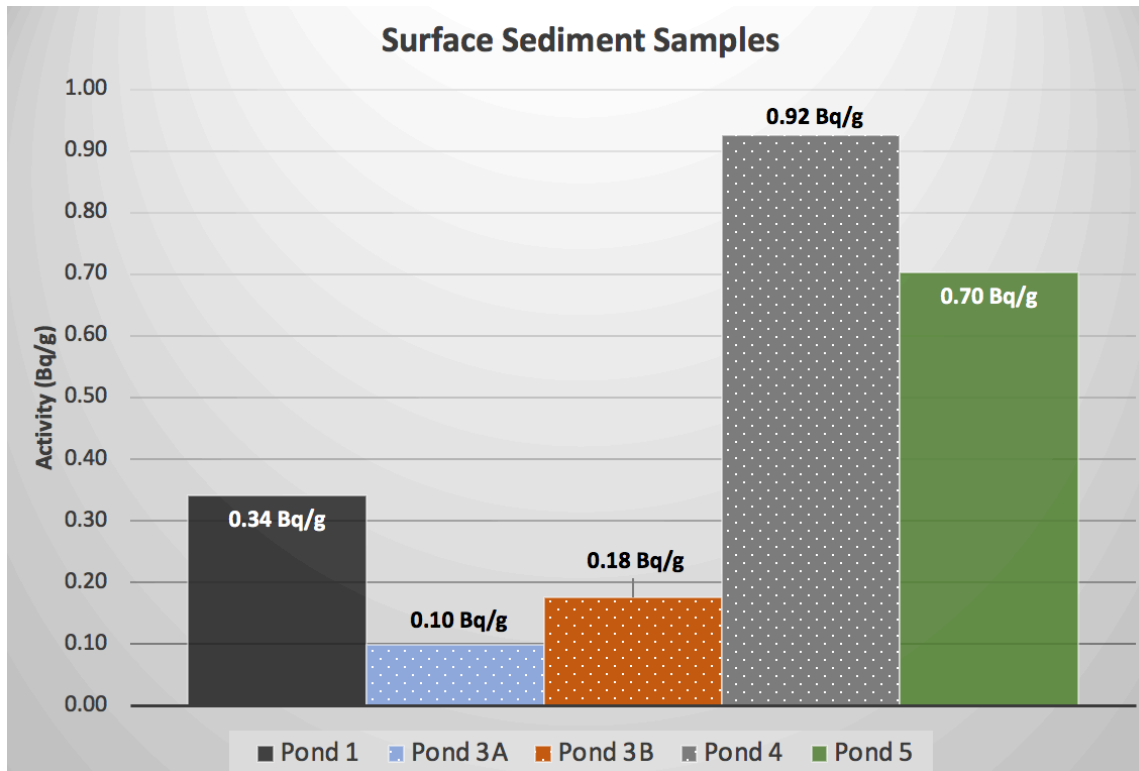


Figure 12. Comparison of ^{137}Cs activities measured in surface sediment samples taken from Pond 3 and 4 locations in Pond B. Inlet Core 1 had a surface activity of $\sim 16 \text{ Bq g}^{-1}$.

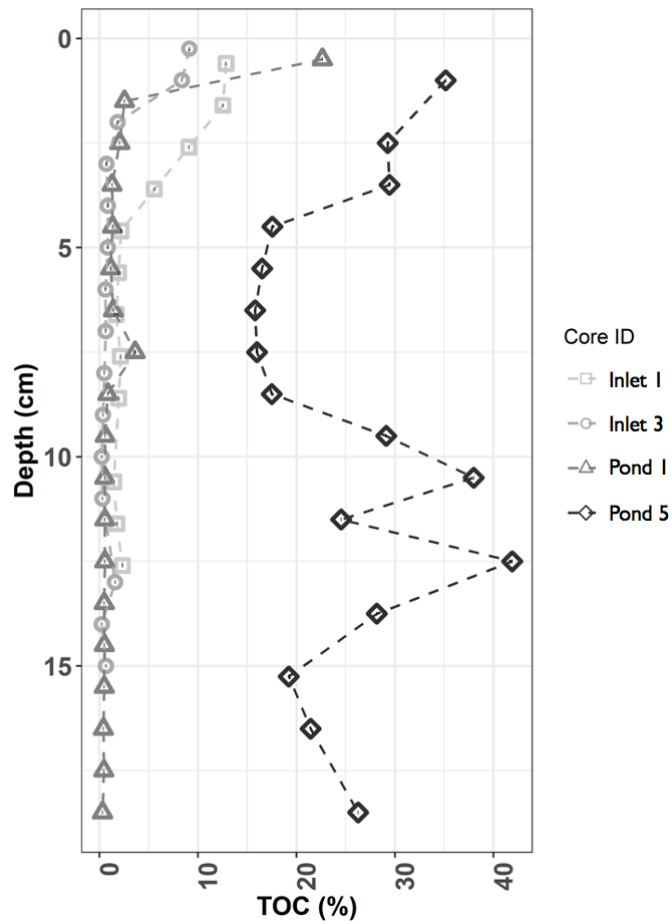


Figure 13. Organic matter percentages in cores sampled from Inlet 1 and 3 and Pond 1 and 5.

Major Ions in Sediment

Major elements sampled from pore waters in the surface sediments of the inlet stream demonstrate temporal differences in concentration with respect to depth (Figure 14). In the warmer, oxygen depleted month of September, ions including Al, Ca, K, Mg, Mn and Na, all were measured with higher concentrations throughout the pore water columns as compared to the colder, more oxygen-rich, month of November. Further, for Al, Ca, Mn, and Mg concentrations in September tend to increase as depth in the soil increases. In contrast, K and Na concentrations

also vary with depth in September, but not to the extent deviation observed with the other ions. However, in the colder months such as October and November, ion concentrations are found to be homogenous and consistently lower than observed in September. ^{137}Cs concentrations have been observed to behave in a similar manner. In past studies, ^{137}Cs concentrations in the water column are consistently greater during the summer months when conditions are more favorable for Cs desorption.

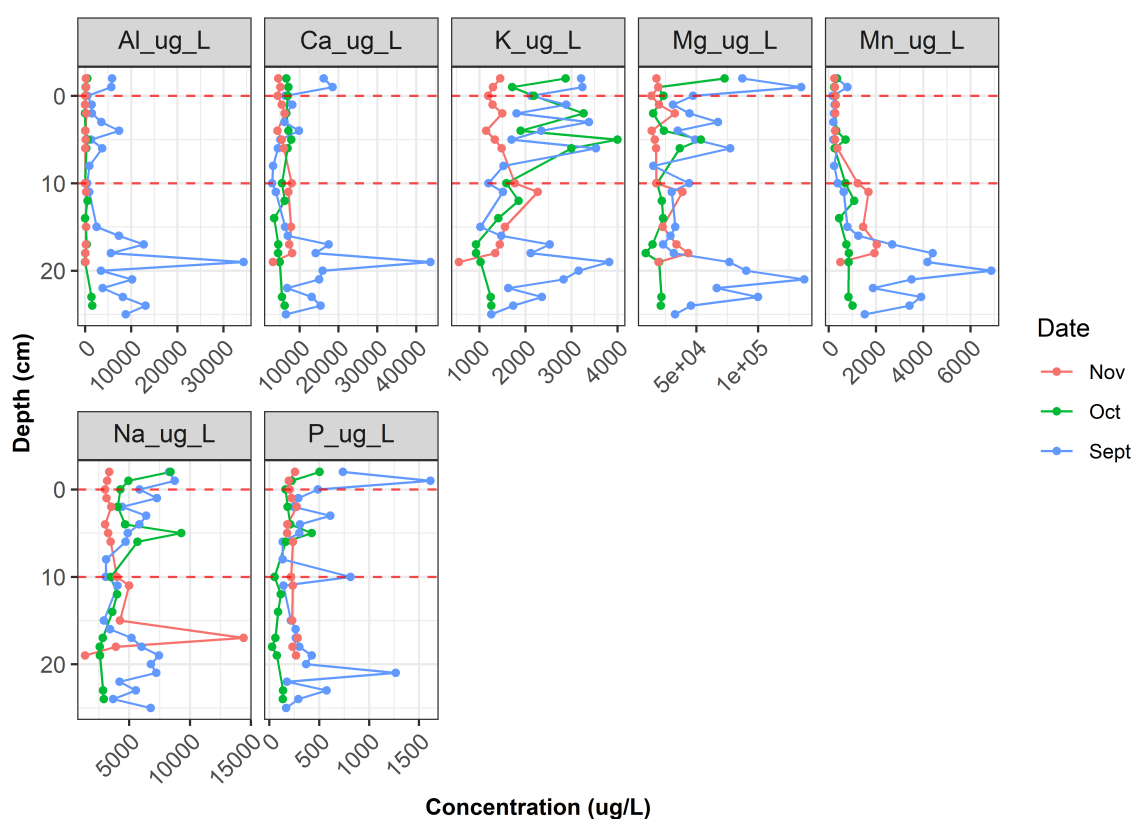


Figure 14. Major ion concentrations in pore water sampled from the inlet stream. The blue trendline was sampled in the warmer month of September, while the green and red trendlines were sampled in the colder months of October and November.

1-D Diffusion Experiment

A soil column with spiked ^{137}Cs was analyzed using a BGO detector to estimate the rate of upward diffusion that occurs in Pond B sediment. After three weeks of measuring ^{137}Cs counts in 1 cm segments, increments were modified to 0.16 cm, as very little upward diffusion was observed at this 1-cm spatial resolution. The detector measured 0.16 μCi in the first cm on Day 6 and 0.15 μCi on Day 28. Once the increments were adjusted to a higher spatial resolution, upward diffusion could be more sensitively measured. As observed in Figure 15, on Day 32, the majority of the ^{137}Cs was measured in the bottom 0.4 cm, corresponding to the location where ^{137}Cs was spiked into the column. However, on Day 42, the measured activities of ^{137}Cs in the bottom 0.4 cm of the column had decreased, but above 0.4 cm the ^{137}Cs increased in measured activity. Specifically, at a height of 0.48 cm, the ^{137}Cs increased from 0.92 μCi to 0.98 μCi , suggesting that upward diffusion had occurred. On Day 52, it was observed that ^{137}Cs had continued to migrate upward, as the bottom of the soil column measured reduced activity while activity measured above 0.8 cm increased. After Day 52, the column became dehydrated, resulting in inaccurate counts and the experiment was stopped. However, the higher spatial resolution data that was collected during these 52 days was enough to demonstrate the natural tendency of ^{137}Cs to move from an area of high concentration to an area of low concentration.

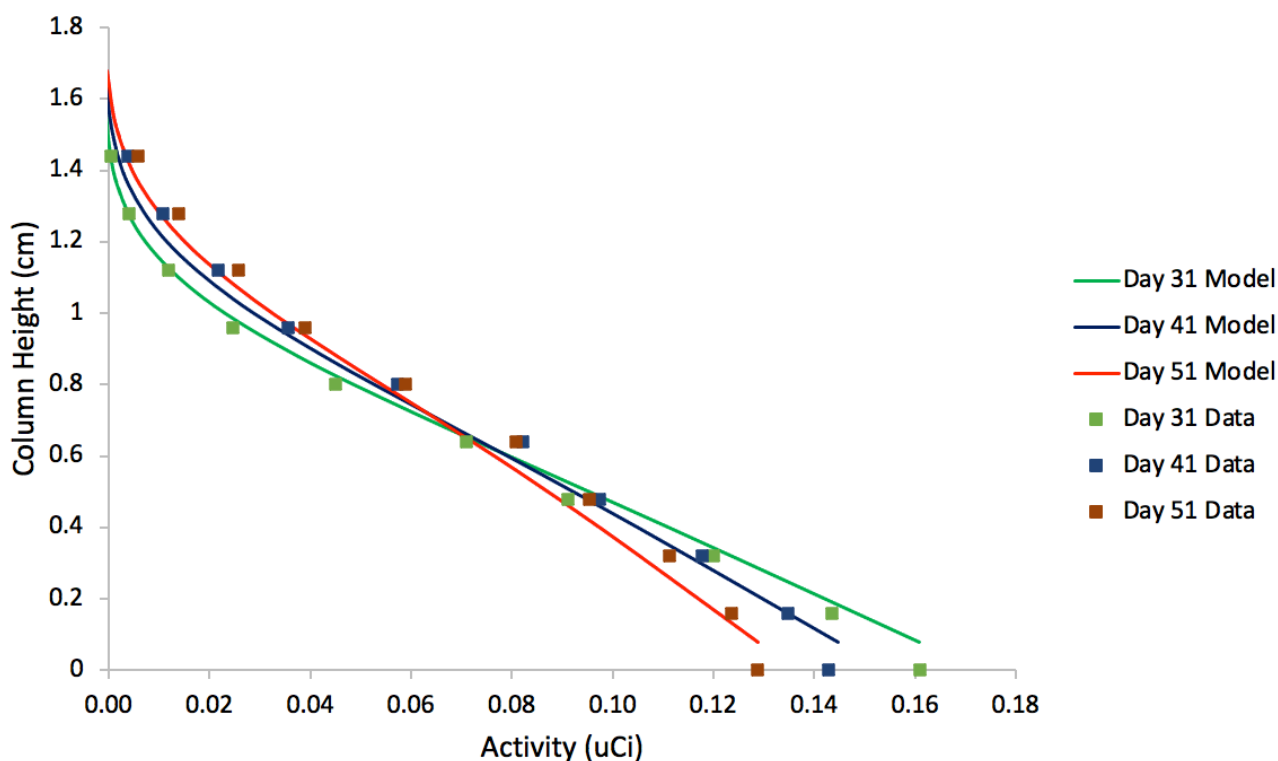


Figure 15. 1-D high spatial resolution of ^{137}Cs upward diffusion.

5. Discussion

Water Chemistry

Measurements of temperature, dissolved oxygen, pH, and ORP throughout the water column in Pond B show drastic variations between seasons (Figure 8). A thermal gradient appears in the summer months beginning in the month of April and becomes very prominent in June. This gradient gradually disappears, and parameters become more homogenous as air temperature becomes colder. Due to this thermal stratification and development of anoxic conditions in the deeper layers, based on previous data, it is hypothesized that ^{137}Cs concentrations increase in

the water column during the summer months as anerobic processes in the hypolimnion release NH_4^+ and as a result, ^{137}Cs releases from sediments due to cation replacement. Another potential mechanism resulting in ^{137}Cs releases involves the dissolution of Fe^{3+} minerals from sediment. As Fe^{3+} minerals are reduced to Fe^{2+} ions, ^{137}Cs that may be attached to these sediments have the potential to be released into the water column with the Fe^{2+} ions. Both the NH_4^+ and Fe^{2+} hypotheses have been verified in past studies at Pond B as higher concentrations of ^{137}Cs were observed in July during stratification compared to both November and December (Mohler et al. 1997). As seen in Figure 10, seasonal variations had little effect on ^{137}Cs concentrations in the water column between March 2019 and June 2020. For both times of year, concentrations were relatively homogenous throughout the water column as a function of depth in the pond. However, concentrations were generally higher in the hypolimnion region as compared to the epilimnion region of the pond. This change in concentration of ^{137}Cs as a function of depth supports the theory of ^{137}Cs dominantly remaining in the lower depths of the water where the Cs sorbs and desorbs from sediment directly below.

The seasonal variation in pH is different than what has been observed in the past by Evans et al. (1983) in Par Pond, where pH was reported as relatively homogenous throughout the water column (Figure 16). The trend toward acidification observed in Pond B may be a result of an increase in metabolites released due to anaerobic metabolism, and/or a result of concentrations of organic carbon (humic substances) present in the water column. As observed in Figure 9, in June 2019 organic carbon concentrations decrease slightly with depth as a result of the presence of vegetation in the epilimnion region. As the abundance of vegetative material decreases with

depth in the water column due to the lack of sunlight, concentrations of organic carbon also decrease as a result of a lack of respiration.

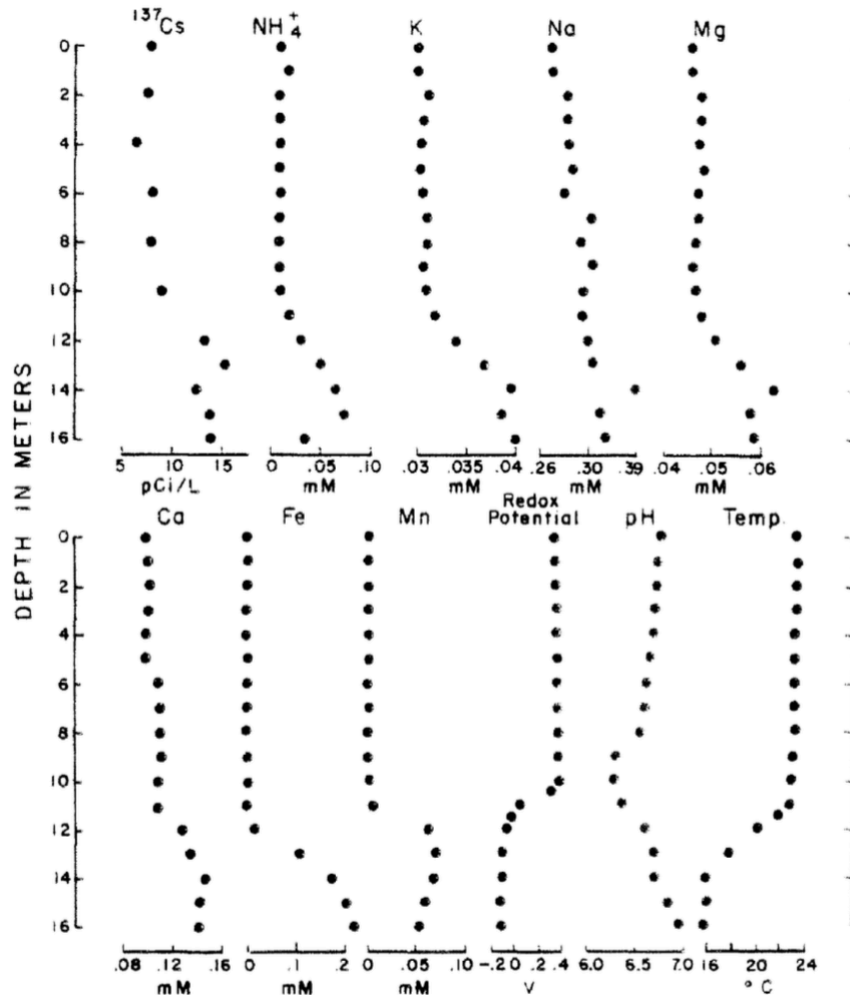


Figure 16. Profiles of dissolved ^{137}Cs and other limnological parameters in Par Pond September 29, 1979 (Evans et al. 1983).

Sediment Cores

Results from sediment cores collected from the inlet stream show higher ^{137}Cs concentrations near the sediment-water interface and decrease as the depth of the core increases. Since the inlet stream serves as the access point for radionuclides to enter the pond,

it can be surmised that this location will likely contain the highest activities of ^{137}Cs . These results are similar to results published by both Whicker et al. (1990) and Pinder et al. (1995), accounting for decay. Cores analyzed in both sets of previous studies were sampled from random locations throughout the pond. However, the decreasing ^{137}Cs concentrations with an increase in depth remains consistent over time. Thus, despite sedimentation occurring, there appears to be a mechanism for maintaining the highest ^{137}Cs concentrations at the surface of sediments. Early studies of ^{137}Cs in Pond B and nearby Par Pond demonstrated a seasonal cycling of increased cesium concentrations in surface waters during the summer months when the ponds have developed a thermocline. The presence of ^{137}Cs in the surface waters may be due to sedimentation of Cs-bearing particles which form in the surface water after the thermocline dissipates, ^{137}Cs diffusion upward into newly sedimented, ^{137}Cs -free sedimentation layer, negligible amount of sediment deposition, and/or introduction of additional ^{137}Cs to the pond from atmospheric deposition or from the influent canal. As sedimentation occurs and soil lacking ^{137}Cs buries the ^{137}Cs rich soil, ^{137}Cs moves from areas of high concentration to areas of low concentration (Robbins, 1974). Estimates of the sedimentation rate of $<0.02 \text{ g cm}^2/\text{y}$ would result in 5 cm of sediment covering the ^{137}Cs laden sediment deposited during reactor effluent releases in 1961-1964. As a result, ^{137}Cs migrates upward in the soil and remains at the highest concentrations near the water-sediment interface. This process, which is further explained by the 1D diffusion experiment discussed below, appears to be responsible for maintaining high concentrations of ^{137}Cs near the sediment/surface water interface and making ^{137}Cs readily available for leaching into the surface waters during the summer months.

There are notable differences in the concentration profiles of ^{137}Cs at each of the sampling locations. Sediment cores sampled from the open water of the pond were observed to vary in their ^{137}Cs concentration profiles versus cores sampled from the inlet stream. Core 1 sampled from Pond 1 exhibited a concentration profile that initially decreased with core depth and then increased to the core's highest concentration, before decreasing once again. The only core profile that has any similarity to Core 1 at Pond 1 can be seen in Pinder et al. (1995). A water depth of 4 m results in a sediment core ^{137}Cs profile that alternates between increasing and decreasing concentrations as the core increases with depth (Figure 17). However, excluding the top 4 cm of the core, the concentration continues to decrease compared to the surface-water interface concentration. While the exact location of this core in Pinder et al. (1995) is unknown, due to the known water depth, it can be assumed that the location was closer to the banks of the pond as compared to the deepest portion of the pond, but deeper than Pond 1. The variation in concentration with depth observed in the Pond 1 core as well as the core seen in Pinder et al. (1995) may be attributed to sedimentation. Since the inlet stream has the highest observed concentration of ^{137}Cs , it can be assumed that the surface sediment is scoured by the higher water flow velocity in the canal and transported into the open pond over time due to the direction of stream flow. Thus, particles containing ^{137}Cs diffuse into the open water, where lower concentrations are observed in the sediment. Applying this rationale, the highest concentrations would be expected in the direct flow path from the stream. However, the core sampled at Pond 1 was sampled slightly off to the side from the flow path of the stream as seen in Figure 18. This difference could contribute to the mixed profile experimentally observed, as sedimentation causes particles with and without ^{137}Cs (depending on the particles' initial locations) to bury ^{137}Cs

deeper into the sediment. The upward diffusion of ^{137}Cs in this soil may also contribute to the varied profile as particles in areas of higher concentrations move to lower concentrations.

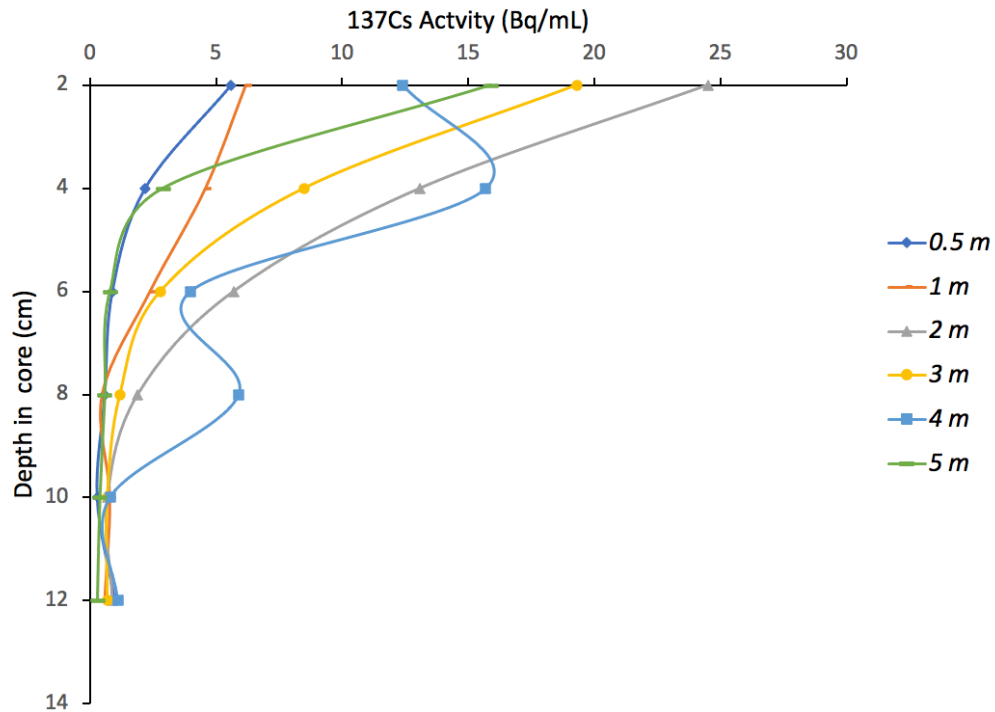


Figure 17. Sediment core results published by Pinder et al. (1995). The legend describes the depth of water from locations where cores were sampled.



Figure 18. Map of Pond B showing Pond Location 1 slightly to the side of the natural movement of water.

The core sampled from Pond 5, closest to the outlet stream, had a very similar ^{137}Cs profile as compared to Inlet Core 3 and a greater surface sediment concentration than the core sampled from Pond 1, being closest to the inlet stream (Figure 11). This increase in concentration at Pond 5 was initially not expected, as it was hypothesized that ^{137}Cs concentrations would decrease as a function of distance from the point of release. However, as past studies have concluded, ^{137}Cs has a tendency to accumulate in areas of high total organic matter due to the high cationic exchange capacity associated with high organic matter. As seen in Figure 13, sediment sampled from Pond 5 has a much greater total organic matter percentage as compared to sediment sampled from Inlet Core 3. Due to the mobility and accumulation of organic matter observed at Pond 5, it can be assumed that the organic matter plays a vital role in the movement of ^{137}Cs across the pond. Also, Pond 5 is much shallower as compared to Pond 3 and 4. As a result, it can be expected that organic matter would typically settle in the shallower regions of the pond, where the natural current of the water moves towards, instead of moving down gradient to the deeper, unmixed portions. Therefore, the original proposed mass-balance model of the pond should be altered to include the movement of ^{137}Cs across the deeper areas of the pond, where it settles with organic matter in the shallower region of Pond 5.

1D Diffusion Experiment

The 1D Diffusion experiment further helps to explain why ^{137}Cs concentrations remain highest near the sediment-water interface in Pond B and decrease with increasing depth. Modelling efforts were conducted using the following equation, where C is the concentration, D is the diffusion rate, t is the time, R is the retardation factor, and z is the distance.

$$C_{(i,j)} = \frac{D\Delta t}{R\Delta z^2} [C_{(i+1,j-1)} - 2C_{(i,j-1)} + C_{(i-1,j)}] + C_{(i,j-1)}$$

Results quantified a diffusion rate of $1.51 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ for ^{137}Cs . This result is similar to a literature based diffusion rate of Cs^+ ions in water of $\sim 2.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. As sedimentation occurs and high concentrations of ^{137}Cs are buried into the soil, ^{137}Cs ions migrate upward and downward to areas of lower concentration where accumulation may occur at the sediment/surface water interface over time. This accumulation may be enhanced by deposition of particles that form in the water column and sorb ^{137}Cs during sedimentation in the winter months. The calculation and observations from the 1D diffusion experiment as well as the results from Pond 1 and 5 ^{137}Cs core profiles suggests that ^{137}Cs has been actively migrating across the pond over time. While the inlet stream continues to have the highest concentrations of ^{137}Cs , the process of upward diffusion allows ^{137}Cs to be potentially remobilized into the water column during warmer months and transported further towards the outlet stream. This process is further explained by the higher concentrations of ^{137}Cs in the sediment at Pond 4 compared to Pond 3 (Figure 11). Once ^{137}Cs is resuspended into the water column, it is able to move with the pond's natural current towards the outlet stream where it settles again once the thermocline begins to disappear. This causes the ^{137}Cs to bypass the deeper portions of the pond (Pond 3). Also, since the core profile resulting from Pond 1 is noticeably different than those collected in the 1980s, it can be assumed that Cs is increasing in mobility with time.

Cs Batch Sorption Experiment

Results from the liquid Cs sorption experiment demonstrated a Freundlich isotherm that increased with the amount of ^{137}Cs sorbed to the soil as the amount of ^{137}Cs aqueous phase concentration increased. Plotting the linearized form of the data resulted in a maximum absorption capacity (K_f) of $\sim 45 \text{ L kg}^{-1}$ (Figure 19). When using the nonlinear Freundlich approach, the data becomes nonlinear at greater Cs concentrations. However, when only plotting the lower concentration values, the data remains linear. The linear Freundlich approach was used to represent this data as it demonstrates the best fit. These results demonstrate that ^{137}Cs is readily able to sorb onto Pond B soils after migrating across the pond during the warmer months. The change from linear to nonlinear occurs due to the limit of available exchange sites in the soil being reached and as a result, the clay is not readily able to absorb Cs at the same magnitude as before. This may be a result of competing Na^+ ions with ^{137}Cs for exchange sites. In the field, this would be consistent with ions such as Na^+ , Ca^{2+} , and Mg^{2+} competing for exchange sites within the soil. As a result, ^{137}Cs can be more readily mobilized into the water column where it can move further downstream.

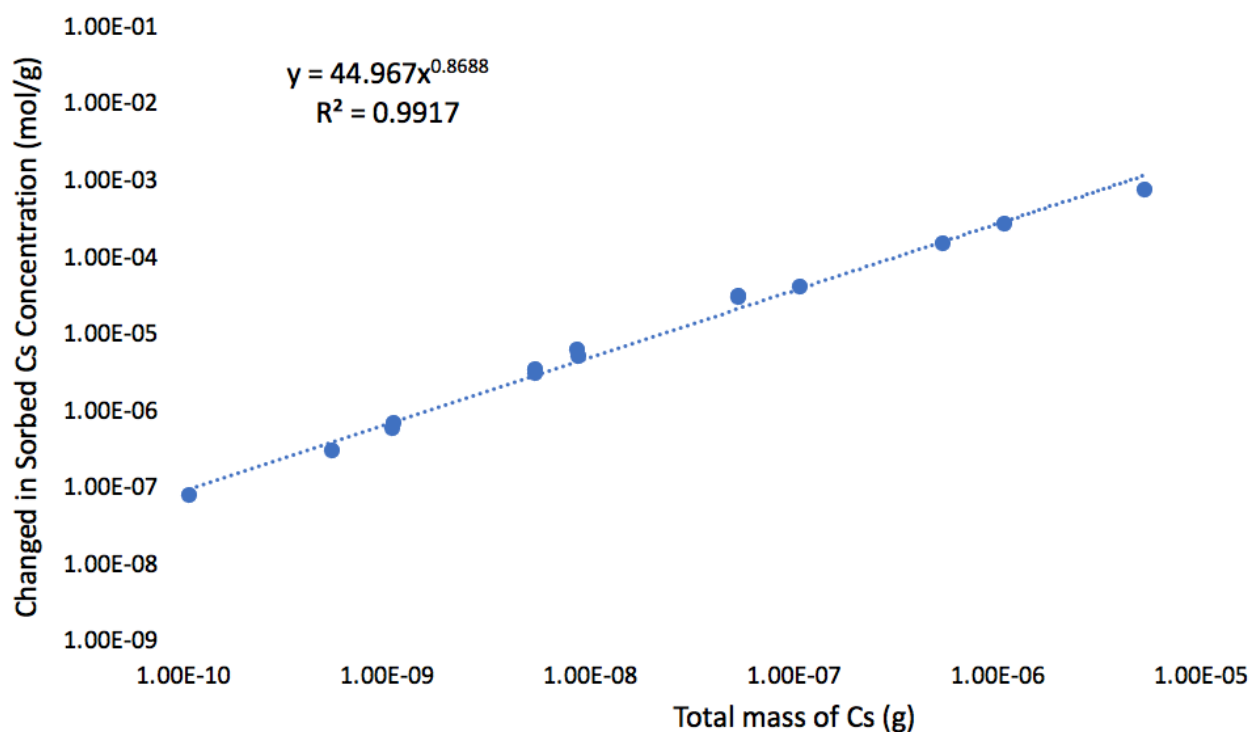


Figure 19. Cs sorption Freundlich isotherm with an K_f value of ~ 45 L/kg. The average aqueous Cs concentration measured in the water column of Pond B was 3.65×10^{-16} mol/L.

XRD analysis of three differing soil horizons in cores sampled from the inlet stream of Pond B demonstrated an abundance of quartz > feldspar > kaolinite. Grain size and soil color of the three samples can be seen in Figure 7. The large amount of kaolinite, and trace amounts of 2:1 clay minerals, are likely responsible for ^{137}Cs sorption via ion exchange and provides another mechanism of ^{137}Cs accumulation throughout the pond. When temperatures are lower and the pond becomes well-mixed, ^{137}Cs sorbs to the kaolinite, containing a 1:1 clay lattice, at the bottom of the pond and becomes sequestered.

6. Conclusion

Pond B sediment geology is comprised of highly weathered soils with an abundance of quartz > feldspar > kaolinite clay mixed with variable concentrations of organic matter. Cesium-137, has the strong ability to absorb onto the lattice of clay particles in the sediment of the pond. However, due to the presence of ammonia in the pond as well as high weatherization of sediment in the Coastal plain area, ^{137}Cs is also readily able to desorb from the clay, diffuse from the sediment pore water, and increase the concentrations in the water column. This process occurs during the summer months when the thermocline is formed and results in elevated ^{137}Cs concentrations in the water column and increased mobility across the pond. Changes in ion concentrations with respect to depth in the warmer months can be a result of the remobilization of ions into the water column as temperatures decrease. Cesium-137 has been observed to behave in a similar manner, except Cs is resuspended into the hypolimnion region of the water column as temperatures increase. This process of ion-exchange that occurs in reducing waters leads to a mobilization of ^{137}Cs in the pond during warmer months. Once temperatures begin to decrease, Cs appears to sorb to particulates suspended in the water column which settle during the winter months. Furthermore, ^{137}Cs appears to have enhanced accumulation in areas of the pond with high organic matter. In this manner, ^{137}Cs is mostly present in the inlet stream locations, closest to the point of release and decreases with distance from this point. However, Pond 5, being the furthest location from the point of release, contains higher surface sediment concentrations of ^{137}Cs than any other location in the pond itself. This enhanced accumulation is hypothesized to be due to the presence of a high concentration of organic matter at location Pond 5.

When comparing this data to historic data from Whicker et al. (1990) and Pinder et al. (1995), there appears to be little change in ^{137}Cs distribution and concentrations in both the water and sediment volumes. As a result, it can be concluded that the Cs is seasonally cycling between the water and sediment volumes and demonstrates undetectable movement. This concept is essential to predicting the risk of bioaccumulation in biota in the area. While plants that are stationary in the water have the ability to accumulate negligible quantities of ^{137}Cs from the water column, the overall risk to all biota in the system is almost nonexistent as Cs has dominantly fluctuated only between the sediment-water interface for the past 30 years.

7. Future Work

After observing the correlation between ^{137}Cs and the presence of organic matter in the pond, it would be useful to continue collecting sediment core samples from new locations throughout the pond including the outlet stream and locations outside of the direct path between the inlet and outlet streams. Sediment cores should be analyzed for ^{137}Cs concentrations, organic matter, and total inorganic/organic carbon. It is expected that Cs concentrations would be greatest between these streams and would decrease as distance from the linearized path increased. Major ion concentrations in the water column should also be determined from these new locations and compared with concentrations measured from locations Pond 1 to 5.

Along with obtaining a greater understanding of the spatial resolution of Cs across the entire pond, a mass-balance simulation of the pond should be produced to assist with determining further mechanisms involved in controlling ^{137}Cs migration. To achieve this

simulation, components including influence rate, effluent rate, precipitation/evaporation rate, and sedimentation rate should be determined. This simulation will also assist with understanding the relationship between the volumes of water above and below the thermocline.

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