^{137}Cs Distribution and Geochemistry in Savannah (Georgia) Riverine, Estuarine and Marsh Environments

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***Abstract*- Sediment radiogeochemistry characteristics of Savannah, Georgia, USA area riverine, marsh and estuarine environments were examined as part of ongoing efforts to determine processes governing the distribution and behavior of radionuclides throughout the Savannah area aquatic system. Analyses were performed to quantify ^{137}Cs and ^{210}Pb$_{xs}$ activities, clay mineralogy, grain-size, elemental cesium (Cs) and manganese (Mn) concentrations. Preliminary results indicate that ^{137}Cs activities in the Savannah area sediments range from below detection limits to 3.42 dpm/g. Radiogeochemistry patterns suggest that in the marsh, downcore particulate ^{137}Cs distribution is primarily controlled by steady-state particle mixing and burial processes whereas non-steady state physical transport processes govern post-depositional ^{137}Cs distribution in the local riverine and estuarine environments. In addition to physical processes, clay mineralogy and grain-size differences may also influence the ^{137}Cs retention ability of the Savannah area aquatic sediments.**

I. INTRODUCTION AND BACKGROUND

Radionuclides in Aquatic Systems

The fate of radionuclides in the aquatic environment is controlled by the: 1) degree of cation competition, a function of salinity and redox reactions; 2) sediment particle characteristics such as mineralogy and grain-size; and 3) physical processes which include water movement, dredging, particle mixing, burial and removal [1]. Upon introduction into the aquatic environment, radionuclides will either: 1) remain near the source region by sorbing onto suspended sediment particles; or 2) be transported away via water mass or particle movement. (The term sorption is used here to describe the overall loss from solution.)

Anthropogenic and naturally occurring radionuclides have been used as tools for examining both particle and water mass movement in aquatic systems. ^{210}Pb$_{xs}$, a naturally occurring radionuclide with a half-life of 22.3 years, is often utilized to investigate particle mixing and burial processes. ^{210}Pb$_{xs}$ is defined as the difference between total and supported ^{210}Pb, a daughter product of ^{226}Ra that is present in the sediment.

During the early 1950's, ^{137}Cs, an anthropogenic radionuclide with a half-life of 30.2 years, was first introduced into the environment primarily as a result of above ground nuclear weapons testing. Since this introduction, ^{137}Cs has been utilized as both a tracer of particle movement in freshwater environments, as well as a tracer of water mass movement in marine and estuarine environments [2, 3, 4, 5, 6, 7, 8, 9].

In freshwater environments, ^{137}Cs is an effective tracer of particle movement because of its ability to adhere to fine-grained, clay-rich particles. In freshwater systems ^{137}Cs is adsorbed and in some instances irreversibly fixed onto clays. In freshwater environments different clay minerals have varying ^{137}Cs adsorption capacities. In general the greatest quantities of ^{137}Cs are adsorbed by smectite followed by illite and kaolinite.

^{137}Cs in the Savannah River Watershed

Sediment ^{137}Cs retention in the Savannah River watershed is controlled by various biogeochemical, physical, environmental and anthropogenic (e.g. dredging, resource management, development and recreation related activities, etc.) factors. The primary ^{137}Cs source to the entire Savannah River watershed is global atmospheric fallout. In addition to the global fallout source, a relatively small amount of radiocesium was directly introduced into this watershed via the U.S. Department of Energy Savannah River Site (US DOE SRS) located in South Carolina [10]. In the past the SRS facility produced and processed significant quantities of nuclear materials. Currently, the 800 km^2 SRS complex is used for the underground storage of radioactive waste material [10]. The only known potential point sources of ^{137}Cs within the Savannah River watershed are the SRS and the Vogtle power generating station, operated in Georgia by

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the Southern Nuclear Company. Some SRS-derived radiocesium (99% ^{137}Cs) was released to on-site surface water streams [10]. There have been no known incidents of environmental radionuclide releases associated with the Vogtle facility [11].

Sediments near the SRS are characterized as sandy coastal plain soils containing kaolinitic clay minerals. Researchers have cited the relatively poor fixation of ^{137}Cs by these sediments as the major factor resulting in the mobility of SRS-derived ^{137}Cs that was introduced into the Savannah River watershed [12, 13, 14, 10]. Once introduced into the Savannah River watershed ^{137}Cs (from global atmospheric fallout, SRS or any other source) may be transported downstream toward the estuarine and marine environments.

Studies have shown that Cs becomes associated with fine particles in coastal environments and that rate, pattern, and extent of accumulation within each coastal system are extremely variable [8]. In this paper, we describe the preliminary results of an on-going investigation of particle-bound ^{137}Cs in the Savannah area aquatic system. For this study we have examined potential factors influencing the distribution and retention of ^{137}Cs in three types of aquatic environments (riverine, marsh and estuarine) located within the Savannah River watershed, near the city of Savannah, Georgia.

II. SAMPLING AND ANALYTICAL METHODS

Sediment cores were collected in the Savannah area aquatic system, using a Glew [15] corer at the Upper Savannah River 32°00.443'N, 80°51.094'W (riverine environment), Turner Creek 32°01.350'N, 80°59.688'W (marsh environment), and Tybee Island 32°01.518'N, 80°55.134'W (estuarine environment). After collection, the sediment cores were extruded and sectioned using a modified Glew extruder [16]. The sectioned samples were stored in "whirl pac" bags, weighed, frozen, freeze-dried and once dry, re-weighed in order to calculate the porosity of each sample. Sediment samples were prepared for radionuclide analyses following techniques described in Alexander et al. [17]. The sediment samples, packaged in low background petri dishes, were assayed for gamma emitters using a planar gamma detector, connected to a Canberra Genie multichannel analyzer. The detector was calibrated using US National Institute of Standards and Technology ^{137}Cs single-line and Ocean Sediment multi-line standards.

After the samples were sealed, ^{226}Ra and ^{214}Pb were allowed to come into secular equilibrium by waiting for a period of no less than 30 days prior to gamma analysis. This period corresponds to approximately 8 half-lives of ^{222}Rn, the immediate daughter of ^{226}Ra. ^{214}Pb is a short-lived daughter product of ^{222}Rn and a precursor to ^{210}Pb. The ^{226}Ra activity was calculated by determining the ^{214}Pb activity. ^{210}Pb$_{xs}$ activities were calculated using activities of total ^{210}Pb and ^{226}Ra (from ^{214}Pb). The activities of the gamma emitters were determined via radionuclide-specific energy peaks located at 661 keV (^{137}Cs), 46.5 keV (^{210}Pb), 295.1 (^{214}Pb), and 351.9 keV (^{214}Pb). Self-adsorption corrections were performed for each sample following techniques of Cutshall et al. [18].

Total Cs and Mn concentrations were determined, using a Perkin-Elmer graphite furnace atomic absorption spectrophotometer. Sample extractions were carried out via a modified *aqua regia* method [19]. Using this method approximately 0.05 g of sediment was extracted with a 1:2 mixture of trace metal grade concentrated HNO_3 and HCl. In order to facilitate the element extraction process, this sediment-diluent mixture was agitated periodically for a period of seven days. A standard dilution procedure was utilized to prepare the samples for Cs and Mn analysis [20]. Appropriate concentration calibrations were performed using an Aldrich multi-elemental standard.

Particle-size distributions were determined using traditional particle filtration and settling techniques [21], as well as sieving and Sedigraph methods [22]. The Sedigraph data was obtained using a Micromeritics Sedigraph 5100 equipped with MasterTech 51 software.

The clay mineralogy of the < 2 µm fractions were identified using X-ray diffraction of oriented mounts. A Phillips X-ray diffractometer with a Bragg-Brentano goniometer was used in this study. Copper radiation was used and filtered with a graphite monochromator. The MDI Databox was used for computer control of the diffraction analyses. The step size was 0.02° 2? and the time step was 2 seconds. XRD analysis was performed on both air-dried and glycol treated samples in order to identify expandable clay minerals.

III. RESULTS AND DISCUSSION

Estuarine environment

The downcore ^{137}Cs activity (Fig. 1) for the Savannah area estuary site (Tybee Island) ranged from below detection limits to 0.08 dpm/g. Tybee Island ^{137}Cs and ^{210}Pb$_{xs}$ profiles are representative of an unstable environment that does not exhibit steady-state particle transport processes. Absence of ^{137}Cs in surface sediments is an indication of older material (material deposited prior to the onset of atmospheric nuclear weapons testing that occurred in the early 1950's). The presence of ^{137}Cs and the elevated ^{210}Pb$_{xs}$ activities in the 20-25 cm depth intervals indicates that these subsurface sediments are comprised of younger material.

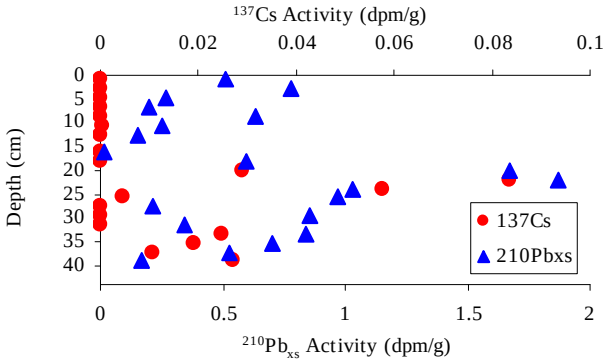

Fig. 1. Savannah area estuarine environment (Tybee Island) ^{137}Cs and ^{210}Pb$_{xs}$ activity (dpm/g) profiles.

At this estuarine location, it appears as though older material was deposited on younger material via irregularly occurring physical transport process(es) (such as storms and dredging). Results from grain-size analysis (Fig. 2) indicate that fine-grained material, suitable for Cs adsorption, is present in varying concentrations throughout the core. Additionally, illite and smectite in the Tybee Island sediments, may have increased the region's ability to retain ^{137}Cs. Elevated concentrations of clay and silt size fractions correspond with increased ^{137}Cs activities and total Cs concentrations (Fig. 3). These results indicate that sediment texture and mineralogy, in addition to the dominant physical particle transport processes may have also influenced the distribution of ^{137}Cs in this estuarine environment. The validity of these interpretations will be investigated via additional analysis.

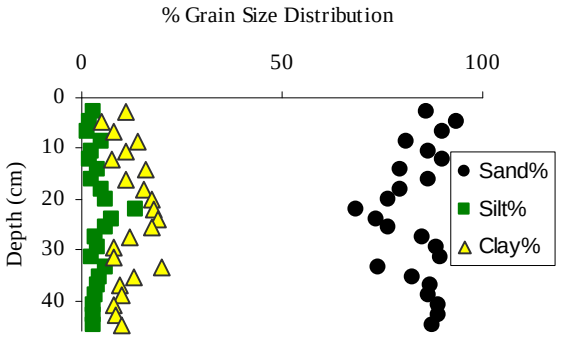

Fig. 2. Savannah area estuarine environment (Tybee Island) downcore grain-size distribution.

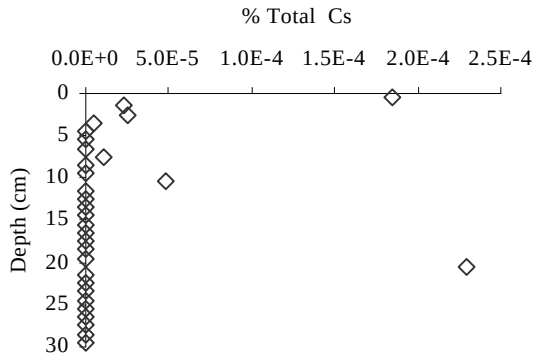

Fig. 3. Savannah area estuarine environment (Tybee Island) total weight % Cs profile.

Riverine environment

Downcore ^{137}Cs activity for the Upper Savannah River site (Fig. 4) ranged from below detection limits in all samples except one, where activity was high: 3.42 dpm/g. ^{137}Cs and ^{210}Pb$_{xs}$ profiles for this riverine environment are representative of an unstable environment. Similar to the Savannah area estuarine site, the absence of ^{137}Cs at various depth intervals in the core collected from the Upper Savannah River may indicate the presence of much older material. The elevated surface and subsurface ^{210}Pb$_{xs}$ activities provide additional support to indicate the deposition of older material being deposited onto younger material.

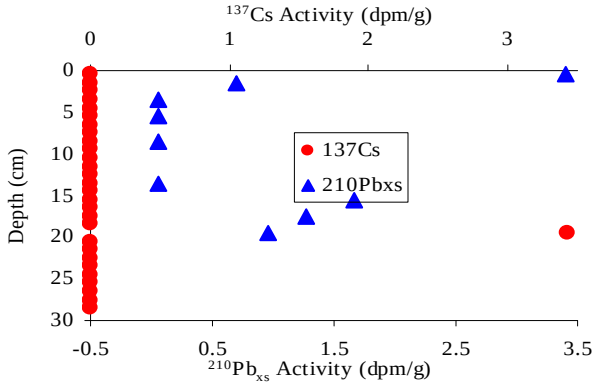

Fig. 4. Savannah area riverine environment (Upper Savannah River) ^{137}Cs and ^{210}Pb$_{xs}$ activity (dpm/g) profiles.

The ^{137}Cs activity profile likely exhibits an alternating pattern of 'old' and 'new' material. In addition to resulting from physical particle transport processes, this type of pattern can also be attributed to post-depositional ^{137}Cs remobilization that can occur in suboxic, anoxic and/or high salinity environments. The elemental Cs concentration profile approximates the distribution of ^{137}Cs (Fig. 5). The Mn profile (Fig. 6) indicates oxidizing conditions likely existed throughout the sediment column. The Mn concentration profile further suggests the presence of older material (lower/reduced Mn concentrations) being deposited on younger oxidized material (higher Mn concentrations). Grain-size analysis of four sediment samples indicate that the riverine site contained at least 20 % clay size particles. The dominant clay mineral present at the Upper Savannah River site is kaolinite. Smectite was not present in this core and illite was identified in only one sample. The radiogeochemistry results indicate that the distribution of ^{137}Cs is primarily influenced by physical transport processes occurring in the Upper Savannah River.

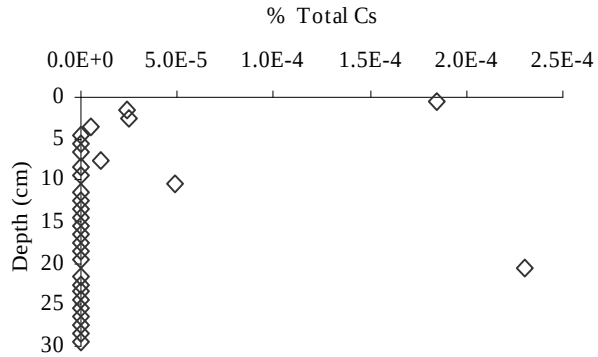

Fig. 5. Savannah area riverine environment (Upper Savannah River) total weight % Cs profile.

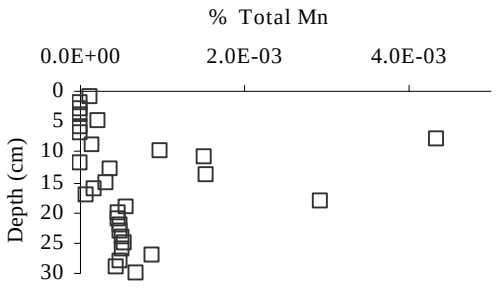

Fig. 6. Savannah River area riverine environment (Upper Savannah River) total weight % Mn profile

Marsh environment

The downcore ^{137}Cs activity (Fig. 7) for the Savannah area marsh site (Turner Creek) ranges from below detection limits to 0.38 dpm/g. The overall ^{137}Cs and ^{210}Pb$_{xs}$ activity profiles are indicative of a stable environment, dominated by steady-state particle transport processes. ^{137}Cs and ^{210}Pb$_{xs}$ profiles indicate that particle mixing is confined to the upper 8 cm, below which burial is the dominant mechanism by which particles are incorporated into deeper sediments.

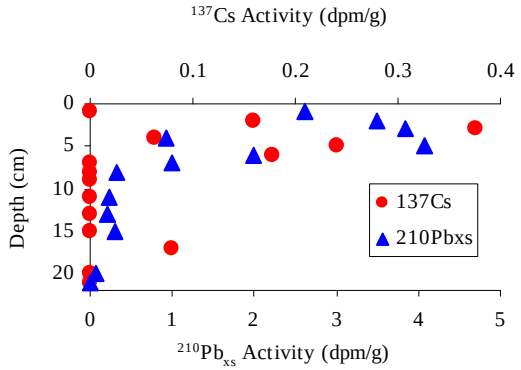

Fig. 7. Savannah River area marsh environment (Turner Creek) ^{137}Cs and ^{210}Pb$_{xs}$ activity (dpm/g) profiles.

Mn was present throughout the sediment core (Fig. 8), indicating the likely absence of reducing conditions in the Turner Creek sediments. The dominant factor controlling the distribution of ^{137}Cs in the marsh sediments appear to be steady state particle mixing and burial.

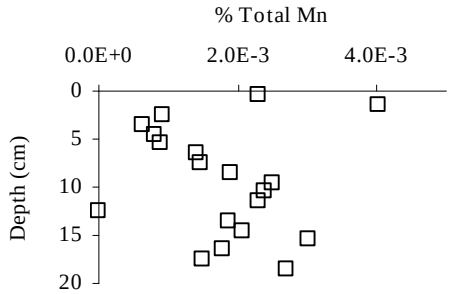

Fig. 8. Savannah River area marsh environment (Turner Creek) total weight % Mn profile

Clay Mineralogy

Smectite, illite and kaolinite, were identified in the Savannah area sediments (Table 1). Additionally vermiculite and chlorite may also be present. Kaolinite is the predominant clay mineral present at each of the sample sites. Smaller quantities of smectite and illite, which possess the greatest ^{137}Cs adsorption capacities, were also present in some of the Savannah area sediments. Smectite was only identified in Tybee Island (estuarine) sediments. Illite was consistently present in all Turner Creek (marsh) sediments, as well as in some samples collected from the riverine (Upper Savannah River) and estuarine (Tybee Island) environments. Future work will include confirming the preliminary interpretation of the mineralogical data which appears to indicate the presence of chlorite and vermiculite in some of the sediment samples. The existence of chlorite in the sediment samples will be confirmed via heat treatments and further XRD analysis. K-saturation sample treatments and additional XRD analysis will be utilized to confirm the presence of vermiculite in the sediment samples.

Table 1. Clay mineralogy of <2 µm sediment fraction. * indicates presence and – indicates absence of the clay mineral.

Sample Site and (Core Depth)	Smectite	Illite	Kaolinite	Chlorite	Vermiculite
Upper Savannah River (6.5 cm)	-	-	*	*	-
Upper Savannah River (9.5 cm)	-	-	*	*	-
Upper Savannah River (11.5 cm)	-	-	*	-	-
Upper Savannah River (21.5 cm)	-	*	*	*	-
Tybee Island (1.9 cm)	-	-	*	*	-
Tybee Island (9.5 cm)	-	-	*	-	-
Tybee Island (20.0 cm)	possible	trace	*	possible	-
Tybee Island (21.9 cm)	*	-	*	-	possible
Tybee Island (44.8 cm)	-	-	*	-	-
Turner Creek (1.0 cm)	-	*	*	-	possible
Turner Creek (2.5 cm)	-	*	*	possible	-
Turner Creek (8.5 cm)	-	trace	*	possible	-

IV. CONCLUSIONS AND FUTURE WORK

The results of this preliminary study appear to indicate that the Savannah area aquatic system does not serve as a permanent retention site for ^{137}Cs-laden particles. Both stable and unstable environments are found within this aquatic system. Factors that are influencing the distribution of radionuclides in these aquatic sediments include physical processes (e.g. storms, dredging, etc.), grain-size differences, clay mineralogy, and possibly biogeochemical processes.

For both the Savannah area riverine and estuarine environments, preliminary results indicate that non-steady state physical processes play major roles in determining the post-depositional distribution, retention and removal of particle-bound ^{137}Cs. In the Savannah area marsh environment, the preliminary results indicate that steady-state particle transport processes influence the post-depositional distribution and retention of ^{137}Cs. Further research is needed to determine the impact of biogeochemical factors and processes to the ^{137}Cs retention capacity and sediment stability of the Savannah area aquatic system.

In addition to particle transport, the retention of ^{137}Cs in this aquatic system is also influenced by various biogeochemical factors. Pevear [23] determined that the concentration of illite in some near-shore environments is elevated due to K^+ uptake by riverine vermiculite. It could be that in the Savannah area aquatic system ^{137}Cs, like K^+, is incorporated into vermiculite particles, resulting in the enrichment of ^{137}Cs concentrations in certain environments. In addition to illite, the preliminary clay mineralogy results indicate the possible presence of vermiculite in the Savannah area sediments. We are currently determining K concentrations (via flame atomic adsorption spectrometry) and completing the elemental, grain size, and mineralogical analysis. Upon the completion of these tasks we will be able to more effectively evaluate the ability of Savannah area near-shore sediment particles to retain and possibly absorbed ^{137}Cs via the proposed near-shore vermiculite/illite uptake process. These lines of inquiry, along with the examination of several other potential biogeochemical factors, are being investigated as part of a larger investigation, which also includes the examination of sediments from additional sites within the Savannah area aquatic system.

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