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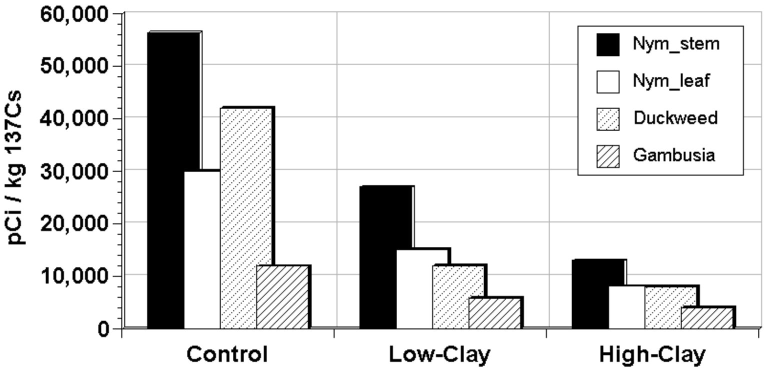
SREL-69 (UC-66E)

Key Words: Cesium, Illite
In situ remediation
Wetlands, Soil Amendment

FIELD DEPLOYMENT OF ILLITE CLAY AS AN *IN SITU* METHOD FOR REMEDIATING ^{137}Cs-CONTAMINATED WETLANDS (U)



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September 25, 2002

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 EXECUTIVE SUMMARY

Radionuclide releases into the aquatic systems of the Savannah River Site (SRS) occurred during the early years of site operation. The releases contaminated numerous aquatic systems on the SRS, such as Par Pond, Ponds A, 2, 4, 5 and B, several creeks (e.g. Steel Creek, Lower Three Runs Creek and Pen Branch), as well as many kilometers of man-made canals that connected the reactors to their cooling ponds. Combined, these aquatic systems represent over 3,000 acres of wetlands that became contaminated with over 500 Curies of radioactive cesium (^{137}Cs).

The problems of contaminated aquatic systems and their associated risks are heightened on the SRS because ^{137}Cs is more biologically available here than at any other Department of Energy (DOE) facility. The enhanced bioavailability of Cs on the SRS is due, in part, to its low adsorptive capability by our kaolinitic-dominated soils. We hypothesized that adding naturally occurring clay minerals with a greater Cs binding capacity to the contaminated wetlands would sequester ^{137}Cs, and reduce its bioavailability. In application, the mineral is broadcast over the surface of the water, where it quickly scavenges ^{137}Cs from the water column as it settles to the bottom sediments. The clay amendments then continue to intercept and adsorb ^{137}Cs from the contaminated sediments, effectively sequestering the contaminant and drastically reducing biological uptake.

We first tested the concept in the laboratory (Hinton et al., 1999b), and found that illite mineral additions to contaminated Pond B sediments effectively adsorbed and retained ^{137}Cs, even in the presence of high concentrations of competing ions, such as ammonium (NH_4^+). The research reported herein centered on a field deployment of the *in situ* remediation method with the goal of learning if the clay amendments reduce the biological availability of ^{137}Cs in contaminated wetlands.

The results were very encouraging. Data analyses from the clay amendment application in Pond A and R-Canal indicate that ^{137}Cs levels in water were reduced 35- to 40-fold, activity concentrations in aquatic plants were reduced 4- to 5-fold, and concentrations in fish were reduced 2- to 3-fold. Equally important, the technique did not destroy the sensitive wetland environment and full-scale deployment costs were estimated to be six times less than the baseline technology, “muck and truck” methods.

This *in situ* technique is a promising remediation tool that allows DOE to reduce the biological availability of an important radioactive contaminant in sensitive wetland environments. While ^{137}Cs is bound to the clay amendment, radioactive decay continually reduces the contaminant concentrations until levels are no longer detectable. The method is a preferred alternative to the extremely destructive and expensive traditional method of “muck and truck”.

2.0 INTRODUCTION

2.1 Cesium Contaminated Wetlands

Radionuclide releases into the aquatic systems of the Savannah River Site (SRS) occurred during the early years of site operation and originated primarily from the reactor areas (Figure 1; RAC, 1999). The releases contaminated numerous aquatic systems on the SRS, such as Par Pond, Ponds A, 2, 4, 5 and B, several creeks (e.g. Steel Creek, Lower Three Runs Creek and Pen Branch), as well as many kilometers of man-made canals that connected the reactors to their cooling ponds. Combined, these aquatic systems represent over 3,000 acres of wetlands that became contaminated with ^{137}Cs, strontium and isotopes of Pu.

The relative risk of these radionuclides to the environment depends upon the quantities released, differences in their potential for concentrating in the environment, and their relative toxicity. Cesium-137 is often the radionuclide of primary concern in these systems because of its biological mobility. Cesium's implication to human health was evident during the draw down of Par Pond. Exposure to ^{137}Cs comprised 95% of the lifetime fatal cancer risks to an adult farmer hypothetically living on the exposed sediments, while strontium and plutonium's contribution to risks were 0.6 and 4.1%, respectively (Whicker et al., 1993).

Cesium-137 was also the primary dose-contributing contaminant to offsite residents during the 1960s and 1970s, the period of major releases (RAC, 1999). Methodology developed by the National Council on Radiation Protection and Measurements (NCRP, 1996) was used by Radiological Assessment Corporation (1999) to assess the relative importance of different radionuclides as potential contributors to offsite radiation dose. The results for surface water contamination showed that ^{137}Cs was the major contributor (~75% of the dose), with ^{60}Co, tritium, ^{131}I, ^{32}P, and ^{90}Sr jointly contributing about another 20%.

Most of the radiocesium released from the SRS in the early years of operation originated from failed fuel elements. The change in ^{137}Cs concentrations in the Site streams over time shows that peak releases occurred in the mid-1960s (Figure 2; RAC, 1999). Annual median release estimates were approximately 0.1 Ci or less before 1955 and after 1976. Over 10 Ci of ^{137}Cs were released annually from 1964–1967, with the highest median release estimate in 1964 of about 20 Ci. RAC (1999) estimated the total ^{137}Cs released for all years to be about 250 Ci with the 5th and 95th percentiles of the distribution estimate equal to 100 and 600 Ci (RAC, 1999). In the early 1990s, Carlton et al. (1992) estimated the inventory of ^{137}Cs within the aquatic systems of the SRS to be 564 Ci. Over 50% of the total ^{137}Cs activity measured in transport in the SRS streams was measured in Steel Creek (Figure 3), which received discharges from L, P and R Reactors. Overall, each of the other streams contributed about 15% of the total quantity of ^{137}Cs.

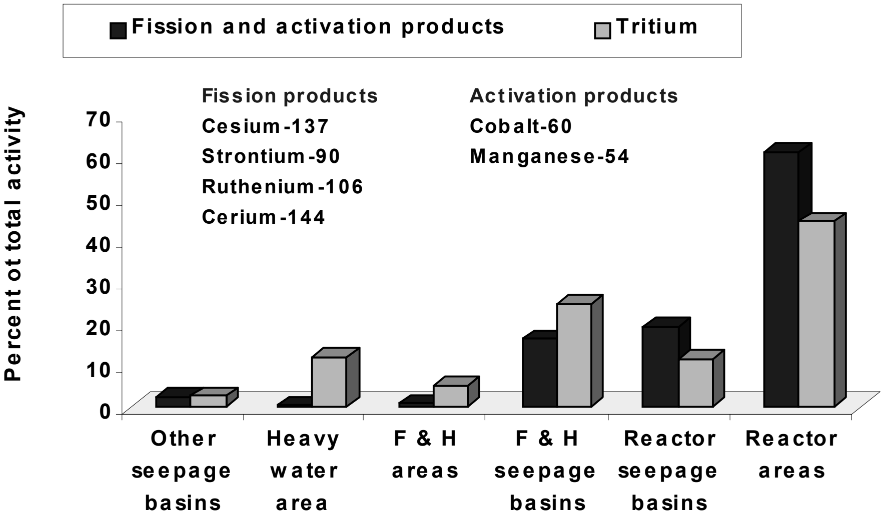


Figure 1. The importance of the reactor areas as contributors of radioactive releases in liquid effluent is shown as a distribution of tritium and beta activity (fission and activation products) in liquid wastes from six sources on the Savannah River Site. These percentages were based on operations in 1965–1969 (RAC, 1999).

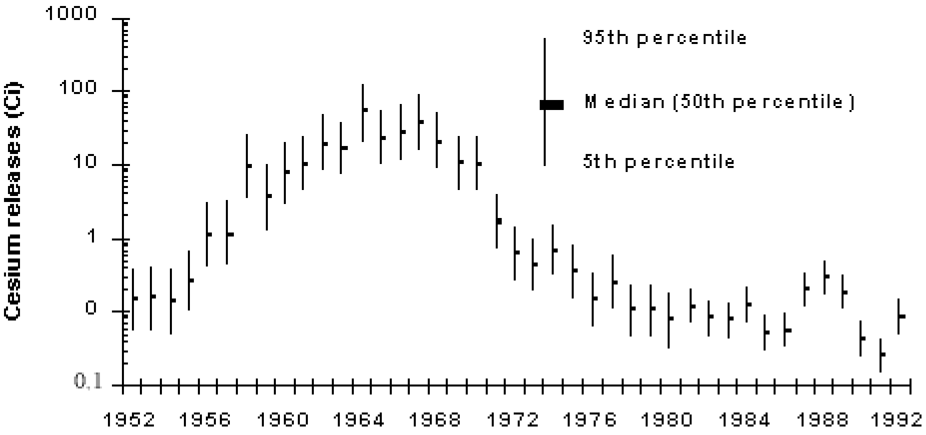


Figure 2. Estimates of ^{137}Cs releases to surface water from the SRS with uncertainty estimates, shown on a logrithmic scale. Each year is represented by a vertical line that represents the 95th (top) and 5th (bottom) percentiles of the distribution of releases with the median or 50th percentile shown as the filled shape in the center (RAC, 1999).

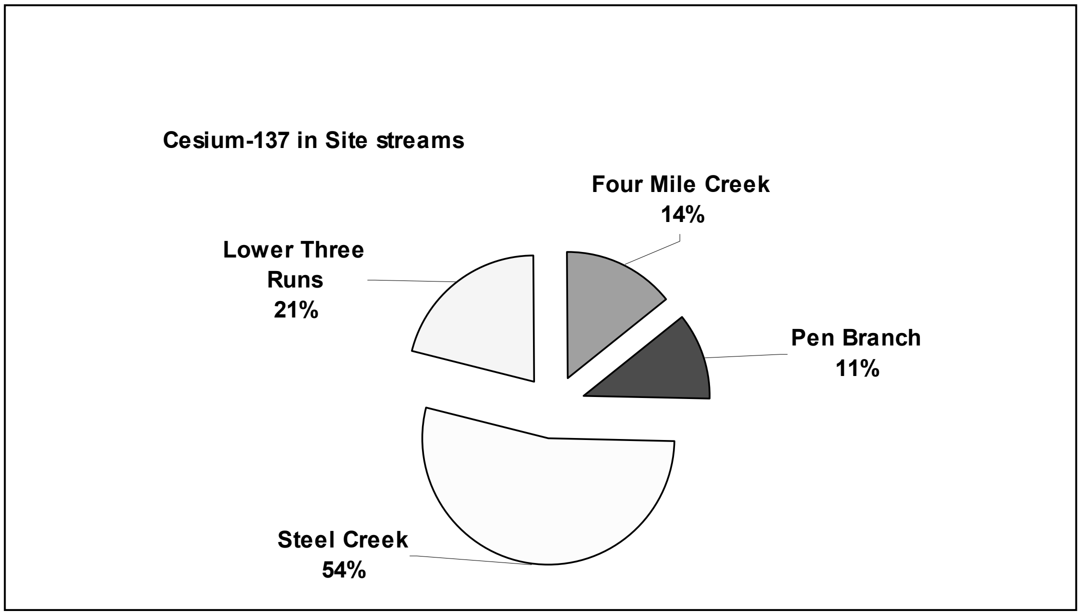


Figure 3. The relative amount of total cesium activity in the major Site streams measured weekly from 1959-1967 in onsite streams at Road A, the last onsite location before the streams emptied into the Savannah River. Over half of the ^{137}Cs activity released during this period was present in Steel Creek (RAC, 1999).

2.2 High Cesium Mobility

The problems of contaminated aquatic systems and their associated risks are heightened on the SRS because ^{137}Cs is more biologically available here than at any other DOE facility. Increased ^{137}Cs availability was documented in these systems during the 1960s era of weapons fallout (Whicker and Schultz, 1982), and the high bioavailability of ^{137}Cs still exists today, as is evident by the propensity of ^{137}Cs to be taken up from the soil by plants. This propensity can be measured using a concentration ratio (CR), where CR = pCi kg^{-1} dried plant / pCi kg^{-1} dried soil. The National Council on Radiological Protection and Measurements recommends a default CR to be used in risk calculations of 0.1. In comparison, CRs for the SRS are generally well above 1.0. Indeed, they are among the highest recorded CRs in the world. Plants from Steel Creek and Par Pond had CRs that ranged from 3 to 7 (Garten and Paine, 1977; Pinder et al., 1980), garden vegetables grown on the exposed lake bed of Par Pond had CRs of 6.8 ± 2.3 (Seels et al., 1995), and early successional species invading Par Pond's exposed lake bed had extremely high CRs of 14.9 ± 2.3 (Hinton et al., 1999). Such large CRs indicate the high bioavailability of ^{137}Cs in the lower coastal plain, and in part, indicate why ^{137}Cs can be the critical contaminant when human and ecological risk analyses are conducted for the SRS.

2.3 Kaolinitic-Dominated Minerals on the SRS

The enhanced bioavailability of ^{137}Cs is thought to be largely due to the low clay content of SRS soils, and the fact that the clays that do exist here are dominated by kaolinite and iron oxides. Soils on the SRS are also weathered of nutrients, particularly potassium, and this too enhances the bioavailability of ^{137}Cs. Sediments of Par Pond provide a typical example: clay comprises only 1 to 3 % of the textural composition of the sediment (Evans et al., 1983), and 85% of that clay is kaolinitic (Ruhe and Matney, 1980). Sediment clay content is important because ^{137}Cs sorption is largely a surface area phenomenon: the greater the proportion of fine-grained clay particles, the more surface area there is for ^{137}Cs to sorb to. However, there are several different binding sites in soils, some result in strong ^{137}Cs bonds, whereas others form appreciably weaker ones. The clay fraction of SRS soils is dominated by kaolinite, which forms very weak bonds with ^{137}Cs. In contrast, mica-like minerals form very strong bonds with ^{137}Cs. Such minerals can sorb ^{137}Cs almost irreversibly, meaning once the ^{137}Cs sorbs to the mineral it is tenaciously held and will not readily desorb. The clay-sized fraction in DOE's Hanford Site sediments typically contain 35% mica-like minerals, and Oak Ridge sediments typically contain 50% of these minerals (Kaplan et al., 1996). Interestingly, SRS sediments do have some mica-like minerals (Ruhe and Matney, 1980), but they are largely ineffective at forming strong bonds with ^{137}Cs (Seaman et al., 2001), presumably because of a lower unit charge from extensive weathering.

An example of the effect of mineralogy on cesium exchange, as measured by the distribution coefficient (K_d), is shown in Table 1. (Data in Table 1 are for stable cesium, Cs, but ^{137}Cs behaves identically and can be substituted for stable Cs in the following discussion). The extent to which other solutes compete with Cs for sorption sites varies greatly between minerals. The vermiculite and kaolinite Cs-K_d values are orders of magnitude greater when no other competing cations are present, as in water, than when sodium (Na) is present as a competing cation. In contrast, mica K_d values are essential the same with or without competing cations (Table 1). This is because mica has a unique mineral structure that permits Cs to enter into its structure and exclude other cations. Micaceous minerals have extreme preferential sorption of Cs; for example, the Cs to Na ratio shown in Table 1 is approximately 1 to 10 trillion. Another important implication of this work and others (reviewed in Ames and Rai, 1978) is that mica, unlike any other mineral, irreversibly sorbs Cs. This is a very important attribute because if Cs is sorbed to micaceous minerals then it is likely to remain there for hundreds of years (Ames and Rai, 1978), and thus be unavailable for biotic uptake. An overview of clay mineralogy relative to Cs fixation can be bound in an earlier report (WSRC, 1999), and also in Appendix A.

2.4 Mechanism for Prolonged Cycling of Cs in Aquatic Systems

Although the primary radioactive releases occurred on the SRS some 40 years ago, bioavailability of ^{137}Cs remains high, rather than decreasing substantially as might be expected with an aged deposit (Hinton et al., 1999). Reoccurring processes within the lakes on the SRS contribute to the continued availability of Cs. Over 95% of the Cs inventory within these lakes resides within the sediments. Each summer, however, when lakes on the SRS thermally stratify, the colder deeper hypolimnion layer becomes anoxic (Figure 4). Anaerobic processes in the anoxic sediments produce NH_4^+, a monovalent cation with a high affinity for displacing ^{137}Cs sorbed to mineral surfaces. A small portion of the total inventory of ^{137}Cs is thus displaced from the sediments into the overlying water column each summer (Evans, et al., 1983). In the fall, the lake loses its thermal stratification, the ^{137}Cs enriched bottom waters mix with the formally stratified upper layers and the ^{137}Cs becomes available for biological uptake by the biota (Figure 4). This annual release of ^{137}Cs from the sediments is thought to contribute to the prolonged cycling of ^{137}Cs in the aquatic systems of the SRS, and is made more pronounced by the ease at which ^{137}Cs is desorbed from the dominant clays on site (i.e., kaolinite).

Table 1. Effect of Mineralogy on Cs Exchange. Distribution coefficients (K_d) indicate the greater sorption of Cs by 2:1 clays (mica and vermiculite) compared to kaolinite, and that only mica continues to adsorb Cs in the presence of competing cations (from Tamura, 1972).

Mineral	Cation Exchange Capacity (meq / 100 g)	Cs-K_d in water (mL / g)	Cs-K_d in 0.1 M NaCl (mL / g)
Mica-like Mineral	20	26,000	28,600
Vermiculite	127	52,000	2,700
Kaolinite	11	2,500	94

2.5 Remediation Challenge

All of these radioactively contaminated aquatic sites on the SRS fall under EPA CERCLA regulations and thus represent a remediation challenge to DOE. Remediation of wetlands is particularly problematic because current cleanup technology for aquatic systems is generally destructive to the ecosystem. If cleanup is required, then a likely scenario would entail draining the impoundment and either immobilizing the sediments, where 95% of the radionuclides reside (Whicker et al. 1990), with some form of grout, or hauling the sediments off for treatment or disposal. These methods are expensive. For example, costs to remediate just the Old-R Discharge Canal have been estimated at over $117,000,000 (ERD, 2002). Additionally, the traditional "muck and truck" methods would expose workers to inhalation doses, and destroy the associated ecosystems.

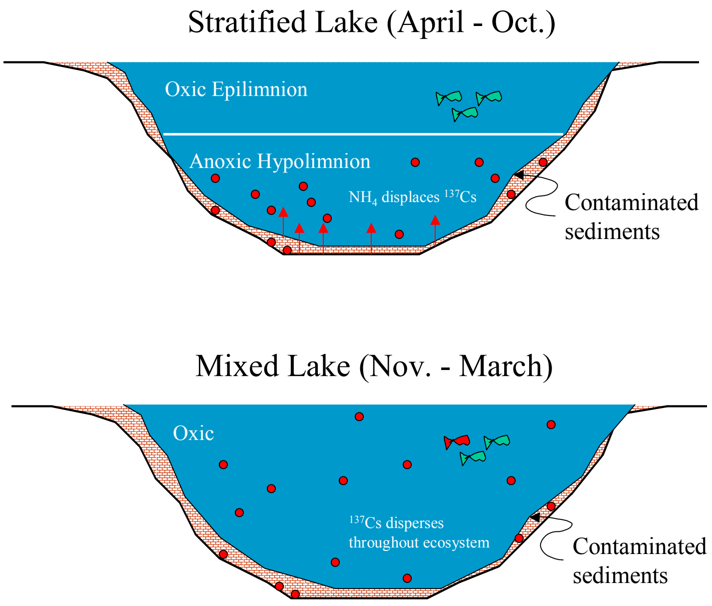
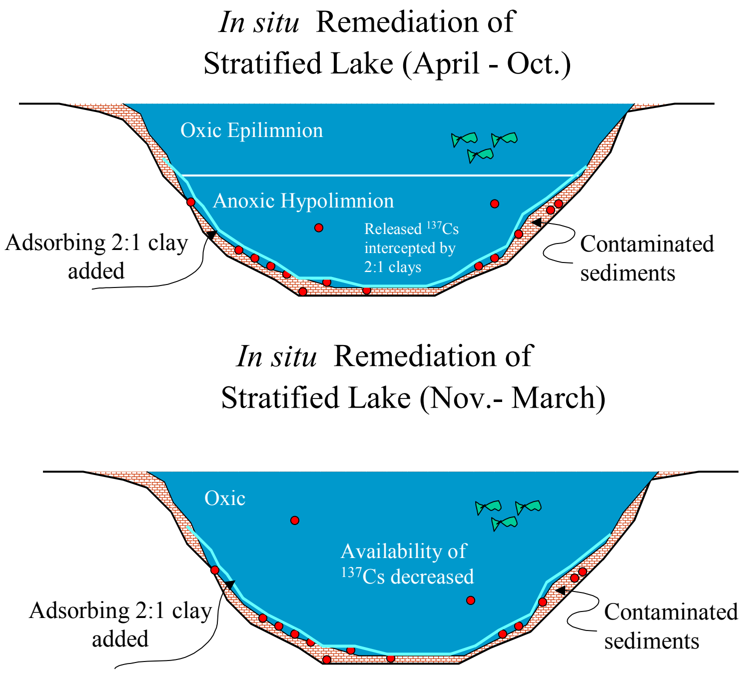


Figure 4. Mechanism for annual ^{137}Cs inputs into stratified lakes. During summer, bacterial buildup of ammonium and dissolution of iron-oxides within the anoxic sediments displaces ^{137}Cs from the sediments into the overlying water column. During the fall, ^{137}Cs is mixed throughout the lake resulting in the contaminant becoming dispersed and available for biological uptake. Although the quantity of ^{137}Cs released is a very small percentage of the total inventory within the sediments, the mechanism does enhance the biological mobility of the contaminant each year.

2.6 Potential Solution: Hypothesis of Initial Proof-of-Concept Study

Because high Cs mobility on the SRS is due, in part, to a low adsorptive capability of the kaolinitic-dominated soils, we hypothesized that adding naturally occurring micaceous minerals to wetlands would sequester ^{137}Cs and reduce its bioavailablity. In application, the naturally occurring minerals would be introduced into the wetlands where they would quickly sorb ^{137}Cs in the water column as they settled to the bottom sediments. The micaceous amendments would then intercept and sorb ^{137}Cs during the annual summer release of ^{137}Cs from the contaminated sediments, effectively sequestering the contaminant and drastically reducing biological uptake (Figure 5). We first tested the concept in the laboratory (Hinton et al., 1999b), and were encouraged to find that additions of clay minerals to Pond B sediments effectively adsorbed and retained ^{137}Cs, even in the presence of high concentrations of NH_4^+. The clay amendments were chosen based on specific characteristics that we tested for within the laboratory. The results were reported to WSRC (Hinton et al., 1999b), and prompted the additional field demonstration reported herein.


In situ Remediation of
Stratified Lake (April - Oct.)

In situ Remediation of
Stratified Lake (Nov.- March)

Figure 5. We hypothesized that an *in situ* remediation method of applying clay amendments that have an affinity for sorbing ^{137}Cs might intercept the yearly release from the sediments and thereby reduce ^{137}Cs bioavailability.

3.0 OBJECTIVES

After conducting successful laboratory proof-of-concept studies (Hinton, et al., 1999b, Hinton et al., 2001), the next step was to enlarge the experiment and perform a moderate-sized field demonstration of the *in situ* remediation method. *The objective of the field demonstration was to reduce the biological availability of* ^{137}*Cs in an aquatic ecosystem by applying clay amendments. The amendments were applied at two rates, and the* ^{137}*Cs concentrations in water, plants and fish were compared to non-treated controls.* Thus, our objectives were to:

1) characterize several commercially available clay minerals for their Cs adsorption and desorption abilities,
2) choose an amendment material based on chemical / physical characteristics of the mineral, costs, and availability,
3) design and conduct a replicated field demonstration of the *in situ* remediation method.

4.0 MATERIALS AND METHODS

4.1 Amendment Materials

Ten clay minerals were purchased from commercial suppliers (Table 2), and examined for their suitability as amendment material. Five illites, three vermiculites and two micas were examined. (See Appendix A: Clay Mineralogy, for a general discussion on the fundamental characteristics of these types of clay minerals).

Table 2. Commercially available clay minerals used in adsorption and desorption experiments.

Company	Trade name	Dominant mineral
Cedar Heights Clay Operations, Oak Hill,Ohio	Fire clay	Illite, mixed layer minerals
	Redart	Illite, mixed layer minerals
W. R. Grace & Co. Cambridge, MA	Expanded vermiculite 01	vermiculite
	Expanded vermiculite 02	vermiculite
	Zolonite	vermiculite
Mineral Mining Company, Inc, Kershaw, SC	3-Xmica	mica (muscovite)
	4-Xmica	mica (muscovite)
Kentucky-Tennessee Clay Company	Ball Clay	Illite
	Stone Clay	Illite
	Todd Light	Illite

4.2 Adsorption of Cs among the 10 Candidate Minerals

The principal characteristic of importance to this experiment is the ability for the mineral to adsorb Cs, and subsequently to retain it in the presence of competing ions (i.e. a low rate of desorption). Each of the 10 minerals (Table 2) was considered as a separate treatment and each was replicated three times. The experiment was conducted in 50mL centrifuge tubes, each containing 0.3 g of mineral. All minerals were equilibrated in 27 mL of filtered (< 0.45 μm) Pond A Water (PAW) by shaking for 1 hr and then centrifuging at 4500 rpm for 30 minutes. After several days, the pH of the clay/PAW suspension was adjusted to ~6.5. Samples were then centrifuged and the solution was discarded. A 30 ml ^{134}Cs (6.9 Bq ml^{-1}) spiked PAW tracer was added to each sample, and was mixed for one week on a slow moving shaker. (^{134}Cs is another Cs isotope with a shorter half-life, and thus more amenable to tracer experiments. Its sorption characteristics are identical to those of ^{137}Cs). The samples were centrifuged, and 5 mL aliquots were assayed for ^{134}Cs activity. These data were used to calculate the Cs distribution coefficient (K_d) for each mineral and to compare their Cs adsorptive abilities:

$$K_d = \frac{(A_{spike} \times V_{spike}) - A_{final}(V_{spike} + V_{\text{int}erstitial\ \ pretreatment})}{A_{final} \times M_{clay}} \tag{1}$$

where:

$V_{interstitial\,pretreatment}$ is the volume of the interstitial solution left after the third pre-equilibration wash (mL),

M_{clay} is the clay mass (g),

V_{spike} is the volume of the ^{134}Cs-amended solution (spike solution) added to the clay (mL),

A_{final} is the ^{134}Cs activity in solution after contact with the sediment (Bq mL^{-1}), and

A_{spike} is the ^{134}Cs activity in the ^{134}Cs -amended solution (Bq mL^{-1}) added to the solids.

4.3 Settling Velocities of 10 Candidate Minerals

The 10 candidate minerals had different densities (g cm^{-3}), and particle size characteristics. These parameters influence mineral settling rates. Thus, our next experiment examined the settling rate of the 10 candidate amendment materials. This was done in the laboratory by adding the various amendment materials to static columns of water and observing their settling behavior (5g of each clay in 200 ml water; duration 24 hrs).

4.4 Adsorption and Desorption of ^{137}Cs Among the Illite Minerals

The tenacity which cesium binds to clay varies among mineral types. Cesium can be desorbed from clays by competing ions. Ammonium ions are particularly effective at displacing cesium. The purpose of this experiment was to compare the ease at which ^{137}Cs desorbs from the illite clays in the presence of NH_4^+. An effective clay amendment should strongly bind cesium and have minimum desorption. The goal of this experiment was to compare the ability of the commercially available illite clays (Redart and Todd Light) and a reference illite clay (Gray Shale) to adsorb/desorb ^{137}Cs. This experiment was conducted in a similar manner to experiments described in the previous section for ^{134}Cs, except that ^{137}Cs was used as a tracer. The experiment was conducted in 50-mL centrifuge tubes, each containing 0.15 g of clay mineral. Adsorption of ^{137}Cs was initiated by adding 10 mL of ^{137}Cs-spiked PAW to each sample. There were two sets of this experiment, in set “A” the spiked PAW contained 171.8 Bq mL^{-1} (4.6 nCi mL^{-1}) of ^{137}Cs, and in set “B” the spiked PAW contained 1718 Bq mL^{-1} (46 nCi mL^{-1}) of ^{137}Cs. Samples were shaken for one week with an automatic shaker, centrifuged, and a 5-mL aliquot removed for ^{137}Cs analysis. Activity of the aliquot was determined on a Packard AutoGamma NaI detector. The amount of ^{137}Cs sorbed by each mineral was calculated using equation 1. Once the adsorption step was completed, the clays were separated from the aqueous phase by centrifugation, and the interstitial liquid was removed by flushing the sediments with unspiked Pond A water. Then 20 mL of 0.1 M NH_4Cl were added and the samples were mixed on an automatic shaker for one week. Following centrifugation, 5 mL of solution were removed and assayed for ^{137}Cs activity. The amount of ^{137}Cs desorbed by each mineral was calculated as a percentage using equations 2, 3 and 4.

$$\%\ desorbed = \left(\frac{A_{desorbed}}{A_{adsorbed}}\right) \times 100 \tag{2}$$

$$A_{adsorbed} = \left(A_{spike} - A_A\right)\left(\frac{V_{spike} + V_{interstitial\ \ pretreatment}}{M_{clay}}\right) \tag{3}$$

$$A_{desorbed} = \frac{A_D\,(V_{NH4Cl} + V_{inerstitial\ \ adsorption}) - A_A\,(V_{interstitial\ \ adsorption})}{M_{clay}} \tag{4}$$

where:

$A_{desorbed}$ = activity of ^{137}Cs desorbed at the end of the desorption experiment (Bq ml^{-1}),
$A_{adsorbed}$ = activity of ^{137}Cs adsorbed at the end of the adsorption experiment (Bq ml^{-1}),
A_D = ^{137}Cs activity in equilibrium desorption solution (Bq ml^{-1}),
A_{spike} = ^{137}Cs activity in (+) control solution (samples without sediment, Bq ml^{-1}),

A_A = ^{137}Cs activity in adsorption solution (Bq ml^{-1}),
V_{spike} = volume of ^{137}Cs -spike solution during adsorption experiment (mL),
V_{NH4Cl} = volume of 0.1 M NH_4Cl added after adsorption experiment, ~10 mL (mL),
$V_{interstitial\ adsorption}$ = volume of interstitial solution after adsorption experiment (mL),
$V_{interstitial\ pretreatment}$ =volume of interstitial solution after pretreatment of clay with Pond A water (mL), and
M_{clay} = mass of clay (g).

4.5 Sequential Extractions

Sediments are a complex mixture of organic and inorganic components in which there are a variety of physical sites available to bind contaminants. For example, associated with the basic mineral is a matrix of other material such as organic matter, iron oxide coatings and carbonates. Researchers have designed chemical methods that are thought to target contaminants residing within these various fractions of the sediment matrix (Tessier, et al., 1979). Knowledge of where a contaminant resides within a sediment matrix can help predict its impact because some sites hold contaminants more tenaciously than others. Contaminants that are loosely bound to sediments are generally more biologically mobile and thus pose a greater risk. Sequential extraction techniques attempt to identify where contaminants are residing within a sediment matrix. Interpretation of the results is rather subjective and researchers often bypass this shortcoming by stating that the various sites that the methods target are “operationally defined”. Nonetheless, results from a sequential extraction procedure can be informative, and a modified Tessier et al. (1979) method was used on samples from Pond A. The generalized sequential extraction method employed is found in Table 3, and details of the procedure are provided in the Appendix.

4.6 Field Deployment Site Description

The *in situ* remediation method was tested in Pond A and the connecting R-canal. Both are remnant structures from R-reactor. Among the five reactors on the SRS, R-reactor was the first to become operational and the first to be shut down. It operated from 1953 to 1964. A canal, leading to a series of cooling ponds, was part of the R-reactor operations. During its operation approximately 221 Ci of ^{137}Cs was released into the canal system (Carlton et al., 1992). A fraction of the releases remained in Pond A, a small pre-cooling pond located in R-canal. Total inventory of ^{137}Cs remaining in Pond A was estimated in 1998 to be 1.1 ± 0.1 Ci (Abraham et al., 2000). Typically the pond is 5.2 ha (12 acres) in area, has a mean depth of 0.5 m and a maximum depth of 1.5 m; although, in the last few years, water levels have fluctuated drastically due to persistent drought. Abraham et al. (2000) found mean concentrations of ^{137}Cs in the sediments to be 213 ± 27 pCi .g^{-1}, and peak concentrations at a 2 to 4 cm depth within the sediments. Greater than 99% of the total inventory was in the top 20 cm of sediments. As mentioned in the Introduction of this report, the sandy textured, nutrient depleted sediments with a low abundance of 2:1 micaceous minerals result in ^{137}Cs being highly bioavailable throughout the aquatic ecosystem of Pond A and R-canal.

Table 3. Sequential extraction regime used in this study.

Sequence	Extractant: Chemical Composition	Targeted Contaminant Fraction	Ref.[a]
1	1.0 M NaOAc; pH 5; repeated twice	Adsorbed/exchangeable/carbonate (AEC)	1
2	0.25 M $NH_2OH{\cdot}HCl$ in 0.25 M HCl; repeated twice	Amorphous Fe oxyhydroxide (Am Fe ox)	1
3	1.0 M $NH_2OH{\cdot}HCl$ in 25% HOAc; repeated twice	Crystalline Fe oxide (Cry Fe ox)	1
4	0.02 N HNO_3 & 30% H_2O_2; repeated twice	Organic Fraction (OM)	2
5	Conc. HCl, H_2SO_4 & HNO_3	Residual (silicates) (R)	

[a] References: 1 = Hall et al., 1995, 2 = Tessier et al., 1979.

4.7 Limnocorrals

The field test was conducted in replicated limnocorrals. A proto-type is shown in Figure 6. Limnocorrals are field-deployed devices that isolate a column of water and its associated sediments. They are made of flexible plastic with a floatation collar at the top that keeps the column's open-end floating on the water surface. Retention rings at mid-depth and at the bottom maintain the column's shape. The bottom is weighted down and inserted into the pond's sediments. After several tests of various designs, 3-m diameter limnocorrals were chosen and constructed for this *in situ* remediation deployment.

Sixteen limnocorrals were randomly placed in R-canal and Pond A during the second week of April 2001 (Figure 7). Initial sediment, water and plant samples were taken to characterize background conditions and variability among the limnocorrals. On 1 May 2001, six limnocorrals were treated with enough clay amendment to cover 0.25 cm of the sediment surface (Low clay application - 60 lbs), six received a treatment 10 times that amount (2.5 cm on the sediment surface: High clay application - 600 lbs), and four limnocorrals served as untreated controls. The clay amendments were added to the limnocorrals by broadcasting the mineral on the surface of the water. This caused the water to become very turbid (Figure 8) for about two weeks. Eventually, water clarity was the same as in the untreated controls.

4.8. Sampling and Analyses of Water

Water samples were periodically collected from each of the 16 limnocorrals. Three-liter samples were drawn 0.5 m from the sediment surface, filtered (0.45 μm), acidified with nitric acid and stabilized with CsCl. The latter two steps were done to prevent ^{137}Cs from plating out on the container walls. The samples were assayed for ^{137}Cs in Marinelli Beakers using a HPGE detector. Subsamples were sent to the University of Georgia for stable element analyses using ICP-MS. Other parameters, such as pH, conductivity, temperature and dissolved oxygen were determined in the field using a HydroLab instrument.

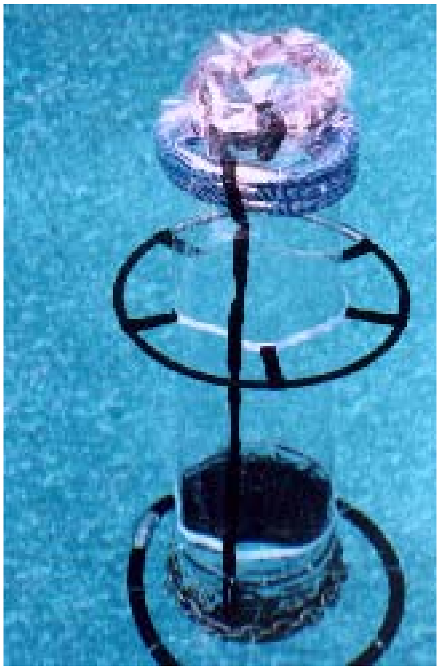


Figure 6. A small, 20 cm diameter, proto-type limnocorral being tested in a swimming pool. A blue floatation collar can be seen at the top of the device, as well as the mid-height ring and weighted bottom section. The device isolates a column of water and its associated sediments. The devices can be replicated and manipulated according to treatment schedules**.**

4.9 Sampling of Sediments

Three sediment cores were taken from each limnocorral prior to the application of the clay amendments. Cores were 5 cm in diameter and typically penetrated the sediments some 30 cm. Cores were sliced into 1 cm sections by forcing the tip end of the core out of the tube with a plunging device. The extruded segment was then cut and placed into a 100 ml beaker. Distilled water was added, resulting in a slurry that was then poured into a 20 ml scintillation vial. The vials were oven-dried at approximately 80º C and homogenized to obtain a consistent geometry for gamma spectroscopy.

Sediments of the limnocorrals were re-cored on 1 April 2002 using the same procedure as described above. Inspection of these cores suggested that smearing of the sediments was occurring along the edge of the core during the extruding procedure. To reduce this bias we re-sampled the limnocorrals on 16 April 2002 using a pre-split core that did not require extruding. Instead, the core is merely split apart (vertically) and samples can be taken at any depth from within the center of the core. This avoids the potential bias of sampling from a smeared edge.

4.10 Sampling and Analyses of Plants

We used two approaches to determine the effect of the clay amendments on ^{137}Cs concentrations in aquatic plants. We introduced uncontaminated plants (duckweed) to the limnocorrals after the treatments had been applied, and we also examined plants (water lily) that were in all of the limnocorrals prior to the addition of any treatments and were contaminated with ^{137}Cs prior to the start of the experiment. The two species of plants are quite different in their growth form and we hypothesized that their response to the treatments would differ. Duckweed (*Lemna* spp.) is a small leafed (3 mm diameter) plant that floats on the surface of the water with a single root that extracts nutrients from the water column. Its root does not reach the sediments. Duckweed is a common plant in household aquaria. In contrast, water lily (*Nymphaea odorata*) is a persistent perennial with extensive rhizomes for roots that intermingle throughout the sediments and contain large tubers. The roots send up long stems that support a fibrous, floating leaf that is commonly 25 cm in diameter (Figure 8).

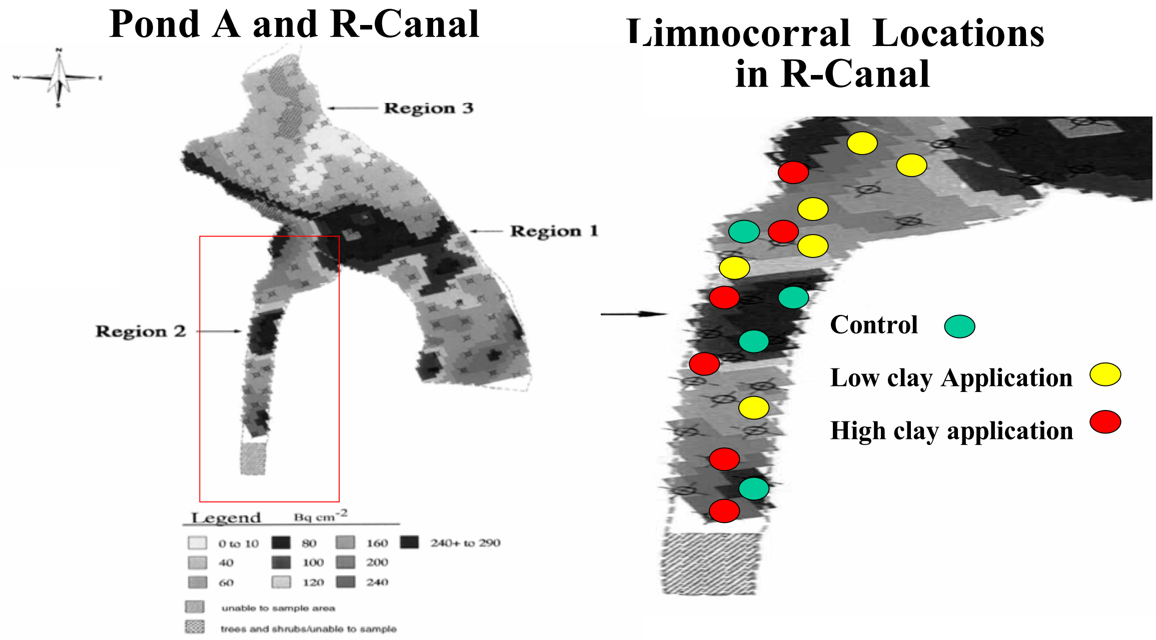


Figure 7. Random locations of limnocorrals placed in R-Canal and Pond A on the Savannah River Site. ^{137}Cs contamination levels, in Bq cm^{-2} are from Abraham et al. (2000). Six limnocorrals were treated with enough clay to cover 0.25 cm of the sediment surface (Low clay application), six received a treatment 10 times that amount (2.5 cm on the sediment surface: High clay application), and four limnocorrals served as untreated controls.

Figure 8. Limnocorral in foreground after receiving the high clay treatment, and a control, untreated limnocorral in the background.

Uncontaminated Duckweed was purchased from a commercial grower and plants were added to all limnocorrals on 5 June 2001, a month after the treatments had been applied. On 20 August 2001, Duckweed was sampled, washed with DI water, dried and assayed for ^{137}Cs.

When the limnocorrals were constructed, no attempt was made to remove the extensive number of water lilies already contaminated with ^{137}Cs. Prior to the addition of the treatments, some water lilies were sampled from each limnocorral, washed with DI water, dried, ground, and assayed for ^{137}Cs. Water lilies were re-sampled for ^{137}Cs on 17 August 2001.

4.11 Sampling and Analyses of Fish

To determine the impact of the *in situ* remediation method on biological availability of ^{137}Cs to vertebrates, we examined ^{137}Cs uptake in *Gambusia,* small fish (2 to 5 cm in length) common in the waters of the southeastern U.S. *Gambusia* are an important component in the vertebrate food web because they are a common food item for many larger fish such as brim and crappie. *Gambusia* eat aquatic insects, particularly mosquito larvae. On 10 May 2001, we electroshocked all limnocorrals to eliminate existing *Gambusia*. Then on 5 June, 2001, (one month after applying the clay treatments) we introduced 30 *Gambusia* into each of the 16 limnocorrals. All fish came from a nearby, uncontaminated control pond. The *Gambusia* successfully reproduced during the course of the summer and we often saw adults and young fish swimming within the limnocorrals. On 17 September, 2001, 30 to 40 fish were sampled from each limnocorral pooled by limnocorral number, and assayed for ^{137}Cs on a high-purity Germanium detector.

4.12 Water Level Fluctuations

Two months after applying the clay amendments, heavy rains caused the water level in R-Canal and Pond A to rise. The extension capability of the limnocorrals' flexible sides was exceeded and ^{137}Cs contaminated water ran over the floatation collar of some units, re-contaminating some of the limnocorrals. Table 4 shows the number of limnocorrals that were flooded as a function of treatment. Water receded over a two-week period, and then continued to decrease throughout the summer from a lack of rain. The drought continued such that by May, 2002 most of the limnocorrals had exposed sediments within them, and by late summer 2002, all of the pond and canal was dry.

4.13. ^{137}Cs Analyses and QA/QC

Analyses of ^{137}Cs in plants, sediments, and sequential extracts were performed on a Packard Autogamma instrument with a well-type NaI crystal (7.6 x 8.3 cm with a 1.5 % relative efficiency). Additional analyses of portions of the sequential extracts were performed on a 70x90 mm^2 high-purity germanium detector. Cs-137 standards, traceable to the National Institute of Standards and Technology, were assayed in the same physical geometry as the samples. Standard QA/QC methods were followed (i.e. use of controls, replicates and blanks for analytical work, as well as split samples sent to two or more laboratories).

Table 4. Number of limnocorrals that were flooded during a two-week period of high water.

Treatment	Number of limnocorrals that were not flooded	Number of flooded limnocorrals
Control	1	3
Low Clay	4	2
High Clay	2	4

4.14 Statistical Analyses

The experimental units in this research are the replicated limnocorrals. Thus sample sizes for statistical analyses were the number of limnocorrals, not the total number of water, plant or fish samples taken. Differences among treatments (controls, low clay, and high clay applications) were compared using analysis of variance (ANOVA). Post hoc tests were performed using Bonferroni's procedure. Statistical analyses were done with the aid of SYSTAT software.

5.0 RESULTS AND DISCUSSION

5.1 Amendment Characterization

Selection of the best amendment material started from an examination of their Cs adsorption characteristics and a calculation of their distribution coefficients (Figure 9). These data revealed that some minerals did not adsorb ^{137}Cs as well as others, and thus allowed us to eliminate all of the micas (Mica-3x and Mica-4x) as candidate remediation material. The materials from Cedar Heights Clay Operations, Oak, Hill, Ohio (Fire-clay and Redart) were eliminated due to the high variation in results (Figure 9) and their higher shipping costs.

We then conducted a series of particle settling experiments in the laboratory. They revealed the poor settling characteristics of the expanded vermiculites (Verm_1K, Verm_2K and Zolonite). These materials did not settle well at all, but instead floated on the water surface (Table 5). We eliminated them as an amendment material. Of the remaining materials, Todd

Light had the best settling characteristics. We therefore conducted our last characterization experiment (i.e. ability to retain Cs in the presence of competing ammonium ions) with it. We compared its Cs retention qualities to a reference Illite (Gray Shale) and a reference Kaolinite (Figure 10). The Todd Light material performed exceptionally, as well as the reference Illite material. We thus chose the Todd Light Illite as the most promising amendment material. Table 6 shows the elemental composition of the Todd Light material we used for the remediation method.

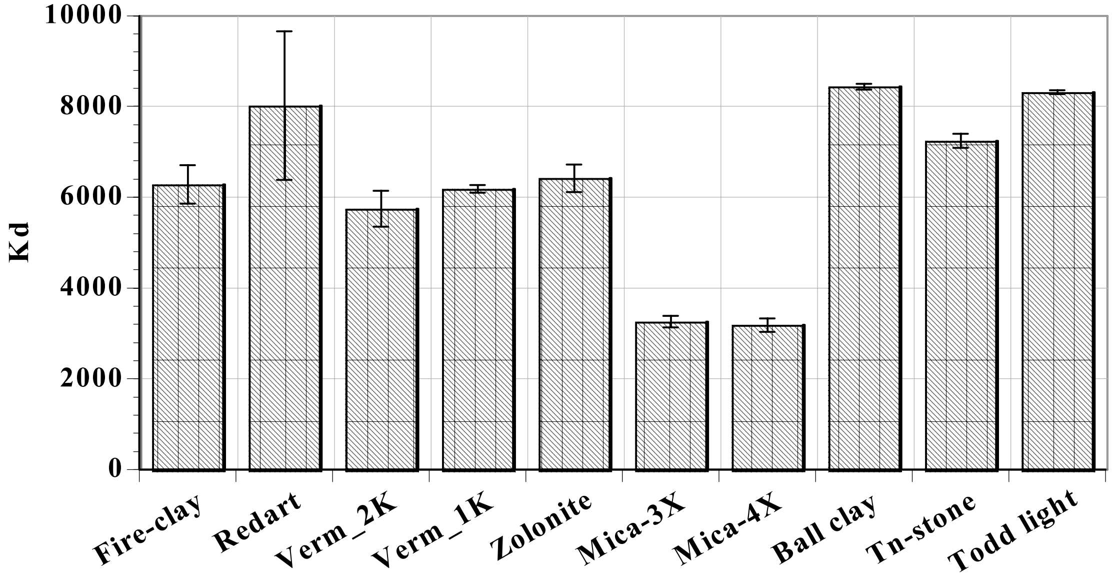


Figure 9. Distribution coefficients (Kd) for clay amendments tested.

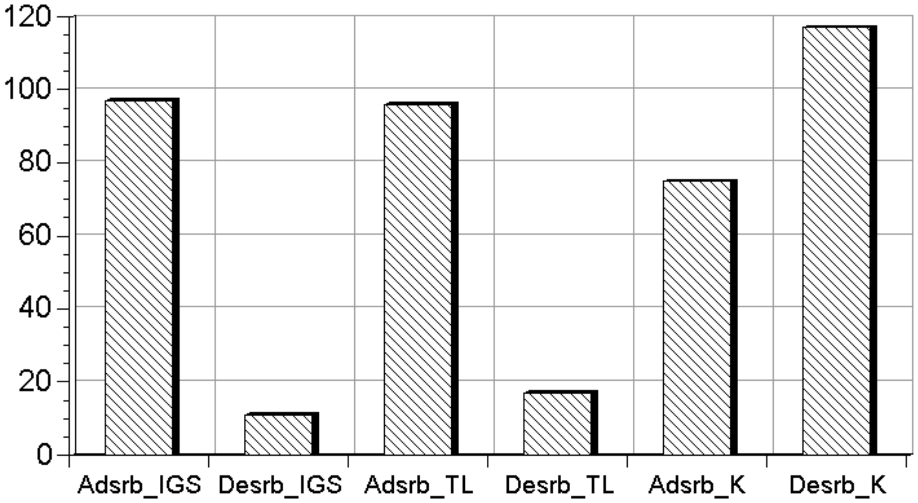


Figure 10. The percentage of adsorbed and desorbed ^{137}Cs by Illite Gray Shale (IGS), Todd Light (TL) and Kaolinite (K)

Table 5. Results of a particle settling experiments using each of the candidate clay minerals.

SAMPLE NAME	SETTLING AFTER 5 min. (%)	SETTLING AFTER 24 hrs (%)
Redart	50	90
Fireclay	50	90
Zonolite	5	5
Expanded Vem_1K	0	0
Expanded Vem_2K	0	0
Mica-3X	80	100
Mica-4X	80	100
Ball Clay	80	100
Todd Light	90	100
Stone Clay	80	100

Table 6 Composition of the Illite chosen as the most promising amendment material (Todd Light).

Element	ppm	Element	ppm
Ag	1	Mn	136
Al	1090	Mo	16
As	162	Na	269
B	15	Ni	2
Ba	52	P	251
Be	25	Pb	47
Ca	1665	Sb	52
Cd	19	Se	87
Co	3	Si	837
Cr	29	Sr	7
Cu	14	Ti	487
Fe	1720	Tl	0
K	749	V	55
Mg	4774	Zn	22

5.2 Limnocorrals

5.2.1 Water

The clay material affectively scavenged ^{137}Cs out of the water column. Concentrations of ^{137}Cs were significantly reduced ($p < 0.01$) by 25- to 30-fold in the water of the clay amended limnocorrals (Figure 11); with similar reductions in the water column of both the low and high clay amended treatments. The increased ^{137}Cs levels observed during week 23 may be due to seasonal differences or, more likely, to a decrease in water level from a prolonged drought. Notice that ^{137}Cs levels in the control limnocorrals increased during this time as well, and that the ratio of ^{137}Cs in the treated limnocorrals to ^{137}Cs in the controls remains fairly constant throughout the study. Analyses of stable element concentrations prior to the start of the experiment and again at week 42 suggest that adding the clay amendments did not significantly alter the water chemistry in the treated limnocorrals (Figure 12). At week 42, there was no apparent difference in stable element concentrations in the water of the control versus clay-amended limnocorrals. This suggests that the addition of the clay amendment will not adversely affect water chemistry.

5.2.2 Sediments

Concentrations of ^{137}Cs in the sediments range from under 10 nCi kg^{-1} to over 1000 nCi kg^{-1}. Concentrations vary as a function of sediment depth (Figure 13) and initial perusal of the data suggested a difference between treated and control limnocorrals. Statistical analyses, however, indicated that the variation in ^{137}Cs concentrations at any one depth was very large, notice the extent of the error bars in Figure 13, and thus the trend was not statistically substantiated. The lower concentration of ^{137}Cs in the upper layer of the treated limnocorrals, compared to the controls, is because the top layer of the treated limnocorrals is comprised of the amendment material, and contains ^{137}Cs that was scavenged from the water column as the clay material settled to the bottom. Concentration of ^{137}Cs in sediment are about 10,000 time greater than in the overlying water, thus it is not surprising that the native sediments have a higher concentration of ^{137}Cs than what the newly added amendment material has scavenged from the water.

The important point to remember is that the dominant native clays (Kaolinites) can adsorb large quantities of ^{137}Cs, but they are unable to retain it in the presence of competing ions such as NH_4, whereas the ^{137}Cs trapped by the amendment material is held tightly while radioactive decay occurs. The real concern to us is a comparison of the bioavailability of ^{137}Cs in the controls and treated limnocorrals, the subject of sections 5.2.3 and 5.3.4.

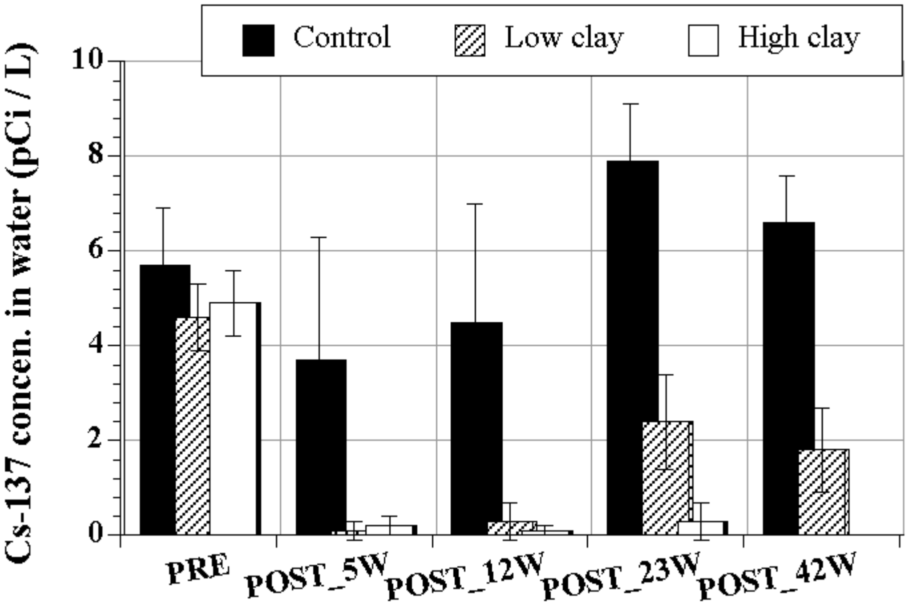


Figure 11. Mean (± SE) activity of ^{137}Cs in water samples collected from control and treated limnocorrals. Data show samples taken prior to the addition of the clay treatment (PRE) and on weeks 5, 12, 23, and 42 subsequent to the treatment. These weeks correspond to the following dates: 4/23/01, 5/29/01, 7/10/01, 9/28/01, and 2/14/02. ^{137}Cs levels in the high clay treatment for week 42 do not appear on the graph because they were below limits of detection.

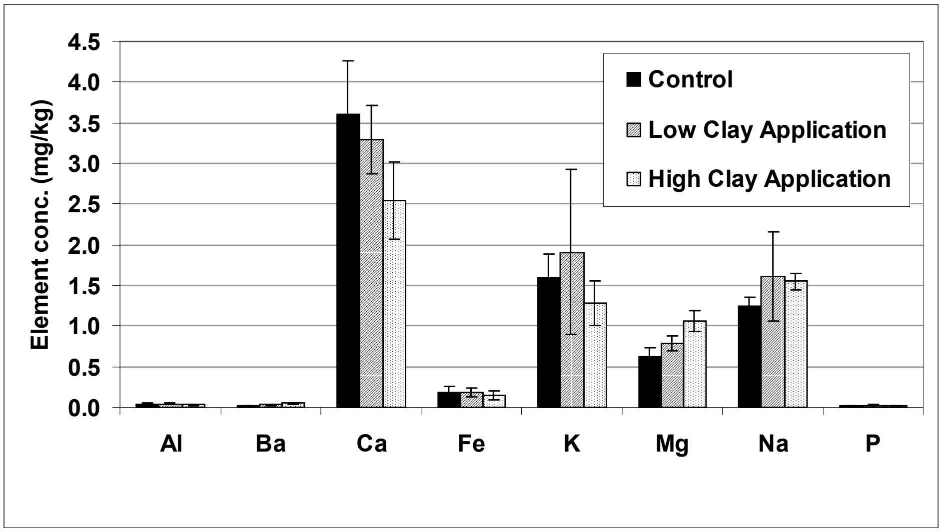


Figure 12. Concentrations (mg / kg) of stable elements in the water column did not differ among control and clay-amended limnocorrals at the 42nd week after applying the treatments.

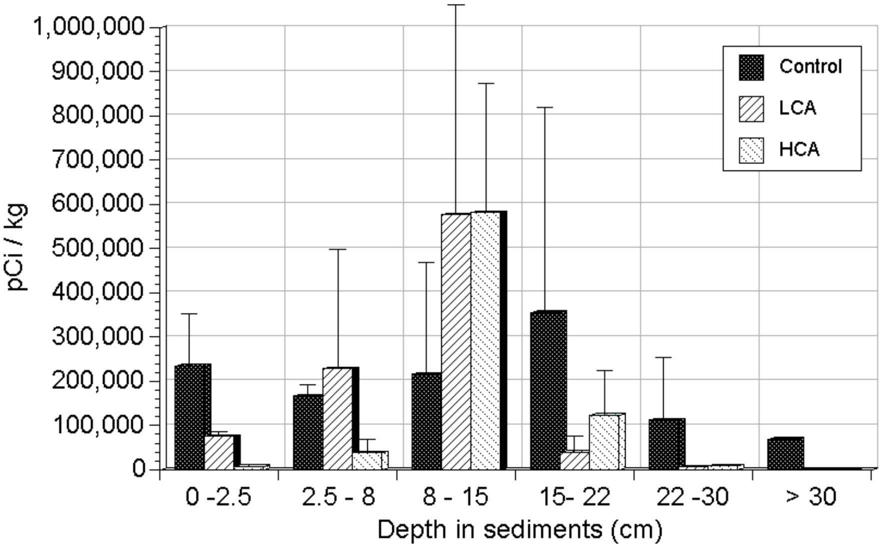


Figure 13. Depth distribution of ^{137}Cs in sediment cores taken from controls, low clay amendments (LCA) and high clay amended (HCA) limnocorrals.

Sequential extractions of the native sediments, as a function of sediment type prior to the addition of the clay amendments, gave an indication of where ^{137}Cs resides within the sediment matrix (Figure 14). As expected, a higher percentage (~ 25%) of the ^{137}Cs was associated with the easily exchangeable fraction of sandy material within the sediments. Cesium was less easily removed from the organic matter (OM; 15%) and clay fractions (15%). The clays retained the highest percentage in the residual portion of the extractions. This portion is thought to be held tightly within the sediment matrix and not available for exchange. The sequential extractions also suggest that the iron oxide fractions have an important role in Cs dynamics within these native sediments. Some 25 to 30% of the Cs was associated with iron oxides, regardless if in a clay, sand or organic matter fraction. Iron oxides, residing on the surface of minerals, are thought to block Cs exchange sites on the mineral itself. Our earlier work indicated that sediments with iron oxide coatings tended to adsorb more Cs than sediments with the coating removed, however, the Cs associated with the iron oxides were also desorbed more easily by competing ions than the Cs attached directly to the mineral.

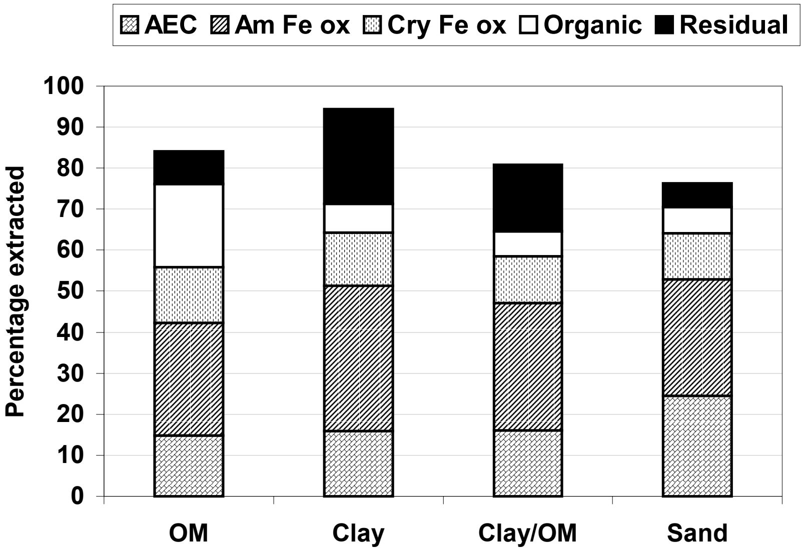


Figure 14. Partition of ^{137}Cs among five fractions in four types of sediment (organic matter, OM; clay; clay/OM mixture; and sand) from R-Canal and Pond A. The five fractions consisted of: AEC – adsorbed/exchangeable/carbonate phase; Am Fe ox – amorphous Fe oxyhydroxide; Cry Fe ox – crystalline Fe oxide; Organic – organic phase; and Residual – silicates**.**

5.2.3. Plants

The bioavailability of ^{137}Cs in control and treated limnocorrals was compared by examining the contaminant concentration in plants. We introduced duckweed into both control and treated limnocorrals about one month after the clay amendments had been added. Duckweed is a small floating-leaved plant with a short single root that derives its nutrients totally from the water column. The clay amendments reduced ^{137}Cs concentrations in Duckweed by a factor of four ($p < 0.01$; Figure 15), with no difference in reduction between the low and high levels of amendment. These results were anticipated, since the duckweed was growing in water that had largely been scavenged of ^{137}Cs during the settling of the amendment material.

The clay amendments also reduced ^{137}Cs concentrations in water lilies that were already contaminated prior to the start of the experiment. Unlike Duckweed, water lilies have an extensive root system within the sediments, and a long stem that extends to the water surface. Stems were almost twice as contaminated with ^{137}Cs as leaves, but both plant components were significantly reduced in activity concentration by the amendment material (Figure 16). These results are particularly encouraging because they suggest that the amendment material reduces

^{137}Cs concentrations in a dominant plant within these wetland ecosystems, even when contaminated prior to the addition of the amendment.

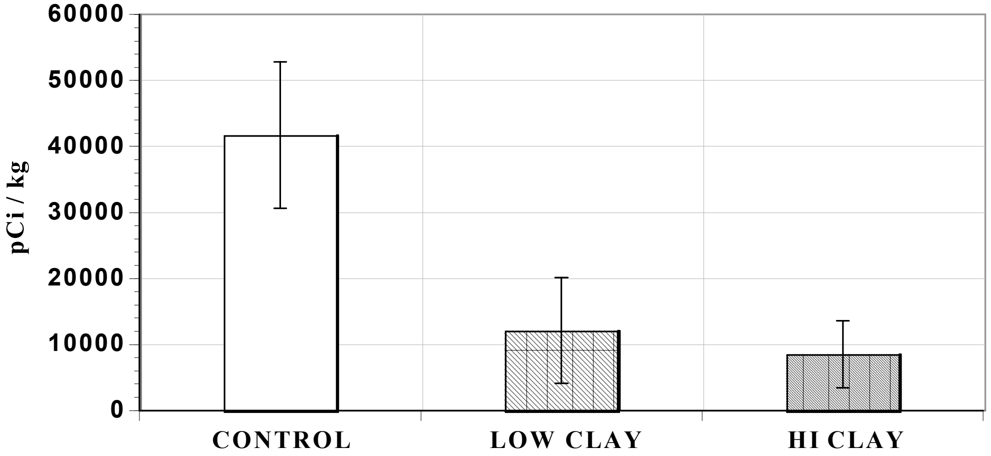


Figure 15. Concentrations of ^{137}Cs in aquatic plants (Duckweed) collected in control and treated limnocorrals. Samples were taken 2½ months after the plants were added to the limnocorrals.

5.2.4 Fish

Reductions in ^{137}Cs concentrations among a vertebrate component of the contaminated ecosystem were tested by introducing Gambusia into the control and treated limnocorrals. Concentrations of ^{137}Cs in fish collected from the control and treated limnocorrals are shown in Figure 17. Significant ($p = 0.02$) reductions in activity concentrations occurred in fish living within the treated limnocorrals. Although activity concentrations were lowest in fish from the high clay treatment, their contaminant burdens were not statistically different than fish in the low clay treatment.

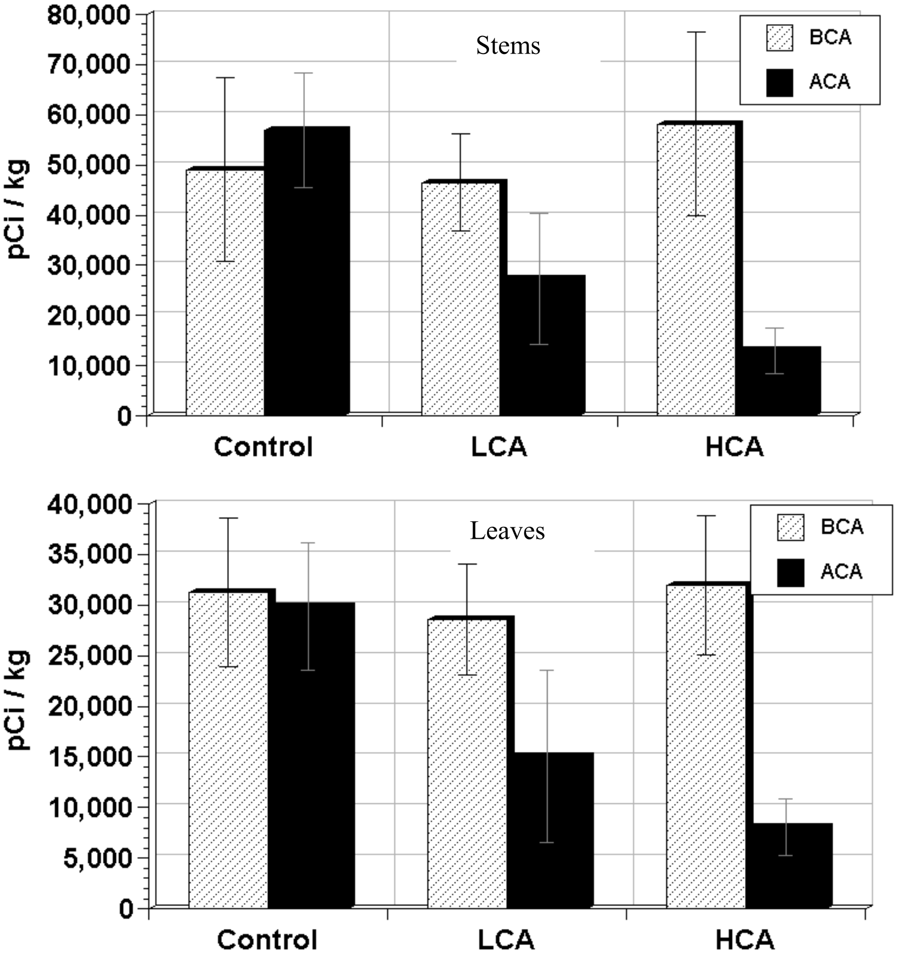


Figure 16. Mean ^{137}Cs concentration in water lily stems and leaves before (BCA) and after (ACA) clay application; control – no clay application, LCA – low clay application treatment (0.25 cm layer of clay on the bottom of the sediment), HCA – high clay application (2.5 cm layer of clay on the bottom of the sediment). Notice that stems have almost twice the activity concentration as leaves.

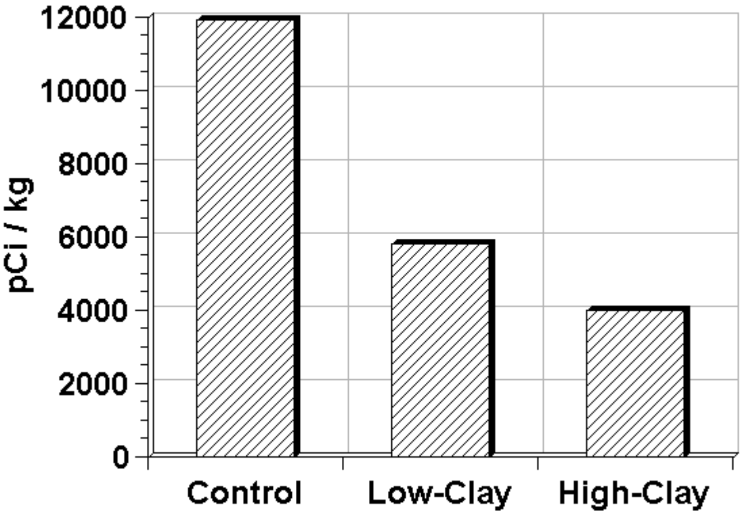


Figure 17. ^{137}Cs concentrations in Gambusia fish in control and treated limnocorrals. Samples were taken 2½ months after the plants were added to the limnocorrals.

6.0 COST ANALYSES

A cost comparison was made between the baseline technology, "muck-and-truck," and the *in situ* clay amendment technology. Budget numbers from the Environmental Restoration Division Baseline Change Log for the Old R-Area Discharge Canal (dated May 6, 2002) were used and compared to estimates for the clay amendment technology. All attempts were made to base the comparisons on similar assumptions.

The first step was to identify those line items that would be similar in both clean-up scenarios. These line items included Administration, Pre-characterization, Characterization, RI Work Plan, Regulatory Documentation, and (RI/BRA, CMS/FS, PD & ROD). The second step was to change the values that would not be the same. Among the assumptions that went into construction and material cost estimates were:

- Old R-Canal length is 7000 ft (WSRC, 1996)
- Width of canal area that required remediation = 30-ft wide canal + 10-ft stream bank on one side + 10-ft stream bank on the other side = 50-ft
- Proportion of area requiring remediation: Based on contamination levels in the New R Canal, ~10% of the canal had >240 Bq/cm^2 (Abraham, et al., 2000)
- Clay bulk density = 1.1 g/cm^3
- 0.1 inch thick illite treatment

Table 7. Comparison of remediation costs for the baseline technology ("muck and truck" removal of the contaminant), application of the clay amendment (Illite), and monitored natural attenuation (MNA). Based on ERD Baseline Change Log 3003 Old R-Area Discharge Canal; May 6, 2002 (in units of $1000).

Component	Baseline	Illite	MNA	Comment
Admin	96	96	96	
Pre-characterization	1520	1520	1520	
RI Work plan	727	727	727	
Characterization	8683	8683	8683	
RI/BRA	1106	1106	1106	
CMS/FS	484	484	484	
PD & ROD	403	403	403	
SUBTOTAL	**13,019**	**13,019**	**13,019**	Subtotal of items with similar costs
Preliminary Engineering	66	250	66	
Design	872	436	436	
Construction	78811	3026	960	Itemized below
Project Supt. Assessment	1118	1118	1118	Same as Baseline; will need to monitor for much longer
Project Supt. Design	278	278	278	Same as Baseline; will need to monitor for much longer
Contingency	7927	1407	1233	
SUBTOTAL	**89,072**	**6,515**	**4,091**	
TOTAL	**102,091**	**19,534**	**17,110**	

- 82.6 m^3 illite needed = 350,000 ft^2 x 0.1 inches think illite x 1.1 g/cm^3 bulk density x 1 ft/12 inches x 1 $m^3/35.3\ ft^3$ x 1000000 cm^3/m^3
- 91,000 kg illite needed = 82.6 m^3 x 1.1 g/cm^3 x 1000000 cm^3/m^3
- Illite cost = $0.15/lb
- To build access road along the 7000 ft stretch of canal, unpaved, 1 lane, 1 turnaround, and a staging area, $1,000,000

- Labor to add illite treatment: Estimate based on time required to add illite to limnocorrals. It took 4 people, 2 days to apply illite by shoveling off boat to 12 limnocorrals. They applied 1700 kg/limnocorral to 6 limnocorrals and 120 kg illite to 6 other limnocorrals. Thus they spread 10,200 + 1,020 kg illite = 11,220 kg illite. 11,220 kg/8 man-days = 1403 kg/man-day.
- 130 man-days of labor for illite application = 91,000 kg illite x 1 man-day/1403 kg illite x 2 (for conservatism)
- 52 man-days of labor for RadCon coverage = watch 5 people work for 26 days x 2 (for conservatism)
- 52 man-days for Field QA/Supervisor = watch 5 people work for 26 days x 2 (for conservatism)
- 182 man-days total labor = 130 + 52 + 52 (see immediately above)
- Delivery cost of Illite (136,500 kg: added extra 50% to the 91,000 kg illite required for task) = $46000

The cost for Design was assumed to be lower than the Baseline because the task is appreciably easier. The cost for Contingency was also assumed to be lower than the Baseline because the total cost of the project is appreciably lower and the uncertainties associated with the cost of deploying the technology are lower than the Baseline.

7.0 CONCLUSIONS AND IMPLICATIONS TO WSRC / DOE

The results of this field demonstration are very encouraging. Application of the clay amendment in Pond A and R-Canal indicate that ^{137}Cs levels in water were reduced 35- to 40-fold, activity concentrations in aquatic plants were reduced 4- to 5-fold, and concentrations in fish were reduced 2- to 3-fold. Equally important, the technique did not destroy the sensitive wetland environment and costs were five times less than traditional “muck and truck” methods.

This *in situ* technique is a promising remediation tool that reduces the biological availability of a dominant radioactive contaminant in sensitive wetland environments. While ^{137}Cs is bound to the clay amendment, radioactive decay continually reduces the contaminant concentrations until levels are no longer detectable. This method is a preferred alternative to the extremely destructive and expensive traditional method of “muck and truck”.

8.0 ACKNOWLEDGEMENTS

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10.0 APPENDICES

- A: Mineralogy Overview
- B: Source of Clay Minerals
- C: Sequential Extraction Procedure
- D: Data Archive
- E: Timeline of Activity

APPENDIX A: MINERALOGY OVERVIEW

Micaceous clays can be transformed into illites, vermiculites, smectites, or kaolinites depending on the amount they have been physically, chemically, and biologically weathered. The extent of weathering increases in the order of: mica < illite < vermiculite < smectite < kaolinite. The amount of weathering has a profound effect on a number of physical and chemical properties that in turn have a direct effect on the clay's propensity and tenacity to sorb Cs.

These minerals can be broadly divided into two classes based on their layer structure. Micas, vermiculites, illites, and smectites have a 2:1 layer structure in which tetrahedral (T) and octahedral (O) sheets are arranged in the sequence T-O-T (extensively reviewed by Bailey 1984 and Fanning et al., 1989). Kaolinites have a 1:1 layer structure arranged in the sequence T-O. The tetrahedral sheets are made up of a Si atom coordinated with four O atoms. The octahedral sheets are made up of either trivalent cations (a dioctahedral 2:1 mineral) or divalent cations (a trioctahedral 2:1 mineral).

Micas, illites, vermiculites, and smectites carry a net negative charge because not all of the cations in the interstices have sufficient positive charge to balance the charge of the oxygen or hydroxyl anions associated with the mineral structures. Most of the charge for micas and illites is derived from substitution of Al for Si in the tetrahedral sheets. For many smectites, including montmorillonite, most of the charge is derived from substitution of a divalent cation for a trivalent cation in the octahedral sheets. Kaolinite derives a very small, barely detectable, amount of its charge from isomorphic substitution. Most of the charge of kaolinite particles comes from the edge sites, whose charge increases with pH. Layer charge is highest for young minerals (i.e. mica) and less for the older minerals (i.e. kaolinite).

The negative charge of the clay layer is balanced by cations that are located in a plane between the 2:1 structures. Although mica and illite crystals carry a large negative charge, most of the charge is nullified by tightly held K ions that cannot be exchanged with other cations. Vermiculite and smectite particles balance their net negative charge with hydrated cations.

Unlike these other minerals, the mineralogical definition of kaolinite is not related to the cations (or anions, when the edge site have a net positive charge) associated with it.

The size of an individual particle, or tactoid, is also a function of a number of mineral properties. Among the most important is the strength of the bond between the 2:1 or 1:1 units. The stronger this bond is, the larger the particle is likely to be. For the 2:1 minerals, the mica particles tend to be larger than vermiculites, which in turn are larger than smectites. Kaolinite is commonly a large particle due to hydrogen bonding between 1:1 units. Surface area of these minerals is inversely related to the tactoid size.

The propensity for clay minerals to exchange cations is sometimes expressed as the cation exchange capacity (CEC), which, theoretically, is the product of the layer charge and the specific surface area (m^2/g). Vermiculites have the highest CEC, primarily as a result of their high layer charge. Smectites also tend to have a high CEC, although this is the result of their larger specific surface area (especially when they are Na saturated). Micas have non-expanding interlayers and thus a low CEC due to their low surface area. Kaolinite has the lowest CEC as a result of low layer charge coupled to small surface area. Since kaolinite is the dominant mineral in SRS sediments, little cation (e.g. cesium) adsorption is expected in these sediments.

The strong affinity of micas and illites for weakly hydrated, large alkaline cations (K^+, Cs^+, and Rb^+) has found its application in radioactive waste disposal. Of these cations, illites and micas sorb Cs^+ the strongest. The reason for this is that the nonhydrated Cs^+ ion fits perfectly into the ditrigonal cavities of the tetrahedral sheets (described above). These sorbed Cs^+ ions are preferentially retained in the presence of hydrated cations, such as Ca^{2+} or Mg^{2+}, which are typically present in the environment in concentrations 5 to 9 orders-of-magnitude greater. Cesium can also out-complete, but slightly less effectively, K^+ and NH_4^+ for these sites (Staunton and Roubaud 1997). Because of the high affinity of Cs for micas and illites, it is commonly found fixed in micaceous and illitic soils in a form that is nonexchangeable (Francis and Brinkley, 1976).

All the clays discussed so far have ditrigonal sites; however, not all of the minerals can "irreversibly sorb" Cs. A number of mineralogical factors are responsible for this (Staunton and Roubaud 1997). One important factor is that the minerals must have a sufficiently high unit layer charge to pull the Cs into the ditrigonal cavity in the tetrahedral sheet while forcing the waters of hydration to remain outside the cavity. All kaolinites and smectites, and most vermiculites do not have a sufficient unit charge. The other mineralogical property affecting "irreversible sorption" of Cs, is the number of high-energy ditrigonal sites assessable to the aqueous Cs. Micas have few assessable high-energy sites because of the tight bound between the 2:1 units. Illites, by definition, have frayed-edge sites which expose high-energy sorption sites. It should be kept in mind that in addition to these high-energy sites, both illites and micas have planar sites, which sorb Cs via cation-exchange, and edge-sites which sorb Cs via surface complexation with surface hydroxides. Kaolinite, vermiculites and smectites only have planar and edge sites.

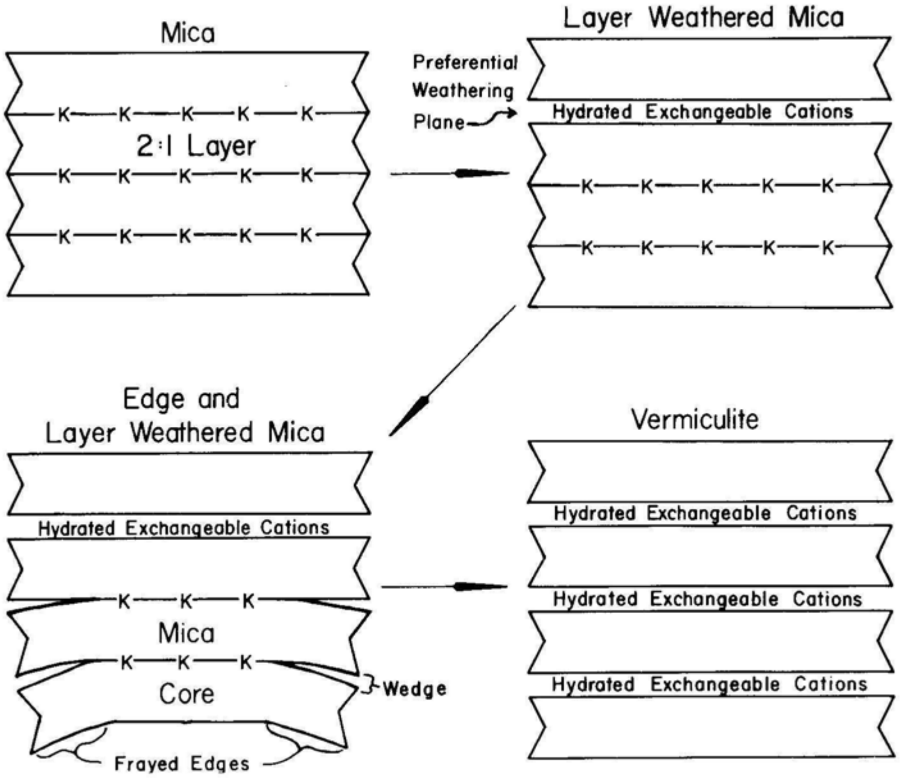

Figure 18. Diagram illustrating the transformation of a mica (with a nonexpanded interlayer containing K) to an illite (with frayed edge sites and expanded layers), and an illite to a vermiculite (with expanded interlayers containing hydrated exchangeable cations.)

Studies of Cs adsorption on clay minerals are an interesting example of the strong preference micas exhibit for Cs. Tamura (1972) studied the effect of ionic strength on the preference for Cs of several clay minerals. In the suspensions containing only Cs cation and no other competing cation, the distribution coefficients (K_d) for Cs were 52,000, 26,000, and 2,500 for <2-µm vermiculite, illite, and kaolinite, respectively. The K_d values decreased with decreasing cation exchange capacity of the three minerals (127 cmol kg^{-1} for vermiculite, 20 cmol kg^{-1} for illite, and

11 cmol kg^{-1} for kaolinite). However, when the experiment was performed with 0.1 *M* NaCl as a background electrolyte, the K_d values were 2,700; 28,600; and 94, respectively. Clearly, Na competed with Cs for the exchange sites on vermiculite and kaolinite, but on illite Cs was highly preferred to Na. Comparable results were reported by Staunton and Roubaud (1997) in a study of Cs exchange with K, Na, and Ca on illite and montmorillonite.

APPENDIX B: SOURCE OF CLAY MINERALS

1. Cedar Heights Clay Operations
   RESCO Products Inc.
   Oak Hill
   OH 45656
   Phone: 740-682-7794
   Fax: 740-682-6438
   Contact person: Steve Blankenbeker – Plant Manager & Ceramic Engineer
   Two samples:
   I. Red shale (Redart Clay) – up to 50% illite
   II. Green shale (Fireclay A/s) – 20% illite

2. BLACKJACK INC.
   Clays-Potter Machinery
   Box 97 Murchison, TX 75778
   Contact Person: Karla Wagner
   Phone: 903 469-3322
   Fax: 903 469-3952
   E-mail: ksw30@aol.com
   One sample:
   I. Red, illitic clay from a deposit located in West Texas near Mineral Wells (on the West Side of Fort Worth). This sample is a crude sample, mined and weathered but it has never been dried (via gas dryers) nor ground. It does contain a rather high percentage of free quartz and quite a bit of calcium/magnesium carbonate and very low in organic material.

3. W.E. GRACE & CO. – Conn.
   62 Whittemore Ave.
   Cambridge, MA 02140
   Phone: 617 876-1400
   Contact person: Eric M Moeller
   E-mail: eric.m. moeller@grace.com
   Three samples:
   I. Enoree, South Carolina Vermiculite Concentrate; Magnesium- Aluminosilicate Mineral
   II. Zonolite Industrial – expended vermiculite (Enoree, South Carolina Source), Magnesium-Aluminosilicate Mineral
   III. Milled Expended Vermiculite (Enoree, South Carolina Source), Magnesium-Aluminosilicate Mineral

4. Mineral Mining Company, Inc.
   Post Office Box 458
   Kershaw, SC 29067
   Phone: 803 285-3965
   Fax: 803-285-5495
   Two samples:
   I. 3-X Mineralite Mica – potassium aluminosilicate (3.64% of K_2O; 70.1% of SiO_2, 20.15% of Al_2O_3, 0.5% of CaO, 0.41% of MgO, and 1.05% of TiO_2); particle size – 7 to 11 microns (average)
   II. 4-X Mineralite mica, pH – 5.5 – 6.5,

5. Kentucky-Tennessee Clay Company
   5080 State Route 45 South
   Mayfield, KY 42066
   Phone: 270 247-3061
   Fax: 270 247-0293
   Contact person: Jamie Cook (sender)
   Wayne Knotts- e-mail address:wknotts@k-tclay.com
   One sample:
   I. Ball Clay – Hydrous Aluminum Silicate, trade name – M&D
      Chemical analysis (in %): 56.6 of SiO_2, 27.8 of Al_2O_3, 1.4 of TiO_2, 2.3 of Fe_2O_3, 0.5 of CaO, 0.7 of MgO, 0.6 of K_2O, 0.2 of Na_2O;
      Specific surface area [m/g] – 43.1
      Particle size- 20 microns and below

APPENDIX C: SEQUENTIAL EXTRACTION PROCEDURE

Fraction 1: Exchangeable

(1) To 2 g of wet sample (or dry sample) in a 50 ml screw-cap centrifuge tube, add 40 ml of 1.0 M CH_3COONa (sodium acetate) at pH 5) and cap.
(2) Vortex contents for 5-10 s and place in a horizontal shaker for 6 h.
(3) Centrifuge for 10 min. at 2800 rpm and decant supernatant liquid into a labeled test-tube. Rinse residue with 10 ml of 0.01 M $CaCl_2$, vortex and centrifuge again; do this twice and discharge supernatant rinses. Make up to the 40ml mark and analyze. If ^{137}Cs counting is below the detection limit, 40 ml of the extract will be evaporated to 20 ml or 10 ml and counting again for ^{137}Cs.
(4) Carry out a second 40 ml 1 M CH_3COONa leach of the residue, repeating steps 2 and 3.

Fraction 2: Amorphous Fe oxyhydroxide

(5) To the residue from step 4, add 40 ml of 0.25 M NH_2OH HCl in 0.25 M HCl, cap and vortex for 5-10 s.
(6) Place in a water bath at 60°C for 2 h with cap loosened. Every 30 min., cap tightly and vortex the contents.
(7) Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 10 ml of 0.01 M $CaCl_2$, vortex and centrifuge again; do this twice and discharge supernatant rinses. Make up to the 40ml mark and analyze. If ^{137}Cs counting is below the detection limit, 40 ml of the extract will be evaporated to 20 ml or 10 ml and counting again for ^{137}Cs.
(8) Carry out a second 0.25 M NH_2OH HCl leach of the residue, but heat for only 30 minutes. Repeat step 7.

Fraction 3: Crystalline Fe oxide

(9) To the residue from step 8, add 40 ml of 1.0 M NH_2OH HCl in 25% CH_3COOH, cap and vortex for 5-10 s.
(10) Place in a water bath at 90 °C for 3 h with cap on tightly. Vortex contents every 20 minutes.
(11) Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 20 ml of 25% CH_3COOH, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to the 60ml mark and analyze. If ^{137}Cs counting is below the detection limit, 60 ml of the extract will be evaporated to 20 ml or 10 ml and counting again for ^{137}Cs.
(12) Carry out a second 1.0 M NH_2OH HCl leach of the residue but heat for only 1.5 h. Then repeat step 11.

Fraction 4: Organic

(13) To the residue from step 12, add 6 ml of 0.02 M HNO3 and 10 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 and the suspension is allowed to digest at least one hour at room temperature (or until it stops bubbling). The mixture will be heated at 80°C for 2 h with occasional agitation (our samples from the top layer – are very rich in organic matter, in that case we might do not heat our samples if the samples are very reactive).
(14) A second 6 ml aliquot of 30% of H_2O_2 (pH 2 with HNO_3) add and the suspension is allowed to digest at least one hour at room temperature (or until it stops bubbling). The mixture will be heated at 80°C for 2 h with occasional agitation (our samples from the top

layer – are very rich in organic matter, in that case we might do not heat our samples if the samples are very reactive).

(15) Add 10 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 and shake for 30 minute.

(16) Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 10 ml of 0.01 M $CaCl_2$, vortex and centrifuge again; do this twice and discharge supernatant rinses. Make up to the 40ml mark and analyze. If ^{137}Cs counting is below the detection limit, 40 ml of the extract will be evaporated to 20 ml or 10 ml and counting again for ^{137}Cs.

(17) Repeat steps 14, 15, and 16. In step 14 add gradually 20 ml of 30% of H_2O_2 .

Fraction 5: Residual

(18) Cesium content in the residual after step 17 will be counting in the solids.

APPENDIX D: DATA ARCHIVE

Table 8. Cesium concentration (Bq/kg) in water lily stems and leaves before (BCA) and after clay application (ACA). Treatments: Control – no clay application; LCA – low clay application (0.25cm layer of clay on the bottom of the sediment; HCA – high clay application (2.5 cm layer of clay on the bottom of the sediment.

Treatment	**Sample location**	**Number of samples in each treatment**	**Stems**		**Leaves**	
			^{137}Cs			
			Bq/kg			
			BCA	**ACA**	**BCA**	**ACA**
Control	LC1	1	2.2031	1.92	1.53	1.03
		2	1.9063	1.92	1.18	1.07
		3	2.9555	1.43	1.69	0.68
		4		1.92		1.02
	LC6	5	1.2066	2.05	0.80	1.22
		6	1.5873	1.49	1.30	0.97
		7	1.3757	2.25	0.94	1.23
		8		2.76		1.18
	LC9	9	2.7778	1.52	1.30	0.88
		10	1.8519	2.56	1.11	1.35
		11	2.3195	3.12	1.20	1.67
		12		1.94		1.17
	LC10	13	0.5869	2.51	0.87	1.01
		14	1.7677	1.99	1.06	0.83
		15	1.2698	2.08	0.90	1.30
		16		1.97		1.10
Treatment avg			**1.82**	**2.09**	**1.16**	**1.11**
Stdev			**0.68**	**0.46**	**0.27**	**0.23**

Treatment	**Sample Location**	**Number of Samples in each treatment**	**Stems**		**Leaves**	
			^{137}Cs			
			Bq/kg			
			BCA	**ACA**	**BCA**	**ACA**
LCA	LC4	1	1.8265	0.83	1.10	0.46
		2	2.0716	0.70	1.05	0.25
		3	2.2447	0.55	1.55	0.45
		4		0.60		0.34
	LC8	5	2.3068	1.24	1.06	0.70
		6	1.8116	1.52	1.09	0.66
		7		1.11		0.51
		8		1.40		0.79
	LC12	9	1.9211	2.25	1.28	0.80
		10	2.3588	1.56	1.33	1.14
		11	1.692	1.31	1.11	0.89
		12		1.48		1.13
	LC13	13	1.2511	1.20	1.02	0.75
		14	1.4109	1.17	0.98	0.59
		15	1.5243	1.27	0.93	0.93
		16		1.38		0.87
	LC15	17	1.3201	0.51	1.22	0.22
		18	1.4815	0.41	0.82	0.19
		19	1.5504	0.38	0.90	0.29
	LC16	20	1.6993	0.55	0.91	0.20
		21	1.2842	0.54	0.90	0.20
		22	1.4815	0.59	0.74	0.24
		23		0.66		0.19
Treatment Avg			**1.71**	**1.02**	**1.06**	**0.56**
Stdev			**0.37**	**0.49**	**0.21**	**0.32**

Treatment	Sample location	Number of samples in each treatment	Stems		Leaves	
			^{137}Cs			
			Bq/kg			
			BCA	ACA	BCA	ACA
HCA	LC2	1	2.6235	0.57	1.5429	0.25
		2	3.1995	0.42	1.7118	0.26
		3	2.4425	0.43	1.2853	0.44
		4		0.66		0.42
	LC3	5	1.742	0.53	1.1489	0.31
		6	1.5046	0.38	1.4724	0.34
		7	1.8779	0.36	1.4555	0.33
		8		0.34		0.33
	LC5	9	1.967	0.30	1.1814	0.14
		10	2.1698	0.51	1.3956	0.15
		11	2.2319	0.47	1.0278	0.22
		12		0.24		0.25
	LC7	13	1.9883	0.08	1.1005	0.11
		14	4.2463	0.47	1.2821	0.25
		15	1.631	0.38	0.9558	0.26
		16		0.48		0.22
	LC11	17	1.7214	0.77	0.9751	0.58
		18	1.8129	0.48	1.0774	0.31
		19	2.4561	0.71	1.1125	0.31
		20		0.80		0.46
	LC14	21	1.5556	0.50	0.7752	0.27
		22	1.6691	0.44	0.907	0.29
		23	1.9192	0.56	0.8916	0.31
		24		0.70		0.34
Avg			**2.15**	**0.48**	**1.18**	**0.30**
Stdev			**0.68**	**0.17**	**0.25**	**0.10**

Table 9. Cesium concentration (Bq/g) in duckweed.

Treatment	Sample location	137Cs Bq/g Each sample	137Cs Bq/g Treatment Average	137Cs Bq/g Treatment Stdev
Ctrl	1	1.00	1.54	0.41
	6	1.83		
	9	1.90		
	10	1.46		
LCA	4	0.28	0.45	0.30
	8	0.32		
	12	0.96		
	13	0.66		
	15	0.19		
	16	0.29		
HCA	2	0.36	0.32	0.19
	3	0.58		
	5	0.12		
	7	0.15		
	11	0.37		

Table 10. Concentration of ^{137}Cs (Bq g^{-1}) as a function of depth in sediment cores collected at R-Canal and Pond A. Blanks within the table mean that the core was shallow and not taken to the depth indicated. Multiply values in the table by 27 to convert to units of pCi g^{-1}.

	Depth of Core Slice (cm)				
Site	0-2.5	2.5-5.0	5.0-7.5	7.5-10	10-12.5
1	7.3	8.06	8.3	12.3	10.2
2	16.9	6.4	6.1	-	-
3	2.2	5.9	4.2	3.4	2.4
4	24.1	19.2	10.9	-	-
5	2.0	6.3	-	-	-
6	7.6	19.0	45.7	42.5	29.1
7	2.0	1.7	2.3	1.8	-
8	2.0	19.2	1.9	1.4	1.2
9	1.6	2.8	8.1	36.5	31.4
10	2.4	14.8	8.0	2.8	1.0
11	2.3	16.0	3.3	-	-
12	0.7	1.1	1.9	0.9	-
13	3.0	3.6	9.5	2.5	0.6
14	1.3	1.9	1.5	1.7	1.8
15	1.1	1.4	1.9	12.4	12.9
16	1.9	21.0	9.7	3.8	-
17	1.9	4.3	8.0	5.0	2.8
18	2.8	13.3	4.6	1.4	1.2
19	5.1	9.6	16.6	10.0	6.6
20	1.7	2.2	1.9	-	-
21	1.9	5.5	1.7	1.5	1.1
22	59.6	6.1	4.6	2.0	-
23	3.9	1.7	0.3	0.1	-
24	1.8	4.7	-	-	-
25	3.6	19.7	7.9	2.8	3.5
26	9.2	19.2	4.6	1.7	0.6
27	1.6	13.3	2.5	0.7	0.5
28	3.5	11.8	4.3	2.6	1.9
29	1.8	1.7	1.8	3.7	6.3
Mean	6.1	9.0	6.7	6.7	6.4
SD	11.5	6.9	8.6	10.9	9.4

Table 11. Concentration of ^{137}Cs concentration (Bq/g) in sediment samples as a function of depth. Samples collected on April 16, 2002 after 11 months of illite application. Treatments: Ctrl – Control, LCA – low clay application, HCA – high clay application.

Treatment	Sample Location	137Cs concentration in Bq/g					
		Depth					
		cm					
		0-2.5	2.5-8	9-15	15-22	22-30	above 30
Control	LC1-A	6.37	7.27	18.36	6.98	2.45	2.45
	LC1-C	6.04	5.76	5.46	32.58	10.09	2.66
	LC10-A	13.74	5.53	0.17	0.04	0.02	
LCA	LC8-A	3.12	19.99	1.11	1.11		
	LC8-B	2.28	2.35	32.93	0.3	0.3	
	LC13-A	2.95	3	30.09	2.99	0.16	0.05
HCA	LC7-A	0.3	2.73	33.91	4.27		
	LC7-B	0.27	1.07	16.13	2.01		
	LC5-A	0.13	0.72	32.2	2.31		
	LC2-A	0.58	2.55	15.47	3.17		
	LC14-A	0.14	0.095	9.95	11.07	0.34	0.05
Average of 137Cs concentration (Bq/g) for each treatment							
Control		8.72	6.19	8.00	13.20	4.19	2.56
LCA		2.78	8.45	21.38	1.47	0.23	0.05
HCA		0.28	1.43	21.53	4.57	0.34	0.05
Standard deviation of 137Cs concentration (Bq/g) for each treatment							
Control		4.35	0.95	9.36	17.14	5.25	0.15
LCA		0.44	10.00	17.61	1.38	0.10	
HCA		0.18	1.16	10.81	3.74		

Table 12. ^{137}Cs concentration ratios (Bq kg^{-1} dried plant / Bq kg^{-1} dried sediment) for water lily samples collected at R-canal and Pond A before clay application. Sediment concentrations of ^{137}Cs were averaged from the 0 - 12.5 cm depth.

Location	^{137}Cs Concentration Ratios of Leaves					^{137}Cs Concentration Ratios of Stems				
	Rep 1	Rep 2	Rep 3	Average	Stdev	Rep 1	Rep 2	Rep 3	Average	Stdev
1	0.058	0.045	0.0641	0.056	0.010	0.084	0.072	0.112	0.089	0.021
2	0.134	0.148	0.1115	0.131	0.019	0.227	0.277	0.212	0.239	0.034
3	0.123	0.158	0.1564	0.146	0.020	0.187	0.162	0.202	0.184	0.020
4	0.102	0.098	0.1439	0.114	0.026	0.169	0.192	0.208	0.190	0.019
5	0.223	0.263	0.1940	0.227	0.035	0.371	0.410	0.421	0.401	0.026
6	0.080	0.130	0.0944	0.102	0.026	0.121	0.159	0.138	0.139	0.019
7	0.371	0.432	0.3223	0.375	0.055	0.671	1.432	0.550	0.884	0.478
8	0.289	0.297	0.0000	0.196	0.169	0.628	0.493	0.000	0.374	0.331
9	0.092	0.079	0.0849	0.085	0.007	0.196	0.131	0.164	0.164	0.033
10	0.087	0.105	0.0891	0.094	0.010	0.058	0.176	0.126	0.120	0.059
11	0.171	0.189	0.1951	0.185	0.013	0.302	0.318	0.431	0.350	0.070
12	0.178	0.185	0.1535	0.172	0.016	0.266	0.327	0.235	0.276	0.047
13	0.217	0.208	0.1964	0.207	0.010	0.265	0.299	0.323	0.296	0.029
14	0.201	0.235	0.2311	0.222	0.019	0.403	0.433	0.497	0.444	0.048
15	0.370	0.248	0.2718	0.297	0.065	0.400	0.449	0.470	0.440	0.036
16	0.208	0.204	0.1680	0.193	0.022	0.386	0.292	0.337	0.338	0.047
Mean	0.181	0.189	0.155	0.175	0.033	0.296	0.351	0.277	0.308	0.082
SD	0.097	0.096	0.082	0.083	0.040	0.176	0.314	0.160	0.192	0.129

APPENDIX E: TIMING OF EVENTS

Dec. 2000	Sediment cores were taken from R-canal and Pond A for baseline data. They were sliced and counted for ^{137}Cs.
Jan. 2001	10 different clay samples from 5 companies were ordered each with various percentages of illite.
Feb.-March, 2001	Lab experiments to determine which clay will adsorb the most ^{137}Cs.
March 5-30,2001	Building of limnocorrals.
April 9-13, 2001	Limnocorrals deployed in R-canal at 16 randomly chosen positions.
April 17-18, 2001	3 Sediment Cores taken from each limnocorral, 1 in each third of a limnocorral.
April 20, 2001	Vegetation samples were collected from each limnocorral, 2 samples were taken in each third of the limnocorral. The aquatic plant sampled was *Nymphaea odorata*.
April 23, 2001	3 liter water samples collected 1 meter off the bottom were taken from each limnocorral. Also, water quality was done on each limnocorral with the hydrolab.
April 23, 2001	Duckweed ordered, will be added to limnocorrals as sampling parameter.
April 26-27, 2001	*Gambusia* collected, will be added to limnocorrals as sampling parameter.
May 1, 2001	Clay application - the limnocorrals were randomly chosen for low clay application, high clay application, and controls (no clay application). 65lbs of clay was added to the low application limnocorrals.
May 2, 2001	650lbs of clay was added to the high application limnocorrals.
May 4, 2001	3-liter water samples and water quality measurements were taken on 2 limnocorrals from each treatment.
May 10-11, 2001	Electroshocked all limnocorrals in an effort to eliminate ambient *Gambusia*.
June 4, 2001	Took water quality measurements on all limnocorrals.
June 5, 2001	Inoculated all limnocorrals with 30 *Gambusia* and 850 ml of duckweed.
June 16, 2001	Installed a staff gauge in the R canal.
June 18, 2001	Took water quality measurements on all limnocorrals. (Do be done every two weeks).
July 2, 2001	Took water quality measurements on all limnocorrals.
July 3-4, 2001	Heavy rain.
July 5	9 of the 16 limnocorrals had most likely exchanged water with the ambient R canal water. The following chart illustrates the impact of this high water event on the experiment.

Treatment	Number of limnocorrals remaining properly isolated	Number of limnocorrals exchanging water
Control	1	3
Low clay application	4	2
High clay application	2	4

July 10, 2001	Took water samples and water quality measurements on all limnocorrals.
July 13, 2001	Found the debris dam causing the high water problem and broke it up. Water level came down very rapidly.
July 24, 2001	All Pond A limnocorrals have been re-isolated from surrounding water.
July 25, 2001	Took water quality measurements on all limnocorrals.

July 30, 2001	Took a preliminary sample of duckweed and *Gambusia* from LC 10 only.
Aug. 7, 2001	Took water quality measurements on all limnocorrals
Aug.17, 2001	Sampled *Nymphaea* stems and leaves from each limnocorral.
Aug.20, 2001	Sampled duckweed from each limnocorral.
Sept. 12, 2001	Took water quality measurements on all limnocorrals.
Sept. 17, 2001	Sampled 30-40 Gambusia from every limnocorral except LC 2.
Sept. 28, 2001	Took water samples and water quality measurements on all limnocorrals
Nov.15-28, 2001	Samples of Nymphaea stems and leaves were ground
Nov. 19, 2001	Water level in R-canal continues to drop. The staff gauge is down to 8cm. (It was 13 cm on 11/14/01). However, all limnocorral sediments are covered with water.
Nov. 27, 2001	Staff gauge on R-canal has dropped to 6cm.
Dec. 4, 2001	Staff gauge is down to 1cm. Limnocorrals 4, 15, and 16 are closest to exposing sediments.
Dec. 10, 2001	Water level in R canal has dropped below the staff gauge approximately -4cm. Sediment in all limnocorrals is still covered by very shallow water.
Dec. 31, 2001	Water level in R canal continues to drop. LC 4 has exposed ~10% of it's sediment. There is a heavy layer of black detritus overlaying. LC 15 and LC 16 are almost totally devoid of standing water.
Feb. 1, 2002	Detailed notes on R-canal low water level situation:

Limnocorral ID	Description	Max depth [cm]
1	No sediment exposure	60
2	No sediment exposure	60
3	No sediment exposure	59
4	10% of sed. exposure	61
5	No sediment exposure	42
6	No sediment exposure	75
7	No sediment exposure	41
8	No sediment exposure	42
9	No sediment exposure	40
10	No sediment exposure	56
11	No sediment exposure	70
12	No sediment exposure	48
13	No sediment exposure	55
14	No sediment exposure	40
15	75% sed. exposure	-
16	100% sed. exposure, LC is dry	-

Water depth in middle of canal is ~60-80cm
There is still a good population of Gambusia in most limnocorral

Feb. 14, 2002

Took water samples from 15 limnocorrals; from LC 16 sample was not taken due to low level of water. Additionally water quality measurements on all limnocorrals were taken (table below).

Limnocorral ID	Temp.	Cond.	DO	pH
1	7.53	45	6.82	7.12
2	7.51	39	5.23	7.23
3	7.67	33	6.93	7.06
4	7.15	51	7.16	7.16
5	8.05	45	6.35	7.12
6	7.84	43	7.09	7.28
7	8.05	36	7.71	7.05
8	7.96	33	7.50	7.04
9	7.76	40	5.35	7.07
10	8.05	34	4.64	7.02
11	8.34	36	5.38	6.78
12	9.22	41	6.36	6.77
13	8.77	34	5.37	6.57
14	9.71	36	6.85	6.71
15 (8 inches water)	7.90	53	7.44	6.74
16 (4 inches water)	Not enough water to do water quality measurements			

Due to low water levels all samples and measurements were taken at the surface

Feb. 22, 2002

Sub-samples of the water samples collected on 4/23/01, 5/4/01, 5/29/01, 7/10/01, 9/28/01, 2/14/02 were sent for ICP-MS analysis for the following elements: Al, B, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, U, and Cs. There was a problem to determine Cs due to CsCl, which was added to the water samples (for more details please see a notebook).

Feb. 25 to
March 25, 2002

Samples of Nymphaea stems and leaves were digested with 10 ml of HNO3 and 7ml H2O2 on Star 6 and diluted to about 50 or 60 ml with DI water

April 1, 2002

18 sediment cores from the following limnocorrals were taken:
Control: LC1 (3SCs), LC6 (1SC), LC9 (1SC), LC (1SC)
Low Clay Application: LC8 (3SCs), LC12 (1SC), LC13 (1SC), LC15 (1SC)
High Clay Application: LC2 (1SC), LC5 (1SC), LC7 (3SCs), LC14 (1SC)

April 16, 2002

The second set of sediment cores (14) were taken from the same limnocorrales as on April 1, 2002, except samples from LC 6 and LC15 were not taken. The split core tubes were used to collect these samples.
Control: LC1 (3SCs), LC9 (1SC), LC (1SC)
Low Clay Application: LC8 (3SCs), LC12 (1SC), LC13 (1SC),
High Clay Application: LC2 (1SC), LC5 (1SC), LC7 (3SCs), LC14 (1SC)