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Use of Illite Clay for In Situ Remediation of ^{137}Cs-Contaminated Water Bodies: Field Demonstration of Reduced Biological Uptake

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We hypothesized that adding micaceous minerals to ^{137}Cs-contaminated aquatic systems would serve as an effective in situ remediation technique by sequestering the contaminant and reducing its bioavailability. Results from several laboratory studies are presented from which an effective amendment material was chosen for a replicated field study. The field study was conducted over a 2-year period and incorporated 16 3.3-m diameter column-plots (limnocorrals) that were randomly placed in a ^{137}Cs-contaminated pond. The limnocorrals received three rates of amendment treatments to their water surfaces. The amendment material was a commercially available mineral with high sorption (K_d > 9000 L kg^{-1}) and low desorption (<20%) characteristics for cesium, even in the presence of high concentrations of the competing cation, NH_4^+. In the treated limnocorrals, ^{137}Cs concentrations were reduced some 25−30-fold in the water, 4−5-fold in aquatic plants, and 2−3-fold in fish. The addition of the amendment did not adversely affect water chemistry, although increased turbidity and subsequent siltation did alter the aquatic macroinvertebrate insect community. This in situ technology provides a valuable, less-environmentally intrusive alternative to costly ex situ technologies that require the contaminated sediment to be excavated prior to treatment, or excavated and disposed of elsewhere.

Introduction

The most costly environmental restoration program in U.S. history is the ongoing cleanup of contamination at the U.S. Department of Energy's (DOE) former nuclear weapons production facilities (*1*). Many of the DOE facilities fall under the Environmental Protection Agency's Comprehensive Environmental Response, Compensation and Liability Act (CERLCA). For example, the entire 800 km^2 area of DOE's Savannah River Site in Aiken, SC, is designated a Superfund site. Similar CERCLA situations exist at DOE's other large facilities.

The Savannah River Site (SRS) produced Pu and tritium between 1953 and 1989 for the U.S. nuclear weapons program. During the early years of operating the SRS, radionuclide releases contaminated numerous aquatic ecosystems, including several natural streams and manmade cooling reservoirs, as well as many kilometers of canals that connected the five nuclear reactors on the SRS to their cooling ponds. Combined, these water bodies cover over 1200 ha in area and remain partially contaminated with radioactive isotopes of Cs, Sr, and Pu. All of these contaminated aquatic systems on the SRS represent a remediation challenge to DOE.

Greater than 95% of the radionuclides in these contaminated water bodies reside in the sediments (*2*). Their remediation is particularly problematic because conventional sediment cleanup technologies can destroy aquatic ecosystems. Cleanup generally entails draining the water body, dredging the sediments, and then trucking them to a disposal landfill. Such traditional methods are very expensive, expose workers to inhalation doses from resuspension of contaminated sediments, and often do more harm to the fragile ecosystems than if the contaminants were left in place. A less destructive, yet effective method of remediating aquatic systems is needed.

Contaminant of Concern. Cesium-137 is the radionuclide that generally drives human and ecological risks on the SRS, and thus the radioactive contaminant targeted during remediation operations. For example, the dominant contribution of ^{137}Cs to human health risks was evident during the draw down of Par Pond, a 10 km^2 contaminated cooling reservoir on the SRS. Exposure to ^{137}Cs comprised 95% of the lifetime fatal cancer risks to an adult farmer hypothetically living on the exposed sediments, while radioactive Sr and Pu's contributions to risks were only 0.6% and 4.1%, respectively (*3*).

The problems of contaminated aquatic systems and their associated risks are heightened on the SRS because ^{137}Cs is more biologically available than at any other DOE facility (*4*). The enhanced bioavailability of ^{137}Cs in this area is evident by the propensity of ^{137}Cs to be taken up by plants. An index of this propensity is the plant-to-soil concentration ratio (CR = Bq kg^{-1} dried plant/Bq kg^{-1} dried soil). In 1996, the National Council on Radiation Protection and Measurements realized that its recommended default CR for ^{137}Cs of 0.1 was too low for the high uptake conditions prevalent in the southeastern coastal plain of the U.S., where the SRS is located, and increased it to 1.0 (*5*). However, CRs for the SRS are generally well above 1.0; indeed, they are among the highest recorded CRs for ^{137}Cs in the world (*4*). For example, CRs for plants from Steel Creek and Par Pond on the SRS ranged from 3 to 7 (*6*), and early successional species invading Par Pond's exposed lake bed had values of 15 ± 2 (*4*). Such large CRs indicate the enhanced bioavailability of ^{137}Cs.

Kaolinitic-Dominated Minerals on the SRS. The enhanced bioavailability of ^{137}Cs in the southeastern U.S. coastal plain is largely due to the low clay content of its sandy soils, and because the clay mineralogy that does exist is dominated by weathered kaolinite (*7, 8*). ^{137}Cs is very weakly bound to kaolinite, whereas the physical structure and ionic charge of several micaceous minerals (e.g., illites) result in Cs tenaciously bonding with the mineral such that ^{137}Cs will not readily desorb, even in the presence of competing ions (*9*−*13*). SRS sediments do have some micaceous minerals, but they are largely ineffective in forming strong bonds with ^{137}Cs (*14*); presumably this is due to a lower particle unit charge, the result of extensive weathering. Tenacious adsorption is important because ^{137}Cs sorbed to illites is likely to be unavailable for biotic uptake.

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Hypothesis. Because high ^{137}Cs mobility on the SRS is due in part to a low retention capacity of the kaolinitic-dominated soils, we hypothesized that adding micaceous minerals to contaminated water bodies would serve as an effective in situ remediation technique by sequestering ^{137}Cs and reducing its bioavailability. The use of micaceous amendments, such as illites, to sequester contaminants, including Cs, is not new (*14–17*). Most previous methods, however, have physically mixed the amendment within the contaminated soil and then tested the effectiveness using chemical adsorptive and/or desorptive tests. Our innovation was in testing whether an application of the amendment to the water surface would reduce biological uptake of the contaminant.

Applying clay to aquatic ecosystems, however, causes turbidity and sedimentation that can have environmental impacts of their own. High levels of turbidity are a common byproduct of activities related to urban development, improper land management practices, deforestation, mining, road construction, and intensive agriculture (*18–20*). Aquatic organisms are affected by increased turbidity, primarily from the limitation of light available to algae and macrophytes, and by siltation. Decreases in algal productivity tend to lower concentrations of dissolved oxygen, harming insects and other organisms, while siltation onto periphyton can lower the quality of food for snails and herbivorous insects (*21*). Therefore, we also examined the environmental impacts of our method.

Specifically, the objectives of this study were to (1) determine, in the laboratory, Cs sorption and desorption characteristics of 10 commercially available clay minerals and choose one for additional field testing; (2) conduct a replicated field test of an in situ remediation method in which we examine its effectiveness at reducing the biological uptake of ^{137}Cs; and (3) evaluate the negative environmental impacts of adding the amendment by examining turbidity, water quality, and changes to the aquatic insect community.

Materials and Methods

Mineral Amendment Characterization. The principal characteristic sought in an amendment was the sorption and retention of ^{137}Cs in the presence of competing ions. We thus evaluated the (ad)sorption/desorption of Cs to 10 minerals that were candidates for amendment material. The 10 clays originated from commercial mining sources, and as such did not represent well-characterized, single-phase minerals. X-ray diffraction analyses (as received, Mg-saturated, glycerol-saturated, and temperature treated for 2 and 4 h at 350 °C, and from 2 to 75 2θ) were conducted on the minerals to assist in their identification. These 10 samples included five minerals dominated by illites, three by vermiculites, and two by micas. Distribution coefficients (K_d: Bq kg^{-1} dry mineral/Bq L^{-1} water) for each mineral were calculated to compare the Cs sorptive capacities among the 10 candidate minerals (3-g mineral: 27-mL μm-filter; pH 6.5; 22 °C; Eh (SHE) = 388 mV; contact time = 1 week; see Experimental Details in Supporting Information).

An effective amendment must not only strongly bind ^{137}Cs, but also retain it in the presence of competing ions. A particularly effective competing ion in natural water is NH_4^+, which has been measured as high as 4 μM in SRS anoxic water (*8*). A desorption experiment with selected minerals was conducted to compare the ease at which Cs desorbed in the presence of an excess of NH_4^+. For purposes of comparison, two well-characterized reference minerals were also included in these desorption tests: Gray Shale (I-API-35; American Petroleum Institution, Washington, DC) and kaolinite (KGa-2; Clay Mineral Society, Denver, CO). The experiment was conducted in triplicate using 50-mL centrifuge tubes, each containing 0.15 g of mineral to which ^{134}Cs was adsorbed as described above. Next, 20 mL of 0.1 M NH_4Cl was added and the samples were mixed on an automatic shaker for 1 week. Following centrifugation, 5 mL of solution was removed and assayed for ^{134}Cs activity. The results were presented in terms of percent of ^{134}Cs desorbed by NH_4^+ from each mineral.

The 10 candidate minerals had different densities and particle size characteristics that influenced settling rates, as determined in the laboratory by adding the various amendment materials to static columns of water and observing their settling behavior (5 g of each clay in 200 mL of water; duration 5 min and 24 h).

In Situ Field Tests. After the candidate mineral was chosen, an in situ remediation method was tested in Pond A, one of a series of cooling ponds on the SRS contaminated with ^{137}Cs. Pond A's total ^{137}Cs inventory was estimated in 1998 to be 41 ± 4 GBq, mean concentrations in the sediments were 7.8 ± 1 kBq kg^{-1}, with maximum concentrations found at a depth of 2–4 cm (*22*). Greater than 99% of the total inventory was in the top 20 cm of sediments. Typically, the pond is 5.2 ha in area, has a mean depth of 0.5 m, and a maximum depth of 1.5 m (parameters vary seasonally).

Our hypothesis was that as the minerals spread over the water surface and settle to the bottom sediments they would quickly sorb ^{137}Cs from the water column. The mineral would then intercept and sorb ^{137}Cs during the annual summer release of ^{137}Cs from the contaminated sediments (*8*), effectively sequestering the contaminant and drastically reducing biological uptake. Annual ^{137}Cs releases are due to summer anoxic conditions in the sediments that result in a buildup of NH_4^+ from bacteria, the dissolution of Cs-binding Fe-oxides, and a subsequent release of ^{137}Cs from the sediments into the overlying water column (*8*).

Clay Application to Limnocorrals. The field test was conducted in replicated limnocorrals. Limnocorrals are field-deployed devices that isolate a column of water and its underlying sediments. Limnocorrals were made of flexible plastic with a flotation collar at the top that kept the column's open end floating above the water surface. Retention rings at mid-depth and at the bottom maintained the column's shape. A skirted bottom was weighted down and inserted into the pond's sediments. After several preliminary tests of various designs, 3.3-m diameter limnocorrals were chosen for this experiment.

Sixteen limnocorrals were randomly placed in Pond A during the second week of April 2001. On May 1, 2001, six limnocorrals were treated with enough mineral amendment to cover the limnocorral's sediment surface to a depth of 0.25 cm (low clay application − 27 kg per limnocorral; referred to as LCA), six received a treatment 10 times that amount (2.5 cm on the sediment surface: high clay application − 270 kg per limnocorral; referred to as HCA), 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. The limnocorrals did not totally isolate the water they contained because some water presumably seeped in/out through the bottom sediments, and rain entered from the open top. The limnocorrals did keep the clay treatments (and added plants and fish, described below) within a confined area and provided an experimental technique whereby replicated study plots could be used within the aquatic system.

Limnocorrals were monitored for 2 years and then we reapplied the same mineral amendment, on July 3, 2003, to determine the negative impacts during the period of peak environmental disturbance. The severity of damage to an aquatic ecosystem from suspended sediments depends on the duration of exposure to conditions of high turbidity (*23*), and turbidity levels are greatest immediately after application of an amendment. The rates and method for the second clay application were identical to the first.

Water Samples. Water samples were periodically collected from each of the 16 limnocorrals. Three-liter samples were drawn 0.5 m from the sediment surface and filtered (0.45 μm) prior to being assayed for ^{137}Cs in Marinelli beakers using a High Purity Germanium detector. Subsamples were analyzed for stable elements using ICP-MS. Other parameters, such as pH, conductivity, temperature, and dissolved oxygen, were determined in the field using a HydroLab instrument. Turbidity samples were taken 2 days prior to the second clay application, and on days 0, 1, 4, 7, 12, 14, and 18 thereafter by filling 30-mL bottles with water collected at 5-cm depth. Turbidity values in nephelometric turbidity units (NTU) were measured using a LaMotte 2020 turbidimeter (LaMotte Co., Chestertown, MD).

Plant Samples. Two approaches were used to evaluate the effect of the clay amendments on ^{137}Cs concentrations in aquatic plants. We introduced uncontaminated plants to the limnocorrals after the first illite treatments had been applied. We also examined native plants that were in all of the limnocorrals prior to the addition of any treatments and that 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 also differ. Duckweed (*Lemna* spp.), the introduced species, 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. The uncontaminated duckweed was purchased from a commercial grower and added to all limnocorrals on June 5, 2001, a month after the treatments had been applied. On August 20, 2001, duckweed was sampled, washed with DI water, dried, and assayed for ^{137}Cs.

In contrast, water lily (*Nymphaea odorata*) is a native perennial with extensive rhizomes that intermingle throughout the sediments and contain large tubers. The roots send up long stems that support a fibrous, floating leaf, commonly 25 cm in diameter. When the limnocorrals were constructed, no attempt was made to remove the extensive number of water lilies present and already contaminated with ^{137}Cs. Prior to the addition of the treatments, 12−18 water lilies from each group of limnocorrals were sampled, washed with DI water, dried, ground, and assayed for ^{137}Cs. No pretreatment differences ($p = 0.29$) were found between the control (mean Bq kg^{-1} ± SD = 1200 ± 300), LCA (1100 ± 200), and HCA (1200 ± 300) leaves, or their stems (control = 1800 ± 700; LCA = 1700 ± 400; HCA = 2100 ± 700; $p > 0.08$). Water lilies were resampled for ^{137}Cs on August 17, 2001, 2.5 months after the clay additions.

Macroinvertebrate Insect Samples. On June 9, 2003, 24 days prior to the second clay additions, 30 Hester−Dendy (H−D) multi-plate aquatic insect samplers were placed in 12 of the 16 limnocorrals (4 replicates for each control, low clay, and high clay treatment). Each sampler consisted of 16, 7.6-cm^2 plates, separated approximately 0.3−1.0 cm, that aquatic insects colonized. Samplers were tied to the sides of the limnocorrals and hung in the water with their tops approximately 15 cm below the water surface. Fourteen pretreatment samplers were collected 4 days prior to illite treatment, and 16 H−D samplers were collected 7 days after clay application. All insects found were preserved in 4% formaldehyde solution and later identified under microscopic examination with the aid of reference materials (*24*, *25*).

Fish Samples. 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 holbrooki*, eastern mosquitofish. *Gambusia holbrooki* are a small fish (2−5 cm in length) and common food for many larger fish in the waters of the southeastern U.S. *Gambusia* eat aquatic insects. On May 10, 2001, we electro-shocked all limnocorrals to eliminate existing *Gambusia*. Next, on June 5, 2001 (1 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 routinely saw adults and young fish swimming within the limnocorrals. On September 17, 2001 (2.5 months after the fish were introduced), 30−40 fish were sampled from each limnocorral, pooled by limnocorral number, and assayed for ^{137}Cs.

Radiocesium Analyses and QA/QC. Analyses of ^{137}Cs in water, plants, sediments, and fish were performed on either a Packard Autogamma instrument with a well-type NaI crystal (7.6 × 8.3 cm with a 1.5% relative efficiency) or a High Purity Germanium detector (HPGE). Analyses of ^{134}Cs for K_d determinations were also performed on an HPGE. ^{134}Cs and ^{137}Cs 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 including use of controls, replicates, and blanks for analytical work.

Statistical Analyses. The experimental units in this research were 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.

Results

Mineral Characterization. All of the commercially available minerals evaluated had relatively high K_d values >3000 L kg^{-1}, 2 orders of magnitude greater than kaolinite's K_d, the dominant clay in SRS sediments (Table 1). Among the candidate amendments, the micaceous minerals (Mica-3x and Mica-4x) sorbed the least Cs (i.e., lowest K_d's), while vermiculites and minerals rich in illites (Redart, Ball Clay, Stone Clay, and Todd Light) adsorbed the most Cs. Studies to determine the mineral settling rates in water revealed that the vermiculites (Vermiculite 01, Vermiculite 02, and Zolonite) settled very little during 24 h (Table 1), a characteristic that would be unfavorable for field application of the material. Of the remaining materials, Todd Light had the best settling characteristics (Table 1). 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 (I-API-35) and a reference kaolinite (KGa-2). The Todd Light material performed exceptionally, as well as the reference illite material. The desorption tests were conducted in the presence of 0.1 M NH_4^+, which is 5−6 orders of magnitude greater than natural NH_4^+ concentrations measured on the SRS (*8*). The Todd Light illite and the reference illite Gray Shale both desorbed about the same percent of adsorbed ^{134}Cs (<20%), whereas all of the ^{134}Cs was desorbed from the kaolinite. We thus chose the Todd Light illite as the most promising amendment material.

X-ray diffraction patterns indicated that the Todd Light illite was a dioctahedral mica and that quartz and small amounts of Fe-rich chlorite or vermiculite were present (Figure 1). Scanning electron microscopy (SEM) images showed that the particles generally ranged in size from about 0.5 to 10 μm, with a vast majority of the individual particles being <2 μm (Figure 1). The aggregated particle size could not be ascertained by SEM, because this measurement is conducted under vacuum.

TABLE 1. Mineral Properties, Cs Sorption, Desorption, and Particle Settling

trade name[a]	dominant mineral[b]	sorption K_d (L/kg)[c]	% settled after 5 min	% settled after 24 h	desorption (%)
Fire Clay[1]	illite	6300 ± 400	50	90	not tested
Redart[1]	illite	8000 ± 1600	50	90	not tested
Vermiculite 01[2]	vermiculite	5700 ± 400	0	0	not tested
Vermiculite 02[2]	vermiculite	6200 ± 100	0	0	not tested
Zolonite[2]	vermiculite	6400 ± 300	5	5	not tested
3x Mica[3]	mica	3300 ± 100	80	100	not tested
4x Mica[3]	mica	3200 ± 100	80	100	not tested
Ball Clay[4]	illite	8500 ± 100	80	100	not tested
Stone Clay[4]	illite	7200 ± 200	80	100	not tested
Todd Light[4]	illite	8300 ± 100	90	100	15
reference (KGa-2)[5] [d]	kaolinite	240 ± 50	not tested	not tested	100
reference (I-API-35)[6] [d]	illite	9300 ± 1000	not tested	not tested	10

[a] Supply Co. 1 = Cedar Heights Clay Operations, Oak Hill, OH; 2 = W. R. Grace & Co., Cambridge, MA; 3 = Mineral Mining Co., Kershaw, SC; 4 = Kentucky–Tennessee Clay Co., Nashville, TN; 5 = mined from Warren County, GA, purchased from Clay Mineral Society, Denver, CO; 6 = American Petroleum Institution, Washington, DC. [b] Based on X-ray diffraction analysis or information provided by vendor. [c] Sorption experiments conducted in triplicate; 0.3 g: 50 mL; pH adjusted to 6.5; initially added 6.9 Bq mL^{-1} ^{134}Cs; background solution was Pond A; equilibration period with ^{134}Cs was 7 days. [d] Reference minerals (not commercially mined minerals) used for comparison and not under consideration for use in the field study.

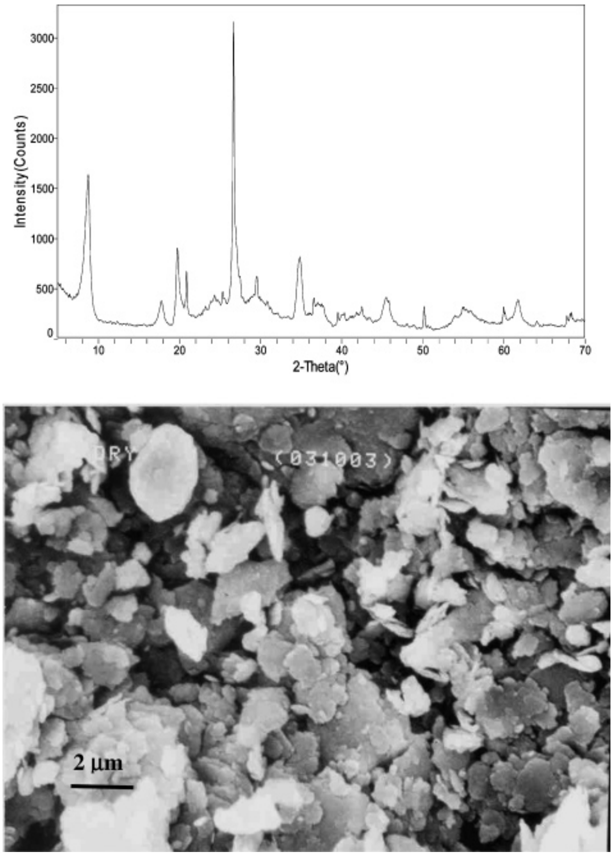

FIGURE 1. X-ray diffraction pattern (top) and SEM image (bottom) of the Todd Light illite used in the limnocorral study.

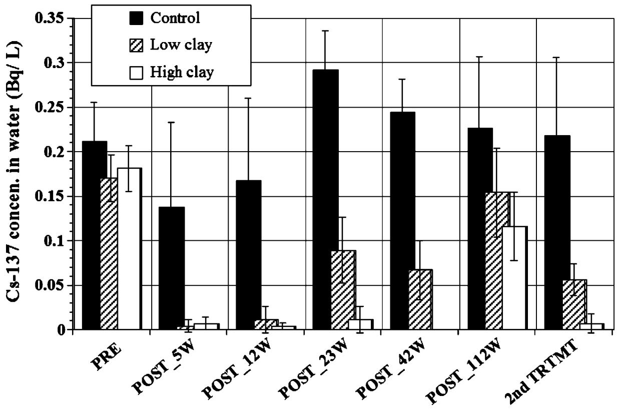

FIGURE 2. Mean (±SE) activity of ^{137}Cs in water samples collected from control and treated limnocorrals. Data show samples taken prior to the addition of the illite treatment (PRE) and for weeks 5, 12, 23, 42, and 112 post-treatment, as well as following a second illite treatment after week-112. Damage was noted to some limnocorrals at week-112, which allowed mixing of treated and untreated pond water.

Effect of In Situ Illite Application on ^{137}Cs Bioavailability. ^{137}Cs Reduction in Water. The illite amendment effectively scavenged ^{137}Cs from the water column, significantly reducing ($p < 0.01$) concentrations by up to 25–30-fold (Figure 2). Similar reductions in ^{137}Cs concentrations occurred from both levels of illite treatment through week-12. From week-12 through week-42, concentrations of ^{137}Cs in the water of the low treatments increased over those that received the high clay application. The increased ^{137}Cs activity concentrations observed during week-23 may be due to decreased water levels from 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 until week-112. ^{137}Cs concentrations in the water of the HCA limnocorrals in week-42 were below detection limits. Some limnocorrals were found to be in ill repair when samples were taken during week-112 and were no longer isolated from the pond's main body of water. Although concentrations continued to be significantly lower in the HCA limnocorrals than in the controls ($p < 0.05$), this means that the efficacy of the method at 2 years post-application cannot be fully addressed and that additional research is required. All limnocorrals were repaired prior to the second application of clay, following week-112.

^{137}Cs Reduction in Biota. The illite treatments successfully reduced the availability of ^{137}Cs to the floating duckweed and the sediment-bound water lilies. Concentrations of ^{137}Cs in duckweed were 4 times lower in the treated limnocorrals than in the controls ($p < 0.01$; Figure 3), with no significant difference between the LCA and HCA treatments. Such large reductions might be expected in the introduced duckweed because its roots did not reach the contaminated sediments and the pond water had already been scavenged of ^{137}Cs during the settling of the illite material.

A reduced bioavailability of ^{137}Cs in water lilies would be more difficult to achieve because of their extensive root system within the sediments, and because the plants were

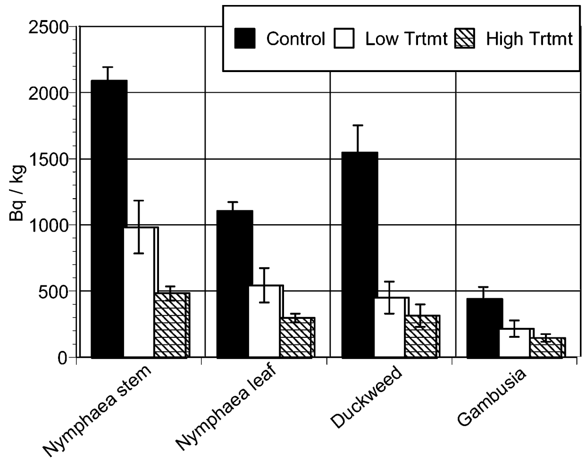

FIGURE 3. Mean concentrations of ^{137}Cs on a dry weight basis (±std error) in water lily (*Nymphaea*) stems and leaves in controls (*n* = 4 limnocorrals), low clay treatment (6 limnocorrals), and high clay treatment (6 limnocorrals). Treatment effects on duckweed and *Gambusia holbrooki* are also depicted. Samples were taken 2.5 months after the fish and duckweed were added to the limnocorrals.

already contaminated prior to the start of the experiment. The illite additions, however, effectively reduced contaminant concentrations in both stems and leaves of the water lilies (Figure 3). These results are particularly encouraging because they suggest that the amendment reduced the contaminant in a dominant plant species, in a sense, decontaminated the plants. The reduction was facilitated by *Nymphaea*'s tendency to take up Cs from the water column (*26*), even though it has an extensive root system within the sediments.

Reduced bioavailability of ^{137}Cs occurred further up the food web as well, evidenced by lowered ^{137}Cs concentrations in the fish, *Gambusia*. Two and a half months after their introduction into the treated limnocorrals, *Gambusia* had significantly ($p = 0.02$) lower ^{137}Cs activity concentrations as compared to untreated controls (Figure 3). Activity concentrations appeared consistently lower in fish from the HCA, although values were not statistically different from those in the LCA ($p = 0.08$). This lack of difference in *Gambusia* ^{137}Cs concentrations between the LCA and HCA treatments was probably because both treatments were equally effective at lowering aqueous ^{137}Cs concentrations during the period the *Gambusia* trial took place (1 month after clay treatment; Figure 2).

Environmental Impacts of Applying the Amendment. Water Quality. Immediately after applying the illite treatments, water turbidity increased 2−3 orders of magnitude. Turbidity in both treatments decreased exponentially, with values recorded 1 day after the application being less than one-half the initial values (Figure 1s, Supporting Information). The addition of the illite amendment did not adversely affect water chemistry. No significant differences occurred among controls and treated limnocorrals when sampled at 4 and 18 d post-treatment for pH (7.1 ± 0.03), electrical conductivity (31.5 ± 15.1 μs cm^{-1}), dissolved oxygen (4.9 ± 2.4 mg L^{-1}), or oxidation−reduction potential (383 ± 9 mV). Electrical conductivity values would be expected to decrease if the illites were absorbing ionic solutes from the water column, such as K^+ or NH_4^+. Thus, the clay application is not likely to decrease the availability of essential plant nutrients in treated waters. Indeed, cursory observations suggested that plant biomass was not affected by the treatments.

Longer-term comparisons of water quality were made examining stable element concentrations prior to the start of the experiment and again at week-42. The data corroborate the short-term results and suggest that adding the clay amendments did not significantly alter the water chemistry in the treated limnocorrals. At week-42, there was no apparent difference in stable element concentrations in the water of the control versus clay-amended limnocorrals (Figure 2s, Supporting Information).

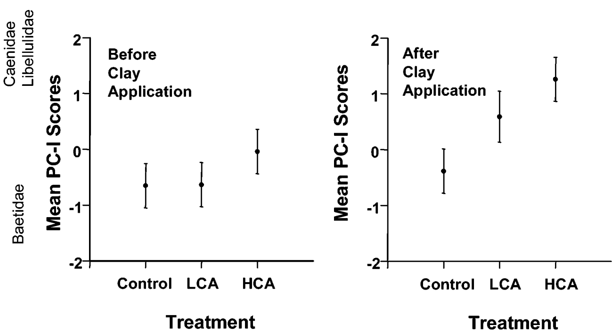

FIGURE 4. Response of PC-I scores to clay treatment. Least squares means saved from ANOVA + 1 standard error. Left panel: Mean scores across treatments before the second clay application; no clay applied (control), low clay application (LCA), and high clay application (HCA). Right panel: Mean scores across treatments after the second clay treatment. Insect families are shown on the *y*-axis of the left panel.

Macroinvertebrate Insects. Macroinvertebrate insects are important components within aquatic food webs and sensitive to ecosystem disturbances, particularly to turbidity and siltation as occurred immediately after the clay amendments were applied. Our analysis examined the macroinvertebrate community structure immediately prior to and after the second clay application (2 years following the first application). The total number of insects was analyzed to compare aquatic insect abundances among treatments; no significant difference ($p > 0.05$) in abundance was found. However, a shift in species composition did occur. Pre- and post-second-treatment macroinvertebrate community structure was analyzed using a principal component analyses (PCA). The analysis produced two components that explained 63% of the variance. Factor loadings listed in Table 1s (Supporting Information) show the correlation of various insect families to the two principal components (PC-I and PC-II). Analysis of variance of the factor scores of PC-I (Table 2s, Supporting Information) confirmed that species assemblages were different before and after the second clay treatment ($p = 0.01$) and also differed among treatments ($p = 0.04$; Figure 4). The response of the insect community was consistent in that not only did the relative abundance of *Caenid* mayflies and *Libellulid* dragonflies increase after the second clay treatment, but this pattern was enhanced in the limnocorrals that received the larger amounts of illite.

The data presented in Figure 4 also show that the insect communities were on a trajectory of recovery from the initial illite treatments applied 2 years prior to the reapplication. Insect community structure in the LCA treatment was similar to the controls, before the second application (Figure 4; left panel), whereas the community structure in the HCA still differed. After the second clay application, the community composition of both low and high treatments diverged further from the controls (Figure 4, right panel).

The initial insect communities within Pond A may have already been indicative of poor quality waters, and the increased turbidity may have had a weaker effect than it would have had on a more pristine area. In undamaged freshwater ecosystems, any given family of insects normally makes up only 3−23% of the total insect community (*27*), whereas control and pretreatment insect samples from our limnocorrals showed that *Chironomidae* and *Coenagrionidae* families already exceeded these percentages. In addition, some taxa of the dominant families (e.g., *Coenagrionidae*) found in the samplers are known to exhibit high tolerances to low water quality, including low dissolved oxygen (*24*).

Changes in composition of algal populations were not examined; however, the lack of impact on dissolved oxygen suggests that algal productivity may not have been seriously impacted. Without changes in algal productivity, the lack of a more severe impact on water quality and insect community becomes less surprising.

The results of this field demonstration are encouraging. This in situ technique is a promising remediation tool that reduces the biological availability of a dominant radioactive contaminant in sensitive aquatic environments at many DOE sites. Reduced biological availability equates to lowered risks. Application of the clay amendment reduced ^{137}Cs levels in water up to 25−30-fold, in aquatic plants 4−5-fold, and in fish 2−3-fold. While ^{137}Cs is bound to the clay amendment, radioactive decay will continually reduce the contaminant concentrations until levels are no longer detectable. An unexpected result was that the clay application caused a decreased ^{137}Cs concentration in aquatic plants whose root systems were well established in contaminated sediments prior to treatment. The treatment essentially decontaminated the plants. Furthermore, there appears to be no adverse effects of illite additions to water chemistry (including pH, dissolved O_2, *Eh*, and essential nutrients). Community level effects on aquatic insect populations were documented, with signs of recovery occurring during the study period. Total costs, including initial site characterization and long-term monitoring post-remediation, were estimated to be 5 times less than traditional “drain and dredge” methods (see Cost Comparison in Supporting Information). The positive attributes of a significant reduction in environmental impacts to the sensitive wetlands, as opposed to draining and dredging, were not included in the costs commutation. Further reductions in environmental impacts could be obtained by staging remediation over time to allow recolonization of biota from untreated areas. This line of research suggests that when remediation of ^{137}Cs contaminated lakes, ponds, and wetlands is warranted (*28*), the in situ technology could provide a valuable alternative to the more environmentally destructive “drain and dredge” approach.

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Supporting Information Available

Additional details on experimental protocols; turbidity and stable element concentrations in water; factor loadings and ANOVA tables from principal components analysis; and details on cost comparison of this method with monitored natural attenuation and “drain and dredge” methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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