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Retention: Permanent

REDUCTION OF CONTAMINANT MOBILITY AT THE TNX OUTFALL DELTA THROUGH THE USE OF APATITE AND ZERO-VALENT IRON AS SOIL AMENDMENTS (U)

Daniel Kaplan, Anna Knox, and Cathy Coffey

SEPTEMBER 27, 2002

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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REVIEWS AND APPROVALS

Daniel I. Kaplan 9/27/02
D. I. Kaplan, Waste Processing Technology Date

Anne S. Knox 9/27/02
A. S. Knox, Waste Processing Technology Date

CP Coffey 9-26-02
C. P. Coffey, Liquid Waste Processing Date

B.T. Butcher 9-27-02
B. T. Butcher, Level 4 Manager, Waste Processing Technology Date

Adrian J Pishko 9-26-02
A. Pishko, Design Check, Waste Processing Technology (SCUREF) Date

WE Stevens 9/30/02
W. E. Stevens, Authorized Derivative Classifier Date

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF APPENDIX TABLES

LIST OF ACRONYMS

AEC	Anion Exchange Capacity
bdl	below detection limit
CEC	Cation Exchange Capacity
COC	Constituent of Concern
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
K_d	Distribution Coefficient
na	not available
SRS	Savannah River Site
TNX OD	TNX Outfall Delta

1.0 EXECUTIVE SUMMARY

The TNX pilot-scale research facility released processed waste, containing high concentrations of several metals and radionuclides into an unlined seepage basin between 1958 and 1980. The contents of this basin have entered the nearby swamp, the TNX Outfall Delta (TNX OD), by subsurface and overland flow. A multi-facetted strategy has been proposed recently for mitigating contaminant migration at the site; it involves:

1) reducing overland flow of drainage, seep, and atmospheric water,
2) permitting a portion of the swamp (the Inner Swamp) to return to its wetter natural state, thereby creating conditions where natural organic matter would build up and the soil would become more chemically reduced, and
3) adding contaminant sequestering soil amendments to the most contaminated portions of the site.

The intent of this remediation strategy is not only to minimize contaminant leaching in a cost-effective manner, but also to minimize harm to the sensitive TNX wetland ecosystem.

The objective of this study was aligned with the third facet of the multi-facetted strategy. Laboratory studies evaluated the effectiveness of adding soil amendments to increase the sequestration of numerous constituents of concern (COC's). The COC's include actinium, arsenic, cobalt, chromium, cesium, mercury, manganese, lead, radium, strontium, thallium, thorium, and uranium.

Two soil amendments were evaluated: zero-valent iron [Fe(0)], apatite, and a combination of both of them. Measurements were made of the COC concentrations in the amended soil leachate and also of how strongly the COC's were retained by the amended soils. The data showed that the simultaneous addition of Fe(0) and apatite to the TNX OD soil greatly stabilized most of the COC's. The amendments increased the K_d values and decreased the potentially leachable fraction (i.e., the source term) for most COC's. One concern was the leaching of As (and possibly Hg) from the apatite itself, however, this potential problem was offset by the addition of Fe(0). A second concern was that thallium showed only a moderate tendency to be retained by apatite and the removal mechanism is likely cation exchange, an ephemeral reaction.

Combined application of the two amendments to the site by surface broadcasting and/or into drilled shallow holes may provide an inexpensive and effective method to reduce the risk of exposure in a cost-effective and environmentally friendly manner for most, if not all, of the COC's.

2.0 INTRODUCTION

The TNX pilot-scale research facility released processed waste into an unlined seepage basin between 1958 and 1980. The basin, referred to as the Old TNX Seepage Basin, was designed to contain wastewater until it could seep into the underlying soils. It was anticipated that the soil would then impede contaminant migration. The waste discharged to the Old TNX Seepage Basin included large quantities of Cr, Hg, Na, U, and Th. The basin contents have entered the nearby inner and outer swamps by subsurface and overland flow; the overland flow is the result of purposely breaching the basin walls and routinely overfilling the basin (Figure 1). Since the basin was closed, contaminant transport is believed to be occurring via two-phase and three-phase (colloid-facilitated) transport in surface water.[1] Among the observations in support of this latter transport mechanism are that: 1) strongly sorbing contaminants are found far from the point source, and 2) high concentrations of strongly sorbing contaminants are found far from the source in sunken depressions, where fine-grain material have accumulated (WSRC 1999). For example, the distribution of soil-Th at the TNX site is >200-m from the point source, i.e., the discharge gully (Figure 2). Traditional two-phase contaminant transport modeling would predict that Th would not travel more than a couple meters from the point source.

A multi-facetted strategy recently proposed for mitigating contaminant migration at the TNX Outfall Delta (TNX OD) involves:

1) reducing overland flow of drainage, seep, and atmospheric water,
2) permitting the Inner Swamp to return to its wetter natural condition, thereby creating conditions where natural organic matter would build up and the soil would become more chemically reduced, and
3) adding contaminant sequestering soil amendments to the most contaminated portions of the site.

The intent of this remediation approach is not only to minimize contaminant leaching in a cost-effective manner, but also to minimize adverse impact to the sensitive TNX wetland ecosystem.

Kaplan (2001) evaluated the second aspect of this remediation approach and concluded that converting the TNX OD site to a wetter, more reduced environment will likely decrease the mobility of Pb, Ra, and U and increase the mobility of Th. It was concluded that by creating a more reducing environment and limiting the amount of overland flow that a large net decrease in overall dissolved radionuclide mobility would be achieved.

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[1] Groundwater contaminant transport is traditionally described as taking place in a two-phase system: a mobile aqueous phase and an immobile solid phase. In a three-phase system, the third phase is a mobile solid phase, or colloidal phase. The net effect of a three-phase system as compared to a two-phase system is that strongly sorbing contaminants, such as actinium, lead, and thorium can move appreciably faster through sediment.

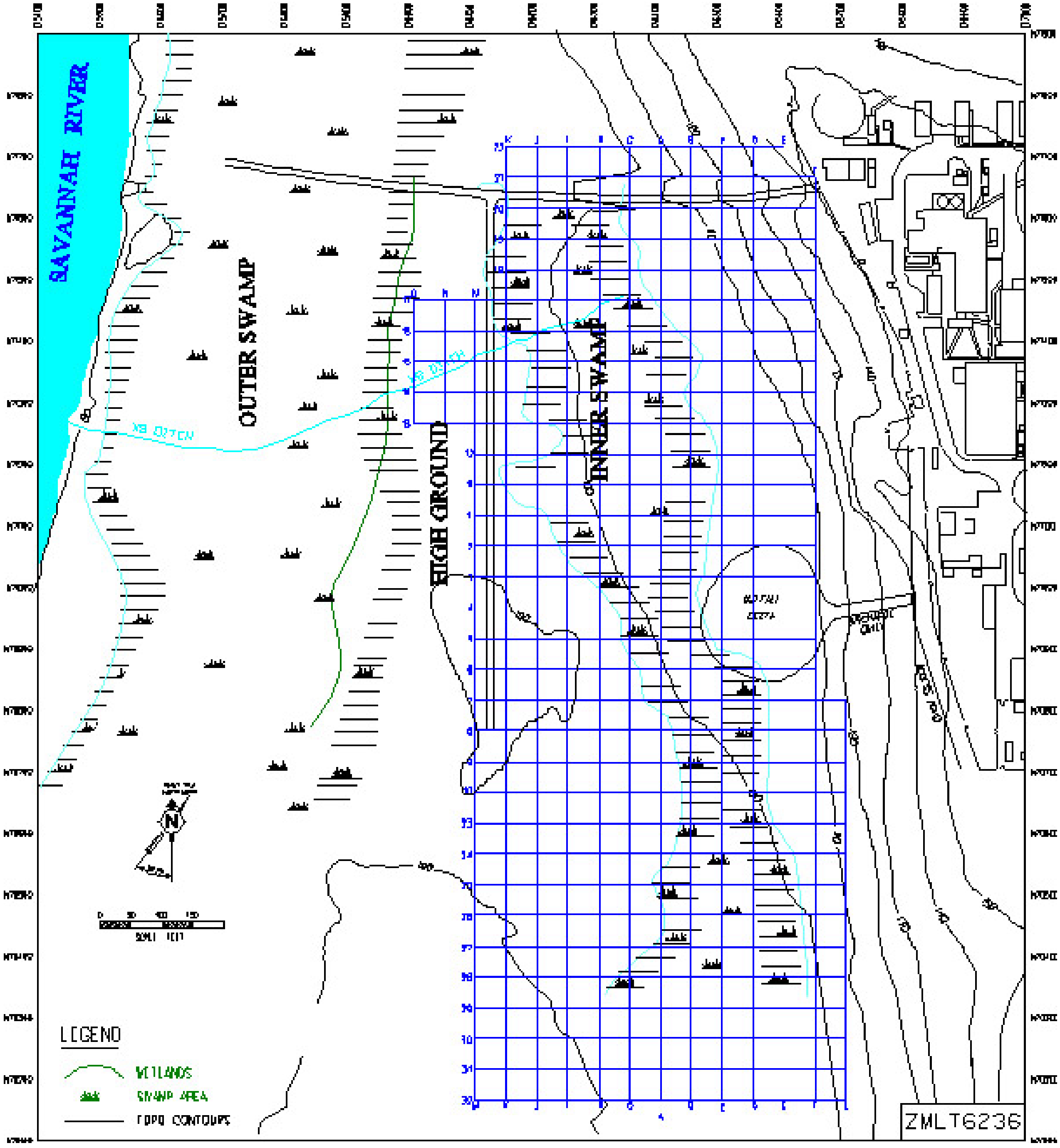

Figure 1. Topographical map of the TNX area showing the Outfall Delta, Inner Swamp, Outer Swamp, Savannah River, and the X8 Drainage Ditch

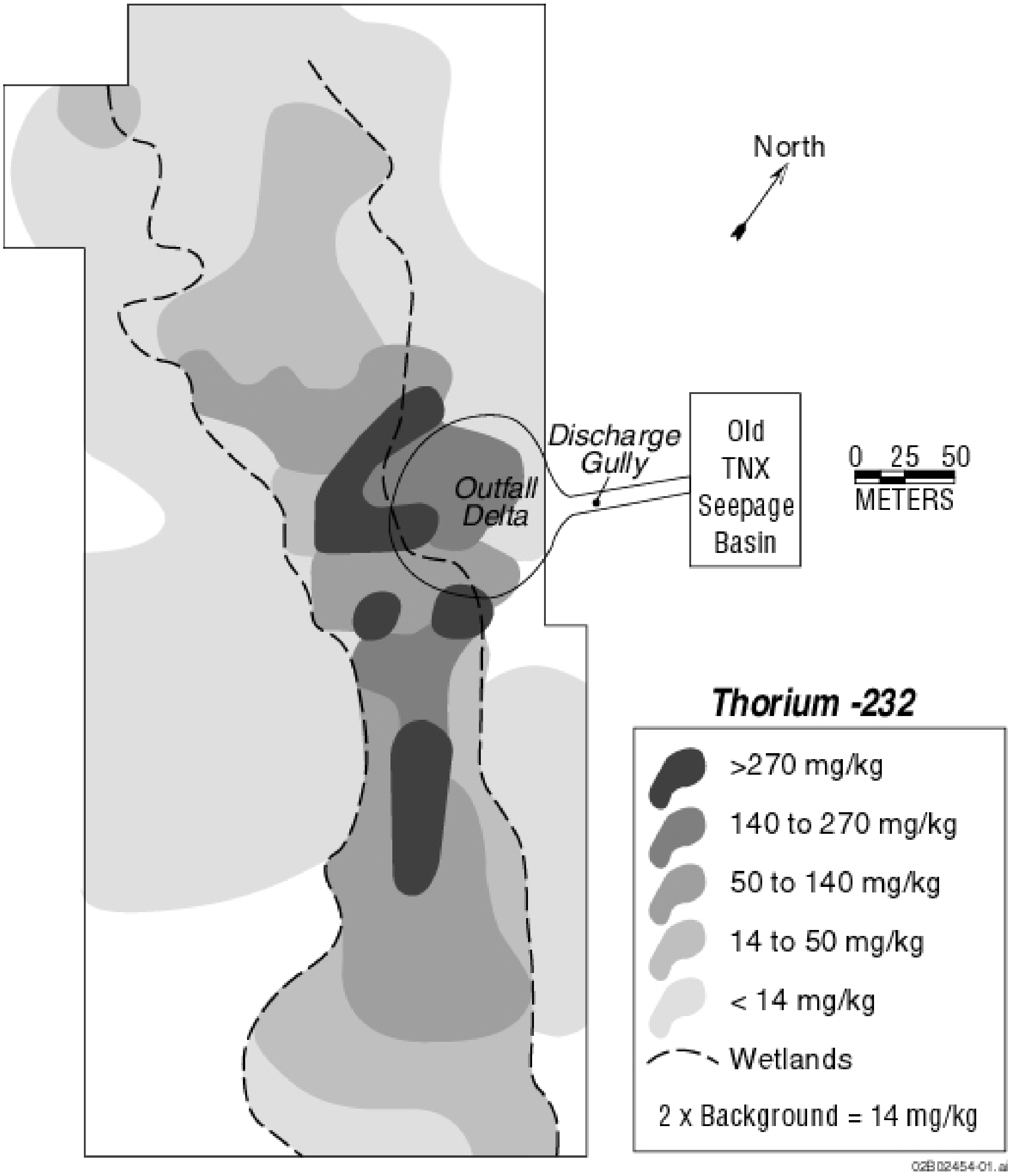

Figure 2. Thorium Concentrations in the Surface Foot of Soil (data from WSRC 1999)

2.1 OBJECTIVE

The objective of this study was to conduct laboratory studies to evaluate the effectiveness of adding soil amendments to increase the sequestration of numerous constituents of concern (COC's). The COC's include Ac, As, Co, Cr, Cs, Hg, Mn, Pb, Ra, Sr, Tc, Tl, Th, and U. There are generally three main classes of soil amendments used to stabilize metal contaminants in soils. They are sulfide sources, phosphate sources, and reducing agents. We elected not to evaluate sulfide sources because one of the key COC's is mercury, and the addition of sulfates to mercury contaminated wetlands has been shown on the A1-Outfall located on the SRS to stimulate the microbiological conversion of elemental mercury to its more mobile and appreciably more hazardous methylated form. The two soil amendments we elected to evaluate were apatite, a calcium-phosphate mineral, and zero-valent iron, Fe(0). Apatite is a common subsurface and surface soil amendment for metal immobilization (reviewed at www.pimsnw.com), whereas Fe(0) is not as commonly used for surface soil applications as it is for subsurface permeable reactive barriers.

An additional objective of this study was to determine whether soil redox conditions would influence the sorption of the COC's by the soil amendments. The concern was whether the soil amendments were equally effective under constantly flooded and wet/dry cycled conditions. The TNX OD contains both types of conditions.

2.2 MECHANISMS BY WHICH APATITE AND Fe(0) REMOVE CONTAMINANTS FROM THE AQUEOUS PHASE

Apatite removes solutes from the aqueous phase through three mechanisms: cation/anion exchange, isomorphic substitution, and precipitation. An example of the removal of lead via cation exchange onto apatite is presented in Equation 1:

$$Ca_{10}(PO_4)_6(OH)_2\mathit{(s)} + x\mathrm{Pb}^{2+}\mathit{(aq)} \rightarrow Ca_{10-x}Pb_x(PO_4)_6(OH)_2\mathit{(s)} + x\mathrm{Ca}^{2+}\mathit{(aq)}. \qquad (1)$$

This removal mechanism is the least desirable from the standpoint of soil stabilization because the bond between the contaminant and the apatite is relatively weak.

Isomorphic substitution is a process in which the contaminant substitutes for a calcium, phosphate, or hydroxide in the apatite structure. This removal mechanism is highly desirable because the contaminant becomes incorporated into the structure of the apatite. Isomorphic substitution is very common in apatite because its crystalline structure is very flexible, therefore several different elements can substitute into it. Calcium exists in apatite in 7-fold and 9-fold coordination. The 7-fold coordinated Ca ions are about 10% smaller than the 9-fold coordinated ions. This difference in atomic size permits a rather large range of contaminants to substitute for Ca, including the following COC's: Sr, Ra, Pb, Cs, Th, U(VI), and Cr(VI) (Deer et al. 1975). Elements that can substitute for phosphate (0.254 nm radius) include TcO_4^- (0.268 nm) and CO_3^{2-} (0.211 nm). Finally, the hydroxyl anion (0.153 nm) can be substituted with Br^- (0.196 nm), Cl^- (0.181 nm) and F^- (0.136 nm).

Concentrations of element impurities in natural apatite samples that were not impacted by contaminants are presented in Table 1. Previous studies have shown that biogenic apatite, while still associated with the living animal, contains very low concentrations of transition metals and actinides (Wright 1990). After deposition onto or into soils biogenic apatite (i.e., bone material) incorporates trace elements at concentration levels that are enriched by one to many orders of magnitude over the levels in the surrounding aqueous solutions (Wright 1990). This comparison of biogenic apatite *in vivo* to biogenic apatite exposed to natural water illustrates that apatite can act as a filter to retard the migration of trace elements in aqueous solution.

Table 1. COC Concentrations in Naturally Occurring Apatite that were Unimpacted by Contamination (Deer et al. 1975)

	Concentration in Apatite (mg/kg)
Sr	190,000
Ce	1840
Pb	200
Cs	6
Th	117
U	227
Cr	760
CO_3^{2-}	300,000

The third mechanism by which apatite removes contaminants from the aqueous phase is by first dissolution (Equation 2), followed by formation of a precipitate with a metal (Equation 3)

$$Ca_{10}(PO_4)_6(OH)_2(s) + 14H^+(aq) \rightarrow 10Ca^{2+}(aq) + 6H_2PO_4^-(aq) + 2H_2O(aq) \qquad (2)$$

$$10M^{2+}(aq) + 6H_2PO_4^-(aq) + 2H_2O(aq) \rightarrow M_{10}(PO_4)_6(OH)_2(s) + 14H^+(aq) \qquad (3)$$

where M^{2+} represents a divalent cation. Phosphate-metal precipitates are typically very stable (Table 2). Another important mechanism by which apatite induces precipitation of metals is through the formation of carbonate phases. As Equation 2 shows, apatite dissolution results in an increased pH, which in turn promotes an increase in carbonate concentrations. These carbonates can form precipitates with several metals. In almost all cases though, carbonate precipitates are more soluble than phosphate precipitates.

Table 2. Solubilities of Some Metal-Phosphate Phases

Mineral Phase	Solubility Product (log K_{sp})
$Pb_5(PO_4)_3(OH,Cl)$	-76.5
$Sr_5(PO_4)_3(OH)$	-51.3
$Zn_3(PO_4)_3$	-35.3
$Cd_3(PO_4)_3$	-32.6
$Pu(PO_4)$	-24.4
Quartz (SiO_2)	-4

The final soil amendment evaluated in this study was Fe(0). Fe(0) removes metals from the aqueous phase by three primary processes: reductive precipitation (by Fe(0) or Fe(II)), coprecipitation with Fe(II/III), and metal sorption by Fe(0)-originating, Fe(II/III)-oxyhydroxides. Reductive precipitation involves the transfer of electrons from Fe(0) to a COC that is less soluble in the reduced from than in the oxidized form. Common contaminants that can be removed from the aqueous phase in this manner are As, Cr, Hg, Mo, Se, Tc, and U. For example, the reductive precipitation of Cr(VI) can be described by Equation 4:

$$CrO_4^{2-}\textit{(aq)} + 1.5Fe^0\textit{(s)} + 5H^+\textit{(aq)} = Cr(OH)_3\textit{(s)} + H_2O\textit{(aq)} + 1.5Fe^{2+}\textit{(aq)}. \qquad (4)$$

In this example, CrO_4^{2-} is both more mobile and toxic than $Cr(OH)_3$, which is a solid phase.

As Equation 4 shows, Fe^{2+} is produced and acidity (H^+) is consumed. Both of these changes are conducive to the formation of Fe(II/III)-oxyhydroxides. If other metals are present, they may coprecipitate with the Fe(II/III)-oxyhydroxide. Chrome removal by Fe(0) is believed to be primarily through this reaction, whereby $Cr/Fe(OH)_3$ solid solutions are formed (Eary and Rai 1987, Sass and Rai 1987).

Fe(0) can remove aqueous contaminants by first oxidizing to form Fe(II/III)-oxyhydroxides, which then can act as an adsorbent. The Fe(II/III)-oxyhydroxides increase the sorption capacity of the system. Contaminant removal in this manner is the least desirable of the three removal mechanisms due to the weak nature of the bond between the contaminant and the Fe(II/III)-oxyhydroxide.

3.0 MATERIALS AND METHODS

A detailed description of the laboratory procedure used in this study is presented in Appendix B: Work Instructions for The Laboratory Study. The following is a brief synopsis.

3.1 MATERIALS

The sediment used in this study came from coordinate B-5 in the TNX OD study site (Figure 1). This sediment was used because it had relatively high contaminant concentrations, yet, based on analytical results, was not classified as either hazardous or radioactive. The sediment sample was collected from the top 15 cm, but did not include the surface organic mat, i.e., the O soil horizon. Granular Fe(0) (Peerless Supply, Columbus, OH) and two forms of apatite were used as sediment amendments. One of the apatite minerals, Apatite-NC, came from a mine in North Carolina (Texas Gulf Mining, Aurora, NC). The second apatite, Apatite-II, is of a biogenic origin: ground fish bones (www.pimsnw.com; PIMS-NW, Richland, WA). Both forms of apatite have been used at several metal-contaminated remediation sites. However, these forms of apatite differ significantly. Apatite-II is appreciably more soluble and therefore would be effective for immediately stabilizing contaminants at a site. Additionally, Apatite-II has much lower concentrations of impurities that may potentially leach into the surrounding groundwater. Apatite-II has only recently been made commercially available, but it has been field tested at a number of sites, including:

- Success Mine, ID (Zn, Pb, and Cd)
- Oak Ridge National Laboratory, TN (U and NO_3^-)
- Camp Stanley, TX (Pb)
- Los Alamos National Laboratory, NM (U)
- Los Alamos National Laboratory, NM (Pu, Am and NO_3^-), and
- Independence Mine (Zn, Pb, and Cd).

The water used in this study was collected from a surface stream located ~1000 m north of the northern boundary of the operable unit. The water was passed through a 0.45-µm filter and stored at 4 °C when not in use.

3.2 METHODS

3.2.1 Laboratory

The experimental design was a randomized block design with 3 replicates, 4 amendments (control, Fe(0), Apatite-NC, and Fe(0) + Apatite-NC) and 2 moisture conditions (flooded and wet/dry-cycled, to simulate cyclic rain events), for a total of 24 treatments. For the flooded treatments, 15-g of B-5 sediment, 0.5-g of appropriate amendment (1-g total for the Fe(0) +

Apatite-NC treatment), and 25-mL of uncontaminated surface water (collected from just north of the study site) were added to 50-mL tubes. The tubes were left on a platform shaker for 7 weeks before separating the solids and liquids for chemical characterization.

For the wet/dry-cycled treatments, 12 disposable filtration units were used. These 115-mL Plexiglas containers consisted of two chambers separated by a 0.45-µm filter membrane. 15-g of sediment and 0.5-g of amendment were mixed and then placed on the filter. 25-mL of the uncontaminated surface water was added on the Friday of each week. Most of the water would remain above the filter until the following Monday, when it was suction vacuumed down through the filter. Twice a day between Monday and Friday, the sediments were mixed with a spatula to facilitate sediment drying. Generally, the sediments were completely air dried by Wednesday. On the next Friday, the leachate would be poured into a 25-mL graduated column and brought up to volume using uncontaminated surface water. Typically, 7-mL of water was required to bring the volume up to 25-mL. This 25-mL solution would then be poured onto the amended sediment. The one-week wet/dry cycle was repeated six times before terminating the experiment by collecting the aqueous phase from the lower chamber of the filtration unit and permitting the sediment to air dry on the filter.

On the day the experiment was terminated, pH, Eh (a measure of the redox status), dissolved O_2, and electrical conductivity (a measure of the total concentration of ions in solution) were measured in the solutions. The solutions were then acidified and analyzed for cations by ICP-MS and ICP-AES. ICP-MS was used to measure As, Co, Cr, Hg, Sr, Th, and U, as several ancillary parameters. ICP-AES was used to measure Mn and Fe, and several ancillary parameters. Of the COC's, only Ac, Ra, and Tl were below detection limit. For these COC's the geochemical behavior of Ce, Ba, and K were monitored and used as analogs for Ac, Ra, and Tl, respectively.

The sediments from the flooded treatments were subjected to a sequential extraction procedure. The details of this procedure are included in Appendix B. Briefly, a subsample of the treated sediments was extracted by a series of solutions that targeted operationally defined contaminant fractions. The extracts were increasingly aggressive at removing contaminants. The resulting five fractions were the exchangeable, amorphous Fe-oxide, organic/sulfide, crystalline Fe-oxide, and structural fractions. A description of what these fractions constitute and the details of the procedure are provided in Tessier et al. (1979) and Hall et al. (1996). The resulting extract solutions were acidified for sample preservation and characterized by ICP-MS and ICP-AES.

3.2.2 Statistics

There were two types of statistics used in this study. The first was the *t*-test to compare two treatment means. The second was Dunett's test to compare all treatment means with a control (Winer 1971). Briefly, there are k treatments, and $k - 1$ comparisons with the Control. Rather than setting a level of significance equal to α for each of the tests, this test sets a level equal to α for the collection of the $k - 1$ decisions, considered as a single decision summarizing the outcomes. Since each of the tests uses the same information on the control condition and a common estimate of experimental error, the tests are not independent. What this means is that the variance of all the means are pooled together. Dunett's test is also a two-tailed test, meaning that it will identify means that are significantly greater and smaller than the control.

3.2.3 Sample Analysis and Quality Assurance

All work conducted in this study followed Standard QA practices described in the WSRC QA Manual 1Q. Eh, pH, electrical conductivity, dissolved O_2, and all sediment characterization measurements were made by SRTC personnel following standard procedures described in detail by Sparks (1996). Blanks and spikes were included where technically appropriate (e.g., there is no blank control for a pH measurement). ICP-MS, ICP-AES, and total inorganic and total organic C analyses were conducted by the Chemical Analysis Laboratory, University of Georgia. This EPA-certified lab provided us with the results of blank and spike controls. Data that were outside of EPA guidelines are not included in this report. There were analytical interferences with some of the ICP-MS Hg data and instrument problems with the ICP-AES Mg data; none of these compromised data are included in the report.

The lab notebook used for this study is WSRC-NB-2001-00133.

4.0 RESULTS AND DISCUSSION

4.1 GROUNDWATER, SEDIMENT, AND SEDIMENT AMENDMENT CHARACTERIZATION

The chemical composition of the surface water used through out this study is presented in Table 3. The acidity and high organic C concentration is characteristic of wetland surface waters. The water contains low concentrations of all the COC's.

Chemical and physical characterization of the B-5 sediment used in this study is presented in Table 4. The textural analysis (sand-silt-clay) indicates that it's a loamy sand. Its low pH, 4.53, and high organic matter content, 1427 mg/kg, are typical of wetland sediments of this area. For purposes of comparison, some elemental concentration data of a background sediment collected just north of the operable unit are included in the table. Among the COC's that are appreciably greater than the background are As, Co, Cr, Hg, Pb, and Th. The U concentration in the B-5 sediment was surprisingly low, essentially the same as in the background sediment.

The Fe(0) contained especially high concentrations of As, Co, Cr, and Cu. It is important to note that some portion of these elements may be leachable, their fate in leach tests must be monitored, the subject of Sections 4.3 and 4.4.

There were two sources of apatite used in this study. Initially, only the mined Apatite-NC was used. But once the elemental data in Table 4 became available, revealing that it contained extremely high concentrations of As, Cr, Hg, Pb, Sr, and U, a second biogenic source of apatite,

Apatite II, was included in the experiment. As expected the Apatite-II generally contained appreciably lower concentrations of the COC's than the Apatite-NC.

The Sr reported in Table 4 is the stable isotope, not the radioactive isotopes; thus, its high concentration in the Apatite-II is not, in itself, of great concern. The same is in principal true of the U concentrations reported in Table 4 (stable ^{238}U accounts for >99% of the naturally occurring U). Although these are not the isotopes of concern, their elevated concentrations may have some adverse effects on the targeted isotopes. For example, they may promote ion exchange, thereby enhancing the desorption of the higher risk isotope.

High concentrations of COC in the Apatite-NC were expected because it is well known that these elements become concentrated into the structure of the apatite mineral (see review presented in Section 2.2). Metal concentration in apatite is the very mechanism that this technology attempts to capitalize on. So in a sense, this data provides part of the data required for a natural analog study that shows that the COC's can be concentrated in the minerals to levels several orders of magnitude greater than that in the uncontaminated natural waters surrounding it. The second part of a natural analog study would need to show whether these COC's remain strongly associated to the apatite. This will be discussed later in the report in association with sequential extraction data of the Apatite-NC (Section 4.5), and leachate COC data from the Apatite-NC (Sections 4.2 and 4.3).

Table 3. Chemical Composition of Uncontaminated Surface Water Collected from Near the TNXOD Operable Unit

Constituent	Concentration (µg/L)	Concentration (mM)	Constituent	Concentration (µg/L)	Concentration (mM)
pH	5.1 (unitless)		Na	357.28	0.016
Al	9.12	0.00034	Ni	1.29	2.2E-05
As	<0.18		Se	<0.61	<0.0013
Ba	64.87	0.0005	Si	4395	0.1565
Ca	3850	0.0962	Sm	0.026	1.74E-07
Ce	0.087	6.2E-07	Sr	33.98	0.00039
Co	0.065	1.1E-06	Th	0.013	5.69E-08
Cr	<0.92		Tl	0.055	2.69E-07
Cs	0.052	3.9E-07	U	<0.01	<4.20E-04
Cu	<0.13		Zn	12.53	0.00019
Eu	0.016	1E-07	Chloride	2061	0.0598
Fe	99.3662	0.00178	Nitrate	186	0.003
Hg	0.076	3.8E-07	Phosphate	<100	<0.0011
K	229.15	0.0058	Nitrite	<100	<0.022
La	0.056	4E-07	Sulfate	13690	0.214
Li	0.55	7.9E-05	Inorganic C	<100	<0.0083
Mg	1117.89	0.046	Organic C	6051	0.504
Mn	57.9	0.001	Summation of Cations		0.325
			Summation of Anions		0.277

Surface water sample collected about 1000 m north of the northern boundary of the operable unit.

Table 4. Sediment and Sediment Amendment Properties

	Units	B-5 Sediment	Background (a)	Apatite-NC	Apatite-II	Metallic Fe	Instrument or Method(b)
As	µg/kg	9221	1520	29396	1078	6155	ICP-MS
Ba	µg/kg	147711	21970	20416	9235	1843	ICP-MS
Cd	µg/kg	na(c)	24830	na	200	380	ICP-MS
Ce	µg/kg	na	4850	na	17	209	ICP-MS
Co	µg/kg	3664	663	897	36	3459	ICP-MS
Cr	µg/kg	38459	2820	76275	166	72956	ICP-MS
Cu	µg/kg	na	2190	na(b)	4859	117632	ICP-MS
Eu	µg/kg	981	na	789	bdl	bdl	ICP-MS
Hg	µg/kg	3507	22	5320	298	229	ICP-MS
Pb	µg/kg	35338	12191	17634	398	1292	ICP-MS
Sr	µg/kg	na	1460	508	40905	1840	ICP-MS
Th	µg/kg	11501	2320	844	bdl	bdl	ICP-MS
U	µg/kg	2663	3780	62103	407	bdl	ICP-MS
Al	mg/kg	2620	1915	1382	8	5	ICP-AES
Ca	mg/kg	na	78.9	>103443	>123069	905	ICP-AES
Fe	mg/kg	16673	889	2627	28	88963	ICP-AES
K	mg/kg	646	87	341	1928	bdl	ICP-AES
Mn	mg/kg	135	84	17	bdl	436	ICP-AES
Mg	mg/kg	na	75	1851	37480	681	ICP-AES
Na	mg/kg	na	25	4831	8722	221	ICP-AES
P	mg/kg	606	787	>101013	>163823	1307	ICP-AES
Se	mg/kg	357	212	156	215	220	ICP-AES
pH	unitless	4.53	4.16	7.93	na	na	1:1 Solid/Liq
Sand-Silt-Clay	wt-%	82-13-5	80-14-6	98-2-0	na	68-32-0	Pipette
Organic C	mg/kg	1427	1395	na	na	na	Wet digestion
CEC	$\text{cmol}_{(+)}$/kg	7.33	4.75	na	na	na	K^+ exchange
AEC	$\text{cmol}_{(-)}$/kg	1.11	1.56	na	na	na	NO_3^- exchange
Fe-oxides	% Fe_2O_3	0.09	na	na	na	na	Dithionite digestable

(a) Kaplan et al. (2000), Sediment 101 is a surface sediment collect just north of the operable unit.

(b) Elemental composition was determined by first digesting in concentrated H_2SO_4, HNO_3, and HCl solution using the Star 6 System® and then the digest was analyzed by ICP-MS and ICP-AES; pH by sediment/water equilibration (Thomas 1996); Organic C by unheated potassium dichromate method (Nelson and Sommers 1996; Cation exchange capacity (CEC) and anion exchange capacity (AEC) were determined by exchange with K and NO_3^- ions on sediments with were not pH adjusted (Sumner and Miller 1996); Particle size distribution, sand-silt-clay, by the micropipette method (Miller and Miller 1987).

(c) na = not analyzed; bdl = below detection limit

4.2 PORE WATER CHEMISTRY OF THE FLOODED AND THE WET/DRY-CYCLED CONTROL TREATMENTS

As mentioned in the Material and Methods section, the experimental design of this study was:

> [4 sediment amendments (Control, Apatite-NC, Apatite-NC + Fe(0), Fe(0)) x 2 moisture regimes (Flooded, Wet/Dry cycled) x 3 replicates] + [1 sediment amendment (Apatite-II) x 1 moisture regime (Flooded) x 3 replicates].

The Apatite-II treatments were added later to the study.

Pore water chemistry of the control treatments (the treatments that did not receive any sediment amendment) will be discussed in this section. In addition to presenting the COC's concentration, a number of ancillary aqueous chemistry parameters will also be presented. These parameters provide important insight into the likely mechanisms by which the COC's are removed from the aqueous phase.

The pore waters from the Flooded and the Wet/Dry-Cycled treatments differed significantly. Comparing the controls, the Flooded samples had significantly lower Eh and dissolved O_2 levels, and higher pH and electrical conductivity levels (Table 5). These are rather profound differences and are surprising given that the only difference between them is the duration that the pore water was in contact with the sediment. It underscores the importance of including the moisture regime variable in the test, because both saturated and intermittently saturated sediments are likely to exist at the site. The Flooded treatment generally had higher ancillary constituent (Table 6) and COC (Table 7) pore water concentrations than the Wet/Dry-Cycled treatment. The longer contact time between the surface water and the sediment in the Flooded treatments permitted more chemical changes to occur, including reduction and COC desorption. Both reactions would generally result in greater elemental pore water concentrations.

Table 5. Comparison of the Pore Water Chemistry for the Flooded and the Wet/Dry-Cycled Control Treatments: Eh, O_2, pH, and Electrical Conductivity

		Eh (mV)	O_2 (ppm)	pH	Conductivity (μS/cm)
Control - Flooded	avg	-145	0.10	5.8 *	505 *
	(stdev)	(23)	(0.06)	(0.2)	(16)
Control - Wet/Dry	avg	287 *	5.5 *	4.5	263
	(stdev)	(11)	(0.5)	(0.1)	(16)

* Indicates a significantly greater mean ($P \leq 0.05$) between the Flooded and Wet/Dry Cycled Treatments.

Table 6. Comparison of the Pore Water Chemistry for the Flooded and the Wet/Dry Cycled Control Treatments: Ancillary Constituent

		Al (ppb)	Ca (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	P (ppm)	Se (ppm)	TIC (ppm)	TOC (ppm)
Control - Flooded	avg	233.83	12.44 *	177.10 *	7.39 *	5.42 *	36.26	1.42	0.46	11.56	240.24 *
	(stdev)	(26.20)	(1.35)	(35.98)	(1.01)	(1.14)	(14.60)	(0.30)	(0.29)	(0.00)	(24.04)
Control - Wet/Dry	avg	306.92 *	4.02	4.11	1.76	0.88	36.84	0.45	0.10	9.83	118.00
	(stdev)	(17.32)	(2.07)	(0.99)	(0.44)	(0.24)	(7.15)	(0.19)	(0.05)	(0.34)	(0.07)

* Indicates a significantly greater mean (P ≤ 0.05) between the Flooded and Wet/Dry Cycled Treatments.

Table 7. Comparison of the Pore Water Chemistry for the Flooded and the Wet/Dry Cycled Control Treatments: Constituents-of-Concern

		As (ppb)	Ba (ppb)	Ce (ppb)	Co (ppb)	Cr (ppb)	K (ppm)	Hg (ppb)	Pb (ppb)	Sr (ppb)	Th (ppb)	U (ppb)
Control - Flooded	avg	18.56 *	462.16 *	49.43 *	20.69	2.83	20.27	AI	7.39 *	122.05 *	15.19	1.85
	(stdev)	(2.72)	(37.77)	(20.81)	(7.14)	(0.75)	(15.93)		(0.67)	(20.23)	(13.51)	(1.19)
Control - Wet/Dry	avg	0.98	106.07	17.53	8.70	2.06	6.76	3.16	1.78	32.52	0.79	0.41
	(stdev)	(0.03)	(34.54)	(1.04)	(3.75)	(0.31)	(2.47)	(3.53)	(0.05)	(2.32)	(0.20)	(0.10)

[a] Ba is used here as an analog for Ra; Ce for Ac; K for Tl.

[b] AI = Analytical Interference

* Indicate a significantly greater mean (P ≤ 0.05) between the Flooded and Wet/Dry Cycled Treatments.

4.3 PORE WATER CHEMISTRY OF THE FLOODED TREATMENTS

For the Flooded treatments, the redox status of the Fe(0), Apatite-NC, and Apatite-NC + Fe(0) treatments were significantly lower than in the Control (Table 8). The Fe(0) lowered the redox status directly through inorganic reduction and indirectly by promoting microbial growth of iron reducing bacteria. Phosphate from the Apatite-NC may have stimulated microbial growth, which in turn may have lowered the redox status. It is not known why the Apatite II did not have any significant effect on the Eh. In fact, the higher solubility of the Apatite-II would lead one to anticipate that it would produce a greater lowering of the Eh than the apatite-NC.

The increase in pH associated with both apatites and the Fe(0) additions can be attributed to the inverse relation that pH and Eh have in sediments, and more directly to the proton consuming nature of the dissolution of apatite in water (Equation 2) and the oxidation of Fe(0) (Equation 4). Furthermore, both apatite minerals likely contain a fair bit of calcium carbonate impurities, which would tend to raise the pH of the system. The elevated electrical conductivity associated with all treatments is the result of a number of geochemical processes including: the dissolution of the apatite and Fe(0), the dissolution of Fe-oxides, and release of species sorbed to the dissolved Fe-oxides. The extremely high electrical conductivity of the Apatite II pore water is indicative of the soluble nature and the large number of salts associated with this material.

Table 8. Water Chemistry of the Flooded Treatments: Eh, O_2, pH and Electrical Conductivity

		Eh (mV)	O_2 (mg/L)	pH	Electrical Conductivity (µS/cm)
Control	avg	-145.3	0.10	5.79	505.0
	(stdev)	(23.4)	(0.06)	(0.22)	(15.6)
Apatite-NC	avg	-175.9 *	0.04	6.63 *	605.3 *
	(stdev)	(3.0)	(0.01)	(0.10)	(19.1)
Apatite-NC + Fe(0)	avg	-185.5 *	0.06	6.69 *	571.3 *
	(stdev)	(2.5)	(0.01)	(0.04)	(17.8)
Fe(0)	avg	-173.3 *	0.11	6.29 *	449.3 *
	(stdev)	(5.5)	(0.11)	(0.03)	(13.6)
Apatite II	avg	-111.57	na	6.65 *	1785.0 *
	(stdev)	(3.01)	na	(0.07)	(106)

"*" identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.
na – not available

The sediment amendments produced significant changes to a number of ancillary parameters, as compared to the unamended treatment (Table 10). Most notable of these differences are those associated with the Apatite-II. The concentrations of Ca, Na, total inorganic C, and total organic

C were much greater than in the Control treatment. This is consistent with the extremely large electrical conductivity value for this treatment (Table 8). Phosphorus pore water concentrations in the Apatite-II, but not in the Apatite-NC, treatment were significantly greater than in the Flooded Control. The significant decrease in Al concentrations for all sediment amendments is due to the concomitant increase in pH (Table 8), which tends to promote Al hydrolysis and precipitation.

Regarding the COC's, the Apatite-NC pore water concentrations of Ba (an analog for Ra), Ce (an analogue for Ac), Co, K (an analog for Tl), and Pb were significantly lower than the Flooded Control (Table 11). The Fe(0) pore water concentrations of As, Ba, Co, Ce, and Pb were significantly lower than the Flooded Control. The Apatite-NC + Fe(0) treatment pore water concentrations of As, Ba, Ce, Co, K, and Pb were lower than the Control. This list suggests that the benefit of combining both sediment amendments into the same treatment is essentially the sum of the benefits from adding each of the amendments individually. The Apatite-II significantly reduced the pore water concentrations of Ba, Ce, and Pb.

These sediment amendments also produced some adverse affects on the pore water chemistry. Both apatite treatments caused significant increases in the amount of As and Sr. The As could have been released from the apatite or it may have been desorbed from the sediment as a result of elevated phosphate concentrations caused by the dissolution of the apatite. The elevated Sr concentration is likely the result of Sr being released from the apatite and Sr being exchanged from the sediment surface sites as a result of elevated concentrations of both Sr and Ca. It is important to keep in mind that the Sr reported here is stable Sr and the Sr of interest is ^{90}Sr. The apatite amendments will only contain stable Sr, thus the only potential detrimental affect of adding apatite to a ^{90}Sr-contaminated sediment is that it would promote the exchange of adsorbed ^{90}Sr (and would not increase the ^{90}Sr concentration as a result of release from the mineral).

By combining Fe(0) with Apatite-NC, the increased As concentrations that originated from the Apatite-NC were lowered (Table 11). Fe(0) is known to be very effective at removing As from the aqueous phase (Melitas et al. 2002; Appelo et al. 2002). By including Fe(0) with the Apatite-NC, the elevated Sr pore water concentration originating from the Apatite-NC was not lowered.

The Apatite-II pore water contained appreciably more Co and K than the Flooded Control. The K is not a problem in itself, but may have the undesirable effect of promoting the exchange of Tl^+ and Cs^+ from the sediment surface. The Apatite-NC did not elevate pore water K concentrations.

Two of the most important risk drivers at the TNX OD site are Th and U. Unfortunately, the pore water concentrations of both COC's were very low, almost at detection limits. These low concentrations were observed in previous studies of TNX OD sediment pore waters and were attributed to their strong sorbing tendency (Kaplan and Serkiz 2000). The low concentrations reduced our ability to detect significant differences between the various treatments and also provided additional data to support the notion that Th and U are indeed strongly associated with the sediment. Apatite is known to be able to remove U from the aqueous phase and maintain its concentration below drinking water limits (Bostick et al. 1999, Conca et al. 2000, Fuller et al. 2002, Rakovan et al. 2002).

4.4 PORE WATER CHEMISTRY OF THE WET/DRY-CYCLED TREATMENTS

The influences of the sediment amendments on pore water chemistry of the Wet/Dry-Cycled treatments (Table 9) were not nearly as large as they were in the Flooded treatments (Table 5). However, many significant differences were detected between the amendment treatments and the Wet/Dry-Cycled Control treatment. Surprisingly, the Apatite-NC treatment tended to cause the Eh to decrease more than the Fe(0). As was the case with the Flooded treatments, all the amendments tended to increase the pH of the Wet/Dry-Cycled treatments.

Table 9. Ancillary Constituent Pore Water Concentrations in the Wet/Dry Cycled Treatments: Eh, O_2, pH and Electrical Conductivity

		Eh (mV)	O_2 (mg/L)	pH	Electrical Conductivity (μS/cm)
Control	avg	286.5	5.52	4.46	263.3
	(stdev)	(11.3)	(0.47)	(0.11)	(15.5)
Apatite-NC	avg	214.4 *	4.29 *	5.20 *	488.3 *
	(stdev)	(10.5)	(0.19)	(0.15)	(77.7)
Apatite-NC + Fe(0)	avg	193.4 *	3.32 *	5.67 *	328.3
	(stdev)	(9.1)	(0.14)	(0.16)	(7.1)
Fe(0)	avg	230.1	3.47 *	5.29 *	190.7
	(stdev)	(53.0)	(0.16)	(0.09)	(18.0)

"*" identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

The concentrations of the elemental ancillary constituents in the Wet/Dry-Cycled treatments (Table 12) followed similar, but less dramatic, trends as in the Flooded treatments (Table 6). The constituent levels in the Fe(0) pore water differed very little from those in the control. In contrast, most of the ancillary parameters in the Apatite-NC pore water differed with those in the Control.

Table 10. Pore Water Chemical Concentrations of Ancillary Parameters in the Flooded Treatments

		Al (ppb)	Ca (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	P (ppm)	Se (ppm)	TIC (ppm)	TOC (ppm)
Control	avg	233.83	12.44	177.10	7.39	5.42	36.26	1.42	0.46	11.56	240.24
	(stdev)	(26.20)	(1.35)	(35.98)	(1.01)	(1.14)	(14.60)	(0.30)	(0.29)	(0.00)	(24.04)
Apatite-NC	avg	67.58 *	75.51 *	118.00	10.55 *	3.66 *	28.41	1.23	0.72 *	12.77	166.0 *
	(stdev)	(6.54)	(4.00)	(7.89)	(0.57)	(0.21)	(1.78)	(0.04)	(0.01)	(1.17)	(19.4)
Apatite-NC + Fe(0)	avg	55.16 *	63.72 *	125.23	11.21 *	4.72	27.04	1.22	0.69	10.78	245.7
	(stdev)	(5.06)	(5.76)	(11.61)	(0.35)	(0.24)	(0.57)	(0.17)	(0.07)	(0.08)	(3.9)
Fe(0)	avg	46.29 *	15.08	171.77	8.81	6.51	24.60	1.34	0.51	10.41	253.6 *
	(stdev)	(7.58)	(0.38)	(9.52)	(0.22)	(0.57)	(1.34)	(0.01)	(0.06)	(0.13)	(5.4)
Apatite-II	Avg	29.52 *	321.77 *	214.47 *	AI	2.26 *	210.10 *	3.38 *	1.75	26.38 *	1653 *
	(stdev)	(4.16)	(8.55)	(4.5)		(0.08)	(60.27)	(0.03)	(0.03)	(2.48)	(89)

* identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

Table 11. Constituent-of-Concern Concentrations in the Pore Water of the Flooded Treatments

		As (ppm	Ba(a) (ppb)	Ce(a) (ppb)	Co (ppb)	Cr (ppb)	K(a) (ppm)	Hg (ppb)	Pb (ppb)	Sr (ppb)	Th (ppb)	U (ppb)
Control	avg	18.56	462.16	49.43	20.69	2.83	20.27	AI	7.39	122.05	15.19	1.85
	(stdev)	(2.72)	(37.77)	(20.81)	(7.14)	(0.75)	(15.93)		(0.67)	(20.23)	(13.51)	(1.19)
Apatite-NC	avg	23.00 *	288.36 *	9.60 *	9.53 *	2.45	7.45 *	AI	1.47 *	336.4 *	3.03	5.84
	(stdev)	(1.30)	(17.83)	(3.12)	(3.14)	(0.79)	(0.24)		(0.96)	(39.65)	(0.74)	(2.80)
Apatite-NC + Fe(0)	avg	7.91 *	285.33 *	5.43 *	6.96 *	1.93	7.51 *	AI	0.67 *	325.9 *	2.11	3.74
	(stdev)	(0.52)	(13.08)	(1.36)	(1.73)	(0.48)	(0.08)		(0.13)	(1.08)	(0.57)	(1.27)
Fe(0)	avg	5.91 *	417.32	10.22 *	6.22 *	1.82	8.28 *	AI	0.76 *	126.3	1.06	1.07
	(stdev)	(0.58)	(17.35)	(1.55)	(0.68)	(0.37)	(0.25)		(0.11)	(4.20)	(0.04)	(0.13)
Apatite-II	avg	47.34 *	186.06 *	1.28 *	39.71 *	2.32	67.97	3.33	0.89 *	109.14	16.36	0.88
	(stdev)	(6.13)	(18.09)	(0.43)	(5.21)	(0.35)	(30.17)	(2.57)	(0.20)	(6.12)	(19.32)	(0.62)

(a) Ba is used here as an analog for Ra; Ce for Ac; K for Tl.

(b) AI = Analytical interference, data not available.

* identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

Perhaps one of the most important points to make regarding Table 12 is that the Apatite-NC pore water had a significantly higher total organic C concentration than the Wet/Dry-Cycled Control. The high organic C concentrations in the leachate were apparent to the naked eye, insofar that the water from this treatment had a brown tinge. The elevated organic C concentrations was likely caused by the increased pH, which would have caused the organic matter to become more negatively charged, and therefore more repulsed from the primarily negatively charged sediment surfaces. Additionally or alternatively, the increased phosphate and Ca concentrations may have promoted the desorption of organic matter from sediment surfaces via anion and cation exchange, respectively. The enhanced total organic C concentration is important for evaluating these sediment amendments because organic matter is a strong complexing agent of many of the COC's and may enhance their mobilization.

The sediment amendments were generally less effective in the Wet/Dry-Cycled treatments (Table 13) than they were in the Flooded treatments (Table 11) at immobilizing COC's. This may be attributed in part to less chemistry taking place in the partially moistened samples. The shorter contact time between the surface water and the treated sediments in the partially moistened systems may have limited the extent that several important sequestration reactions occurred. These reactions may have included COC desorption followed by re-adsorption, apatite dissolution, Fe(0) reduction, and microbial reduction. Fe(0) and Apatite-NC were very effective at removing Pb. The adverse influence of the Apatite-NC on As and Sr concentrations observed in the Flooded treatments were also observed in the Wet/Dry-Cycled treatments.

Table 12. Pore Water Chemical Concentrations of Ancillary Parameters in the Wet/Dry Cycling Treatments

		Al (ppb)	Ca (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	P (ppm)	Se (ppm)	TIC (ppm)	TOC (ppm)
Control	avg	306.92	4.02	4.11	1.76	0.88	36.84	0.45	0.10	9.83	118.00
	(stdev)	(17.32)	(2.07)	(0.99)	(0.44)	(0.24)	(7.15)	(0.19)	(0.05)	(0.34)	(0.07)
Apatite-NC	avg	474.68	39.35 *	1.20 *	4.58 *	0.40	47.33	1.00 *	0.30 *	10.19	228.3 *
	(stdev)	(67.68)	(9.27)	(0.55)	(1.10)	(0.26)	(8.07)	(0.13)	(0.06)	(0.29)	(31.4)
Apatite-NC + Fe(0)	avg	866.12 *	15.90	1.34 *	2.39	0.21	36.97	0.64	0.14	10.19	143.6
	(stdev)	(55.11)	(0.74)	(0.42)	(0.07)	(0.07)	(2.14)	(0.06)	(0.03)	(0.02)	(6.6)
Fe(0)	avg	302.56	2.27	1.26 *	0.74	0.38	27.15	0.45	0.05	10.51	115.3
	(stdev)	(31.44)	(1.17)	(0.42)	(0.33)	(0.18)	(2.47)	(0.09)	(0.02)	(0.00)	(3.6)

* identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

Table 13. Constituent-of-Concern Concentrations in the Pore Water of the Wet/Dry Cycled Treatments

		As (ppb)	Ba(a) (ppb)	Ce(a) (ppb)	Co (ppb)	Cr (ppb)	K(a) (ppm)	Hg (ppb)	Pb (ppb)	Sr (ppb)	Th (ppb)	U (ppb)
Control	Avg	0.98	106.07	17.53	8.70	2.06	6.76	3.16	1.78	32.52	0.79	0.41
	(stdev)	(0.03)	(34.54)	(1.04)	(3.75)	(0.31)	(2.47)	(3.53)	(0.05)	(2.32)	(0.20)	(0.10)
Apatite-NC	avg	2.35 *	104.28	13.88	4.19	3.75 *	7.15	2.97	0.86 *	249.22 *	1.21	0.32
	(stdev)	(0.39)	(29.70)	(4.20)	(1.73)	(0.51)	(0.98)	(0.48)	(0.15)	(76.77)	(0.35)	(0.06)
Apatite-NC + Fe(0)	avg	1.18	45.95	2.94	0.97	1.46	5.38	2.15	0.87 *	90.56	0.72	0.20 *
	(stdev)	(0.22)	(3.77)	(0.45)	(0.25)	(0.47)	(0.18)	(1.43)	(0.29)	(5.45)	(0.02)	(0.05)
Fe(0)	avg	0.66	52.48	3.58	2.46	0.62	3.60	1.21	0.57 *	13.59	0.25	0.16 *
	(stdev)	(0.15)	(20.24)	(1.99)	(1.79)	(0.33)	(0.89)	(0.23)	(0.19)	(3.08)	(0.09)	(0.06)

(a) Ba is used here as an analog for Ra; Ce for Ac; K for Tl.

* identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

4.5 SEQUENTI AL EXTRACTIONS AND "POTENTIALLY LEACHABLE SOURCE-TERM FRACTION"

Sequential extractions were conducted on the sediments from the Flooded treatments (except for the Apatite-II treatment, Figure 3 through Figure 6, the means and standard deviations associated with these data are presented in Appendix Table 4 through **Appendix Table 7**).

There are two important factors that come into play when interpreting sequential extraction data. The first is that the various fractions are operationally defined, and that the targeted fraction may or may not be entirely recovered by a given extraction procedure. The other important consideration is that in order to observe a positive response (COC immobilization) to the sediment amendment through measurements of the solid phase, the COC must first desorb from the sediment and re-sorb onto or into the sediment amendment. These are generally kinetically hindered reactions and often take several months to reach steady state. Although such durations are long with respect to this study, they are not long with respect to their application at the TNX OD site. The net effect of collecting data prior to achieving steady state is that less transition of the COC into the immobilized fractions will be measured. Additional discussions about interpreting the results of this short-term study in relation to the long-term reaction rates are presented in Section 4.6. Given these two important caveats, namely the operational definition of the fractions and the incomplete desorption and re-sorption into the sediment amendments, it is possible to discuss the data in a less rigorous manner, being cautious not to over interpret the data.

The main intent of conducting sequential extractions is to determine how strongly the COC's are bound to the solid phase. Early extraction steps (the exchangeable, amorphous Fe-oxide and the organic/sulfide fractions) tend to recover COC fractions that are less strongly bound than the fractions collected in the latter extraction steps (crystalline Fe-oxide and residue fractions). Thus, an indication that a given sediment amendment is sequestering a COC in a desirable manner would be an increase in the crystalline Fe-oxide and residue fractions when compared to the untreated Control sediment (Table 14 and Table 15). Such a shift was observed with:

- As for the Apatite-NC + Fe(0) treatment and the Fe(0) treatment,
- Ba for the Fe(0) treatment,
- Co for the Apatite-NC + Fe(0) treatment and the Fe(0) treatment,
- Hg for the Apatite-NC + Fe(0) treatment and the Fe(0) treatment, and
- Th for the Apatite-NC + Fe(0) treatment and the Fe(0) treatment.

The sequential extractions also revealed some undesirable shifts in the COC concentrations as a result of adding sediment amendments. They include a decrease in the sum of the Crystalline Fe-oxide and Residual Fractions for the following:

- Co for the Apatite-NC treatment,
- Pb for the Apatite-NC + Fe(0) treatment and the Fe(0) treatment,
- Sr for the Apatite-NC treatment,
- Th for the Apatite-NC treatment, and

- U for the Apatite-NC + Fe(0) treatment and the Apatite-NC treatment.

The COC's that existed in appreciably higher concentrations in the Apatite-NC than in an uncontaminated sediment collected from near the TNX OD site were As, Cr, Hg, Pb, and U (Table 4). These high concentrations may confirm the ability of the apatite to concentrate the COC's from water with low COC levels during geological time frames. Alternatively, if these elements were present at the time the apatite was formed, then these data indicate that the apatite has been able to retain them for very long periods of time. The high As concentrations are not surprising because arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) have similar geochemical behavior. The high concentrations of Cr, Hg, Pb and U are indicative of the high retention potential of apatite for these elements.

Sequential extractions were also conducted on the Apatite-NC amendment (Table 16). For purposes of comparison, the same sequential extraction procedure used with the sediments was used for the apatite. Although this eases comparison, the sequence of extractions is not optimal for phosphate phases, such as apatite. Instead, a sequential extraction designed specifically for phosphate would be more meaningful in terms of chemistry (e.g., Kuo 1996). For example, the Organic/Sulfide Fraction accounted for as much as 33% of the COC, yet neither organic nor sulfide exist to any appreciable extent in the Apatite-NC. Thus, the hydrogen peroxide used in this step removes some fraction that is likely not comprised of organics or sulfides. Instead it dissolves some other phases that are oxidizable by H_2O_2. (For this reason, many scientists prefer to refer to the sequential extraction steps by their extractants, rather than their targeted fraction.)

Between 86% and 92% of As, Cr, Hg, Pb, or U (the COC's that existed in high concentrations in the Apatite-NC; Table 4) was associated with the two least labile (most mobile) fractions (Table 16).[2] Of these COC's, the sequential extraction results for the Hg elicit the most concern. Given the extremely low permissible environmental limits imposed by regulators, introducing into the TNX OD 0.69 mg/kg of Hg (13% of 5.32 mg/kg Hg; Table 16) with the Apatite-NC requires close scrutiny. Another potential problem may exist with the amounts and proportions of mobile As in the Apatite-NC amendment. The leach test indicated that the As concentrations in the Apatite-NC treatments were significantly greater than in the Control in the Flooded treatment (Table 11) and in the Wet/Dry-Cycled treatment (Table 13). Leachate Cr in the Wet/Dry-Cycled, but not in the Flooded, treatments was also significantly higher in the Apatite-NC amended sediment than in the Control.

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[2] In discussing the sequential extractions of the quarried apatite, Apatite-NC, the mobile phase will be defined as that associated with the first two extraction steps (1-M CH_3COONa, pH = 5; and 0.25 M NH_2OH-HCl), the hydrogen peroxide oxidation fraction, referred to as the Organic/Sulfide Fraction, will be considered as part of the immobile fraction. This exception is used because there is essentially no organic matter in this the apatite and the only reason that the Organic/Sulfide fraction was included in the "mobile fraction" was because of the relatively rapid rate at which organic matter, compared to likely inorganic soil phases, oxidizes. Since there is no organic matter in the Apatite-NC, this conservative assumption, which errors on the side of assuming more COC is associated with the mobile phase, is not warranted.

Another way of viewing this same data is through the concept of the potential leachable source-term fraction, as defined by:

$$\text{\% Potential Leachable Source-Term} = 100 - (\text{Strongly Sorbing Fraction}) \qquad (5)$$

where the Strongly Sorbing fraction is the sum of the Crystalline Fe-oxide fraction (Fraction #3 and the Residual fraction (Fraction #5). This construct provides a conservative estimate of the percentage of a COC in the source term (contaminated sediment) that has the potential to leach. This is conservative because, as mentioned above, had the experiment been conducted over a longer period, more of the COC's would have had time to desorb from the sediment and resorb onto or into the amendments. For example, Table 14 shows that 80.5% of the As in the sediment was associated with the strongly sorbing fraction of the Apatite-NC + Fe(0) treatment. Using Equation 5, the percent of As that may potential leach from the sediment is 19.5%, or 1.79 mg/kg As (19.5% of 9.2 mg/kg As Table 4). By not adding any amendment to the sediment, 22.7% of the As in the sediment is leachable. By adding Apatite-NC + Fe(0), this fraction significantly decreases to 19.5%. Perhaps the most striking data in Table 14 deals with Cr. In the Control, only 19.3% of the total Cr pool is leachable. Although the addition of Apatite-NC + Fe(0) did not further reduce the leachable fraction, it does indicate that the Cr on the site is likely not the mobile Cr(VI) species, but more likely the immobile Cr(III) species. No benefit was realized for immobilizing the Cr through the addition of Fe(0) because all the Cr was presumably already in the reduced form.

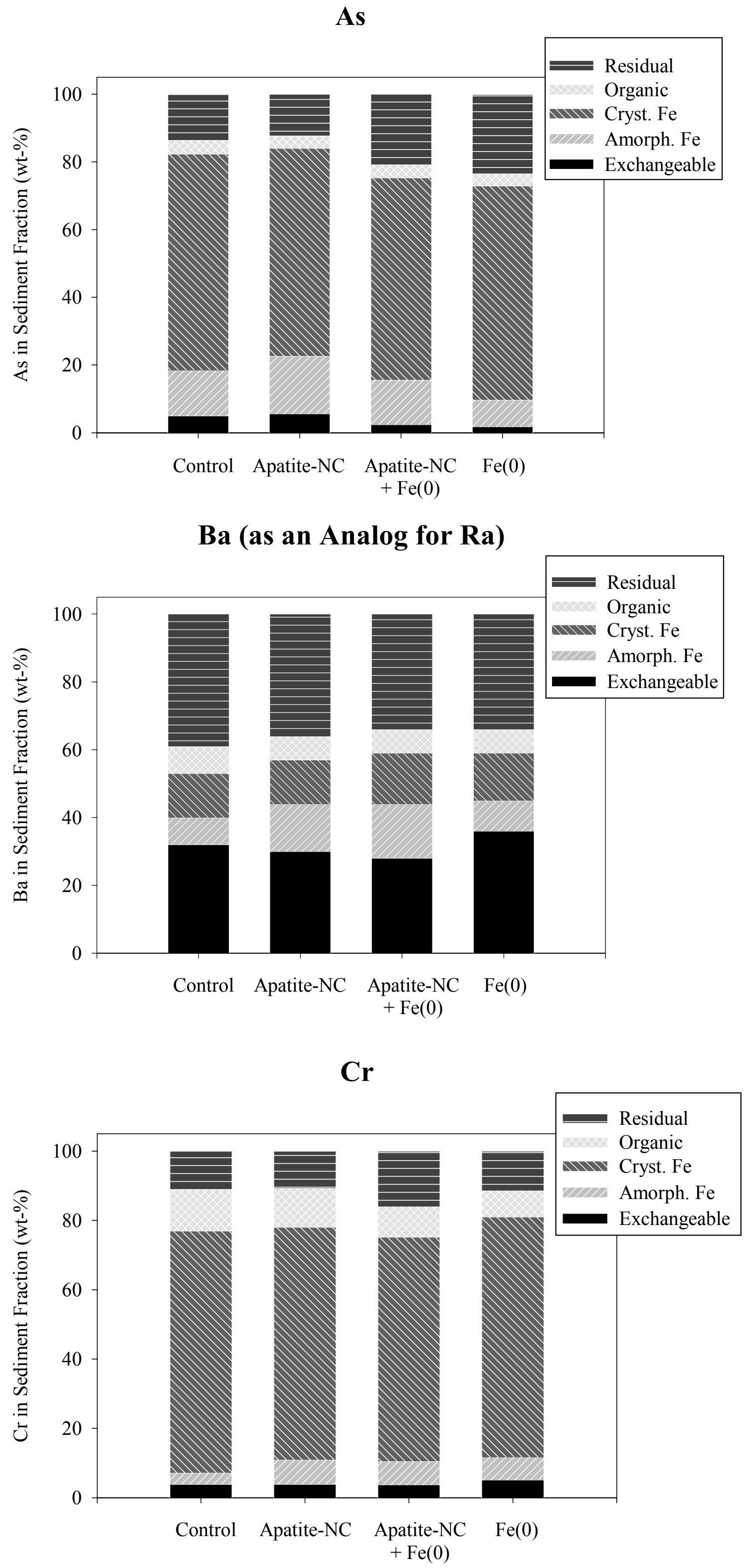
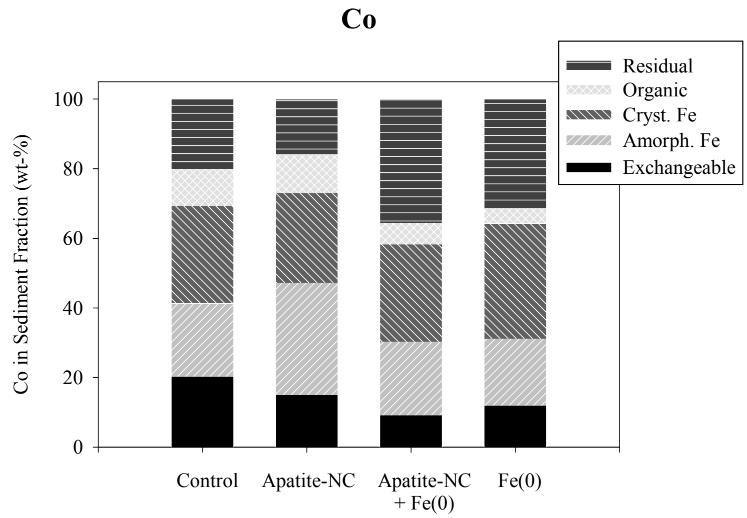
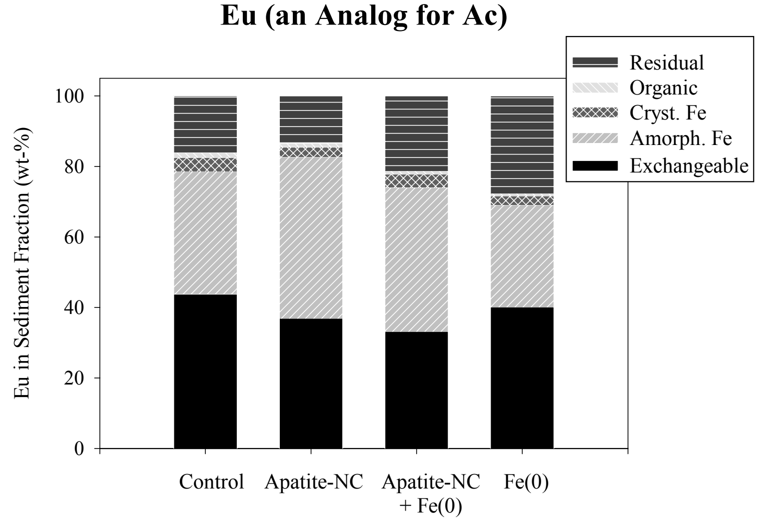


Figure 3. Sequential Extraction of Sediment As, Ba, and Cr After 7-weeks of Contact Time





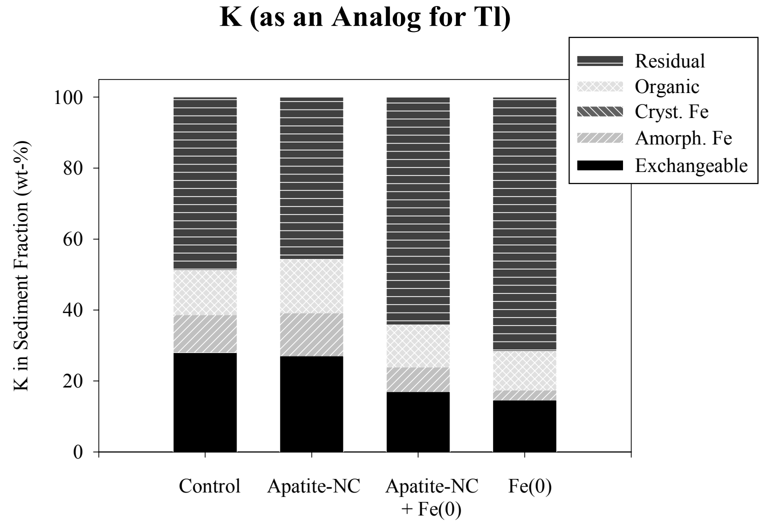


Figure 4. Sequential Extraction of Sediment Co, Eu, and K After 7-weeks of Contact Time

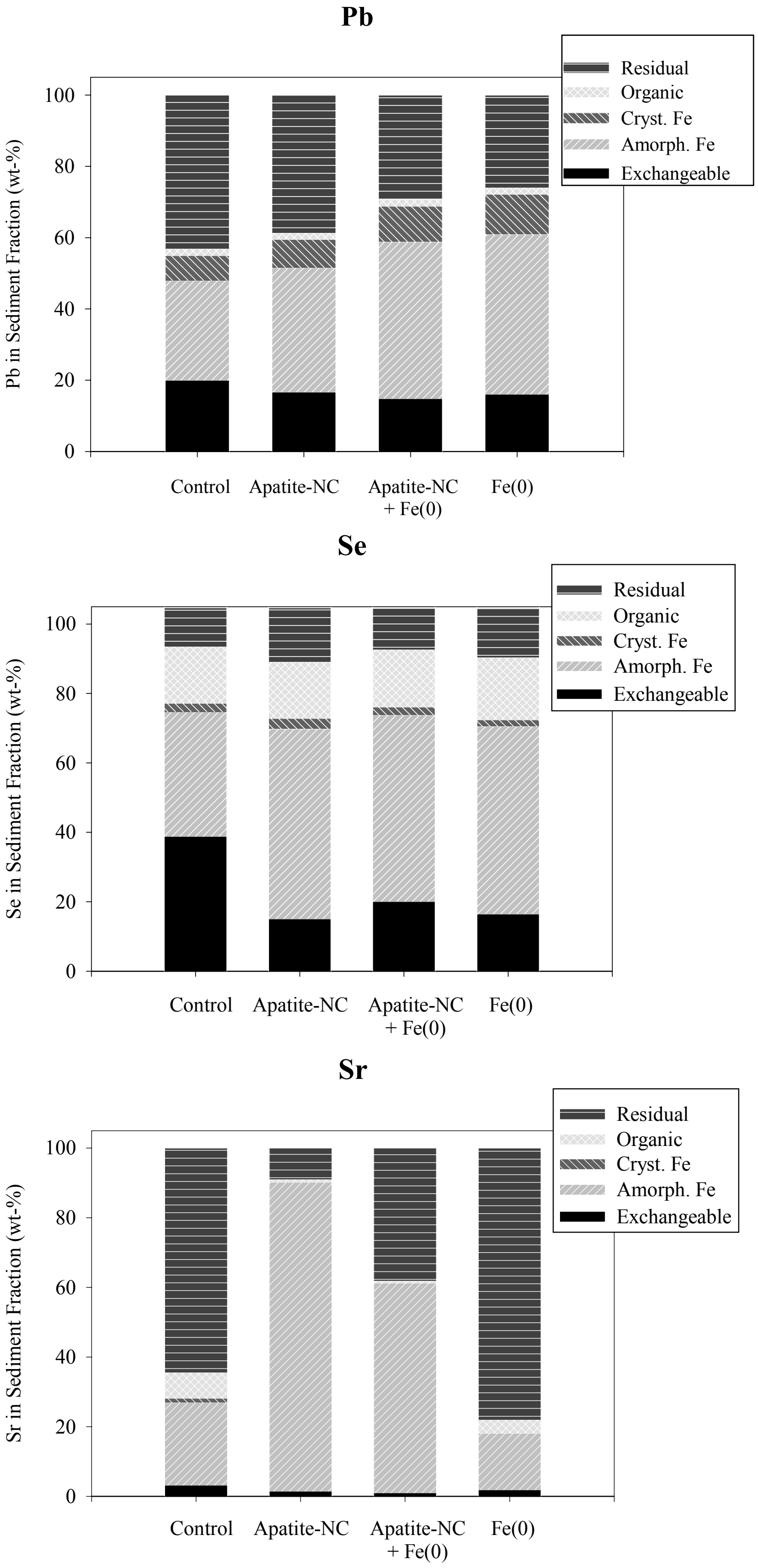


Figure 5. Sequential Extraction of Sediment Pb, Se, and Sr After 7-weeks of Contact Time

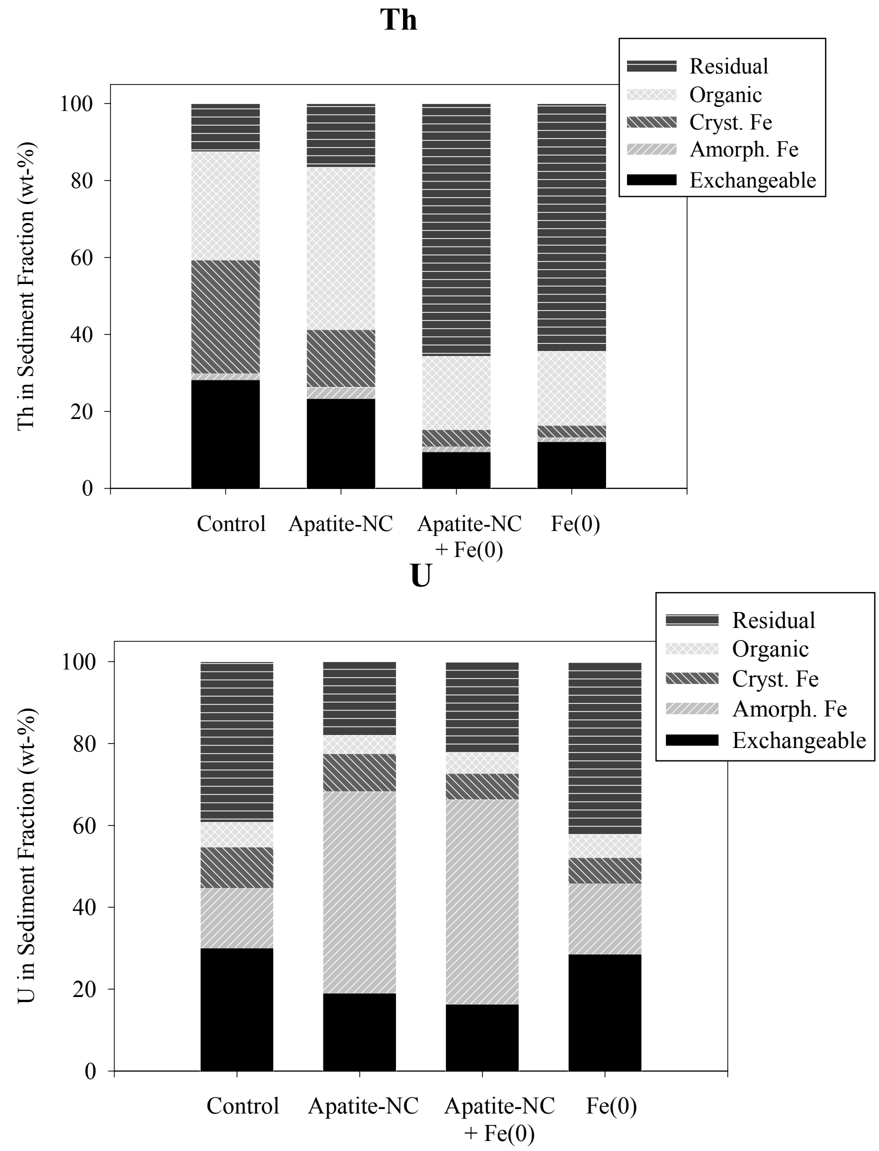


Figure 6. Sequential Extraction of Sediment Th and U After 7-weeks of Contact Time

Table 14. Percentage of Constituent-of-Concern Associated with Strongly Sorbing Fraction (100 – Strongly Sorbing Fraction = % of Source Term That is Potentially Leachable; Equation 5)

		As	Ba	Eu	Co	Cr	Hg	K	Pb	Sr	Th	U
Control[(a)]	avg	77.3	51.9	20.0	48.1	80.7	56.1	48.5	50.5	65.5	41.6	49.2
	(stdev)	(1.0)	(0.3)	(2.7)	(1.8)	(1.0)	(5.0)	(2.7)	(0.7)	(5.5)	(5.0)	(1.8)
Apatite-NC	avg	73.5 *	49.6	16.2	41.7 *	77.7	61.5	46.0	46.7	9.0 *	31.3 *	27.2 *
	(stdev)	(0.3)	(0.9)	(3.1)	(0.8)	(0.9)	(2.7)	(7.7)	(0.2)	(1.9)	(1.9)	(1.4)
Apatite-NC + Fe(0)	avg	80.5 *	49.0	25.0	63.5 *	80.7	72.1 *	81.5	39.1 *	31.6	69.8 *	28.3 *
	(stdev)	(0.9)	(0.7)	(2.6)	(2.5)	(1.2)	(1.5)	(25.0)	(6.8)	(24.9)	(2.5)	(0.6)
Fe(0)	avg	86.6 *	47.7 *	29.9	64.4 *	80.7	71.8 *	70.6	37.2 *	77.7	67.4 *	48.4
	(stdev)	(0.6)	(2.1)	(6.2)	(0.3)	(0.3)	(0.1)	(7.8)	(0.1)	(5.3)	(1.6)	(1.6)

"*" identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

(a) Data used to generate these data are presented in Figure 3 through Figure 6. Ba, Eu and K are used here as analogs for Ra, Ac, and Tl. The Strongly Sorbing fraction equals the sum of Fractions 3 and 5 of the sequential extraction data.

Table 15. Percentage of Ancillary Constituents Associated with Strongly Sorbing Fraction (100 – Strongly Sorbing Fraction = % of Source Term That is Potentially Leachable)

		Al	Fe	Mn	P	Se
Control	avg	30.7	65.6	40.8	66.2	52.1
	(stdev)	(1.6)	(1.2)	(3.9)	(1.5)	(3.2)
Apatite-NC	avg	25.1	62.6	34.6 *	11.7 *	72.1 *
	(stdev)	(4.1)	(0.5)	(1.3)	(0.7)	(9.1)
Apatite-NC + Fe(0)	avg	7.1 *	56.6 *	46.3	16.0 *	70.4
	(stdev)	(2.6)	(2.1)	(0.5)	(0.9)	(0.5)
Fe(0)	avg	5.2 *	39.9 *	39.0	57.8 *	72.1 *
	(stdev)	(0.8)	(0.1)	(1.4)	(1.1)	(2.5)

"*" identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

(a) Data used to generate these data are presented in Figure 3 through Figure 6.

Table 16. Elemental Concentration and Sequential Fractionation of Apatite-NC

	Total Concentration (mg/kg)	Exchangeable Fraction (%)	Amorphous Fe-oxide (%)	Crystalline Fe-oxide (%)	Organic/Sulfide Fraction (%)	Residual Fraction (%)
Al	1382	0	19	67	1	13
As	29.3	3	9	28	33	26
Ba[(a)]	20.4	6	17	12	5	60
Co	0.8	4	13	10	13	60
Cr	76.3	1	5	25	5	64
Eu[(a)]	0.78	0	1	0	7	93
Fe	2627	1	6	6	18	69
Hg	5.32	13	1	8	2	76
K[(a)]	341	6	5	0	4	85
Mn	17	9	30	15	13	32
P	>101,000	1	31	27	15	25
Pb	17.6	0	8	11	8	73
Se	156	4	30	21	4	41
Sr	0.51	2	0	21	0	77
Th	0.84	1	1	4	1	94
U	62.1	1	8	7	20	64

(a) Ba, Eu, and K are included as analogs for Ra, Ac, and Tl, respectively.

4.6 INFLUENCE OF SEDIMENT AMENDMENTS ON CALCULATED SOURCE TERM AND KD VALUES

Desorption distribution coefficient (K_d) values were operationally defined as:

$$K_d = \frac{C_{Exch} + C_{AmFe} + C_{Org/Sulf}}{C_{Aq}} \qquad (6)$$

where *C* represents concentration, and the subscripts *Exch, AmFe,* and *Org/Sulf*, represent the first, second and fourth fraction of the sequential extractions, respectively, and *Aq* represents the concentration in the aqueous phase collected from the Flooded treatments at the end of the equilibration period. These fractions of the solid phase were selected for two primary reasons: 1) the K_d construct assumes a reversible reaction (adsorption rate is the same as the desorption rate) and these fractions most closely approach this condition, and 2) to be conservative (predict a low K_d value), the total COC solids concentration was not used.

In order to measure an increase of K_d in the amended treatments, the COC sorbed to the sediment must first desorb and then re-sorb into the immobilizing phase. Thus, if the sediment amendment is working as designed, then the longer the contaminated sediment is in contact with the amendments, the greater proportion of the total COC pool will become immobilized until steady state conditions are obtained. It is likely that steady state conditions were not achieved during the six to seven week duration of this study. Instead, the system was kinetically hindered with respect to several key reactions involving Fe(0) and apatite stabilization. Thus, the steady state conditions assumed in the operational definition of K_d (Equation 6), were likely not obtained during the length of this experiment for several important reactions governing the immobilization of the COC. Three processes in particular are known to be very slow, they are:

- reductive dissolution of Fe-oxyhydroxides that may result in the release of some of the COC's into the aqueous phase for subsequent re-adsorption into less available phases in the sediment amendments (applicable to treatments receiving Fe(0)),[3]
- diffusion of adsorbed COC's into strongly retained phases, whereby the COC becomes incorporated into the mineral structure through isomorphic substitution (applicable to treatments receiving apatite), and
- desorption of polyvalent ions is generally a kinetically hindered reaction that often takes weeks to months to come to steady state (as compared to adsorption, which general comes to steady state in the order of hours to days) (Stumm and Morgan 1996).

The implications of the system being kinetically hindered is that the K_d values calculated by Equation 6 are lower than if the K_d values had been measured over a longer duration, for instance, after 1 year.

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[3] In the natural environment, reductive dissolution takes years to come to steady state (Vepraskas 1996).

The following conclusions are based on Table 17:

- The Apatite-NC treatment had significantly greater K_d values than the Control for Ba, K, and Sr.
- The Fe(0) treatment had significantly greater K_d values than the Control for As, Co, Cr, Pb, and Th.
- The Apatite-NC + Fe(0) treatment had significantly greater K_d values than the Control for all COC's except Hg and U.
- None of the treatments significantly decreased the K_d values for any COC's (except the Sr-K_d value in the Fe(0) treatment).

All three amendments lowered the Se K_d values (which is not a COC, but an ancillary parameter) with respect to the Control.

Potassium showed only a moderate tendency to be retained by apatite and the removal mechanism is likely an ephemeral cation exchange process.

Unfortunately, there was a great deal of variability associated with the Hg, Sr, and U K_d measurements. It is not known whether this variability originated from analytical measurements, experimental techniques, or inherent sediment variability. Furthermore, it is very possible that the contaminated sediment had not released a significant amount of Hg and U during the 7-week equilibration time to permit a noticeable difference between the Control and the amendments. Wright et al. (1995) reported significant aqueous U removal through the use of the same source of apatite as was used in this experiment, Apatite-NC. Kaplan et al. (2001) previously reported Hg K_d values with Fe(0) between 1364 ± 117 mL/g and 6270 ± 719 mL/g. It is not known why these results did not support these previous findings indicating that Fe(0) and apatite can immobilize Hg and U, respectively.

Table 17. Influence of Sediment Amendments on K_d Values for Contaminated Sediments

		Control (mL/g)	Apatite-NC (mL/g)	Apatite-NC + Fe(0) (mL/g)	Fe(0) (mL/g)
As	avg	123(a)	113	333 *	367 *
	(stdev)	(1)	(10)	(31)	(6)
Ba(b)	avg	94	154 *	158 *	96
	(stdev)	(1)	(2)	(2)	(12)
Co	avg	110	244	436 *	524 *
	(stdev)	(29)	(41)	(45)	(78)
Cr	avg	15014	18463	32094 *	48353 *
	(stdev)	(1524)	(2844)	(867)	(4998)
Ce(b)	avg	53.3	363	552 *	298
	(stdev)	(1.8)	(158)	(109)	(25)
Fe	avg	43	59	109	92
	(stdev)	(7.5)	(4.6)	(35.1)	(4.7)
K(b)	avg	8.2	20.7 *	16.2	13.4
	(stdev)	(5.7)	(0.9)	(0.3)	(1.5)
Pb	avg	2377	16090	30210 *	26575 *
	(stdev)	(192)	(11750)	(9878)	(3135)
Se	avg	344	92 *	152 *	185 *
	(stdev)	(66)	(55)	(12)	(10)
Sr	avg	27	154 *	150 *	16 *
	(stdev)	(2)	(25)	(29)	(2)
Th	avg	706	2251	3414 *	6046 *
	(stdev)	(601)	(380)	(848)	(1044)
U	avg	1239	975	1316	1547
	(stdev)	(540)	(599)	(369)	(188)
Hg(c)	avg	383	339	174	101
	(stdev)	(164)	(103)	(49)	(355)

(a) K_d = distribution coefficient, operationally defined in Equation 6. Importantly, several of these constituents may be better represented by the solubility construct, but for ease of data presentation and comparison, only K_d values are presented. Experiment did not reach steady state and therefore are lower values than is expected *in situ*.

(b) Ba, Ce, and K are used here as analogs for Ra, Ac, and Tl.

(c) Due to analytical interference with the Hg measurement of the pore water solution collected from the equilibrated solutions, Hg K_d values were calculated with the Hg aqueous concentrations measured in the first leachates collected from the Wet/Dry-Cycled Treatments.

* identifies a treatment mean concentration that is significantly ($P \leq 0.05$) different than the control mean concentration, according to Dunett's Test.

5.0 CONCLUSIONS

Several parameters were measured to evaluate the effectiveness of the sediment amendments to sequester COC's. Among these parameters were the COC concentrations in sediment leachate and sequential extractions. Four metrics were calculated from these measurements, the Flooded treatment leachates, the Wet/Dry-Cycled leachates, %-COC Immobilized (inversely related to % Potential Leachable Source Term), and COC K_d Values. Perhaps the Flooded treatment leachate data is the single best parameter to use to evaluate the efficacy of the sediment amendments. It indicates that the Apatite-NC + Fe(0) treatment was the best overall treatment and chemically behaved like the sum of the individual Fe(0) and Apatite-NC amendments (Table 18). The Fe(0) treatment tended to remove more different COC than either type of apatite. The Apatite-NC + Fe(0) treatment significantly lowered the COC leaching for all elements except Cr, Sr, Th, and U (Table 18). There was little difference between the COC concentrations in the Wet/Dry-Cycled treatments and the Controls because the reduced moisture concentration slowed down many of the important reactions responsible for amendment COC sequestration (Table 18).

The K_d values calculated for this report provide a less direct measure of the efficacy of the treatments and require additional assumptions, but have the distinct advantage over the other parameters in that they can be used directly in risk modeling and are easy to understand. The K_d values for the combined Apatite-NC + Fe(0) treatments were significantly greater than the Controls for 8 of the 11 COC, all except Tl, Hg, and U. Uranium concentrations in the contaminated sediment were near that of background, therefore the fact that little enhanced sequestration was measured in the presence of the amendments is not surprising. Previous work conducted on SRS and elsewhere indicate that both Hg and U should be readily removed from the aqueous phase in the presence of Fe(0) and/or apatite (Wright et al. 1995, Kaplan et al. 2001, Rakovan et al. 2002, Fuller et al. 2002).

The % Potential Leachable Source Term (Equation 5) is important in that it provides a sound estimate of the COC fraction that can leach from the sediments. This can be thought of as the true source term, as compared to the total COC pool, which may require that very strong bonds (e.g., mineral structural bonds) be broken before a COC enters the groundwater. As Table 18 indicates, the Apatite-NC + Fe(0) treatment significantly immobilized (reduced the source term) As, Co, Hg, and Th compared to the Control. It should be noted that the relatively short duration of these experiments, 6 to 7 weeks, likely produced results that would underestimate the actual magnitude of immobilization that a longer-term experiment would produce.

Two very different sources of apatite were evaluated by the leach test. Both types of apatite have been used to remediate other contaminated sites, including mining sites and DOE sites (Moody and Wright 1995, Wright et al. 1995, www.pimsnw.com). Apatite-NC is a mined mineral, with an appreciably lower solubility than the Apatite-II, a biogenic material. As is the case with other sources of mined apatite, Apatite-NC had especially high concentrations of contaminants, including As, Cr, Hg, Pb, and U. These high concentrations are indicative of the ability of this material to sequester these constituents over geologic timeframes. Sequential extractions of the Apatite-NC showed that >86% of these COC's were strongly bound by the mineral structure and were not likely to leach into the pore water. The presence of As and Hg in the Apatite-NC may be a potential problem, but one that can be resolved by including Fe(0) with the Apatite-NC; the Fe(0) readily removes As and Hg through reduction.

In conclusion, these data show that the addition of both Fe(0) and apatite to the TNX OD sediment will greatly stabilize most of the COC's. Together, these amendments will increase the K_d values and decrease the potentially leachable fraction of the source term for a majority of the COC's. One concern was the leaching of As (and possibly Hg) from the apatite itself, but this potential problem may be offset by including Fe(0). Thallium showed only a moderate tendency to be retained by apatite and the removal mechanism is likely cation exchange, a weak removal mechanism.

Table 18. Summary of Sediment Amendments Effects on Various COC-Concentration Parameters With Respect to the Controls ("L" = Significantly Lower, "H" = Significantly Higher, Empty = No Significant Difference)

	Leach COC Concentrations - Flooded[a]				Leach COC Concentrations – Wet/Dry-Cycled[b]			% COC Immobilized[c]			K_d[d]		
	Apatite -NC	Fe(0)	Apatite -NC + Fe(0)	Apatite -II	Apatite -NC	Apatite -NC + Fe(0)	Fe(0)	Apatite -NC	Apatite -NC + Fe(0)	Fe(0)	Apatite -NC	Apatite -NC + Fe(0)	Fe(0)
Ac[e]	L[f]	L	L	L								H	
As	H	L	L	H	H			L	H	H		H	H
Co	L	L	L	H				L	H	H		H	H
Cr					H							H	H
Hg	AI[g]	AI	AI	AI					H	H			
Pb	L	L	L	L	L	L	L		L	L		H	H
Ra[e]	L		L	L						L	H	H	
Sr	H		H		H			L			H	H	L
Th								L	H	H		H	H
Tl[e]	L	L	L								H		
U						L	L	L	L				

[a] Data taken from Table 11.

[b] Data taken from Table 13.

[c] Data taken from Table 14.

[d] Data taken from Table 17.

[e] Ac, Ra, and Tl were not measured directly. Instead measurements were made of Eu/Ce, Ba, and K, and treated as analogs for Ac, Ra, and Tl, respectively.

[f] L = significantly ($P \leq 0.05$) lower mean than the control treatment mean; H = significantly ($P \leq 0.05$) higher mean than the Control treatment mean; no entry indicates not significantly ($P \leq 0.05$) different from the Control treatment according to Dunett's test.

[g] AI = Analytical Interference

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7.0 APPENDIX A: ADDITIONAL DATA

Appendix Table 1. Pore Water Chemistry of Leachate at End of Experiment: Eh, O_2, pH and Conductivity

Trt ID	Amendment	Eh (mV)	O_2 (mg/L)	pH	Conductivity (µS/cm)
301	Control-Flooded	-136	0.06	5.54	
302	Control-Flooded	-128	0.17	5.94	516
303	Control-Flooded	-172	0.06	5.88	494
304	Apatite-Flooded	-176.5	0.04	6.52	608
305	Apatite-Flooded	-172.6	0.04	6.68	623
306	Apatite-Flooded	-178.6	0.05	6.7	585
307	Apatite+Fe(0)-Flooded	-182.9	0.05	6.73	552
308	Apatite+Fe(0)-Flooded	-187.8	0.07	6.7	575
309	Apatite+Fe(0)-Flooded	-185.9	0.06	6.65	587
310	Fe(0)-Flooded	-179.4	0.05	6.26	442
311	Fe(0)-Flooded	-168.8	0.04	6.32	441
312	Fe(0)-Flooded	-171.6	0.23	6.28	465
313	Control-Wet/Dry	273.6	6	4.36	281
314	Control-Wet/Dry	294.6	5.5	4.44	252
315	Control-Wet/Dry	291.2	5.06	4.58	257
316	Apatite-Wet/Dry	209.4	4.43	5.04	578
317	Apatite-Wet/Dry	207.4	4.36	5.33	442
318	Apatite-Wet/Dry	226.5	4.08	5.22	445
319	Apatite + Fe(0)-Wet/Dry	203.2	3.37	5.49	327
320	Apatite + Fe(0)-Wet/Dry	191.7	3.16	5.75	336
321	Apatite + Fe(0)-Wet/Dry	185.2	3.43	5.78	322
322	Fe(0)-Wet/Dry	290.8	3.58	5.19	208
323	Fe(0)-Wet/Dry	193	3.29	5.36	172
324	Fe(0)-Wet/Dry	206.6	3.53	5.33	192

Appendix Table 2. Pore Water Chemistry of Leachate at End of Experiment: ICP-MS data (μg/L)

Trt ID	Amendment	Al	Cr	Co	As	Sr	Ba	Hg	Pb	Th	U	Ce
301	Control-Flooded	225.35	2.65	20.9	17.167	131.86	451.58	AI	6.913	24.75	1.5016	62.889
302	Control-Flooded	249.24	2.1901	13.452	16.812	98.775	430.81	AI	7.8634	5.638	0.87663	59.946
303	Control- Flooded	196.9	3.6633	27.719	21.695	135.5	504.09	10.402			3.1746	25.465
304	Apatite-Flooded	69.781	1.787	7.0231	21.619	364.44	284.67	AI	2.5662	3.5557	7.0663	13.016
305	Apatite-Flooded	60.229	2.2416	8.5151	24.192	308.36	272.67	AI	0.82285	2.5114	2.6375	6.8842
306	Apatite- Flooded	72.733	3.325	13.051	23.197		307.75	0	1.0082		7.8191	8.908
307	Ap+Fe(0)-Flooded	51.032	1.6872	6.2394	8.2013	325.2	272.67	AI	0.82285	2.5114	2.6375	6.8842
308	Ap+Fe(0)-Flooded	60.799	1.6221	5.7122	7.3085	326.73	284.51	AI	0.57665	1.7004	3.4779	5.1978
309	Ap+Fe(0)- Flooded	53.638	2.4842	8.9383	8.2217	225.1	298.8	0	0.62168		5.0919	4.1978
310	Fe(0)-Flooded	54.209	1.5794	5.5769	6.4433	129.3	437.23	AI	0.67679	1.0901	1.0432	11.691
311	Fe(0)-Flooded	45.46	1.6458	6.9333	5.9856	123.36	409.26	AI	0.88068	1.0268	0.95978	10.37
312	Fe(0)- Flooded	39.109	2.2464	6.1354	5.2921	122.04	405.46	0	0.70928		1.2095	8.6073
325	Apatite-II- Flooded	31.322	2.6545	45.263	54.07	115.29	204.72	6.2729	0.86469	38.641	1.584	1.7667
326	Apatite-II- Flooded	32.493	1.95	34.934	42.057	109.06	168.61	2.2114	1.1066	6.1459	0.44405	1.1203
327	Apatite-II- Flooded	24.78	2.358	38.944	45.902	103.06	184.86	1.5035	0.70406	4.2815	0.61204	0.94542
313	Control-Wet/Dry	313.93	2.1612	4.3845	0.94685	32.491	66.442	AI	1.5658	0.92879	0.33819	3.7893
314	Control-Wet/Dry	319.63	1.7167	10.529	0.982	35.774	129.72	AI	1.6379	0.64277	0.4727	18.26
315	Control- Wet/Dry	287.19	2.3111	11.19	1.0084	29.292	122.06	0	2.1497		0.57152	16.795
316	Apatite-Wet/Dry	550.22	4.2758	6.1742	2.7814	336.34	138.31	AI	1.0279	1.4521	0.22531	18.591
317	Apatite-Wet/Dry	419.55	3.2628	3.4178	2.2497	219.88	90.929	AI	0.73444	0.96314	0.30525	12.541
318	Apatite- Wet/Dry	454.27	3.7064	2.9808	2.022	191.45	83.591	3.518	0.80866		0.42074	10.511
319	Ap+Fe(0)-Wet/Dry	827.15	1.2303	0.85699	1.0738	96.84	47.053	AI	0.82201	0.73438	0.1883	3.384
320	Ap+Fe(0)-Wet/Dry	905.09	1.1514	0.78571	1.0315	86.988	41.75	AI	0.59735	0.70384	0.15292	2.4758
321	Ap+Fe(0)- Wet/Dry		2.0076	1.2531	1.4324	87.858	49.045	0.49748	1.1788		0.24639	2.9607
322	Fe(0)-Wet/Dry	324.79	0.92928	0.78147	0.72814	17.043	29.775	AI	0.68071	0.30977	0.08889	1.2998
323	Fe(0)-Wet/Dry	280.33	0.27238	2.2536	0.76248	11.117	59.014	AI	0.35443	0.18571	0.19804	4.9323

AI – Analytical Interference

Appendix Table 3. Pore Water Chemistry of Leachate at End of Experiment: ICP-AES data (µg/L)

Trt ID	Amendment	Ca	Cr	Fe	K	Na	P	Se
301	Control-Flooded	12.8	0.0168	185.7	38.5 .		1.464	0.5716
302	Control-Flooded	10.95	0.0195	137.6	13.31	46.58	1.11	0.1374
303	Control-Flooded	13.58	0.0464	208	9.001	25.93	1.7	0.6802
304	Apatite-Flooded	73.68	0.001	119.4	7.728	29.95	1.216	0.7043
305	Apatite-Flooded	80.1	0.0095	125.1	7.403	28.82	1.203	0.7126
306	Apatite-Flooded	72.76	0.0413	109.5	7.265	26.47	1.284	0.7293
307	Ap+Fe(0)-Flooded	59.64	0.0054	139.1	7.566	27.25	1.203	0.6527
308	Ap+Fe(0)-Flooded	67.79	0.002	118.1	7.45	27.47	1.065	0.6445
309	Ap+Fe(0)-Flooded		0.0415	120	7.79	26.39	1.402	0.7695
310	Fe(0)-Flooded	15.51	0.0059	180.9	8.285	26.13	1.329	0.533
311	Fe(0)-Flooded	14.92	0.0051	161.9	8.03	23.68	1.334	0.4842
312	Fe(0)-Flooded	14.81	0.0406	172.5	8.537	23.98	1.343	0.6087
325	Apatite-II-Flooded	311.9	0.0576	218	102.8	279.6	3.347	1.748
326	Apatite-II-Flooded	327.1	0.0618	216	51.38	178.5	3.398	1.775
327	Apatite-II-Flooded	326.3	0.0604	209.4	49.73	172.2	3.386	1.716
313	Control-Wet/Dry	6.341	0	4.812	9.492	44.42	0.5401	0.044
314	Control-Wet/Dry	3.348	0	3.417	6.104	35.88	0.2336	0.1457
315	Control-Wet/Dry	2.369	0.0186		4.682	30.21	0.5861	0.0964
316	Apatite-Wet/Dry	50.02	0.0663	1.826	8.276	56.62	1.139	0.3754
317	Apatite-Wet/Dry	34.81	0.0526	0.8001	6.531	43.3	0.9845	0.2624
318	Apatite-Wet/Dry	33.22	0.0188	0.9635	6.64	42.07	0.8843	0.2673
319	Ap+Fe(0)-Wet/Dry	16.75	0.0224	1.237	5.346	36.11	0.5834	0.1149
320	Ap+Fe(0)-Wet/Dry	15.6	0.0215	0.9879	5.211	39.41	0.629	0.129
321	Ap+Fe(0)-Wet/Dry	15.36	0.0191	1.808	5.57	35.39	0.6983	0.164
322	Fe(0)-Wet/Dry	4.294	0.0133	0.8011	4.607	29.63	0.4945	0.0443
323	Fe(0)-Wet/Dry	1.376	0.0137	1.335	3.131	24.69	0.3464	0.0462
324	Fe(0)-Wet/Dry	1.141	0.0174	1.633	3.047	27.13	0.4944	0.0721

Appendix Table 4. Sequential Extractions of the Control Sediment (2 replicates)

	Fraction 1 (avg %-wt)	Fraction 2 (avg %-wt)	Fraction 3 (avg %-wt)	Fraction 4 (avg %-wt)	Fraction 5 (avg %-wt)
Ba(a)	29.2	11.9	15.0	9.9	33.9
Co	21.0	38.8	7.4	12.6	20.3
Cr	9.4	30.0	2.0	23.7	34.9
Eu	43.8	34.8	3.9	1.4	16.1
K	28.0	10.7	0.0	12.5	48.8
Pb	8.7	26.9	2.2	6.8	55.4
Sr	3.2	23.8	1.1	7.5	64.4
Th	28.2	1.7	29.5	28.2	12.5
U	30.1	14.7	10.0	6.1	39.2
Fe	7.1	22.8	32.4	4.5	33.2
Mn	37.5	14.0	18.7	7.6	22.1
P	3.2	6.3	25.7	24.3	40.5

	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)
Ba	1.4	0.7	1.2	0.1	0.3
Co	3.8	4.5	1.4	1.4	28.7
Cr	4.2	2.8	0.8	0.8	7.8
Eu	1.6	0.3	0.1	0.1	2.9
K	1.1	0.0	0.2	0.2	14.0
Pb	0.5	1.4	0.4	0.4	12.2
Sr	3.8	1.6	0.7	0.7	8.6
Th	0.3	12.1	1.6	1.6	1.0
U	1.0	1.4	0.0	0.0	1.3
Fe	0.4	1.7	0.1	0.1	1.2
Mn	0.5	2.8	0.2	0.2	3.4
P	0.3	1.3	0.2	0.2	0.9

(a) Ba is used in this study as an analog for Ra, Eu for Ac, and K for Tl.

Appendix Table 5. Sequential Extractions of the Apatite-NC Amended Sediment (2 replicates)

	Fraction 1 (avg %-wt)	Fraction 2 (avg %-wt)	Fraction 3 (avg %-wt)	Fraction 4 (avg %-wt)	Fraction 5 (avg %-wt)
Ba[(a)]	26.0	19.4	15.1	8.5	30.9
Co	33.1	48.8	0.2	17.9	0.0
Cr	13.2	36.8	0.0	21.8	28.2
Eu	36.9	45.8	2.8	1.1	13.4
K	27.1	12.2	0.0	15.2	45.6
Pb	16.5	38.3	0.4	6.9	37.9
Sr	1.5	88.7	0.0	0.8	9.0
Th	23.4	2.9	15.0	42.3	16.4
U	19.1	49.2	9.3	4.5	17.9
Fe	6.8	25.9	32.0	4.8	30.6
Mn	34.7	23.3	17.1	7.4	17.5
P	0.7	84.4	7.0	3.3	4.7
	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)
Ba	1.1	0.5	0.4	0.3	2.2
Co	23.3	8.6	0.4	0.6	0.0
Cr	12.7	3.7	0.0	0.6	3.7
Eu	7.7	1.3	0.8	0.1	2.7
K	9.0	2.2	0.0	1.0	4.4
Pb	10.4	1.6	0.8	0.2	2.9
Sr	0.0	6.6	0.0	0.0	1.7
Th	1.3	0.2	3.0	4.3	1.5
U	0.6	7.2	1.4	0.4	2.1
Fe	0.8	2.7	1.5	0.0	0.4
Mn	0.8	0.8	0.9	0.1	0.7
P	0.2	6.9	0.3	0.1	0.2

(a) Ba is used in this study as an analog for Ra, Eu for Ac, and K for Tl.

Appendix Table 6. Sequential Extractions of the Apatite-NC + Fe(0) Amended Sediment (2 Replicates)

	Fraction 1 (avg %-wt)	Fraction 2 (avg %-wt)	Fraction 3 (avg %-wt)	Fraction 4 (avg %-wt)	Fraction 5 (avg %-wt)
Ba(a)	25.7	19.2	15.5	7.7	31.9
Co	7.0	35.7	16.7	9.4	31.2
Cr	3.7	26.4	40.5	15.3	14.1
Eu	33.2	40.8	3.8	1.0	21.2
K	17.0	7.0	0.0	12.0	64.0
Pb	4.2	35.7	3.2	3.8	53.2
Sr	1.0	85.0	0.0	1.0	12.0
Th	9.5	1.5	4.3	19.2	65.5
U	16.4	50.0	6.4	5.3	22.0
Fe	8.7	32.4	37.3	2.3	19.3
Mn	26.9	22.4	27.0	4.3	19.4
P	0.5	80.1	9.8	3.5	6.2

	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)
Ba	1.4	1.1	0.9	0.2	2.9
Co	2.2	1.8	4.0	0.8	44.1
Cr	1.3	2.9	3.0	0.3	20.0
Eu	2.0	0.8	0.3	0.1	2.7
K	1.1	0.6	0.0	0.3	4.0
Pb	0.1	1.3	0.1	0.3	4.5
Sr	0.0	16.7	0.2	0.0	0.4
Th	0.2	0.0	0.2	0.5	6.2
U	0.1	6.7	0.5	0.2	2.9
Fe	0.2	2.1	8.9	0.1	7.3
Mn	0.7	3.1	8.5	0.7	10.9
P	0.0	15.1	0.3	0.0	1.5

(a) Ba is used in this study as an analog for Ra, Eu for Ac, and K for Tl.

Appendix Table 7. Sequential Extractions of the Fe(0) Amended Sediment (2 replicates)

	Fraction 1 (avg %-wt)	Fraction 2 (avg %-wt)	Fraction 3 (avg %-wt)	Fraction 4 (avg %-wt)	Fraction 5 (avg %-wt)
Ba(a)	32.8	11.9	14.4	9.1	31.7
Co	8.8	31.4	18.3	4.0	37.4
Cr	7.8	17.5	51.8	9.7	13.2
Eu	40.1	29.0	2.5	0.8	27.6
K	14.6	2.9	0.0	11.0	71.5
Pb	6.1	30.7	5.8	3.7	53.6
Sr	1.8	16.3	0.0	3.9	77.9
Th	12.1	1.1	3.1	19.4	64.2
U	28.6	17.3	6.3	5.8	42.1
Fe	16.4	42.3	30.3	1.4	9.6
Mn	27.8	28.8	29.4	4.3	9.7
P	3.8	20.7	27.4	17.7	30.4

	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)	(stdev %-wt)
Ba	0.9	6.9	3.4	0.3	0.4
Co	3.5	6.9	5.0	1.2	2.6
Cr	2.1	4.5	26.3	1.6	0.5
Eu	2.9	9.7	0.3	0.3	0.7
K	0.7	2.7	0.0	1.2	19.9
Pb	1.9	4.0	1.5	0.2	9.0
Sr	0.0	295.6	0.9	0.2	2.0
Th	0.8	0.5	1.2	3.6	15.2
U	2.7	46.5	3.3	3.1	3.9
Fe	2.9	14.7	0.6	0.1	0.1
Mn	1.4	10.3	4.6	0.6	0.8
P	1.0	286.6	22.9	3.4	0.2

(a) Ba is used in this study as an analog for Ra, Eu for Ac, and K for Tl.

8.0 APPENDIX B: WORK INSTRUCTIONS FOR THE LABORATORY STUDY

Work Instructions for The Laboratory Study of the Effects of Sediment Amendments on Contaminant Immobilization in a TNX Outfall Delta Soil

Dan Kaplan
February 5, 2002

Objectives

Determine if additions of commercially available Fe(0) and apatite to a contaminated TNX sediment can reduce contaminant mobility (extractability).

Experimental Set-up

Materials

1. B-5 TNX OD contaminated soil, a non-rad and non-hazardous soil
2. granular Fe(0)
3. North Carolina apatite
4. TNX uncontaminated surface water
5. 12 50-mL Oak Ridge tubes
6. 12 disposable filtration assemblies

Methods

1. Experimental Design: Completely randomized block design, 3 reps x 4 additives (control, Fe(0), Apatite, and Fe(0) + Apatite) x 2 moisture conditions (flooded and simulated cyclic rain events) = 24 treatments. Label containers as shown in Table 1B. 50-mL Oak Ridge tubes will be used for "flooded" treatments and disposable filtration assemblies will be used for the "wet/dry cycle" treatments.
2. Add 15-g of soil to each tube. Add 0.5-g of appropriate amendments to each tube. For the "Apatite+Fe(0) treatment" add 1-g of each. "Controls" receive no amendment.
3. Add 25-mL of uncontaminated surface water to the "flooded" treatments. Cap samples, place in a light-proof box, then place box on slow moving platform shaker.
4. For "wet/dry cycle" treatments, add 25-mL of uncontaminated surface water. Mix well by hand. Let water sit on soil for 1 day, then apply vacuum. With a tiny spatula, stir soil to permit air to dry soil. Repeat water addition 3 working days later using 25-mL water. This 25-mL of water will be composed of the water collected from lower reservoir (recycle water) and make-up water from uncontaminated surface water. The cycle will be 1 day wet, followed by 3 days dry. We will evaluate whether this cycle accomplishes the full drying desired.
5. Terminate equilibration period 4-weeks after initial water addition.
6. To terminate "flooded" samples, immediately after opening cap, filter enough sample to permit rapid measurement of pH, O_2, Eh, and conductivity (measure O_2 first to reduce amount of O_2 from the air to diffuse back into sample. Reuse sample used in the O_2 measurement in the in-line measurements of pH, Eh, and conductivity. Separate the remaining solids from liquids by centrifugation. Save both phases. Pass remaining aqueous through a 0.45-µm filter. Acidify ~½ sample by adding 0.75-µL of Ultrex HNO_3 for metal

analyses. Don't acidify the half of the aqueous sample; it will be used for anion analysis. Label samples: 301pw, 302pw/a, etc… Save moistened solids in tared containers labeled 301s, 302s, etc… Parafilm or tape caps securely to the containers and store in dark in refrigerator.

7. To terminate "wet/dry cycled" samples, add 25-mL water as if initiating another wet/dry cycle. Shake vigorously to get the soil into suspension. After 1-day contact time, vacuum filter and pass liquids through 0.45-µm filter. Rapidly measure pH, O_2, Eh, and conductivity (again, measure O_2 first to reduce amount of O_2 diffusing back into sample). Complete the separation of solids from liquid. Acidify ½ the aqueous sample by adding 0.75-µL Ultrex HNO_3. Don't acidify the remaining sample; it will be used for anion analysis. Label samples: 313pw, 313pw/a, etc… Save moistened solids in tared containers labeled 313s, 314s, etc… Parafilm or tape caps securely to the containers and store in refrigerator in dark.
8. Do 4 step sequential extraction on 2 of the 3 replicated soils, as described below.

Table 1B. Treatment I.D.'s.

Treatment ID	Moisture Condition	Amendment	Replicate
301	Flooded	Control	1
302			2
303			3
304		Apatite	1
305			2
306			3
307		Apatite and Fe(0)	1
308			2
309			3
310		Fe(0)	1
311			2
312			3
313	Wet/Dry Cycling	Control	1
314			2
315			3
316		Apatite	1
317			2
318			3
319		Apatite and Fe(0)	1
320			2
321			3
322		Fe(0)	1
323			2
324			3

Sequential Extraction Method

Fraction 1: Exchangeable

1. To 1 g of wet sample (or dry sample) in a 50 ml screw-cap centrifuge tube, add 20 ml of 1.0 M CH3COONa (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 5 ml of DI water, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to the 30ml mark and analyze.
4. Carry out a second 20 ml 1 M CH_3COONa leach of the residue, repeating steps 2 and 3.

Table 2B. Weights used in exchangeable fraction.

ID#	Sediment Description	Rep	Centrifuge tare wt. (g)	Tare + sed. wet wt. at start of Exchangeable fraction (g)	Tare + wet sed. + extract wt. for exchangeable fraction (g)
301	Flooded/Control	1			
302		2			
304	Flooded/Apatite	1			
305		2			
307	Flooded/Ap&Fe(0)	1			
308		2			
310	Flooded/Fe(0)	1			
311		2			
313	Wet-Dry/Control	1			
314		2			
316	Wet-Dry/Apatite	1			
317		2			
319	Wet-Dry/Ap&Fe(0)	1			
320		2			
322	Wet-dry/Fe(0)	1			
323		2			

Fraction 2: Amorphous Fe oxyhydroxide

1. To the residue from step 4 of exchangeable fraction, add 20 mL of 0.25 M NH_2OH HCl in 0.25 M HCl, cap and vortex for 5-10 s.
2. Place in a water bath at 60^oC for 2 h with cap loosened. Every 30 min., cap tightly and vortex the contents.
3. Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 5 ml of DI water, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to the 30 mL mark and analyze.
4. Carry out a second 0.25 M NH_2OH HCl leach of the residue, but heat for only 30 minutes. Repeat step 3.

Fraction 3: Crystalline Fe oxide

1. To the residue from step 4 of amorphous Fe oxyhydroxide, add 30 ml of 1.0 M NH_2OH HCl in 25% CH_3COOH, cap and vortex for 5-10 s.
2. Place in a water bath at 90 ^oC for 3 h with cap on tightly. Vortex contents every 20 minutes.
3. Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 10 ml of 25% CH_3COOH, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to the 50ml mark and analyze
4. Carry out a second 1.0 M NH_2OH HCl leach of the residue but heat for only 1.5 h. Then repeat step 3.

Fraction 4: Organic/Sulfide

1. To the residue from step 4 of crystalline Fe oxide, add 3 ml of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and allow the suspension to digest at least one hour at room temperature (or until it stops bubbling). The mixture will be heated at 80^oC for 2 h with occasional agitation.
2. A second 3 ml aliquot of 30% of H_2O_2 (pH 2 with HNO_3) is added 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^oC for 2 h with occasional agitation.
3. Add 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 and shake for 30 minutes.
4. Centrifuge for 10 min. and decant supernatant liquid into a labeled test-tube. Rinse residue with 5 ml of DI water, vortex and centrifuge again; do this twice and add supernatant rinses to the test-tube. Make up to the 30ml mark and analyze.
5. Repeat steps 2, 3, and 4 if necessary. In step 4 add gradually 30% of H_2O_2.

Fraction 5: Residual

1. Sub-sample of 0.6 gram (dry) from step 4 of organic/sulfide was digested in the system Star 6 with HNO_3 (10ml), H_2SO_4 (4.0 ml), HNO_3 (4.5 ml), and HCl (2ml). Samples were filtered and diluted to 100 ml.

Additional Characterization

The following analyses were be conducted on an un-treated soil.

- pH (Cathy)
- particle size distribution (Anna)
- total organic carbon (combustion, Anna)
- cation exchange (Cathy)
- Uncontaminated surface water
- Cation/anions: ICP-MS (primary program + Ce, Th, U, and S specialty programs) + ICP-ES (31 elements) (UGa, Anna)
- TIC/TOC (UGa, Anna)
- pH, EC, Eh, and O_2 (Cathy)

<u>Apatite</u>

- Total digestion by STAR 6 program followed by Cation/anions: ICP-MS (primary program + Ce, Th, U, and S specialty programs) + ICP-ES (31 elements) (UGa, Anna)

<u>Fe(0)</u>

- Total digestion by STAR 6 program followed by Cation/anions: ICP-MS (primary program + Ce, Th, U, and S specialty programs) + ICP-ES (31 elements) (UGa, Anna)
- Used Fe(0); at end of experiment, remove some Fe(0) particles from soil. Rinse soil off particles. Place used Fe(0) in centrifuge tube containing ~40-mL water. Place tubes on slow moving platform shaker for 2 hours. Pick out Fe(0) particles. Submit 3 replicates for chemical analysis. (Dan)
- Total digestion by STAR 6 program followed by Cation/anion analyses: ICP-MS (primary program + Ce, Th, U, and S specialty programs) + ICP-ES (31 elements) (Dan)

Chemical Analyses

Table 3b contains the types of analyses to be performed on each sample.

Table 3B. Samples to be submitted for chemical analyses.

	Sample ID	Description	Water	Analysis[(a)]
1	301pw	Control, Pore Water	Flooded	2
2	301pw/a	Control, Pore Water Acidified	Flooded	1
3	301exch	Control, Exchangeable	Flooded	1
4	301org	Control, Organic	Flooded	1
5	301Fe	Control, Crystalline Fe-oxide	Flooded	1
6	301Tot	Control, Total Residue	Flooded	1
7	302-pw	Control, Pore Water	Flooded	2
8	302pw/a	Control, Pore Water Acidified	Flooded	1
9	302exch	Control, Exchangeable	Flooded	1
10	302org	Control, Organic	Flooded	1
11	302Fe	Control, Crystalline Fe-oxide	Flooded	1
12	302Tot	Control, Total Residue	Flooded	1
13	304pw	Apatite, Pore Water	Flooded	2
14	304pw/a	Apatite, Pore Water Acidified	Flooded	1
15	304exch	Apatite, Exchangeable	Flooded	1
16	304org	Apatite, Organic	Flooded	1
17	304Fe	Apatite, Crystalline Fe-oxide	Flooded	1
18	304Tot	Apatite, Total Residue	Flooded	1
19	305pw	Apatite, Pore Water	Flooded	2
20	305pw/a	Apatite, Pore Water Acidified	Flooded	1
21	305exch	Apatite, Exchangeable	Flooded	1
22	305org	Apatite, Organic	Flooded	1
23	305Fe	Apatite, Crystalline Fe-oxide	Flooded	1
24	305Tot	Apatite, Total Residue	Flooded	1
25	307pw	Apatite&Fe(0), Pore Water	Flooded	2
26	307pw/a	Apatite&Fe(0), Pore Water Acidified	Flooded	1
27	307exch	Apatite&Fe(0), Exchangeable	Flooded	1
28	307org	Apatite&Fe(0), Organic	Flooded	1
29	307Fe	Apatite&Fe(0), Crystalline Fe-oxide	Flooded	1
30	307Tot	Apatite&Fe(0), Total Residue	Flooded	1
31	308pw	Apatite&Fe(0), Pore Water	Flooded	2
32	308pw/a	Apatite&Fe(0), Pore Water Acidified	Flooded	1
33	308exch	Apatite&Fe(0), Exchangeable	Flooded	1
34	308org	Apatite&Fe(0), Organic	Flooded	1
35	308Fe	Apatite&Fe(0), Crystalline Fe-oxide	Flooded	1
36	308Tot	Apatite&Fe(0), Total Residue	Flooded	1
37	310pw	Fe(0), Pore Water	Flooded	2
38	310pw/a	Fe(0), Pore Water acidified	Flooded	1
39	310exch	Fe(0), Exchangeable	Flooded	1
40	310org	Fe(0), Control, Organic	Flooded	1
41	310Fe	Fe(0), Control, Crystalline Fe-oxide	Flooded	1
42	310Tot	Fe(0), Control, Total Residue	Flooded	1
43	311pw	Fe(0), Control, Pore Water	Flooded	2
44	311pw/a	Fe(0), Pore Water Acidified	Flooded	1
45	311exch	Fe(0), Control, Exchangeable	Flooded	1
46	311org	Fe(0), Organic	Flooded	1
47	311Fe	Fe(0), Crystalline Fe-oxide	Flooded	1
48	311Tot	Fe(0), Total Residue	Flooded	1
49	313pw	Control, Pore Water	Wet/Dry	2

50	313pw/a	Control, Pore Water Acidified	Wet/Dry	1
51	313exch	Control, Exchangeable	Wet/Dry	1
52	313org	Control, Organic	Wet/Dry	1
53	313Fe	Control, Crystalline Fe-oxide	Wet/Dry	1
54	313Tot	Control, Total Residue	Wet/Dry	1
55	314-pw	Control, Pore Water	Wet/Dry	2
56	314pw/a	Control, Pore Water Acidified	Wet/Dry	1
57	314exch	Control, Exchangeable	Wet/Dry	1
58	314org	Control, Organic	Wet/Dry	1
59	314Fe	Control, Crystalline Fe-oxide	Wet/Dry	1
60	314Tot	Control, Total Residue	Wet/Dry	1
61	316pw	Apatite, Pore Water	Wet/Dry	2
62	316pw/a	Apatite, Pore Water Acidified	Wet/Dry	1
63	316exch	Apatite, Exchangeable	Wet/Dry	1
64	316org	Apatite, Organic	Wet/Dry	1
65	316Fe	Apatite, Crystalline Fe-oxide	Wet/Dry	1
66	316Tot	Apatite, Total Residue	Wet/Dry	1
67	317pw	Apatite, Pore Water	Wet/Dry	2
68	317pw/a	Apatite, Pore Water Acidified	Wet/Dry	1
69	317exch	Apatite, Exchangeable	Wet/Dry	1
70	317org	Apatite, Organic	Wet/Dry	1
71	317Fe	Apatite, Crystalline Fe-oxide	Wet/Dry	1
72	317Tot	Apatite, Total Residue	Wet/Dry	1
73	319pw	Apatite&Fe(0), Pore Water	Wet/Dry	2
74	319pw/a	Apatite&Fe(0), Pore Water Acidified	Wet/Dry	1
75	319exch	Apatite&Fe(0), Exchangeable	Wet/Dry	1
76	319org	Apatite&Fe(0), Organic	Wet/Dry	1
77	319Fe	Apatite&Fe(0), Crystalline Fe-oxide	Wet/Dry	1
78	319Tot	Apatite&Fe(0), Total Residue	Wet/Dry	1
79	320pw	Apatite&Fe(0), Pore Water	Wet/Dry	2
80	320pw/a	Apatite&Fe(0), Pore Water Acidified	Wet/Dry	1
81	320exch	Apatite&Fe(0), Exchangeable	Wet/Dry	1
82	320org	Apatite&Fe(0), Organic	Wet/Dry	1
83	320Fe	Apatite&Fe(0), Crystalline Fe-oxide	Wet/Dry	1
84	320Tot	Apatite&Fe(0), Total Residue	Wet/Dry	1
85	322pw	Fe(0), Pore Water	Wet/Dry	2
86	322pw/a	Fe(0), Pore Water Acidified	Wet/Dry	1
87	322exch	Fe(0), Exchangeable	Wet/Dry	1
88	322org	Fe(0), Control, Organic	Wet/Dry	1
89	322Fe	Fe(0), Control, Crystalline Fe-oxide	Wet/Dry	1
90	322Tot	Fe(0), Control, Total Residue	Wet/Dry	1
91	323pw	Fe(0), Control, Pore Water	Wet/Dry	2
92	323pw/a	Fe(0), Pore Water acidified	Wet/Dry	1
93	323exch	Fe(0), Control, Exchangeable	Wet/Dry	1
94	323org	Fe(0), Organic	Wet/Dry	1
95	323Fe	Fe(0), Crystalline Fe-oxide	Wet/Dry	1
96	323Tot	Fe(0), Total Residue	Wet/Dry	1

Table 4B. Dry weight measurements.

ID#	Treatment	Rep	Al Pan Tare Wt, betw. 2 & 3 g (g)	Al Pan + Wet Soil Wt (g)	Al Pan + Dry Soil Wt. (g)
301a	301	A			
301b	301	B			
302a	302	A			
302b	302	B			
304a	304	A			
304b	304	B			
305a	305	A			
305b	305	B			
307a	307	A			
307b	307	B			
308a	308	A			
308b	308	B			
310a	310	A			
310b	310	B			
311a	311	A			
311b	311	B			
313a	313	A			
313b	313	B			
314a	314	A			
314b	314	B			
316a	316	A			
316b	316	B			
317a	317	A			
317b	317	B			
319a	319	A			
319b	319	B			
320a	320	A			
320b	320	B			
322a	322	A			
322b	322	B			
323a	323	A			
323b	323	B			