In Situ Treatment of Metals in Contaminated Soils with Phytate

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ABSTRACT

Batch experiments were conducted to evaluate the ability of various forms of phytate, the hexaphosphoric form of myo-inositol (IP6), to immobilize U, Ni, and other inorganic contaminants in soils and sediments. A Ca–phytate precipitate (Ca_n–IP6), dodeca sodium–phytate (Na_{12}–IP6), and hydroxyapatite (HA) were added to contaminated soil at rates of 0, 10, 25, and 50 g kg^{-1} and equilibrated in 0.001 M CaCl$_2$. The samples were then centrifuged, the solution pH was measured, and the supernatants were filtered prior to analysis for dissolved organic carbon (DOC), U, Ni, P, and other inorganic contaminants, such as As, Cr, Se, and Pb. The residual sediments were air-dried prior to characterization by analytical electron microscopy and extraction with the Toxicity Characteristic Leaching Procedure (TCLP). The solubility of several metals (e.g., U, Pb, Cu) increased with increasing Na_{12}–IP6 when compared with the nonamended control. In some cases immobilization was observed at the lowest Na_{12}–IP6 application rate (10 g kg^{-1}) with an increase in solubility observed at the higher rates, demonstrating the importance of metal to ligand ratio. In contrast, Ca_n–IP6 and HA decreased the solubility of U, Ni, Al, Pb, Ba, Co, Mn, and Zn. For example, soluble U decreased from 2242 to 76 µg kg^{-1} and Ni from 58 to 9.6 mg kg^{-1} with the Ca_n–IP6 addition, similar to the results observed for HA. Arsenic and Se solubility increased for HA and both forms of IP6, but to a much greater degree for Na_{12}–IP6, suggesting that the increase in pH observed for HA and Na_{12}–IP6, combined with added competition from PO$_4$ and IP6 for sorption sites, resulted in the release of sorbed oxyanion contaminants. The analytical electron microscopy results indicated that metals such as U and Ni were closely associated with secondary Al-rich precipitates in the HA-treated soils, rather than unreacted HA. The analytical electron microscopy results were less definitive for the Ca_n–IP6-treated soil, although the residual P-containing material was enriched in Al, with lesser amounts of U and Ni.

CONVENTIONAL REMEDIATION techniques that involve excavation and some form of ex situ treatment (i.e., soil washing, solidification, etc.), followed by disposal and long-term monitoring are expensive and disruptive to the landscape and existing ecosystem. However, recent studies have demonstrated that in situ contaminant immobilization may be the preferred approach for remediating shallow contaminated soils and sediments (Knox et al., 2000; Seaman et al., 2001a). In addition to reducing cleanup costs, nondestructive in situ treatment options can potentially decrease environmental disturbance and worker exposure.

In situ immobilization treatment methods typically reduce the mobility and bioavailability of the target contaminant by redirecting solid-phase speciation in favor of less labile phases either through preferential sorption or contaminant precipitation. For instance, the addition of illitic clays to coarse-textured soils and sedi-

ments can enhance the interlayer fixation of ^{137}Cs (Hinton et al., 2001; Seaman et al., 2001a). As another example, the addition of apatite minerals [$Ca_5(PO_4)_3X$, where X = halide or hydroxyl] and even phosphoric acid has proven effective in stabilizing many transition and heavy metals, metalloids, and radionuclides through sorption to HA or the formation of secondary phosphate precipitates that remain stable over a range of geochemical conditions (Berti and Cunningham, 1997; Bostick et al., 2000; Fuller et al., 2002; Laperche et al., 1997; Ma et al., 1993; Manecki et al., 2000; Traina and Laperche, 1999; Wright et al., 1995; Yang et al., 2001). To overcome the limitations encountered when using a sparingly soluble immobilizing agent, such as HA or illitic clays, researchers have proposed introducing the material as part of a passive flow-through contaminant barrier for intersecting the migrating plume (Bostick et al., 2000; Fuller et al., 2002).

Recent studies have demonstrated the ability of HA to reduce the mobility and bioavailability of U, Ni, and other inorganic contaminants from shallow sediments on the Department of Energy's Savannah River Site (SRS), located near Aiken, SC (Arey et al., 1999; Seaman et al., 2001a; Seaman et al., 2001b). Tims Branch, a second-order stream that drains approximately 16 km^2 on the SRS and eventually feeds the Savannah River, received significant amounts of U, Ni, Pb, Cr, Cu, Th, and other contaminants resulting from nuclear materials production and refinement on the SRS (Evans et al., 1992; Pickett, 1990). Significant deposition of contaminants and suspended sediments occurred within Steed Pond, a former farm pond on Tims Branch, due to the longer residence times and reduced flow velocities (Batson, 1994; Batson et al., 1996; Evans et al., 1992). The wooden dam ruptured in 1984, draining the pond and exposing the contaminated sediments to erosion (Pickett, 1990). No attempt was made to rebuild the dam and revegetation has been hampered somewhat by metal toxicity that continues to limit plant growth (Batson, 1994; Punshon, unpublished data, 2002).

Steed Pond is an ideal site for in situ immobilization methods due to the large expanse of the affected area (approximately 5.3 ha) and the relatively shallow nature of the contamination, most of which is restricted to the upper 50 cm. In situ immobilization methods are typically limited to surficial contamination where the poorly soluble stabilizing agents (e.g., hydroxyapatite [HA], zeolites, and illitic clays) can be actively incorporated within contaminated soils and sediments. However, incorporation of HA to a depth of 50 cm would
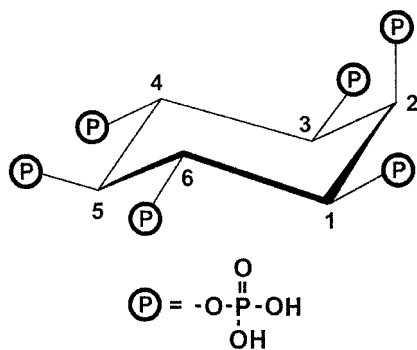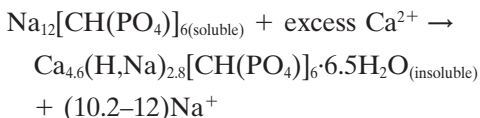
Fig. 1. The structure of phytate (IP6) in a dilute solution (redrawn from Graf [1983]).

greatly disturb the functioning, albeit contaminated, ecosystem and possibly result in greater contaminant redistribution due to erosion. Remediating additional contaminated areas adjacent the active streambed along Tims Branch could be even more problematic with poorly soluble amendments.
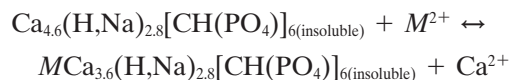
Recent studies have suggested that phytate (IP6), a natural organophosphorus compound, can be applied in a soluble form for delivery to remote contaminated sediments, where it undergoes various reactions that eventually result in the precipitation of the contaminant metals (Jensen et al., 1996; Nash et al., 1997, 1998a,b). A natural by-product of fermentation processes and a waste product in the fermentation industry, IP6, the hexaphosphoric acid of myo-inositol, is a major component of plant seeds with six orthophosphate moieties that provide twelve coordinate ligands for binding metal ions (Fig. 1). Metal interactions with the numerous phosphate ligands present on IP6 can lead to both intra- and intermolecular bonding resulting in the simultaneous formation of numerous monomeric and polymeric species, which can lead to the coprecipitation of nonstochiometric solid-phase mixtures, as the metal to ligand ratio increases (Wise, 1986). Phytate is the dominant form of organic phosphorus present in poultry and swine manure, because these animals lack an important enzyme system for efficient IP6 breakdown (Sharpley and Moyer, 2000; Sharpley et al., 1994); therefore, significant research has been conducted to evaluate the role of IP6 in eutrophication associated with high levels of P that can accumulate in animal waste–amended soils.

The use of IP6 for contaminant immobilization has been described by Nash and coworkers (Jensen et al., 1996; Nash et al., 1997, 1998a,b) as a multistep process. First, IP6 is surface-applied or injected in the subsurface in a soluble form, probably dodeca Na–phytate (Na_{12}–IP6). As the IP6 migrates through the material of interest, it precipitates with native polyvalent cations (Jensen et al., 1996; Nash et al., 1997, 1998a), such as Ca or Mg:

$$Na_{12}[CH(PO_4)]_{6(soluble)} + excess\ Ca^{2+} \rightarrow$$

$$Ca_{4.6}(H,Na)_{2.8}[CH(PO_4)]_6 \cdot 6.5H_2O_{(insoluble)}$$
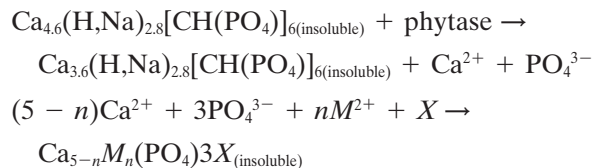
$$+ (10.2–12)Na^+$$

Contaminant metal immobilization then occurs through either coprecipitation during initial solid-phase

formation or exchange between the major solid-phase cation (Ca in the present case), and the soluble contaminant metal of interest (M^{2+}) (Nash et al., 1997, 1998a,b):

$$Ca_{4.6}(H,Na)_{2.8}[CH(PO_4)]_{6(insoluble)} + M^{2+} \leftrightarrow$$

$$MCa_{3.6}(H,Na)_{2.8}[CH(PO_4)]_{6(insoluble)} + Ca^{2+}$$

Contaminant metals may be coprecipitated or exchanged with Ca in Ca_n–IP6 at concentrations that are insufficient to promote precipitation by themselves (Wise, 1986). Additionally, metals such as Pb may be strongly sorbed to precipitated Ca_n–IP6 without resulting in the stochiometric release of Ca^{2+} (Wise, 1986). Although coprecipitation or metal exchange with Ca_n–IP6 may initially reduce contaminant metal solubility, Nash and coworkers (Jensen et al., 1996; Nash et al., 1997, 1998a,b) suggest Ca_n–IP6 hydrolysis and mineralization release inorganic PO_4, which can result in further contaminant immobilization through the formation of insoluble secondary contaminant–phosphate precipitates in a manner similar to the addition of HA to metal-contaminated soils:

$$Ca_{4.6}(H,Na)_{2.8}[CH(PO_4)]_{6(insoluble)} + phytase \rightarrow$$

$$Ca_{3.6}(H,Na)_{2.8}[CH(PO_4)]_{6(insoluble)} + Ca^{2+} + PO_4^{3-}$$

$$(5 - n)Ca^{2+} + 3PO_4^{3-} + nM^{2+} + X \rightarrow$$

$$Ca_{5-n}M_n(PO_4)3X_{(insoluble)}$$

To date, studies evaluating the efficacy of IP6 as an in situ immobilizing agent have focused mainly on the reactions involved in metal sorption and exchange once the IP6 has arrived at the zone of interest and precipitated in the Ca_n–IP6 form. However, IP6 can strongly sorb to hydrous oxides such as goethite (Celi et al., 1999, 2001; Ognalaga et al., 1994), which might tend to limit the ability to deliver the reactant to the contaminated zone of interest in a controlled manner. In addition, the solubility of metal–IP6 complexes depends greatly on the metal to ligand ratio in that equimolar concentrations of most metals are highly soluble (Graf, 1986), possibly resulting in the enhanced mobilization of the target contaminant. Therefore, the objective of the current study was to evaluate the ability of various forms of IP6 in comparison with HA to immobilize U and other inorganic contaminants in Steed Pond sediments collected from the Department of Energy's Savannah River Site located near Aiken, SC.

MATERIALS AND METHODS

Steed Pond sediments are characteristic of the highly weathered soils and sediments of the Atlantic Coastal Plain (Table 1), and display elevated levels of U, Ni, Cr, Cu, and Pb that are several times higher than the reported values for nonimpacted soils on the Savannah River Site (Pickett, 1990; Pickett et al., 1985; Zeigler et al., 1986). The levels of U and Ni are several hundred times higher than "normal," and apparently limit revegetation in localized areas. The sediments tend to be acidic (pH 4.0–4.5) with variable levels of organic carbon and a clay fraction that is dominated by kaolinite with lesser amounts of hydroxy-interlayered vermiculite (HIV), gibbsite, and goethite (Arey et al., 1999; Batson, 1994). After

collection, the study sample was stored in a field-moist state at 4°C until used in the batch study.

Batch Equilibrations

Three amendment materials were evaluated in a series of batch equilibration experiments: reagent-grade Na_{12}–IP6 (Na_{12} $C_6H_6O_{24}P_6$), a Ca_n–IP6 precipitate, and reagent-grade HA (Ca_5 $(PO_4)_3OH$). The Ca_n–IP6 {$Ca_{4.41}Na_{0.09}H_{3.09}[CH(PO_4)]_6 \cdot 7 \cdot 2H_2O$} was produced with the method outlined by Nash et al. (1998a). Briefly, a sufficient volume of 1 M $Ca(NO_3)_2$ solution was added to a pH 7.0, 0.049 M Na_{12}–IP6 solution to achieve a 6:1 Ca to IP6 ratio. The resulting white precipitate was stirred overnight and then washed four times with deionized water prior to oven-drying at 60°C. A soluble Ca_1–IP6 salt is commercially available ($CaC_6H_{16}O_{24}P_6 \cdot nH_2O$, n = approximately 3.1), but precipitation with additional Ca and pH adjustment to counter the inherent acidity would still be required before such material could be used as a soil amendment. In preliminary batch experiments, the commercially available Ca_1–IP6 decreased the soil pH to approximately 3.6, in contrast to the pH increase observed for all amendments used in the current study. The Ca_1–IP6 also increased contaminant metal solubility as well, to a level similar to that observed for Na_{12}–IP6 (data not shown).

Three grams (dry wt.) of field-moist sediment were placed in centrifuge tubes with three replicates for each treatment. Four levels of amendment were tested: 0, 10, 25, and 50 g kg^{-1}, which correspond to 0, 1.0, 2.5, and 5.0% by weight. Fifteen milliliters of 0.001 M $CaCl_2$ was used as a background solution. Samples were equilibrated on a reciprocating shaker for 136 h at 25°C. Preliminary kinetic studies indicated that such a reaction time was sufficient to reach equilibrium with respect to metal immobilization. After equilibration, the pH of the sediment suspensions was measured. The suspensions were centrifuged at 10 000 rpm for 20 min with a Sorvall RC2-B supercentrifuge (Sorvall Kendro Laboratory Products, Newton, CT) and the supernatants were then passed through 0.22-μm pore-size polycarbonate filters. A fraction of the filtered supernatant was analyzed for DOC with a Shimadzu (Kyoto, Japan) TOC-5000A organic carbon analyzer. The remaining supernatants were acidified (1% nitric acid) and analyzed for metals by inductively coupled plasma mass spectrometry (ICP–MS) (Elan 6000; PerkinElmer, Wellesley, MA) following the quality assurance–quality control protocols outlined in USEPA Method 6020 (USEPA, 1994). Following batch equilibration, the samples were air-dried for scanning electron (SEM) and transmission electron microscopy (TEM)–based spectroscopic microanalysis.

Toxicity Characteristic Leaching Procedure Extraction

A subsample of the air-dried replicates for each treatment was extracted with the USEPA standardized Toxicity Characteristic Leaching Procedure (TCLP; USEPA, 1992). The TCLP leaching solution is comprised of 0.1 M glacial acetic acid and 0.0643 M NaOH, with a final pH of 4.93. Ten milliliters of leaching solution were added to 0.5 g of treated sediment, the mixture was agitated on a reciprocating shaker for 18 h at 25°C, and then centrifuged as described above. After centrifugation, the supernatants were filtered through 0.22-μm pore-size polycarbonate filters, acidified to 1% HNO_3, and analyzed for metals with ICP–MS.

Table 1. Physical and chemical characteristics of the contaminated sediment from Steed Pond (Arey et al., 1999; Batson, 1994).

Characteristic	Value
pH†	4.1
CDB‡-extractable Fe, % (w/w)	3.2
CDB-extractable Al, % (w/w)	2.3
Organic carbon, g kg^{-1}§	49
Particle size distribution¶, %	
Sand	19.2
Silt	45.2
Clay	35.6
Mineralogy#	
Sand	q ≫ fel
Silt	q > k ≫ fel
Clay	k ≫ HIV > gibb > goe > q
Metal concentration, mg kg^{-1}	
As	17.4
Ba	78.6
Cd	1.1
Co	11.0
Cr	175 (38)††
Cu	76.5 (18)††
Ni	1922 (10)††
Pb	91.6 (13)††
U	2260 (2)††
Zn	215

† 2:1 solution to soil ratio in deionized water.
‡ Citrate–dithionite–bicarbonate extraction (Jackson et al., 1986).
§ Total organic carbon, dry combustion method (Nelson and Sommers, 1982).
¶ Micropipette method (Miller and Miller, 1987).
# Mineralogy determined by X-ray diffraction (Whittig and Allardice, 1986); fel is feldspar, k is kaolinite, HIV is hydroxy-interlayered vermiculite, gibb is gibbsite, q is quartz, and goe is goethite.
†† Values in parentheses are the background levels for soils on the Savannah River Site (Pickett et al., 1985).

Electron Microscopy Analysis

Analytical electron microscopy was used to identify solid phases that may influence contaminant metal solubility. Air-dried soils from the batch experiments were secured with carbon tape to a scanning electron microscope sample stub and coated with evaporated carbon prior to energy dispersive X-ray analysis (EDXA) and imaging with a JEOL (Peabody, MA) JSM 6400 scanning electron microscope (tungsten filament) equipped with a Noran Voyager EDXA system (Thermo NORAN, Middleton, WI). For comparison, the initial soil amendments (i.e., Ca_n–IP6, Na_{12}–IP6, reagent-grade CaC_6H_{16} $O_{24}P_6 \cdot nH_2O$, and HA) were also analyzed with the same method. To improve spatial resolution during EDXA analysis, a small fraction of each treated soil and the control soil was embedded in a low viscosity fixative and cured overnight prior to sectioning. The fixed samples were cut into thin sections (approximately 70 nm) with an ultramicrotome equipped with a diamond knife and mounted on transmission electron microscopy grids prior to analysis with a JEOL 2010 transmission electron microscope equipped with a thin-window EDXA detector for quantifying lighter elements ($Z \geq 6$).

RESULTS AND DISCUSSION

Batch Results

Metal concentrations derived from batch equilibrations are plotted as a function of amendment level. Error bars have been included to reflect the standard deviation of the treatment means. In all but a few cases, the standard deviation is smaller than the actual treatment symbol in the figure. For all inorganic contaminants tested
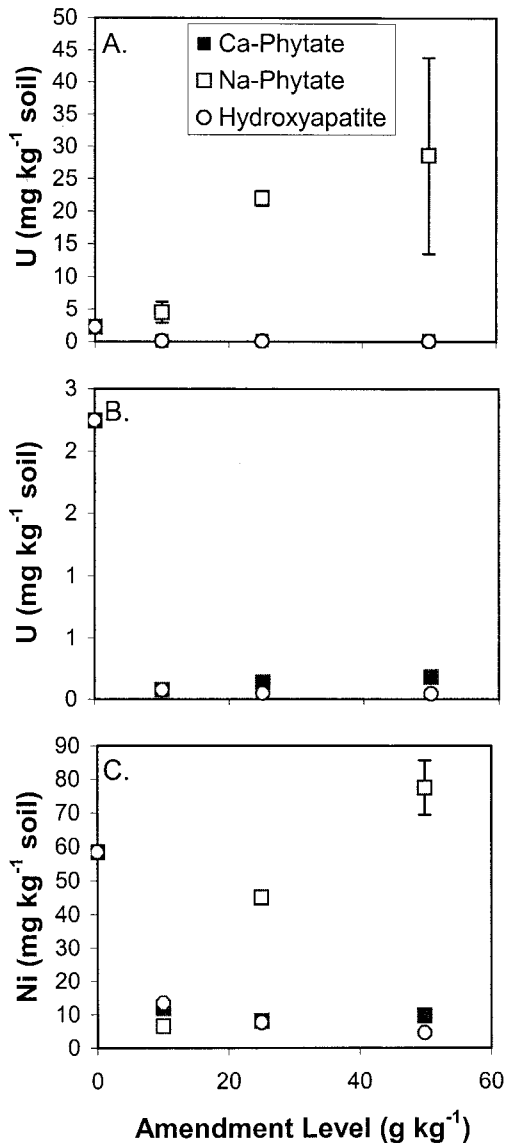
Fig. 2. Effect of calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA) addition on soluble U (*A* and *B*) and Ni (*C*) after equilibration for 136 h in 0.001 *M* CaCl$_2$. *B* reflects the expanded scale for *A*. Error bars represent the standard deviation of the treatment means.

Fig. 3. Effect of calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA) on soluble Al (*A*), Pb (*B*), Ba (*C*), and Cu (*D*) after equilibration for 136 h in 0.001 *M* CaCl$_2$. Error bars represent the standard deviation of the treatment means.

in this study, Ca$_n$–IP6 performed quite similar to HA in decreasing the solubility of several contaminant metals, including U and Ni (Fig. 2), during the initial equilibrations. For example, the level of soluble U and Ni decreased from 2.3 to <0.1 (Fig. 2B) and 59 to <10 (Fig. 2D) mg kg^{-1} soil, respectively. In sharp contrast, the soluble form of IP6, Na$_{12}$–IP6, was often ineffective at immobilizing the metals. For U, the solubility increased directly with increasing Na$_{12}$–IP6 amendment level, but for Ni there was an initial decrease in solubility at the lowest treatment level, 10 g kg^{-1}, similar to the results observed for Ca$_n$–IP6 and HA, followed by an increase in solubility with increasing amendment. A closer examination of the HA and Ca$_n$–IP6 data suggests that U solubility increases slightly for the Ca$_n$–IP6 treatments at the higher amendment treatment levels, that is, 25 and 50 g kg^{-1}.
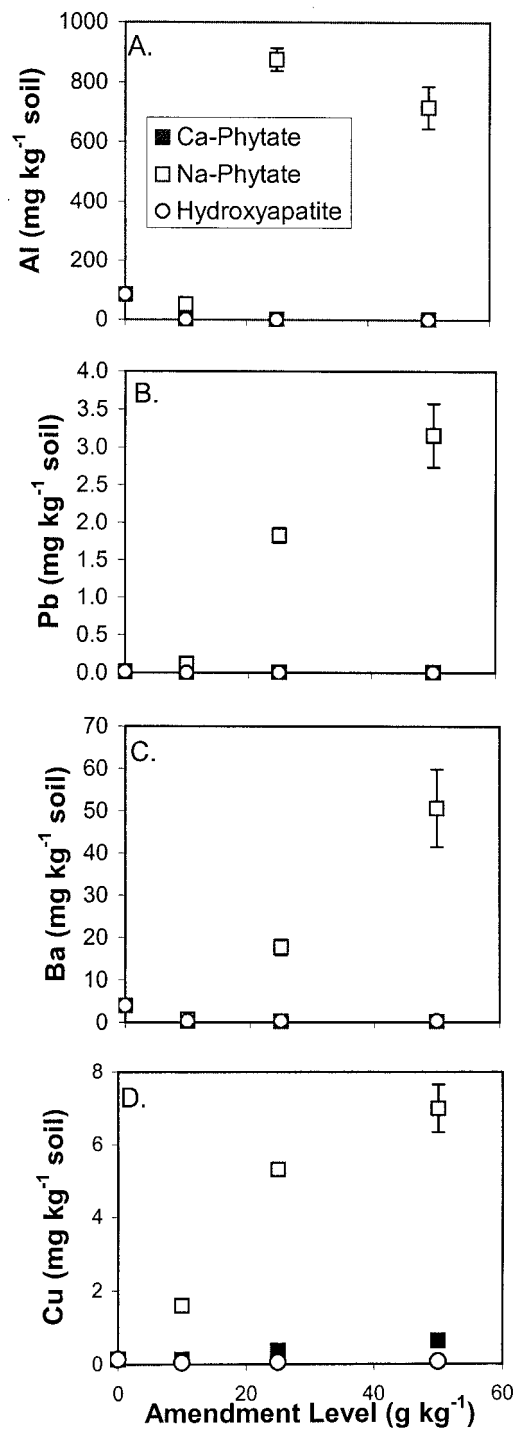
Uranium and Ni represent the two major amendment responses to Na$_{12}$–IP6 treatments observed for the inorganic contaminants monitored in the current study. Increased metal solubility with Na$_{12}$–IP6 treatment was also observed for Pb and Cu (Fig. 3). At the lower treatment levels, Al and Ba responded in a manner
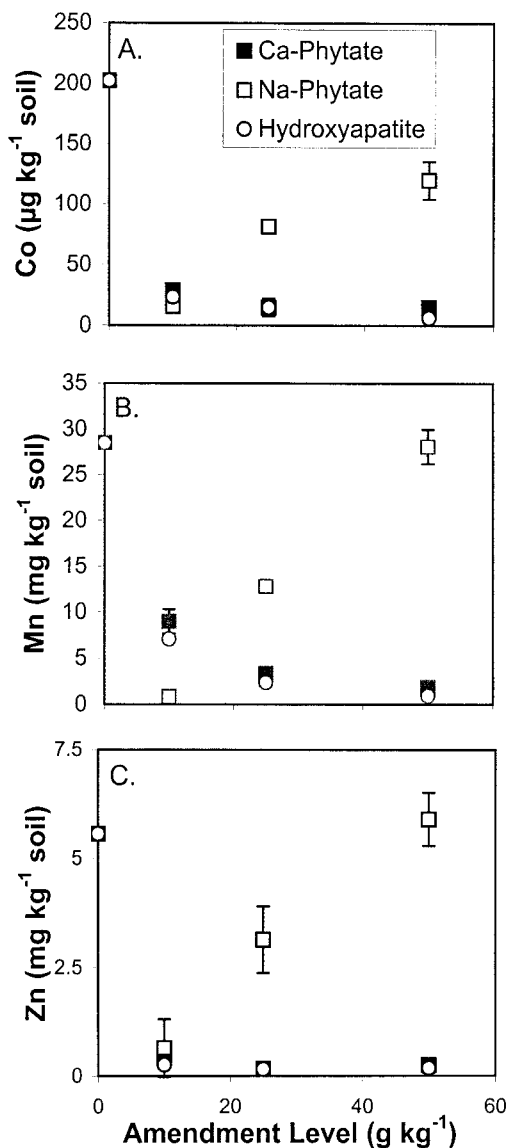
Fig. 4. Effect of calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA) on soluble Co (A), Mn (B), and Zn (C) after equilibration for 136 h in 0.001 M CaCl$_2$. Error bars represent the standard deviation of the treatment means.

Fig. 5. Effect of calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA) on pH (A), P (B), and dissolved organic carbon (DOC) (C) after equilibration for 136 h in 0.001 M CaCl$_2$. Error bars represent the standard deviation of the treatment means.

similar to Ni, that is, an initial decrease in solubility at the lowest amendment level, 10 g kg^{-1}, but increased solubility with increasing Na$_{12}$–IP6 beyond that of the nonamended control. As reported earlier, enhanced metal solubilization was also observed in preliminary batch studies with reagent-grade Ca$_1$–IP6 (CaC$_6$H$_{16}$O$_{24}$P$_6$· nH$_2$O, n = approximately 3.1) as a soil amendment. Such behavior illustrates the importance of metal to ligand ratio in controlling metal–IP6 precipitation. In fact, IP6 has been used in cleaning solutions to solubilize Fe and Ca, despite the fact that it forms fairly insoluble precipitates with both cations (Graf, 1983).

Behavior similar to that observed for Ni (i.e, immobilization at low amendment levels and greater metal solubility approaching that observed for the control with increasing amendment level) was observed for several
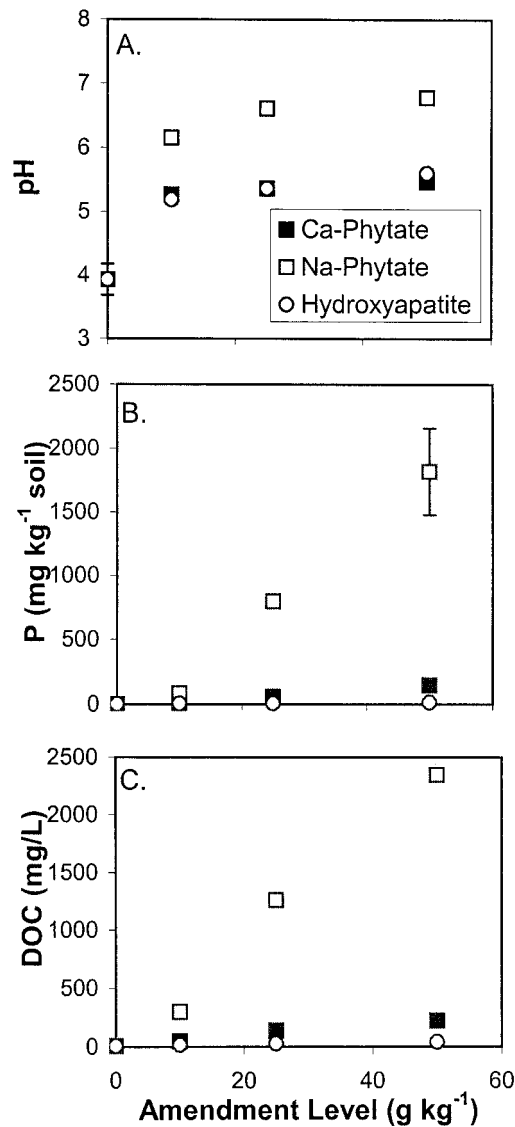
other metal contaminants, such as Co, Mn, and Zn (Fig. 4). This suggests that metal to ligand ratios for the low-level Na$_{12}$–IP6 treatment in the 0.001 M CaCl$_2$ background solution favored IP6 precipitation necessary for metal immobilization, while higher treatment levels favored metal solubilization. Other solution factors support such a hypothesis. The Na$_{12}$–IP6 increased the solution pH to a greater degree than was observed for HA or Ca$_n$–IP6 (Fig. 5). All three amendments increased the level of soluble P to some degree in a relatively linear manner with increasing amendment level, with soluble P being much higher for the Na$_{12}$–IP6 treatments compared with HA (slope = 0.21, P = 1.79 × 10^{-8}) and Ca$_n$–IP6 (slope = 3.49, P = 1.48 × 10^{-9}), presumably indicative of the role IP6 is playing in metal solubilization for the high-level Na$_{12}$–IP6 treatments. An examination of the slope and intercept for soluble P in

the Na_{12}–IP6 treatments suggests that some base level of IP6 was initially sorbed or precipitated from all treatments, that is, intercept < 0 ($P = 0.036$), which supports the contention that IP6 precipitation at low treatment levels favors metal immobilization observed for Ni and other metals. To a lesser degree, a similar supporting trend was also observed for DOC, that is, intercept < 0 ($P = 0.104$).

Hydroxyapatite and Ca_n–IP6 reduced the solubility of Al, Pb, Ba, Co, Mn, and Zn during batch equilibration (Fig. 3 and 4), demonstrating the potential efficacy of Ca_n–IP6 and HA in addressing soils and sediments with multiple contaminant metals. For example, Ca–IP6 and

HA reduced the solubility of Pb from 16 $\mu g\ kg^{-1}$ in the unamended soil to $<5\ \mu g\ kg^{-1}$. The Ca–IP6 was ineffective in reducing the solubility of Cu when compared with the control or HA-treated samples (Fig. 3D). However, Na_{12}–IP6 increased the solubility of several
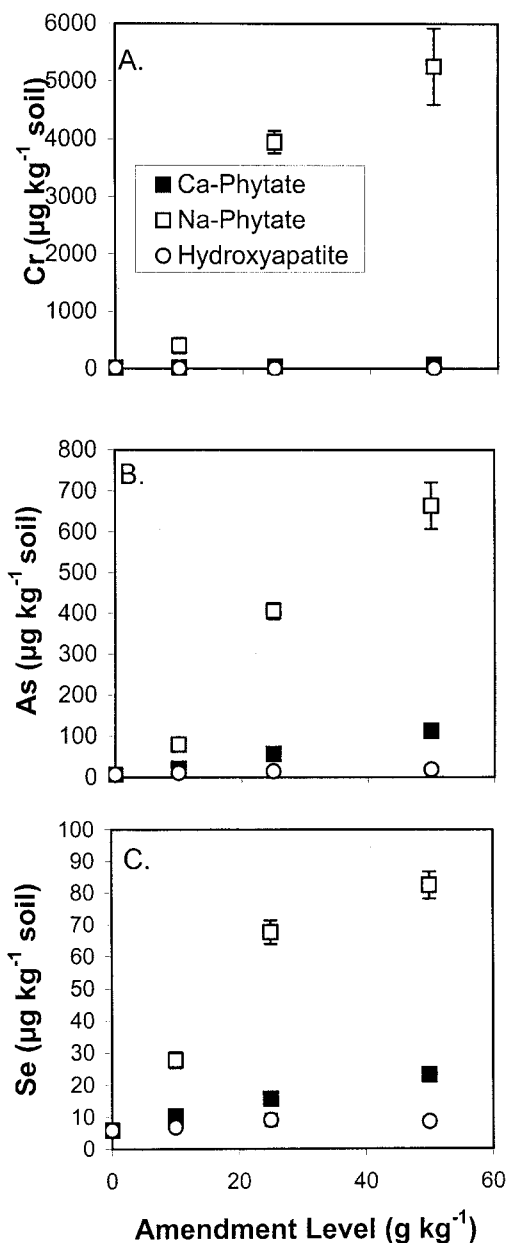

Fig. 6. Effect of calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA) on soluble Cr (A), As (B), and Se (C) after equilibration for 136 h in 0.001 M CaCl$_2$. Error bars represent the standard deviation of the treatment means.
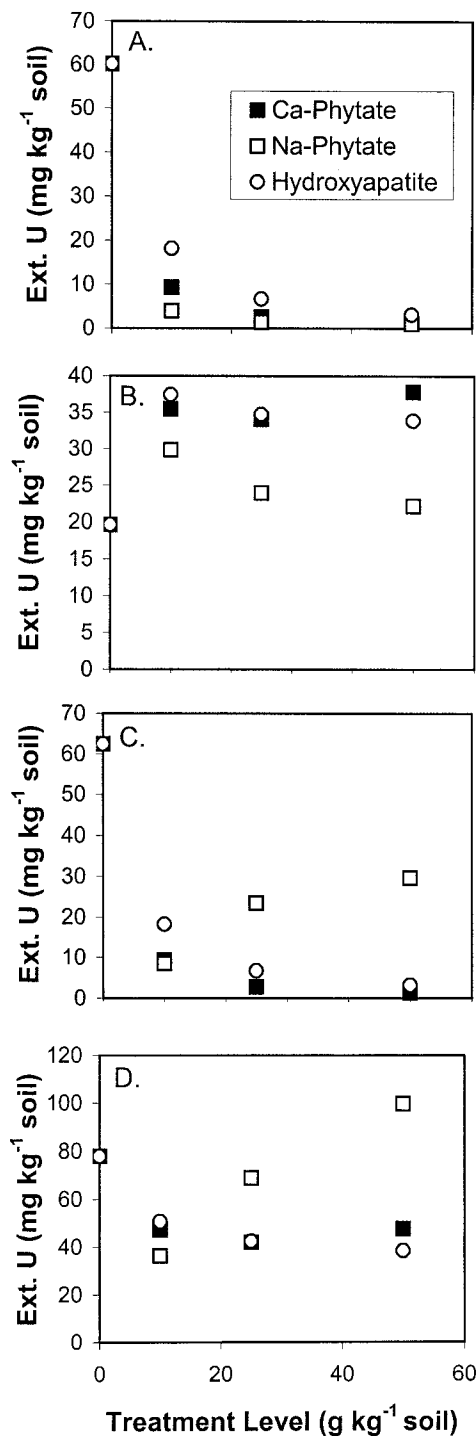
Fig. 7. Toxicity Characteristic Leaching Procedure (TCLP)–extractable U (A) and Ni (B) for contaminated soil amended with calcium–phytate precipitate (Ca$_n$–IP6), dodeca sodium–phytate (Na$_{12}$–IP6), and hydroxyapatite (HA). In C and D, the TCLP extractable U and Ni values were corrected for metal removal during the initial equilibration phase of the study and reported on a soil mass basis.

other metals as observed for U, especially at the two highest amended treatment levels (e.g., Al, Pb, Ba, and Cu; Fig. 3), and decreased the solubility of other metals at low amendment levels while metal solubility approached that of the control treatment at higher treatment levels in a manner similar to that observed for Ni (e.g., Co, Mn, and Zn; Fig. 4). The 0.001 M background level of Ca and certain contaminant metals appear to be insufficient to result in full Ca_n–IP6 precipitation for the high-level Na_{12}–IP6 treatments. At the higher Na_{12}–IP6 amendment levels, IP6 apparently acted as chelator for several polyvalent metals, such as U, Al, Pb, Ba, and Cu, enhancing their solubility beyond that of the control, while resulting in partial immobilization for other metals (Fig. 4). At the amended treatment level (10 g kg^{-1} soil), it appears that a significant portion of the Na_{12}–IP6 did precipitate, resulting in a lower level of both soluble P and DOC, and the immobilization of several contaminant metals to a level similar to that observed for HA and Ca_n–IP6.

All three amendments were ineffective at immobilizing As, Se, and Cr, with Na_{12}–IP6 enhancing their solubility to the greatest degree followed by Ca_n–IP6 and HA (Fig. 6; P values for all amendments < 0.05). This increase in solubility can be attributed to the competition between phosphate ligands and the oxyanion species of As, Se, and Cr for anion–ligand exchange sites (Celi et al., 1999; James and Bartlett, 1983; Ognalaga et al., 1994; Peryea, 1991), demonstrating that all three amendments would be ineffective for remediating such oxyanion contaminants. Increasing pH can also enhance this effect and could have been a contributing factor with these samples. However, chelation of Cr(III) by IP6 cannot be discounted as a possible cause of increased solubility. Regardless, soils contaminated with As, Se, and Cr should receive special consideration when implementing similar remedial agents.

Toxicity Characteristic Leaching Procedure Results

All three amendments appear to be similarly effective at reducing TCLP-extractable U (Fig. 7A), which at first seems surprising given the greater solubility of U in the high-level Na_{12}–IP6 treatments (25 and 50 g kg^{-1}). The Na_{12}–IP6 apparently removed a significant portion of the readily extractable fraction during the initial batch equilibrations, leaving less U available for subsequent TCLP extraction. The trends for Ni are even more complicated with all amendments resulting in extractable Ni values similar to or greater than the nonamended control (Fig. 7B). In a previous study, Seaman et al. (2001b) attributed such anomalous behavior to contami-
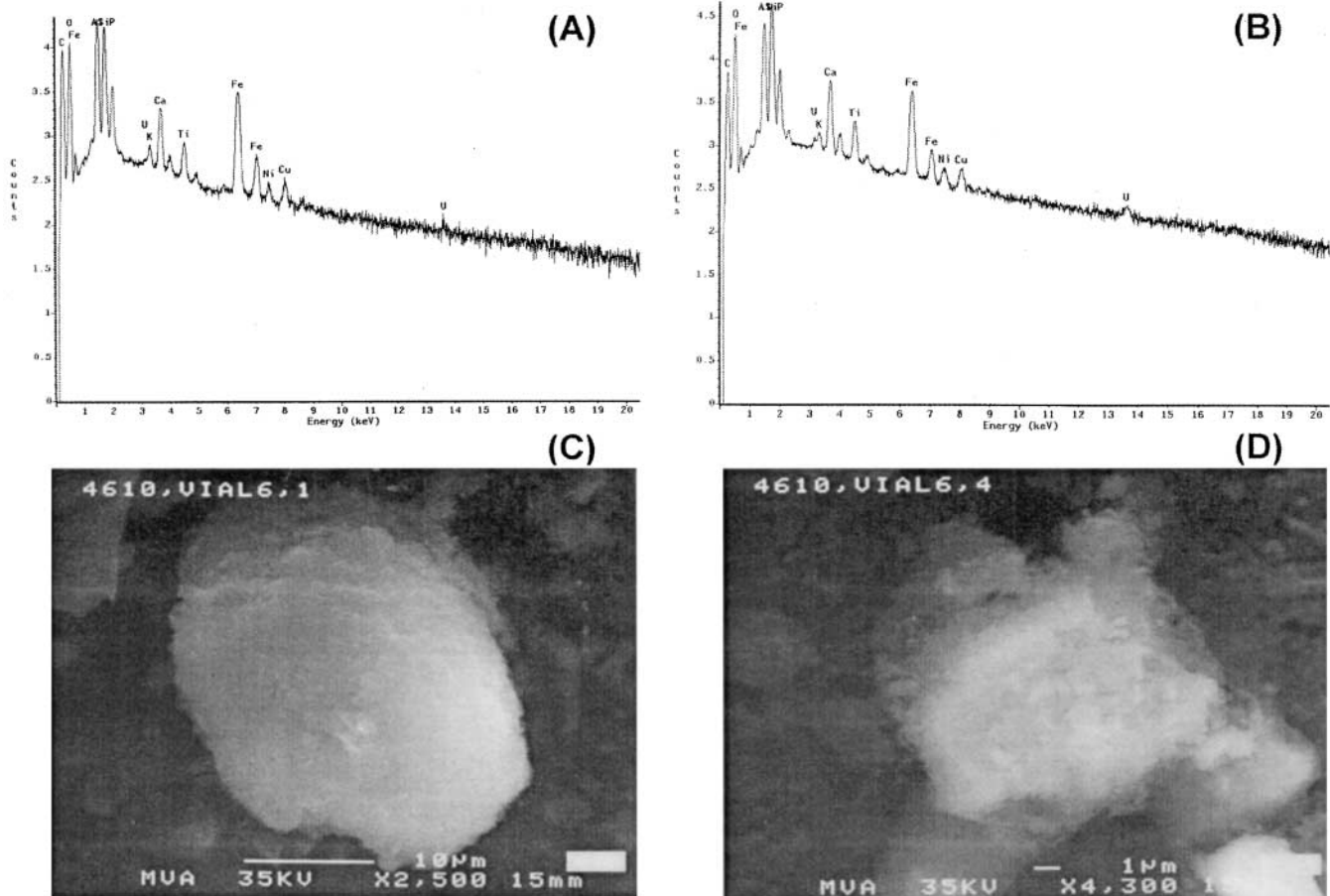

Fig. 8. Typical scanning electron microscope energy dispersive X-ray analysis (EDXA) spectra (*A* and *B*) and micrograph images (*C* and *D*) for phosphorus-rich particles observed in the calcium–phytate precipitate (Ca_n–IP6)-treated (50 g kg^{-1}) soil.

nant metal extraction that occurred during the initial batch equilibration. To correct for such bias, the amounts of U and Ni removed during the initial equilibration phase of the study were added back to the TCLP extraction results (Fig. 7C,D). After such correction, Ca_n–IP6 and HA are similarly effective at reducing TCLP-extractable Ni and U, and the initial extraction of U from the highest Na_{12}–IP6 treatment levels becomes apparent (Fig. 7C), even though the total U extracted in the two combined steps was less than the nonamended control. The combined data for Ni display a similar trend with lesser amounts extracted from the low-level Na_{12}–IP6 treatment, with greater overall solubilization at high Na_{12}–IP6 amendment levels. At the very least, such results demonstrate the potential experimental bias that can occur during multistep equilibration-type experiments.

Analytical Electron Microscopy

Based on particle morphology and elemental peak ratios, residual HA was clearly identified in the HA-treated soils. A secondary Al-rich precipitate identified in the previous HA-based contaminant immobilization studies of Arey et al. (1999) and Seaman et al. (2001a,b) was also observed. As reported previously, U, Ni, and to a lesser degree other contaminant metals evaluated in the present study were generally associated with the secondary Al-rich, P-containing precipitate, and not the residual HA (Arey et al., 1999; Seaman et al., 2001a,b).

In Fig. 8, the EDXA spectra and secondary electron images are presented for the Ca_n–IP6-treated soil (50 g kg^{-1} soil). The poor image quality and high signal background reflect the small particle size and high excitation voltage necessary to collect the full EDXA spectra. At such an excitation voltage, the spatial resolution is compromised as greater beam spread and secondary scattering generate X-ray signals from a greater region within and possibly outside the particle of interest (Goldstein et al., 1992; Seaman, 2000). For the Ca_{12}–IP6-treated soil, the PO_4–rich particles appear to be enriched in Al and Fe, with minor levels of U and Ni, and somewhat lesser amounts of Ca when compared with the original unreacted IP6 amendments. An Al-rich secondary PO_4 precipitate was identified in the transmission electron microscopy thin sections for the Ca_n–IP6-treated soils that was quite similar in composition to the secondary Al-rich precipitate identified in previous HA-based contaminant immobilization studies (Arey et al., 1999; Seaman et al., 2001a,b). However, lesser amounts of U and Ni were observed to be associated with the secondary IP6 precipitate in the current study.

CONCLUSIONS

Results from the current study clearly illustrate some possible obstacles to the effective use of IP6 as a contaminant immobilizing agent. Despite the assertion that soluble IP6 can be used to immobilize metals in soils or sediments where it would be difficult to introduce an insoluble chemical agent, such as HA, previous studies focused on metal immobilization after formation of an IP6 precipitate. In the current study, Ca_n–IP6 was similar in effectiveness to HA at immobilizing several contaminant metals, including U, Ni, Pb, Ba, Co, Mn, and Zn, demonstrating the potential utility of IP6 for remediating a wide range of metal-contaminated sites. However, the commonly available soluble form of IP6, Na_{12}–IP6, and even the reagent-grade Ca_1–IP6, may actually increase the solubility of certain contaminant metals, depending on the solution conditions, as well as the type and concentration of a given metal of interest and the concentration of IP6 (Graf and Eaton, 1984). In addition, all three materials enhanced the solubility, and possibly the migration potential, of oxy-anion contaminants such as As, Se, and Cr. Therefore, caution must be used in the field application of IP6 until we better understand such processes within a specific contamination scenario.

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