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Title: PHYTOSIDEROPHORE EFFECTS ON SUBSURFACE ACTINIDE CONTAMINANTS: POTENTIAL FOR PHYTOSTABILIZATION AND PHYTOEXTRACTION

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PHYTOSIDEROPHORE EFFECTS ON SUBSURFACE ACTINIDE CONTAMINANTS: POTENTIAL FOR PHYTOSTABILIZATION AND PHYTOEXTRACTION

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In recognition of the need for a safe, effective technology for long term Pu/Th/Actinide stabilization or removal from soils, we have begun an investigation of the potential for phytoremediation (phytostabilization and/or phytoextraction) of Pu and other actinide soil contaminants at DOE sites using phytosiderophore producing plants, and are investigating the contribution of phytosiderophores to actinide mobility in the subsurface environment. Phytoremediation and Phytostabilization have been proven to be a cost-effective, safe, efficient, and publicly acceptable technology for clean up and/or stabilization of contaminant metals. However, no phyto-based technologies have been developed for stabilization or removal of plutonium from soils and groundwater, and very few have been investigated for other actinides. Current metal-phytostabilization and phytoremediation techniques, predominately based around lead, nickel, and other soft-metal phytoextraction, will almost certainly be inadequate for plutonium due its distinct chemical properties. Phytosiderophore-based phytoremediation may provide technically and financially practical methods for remediation and long-term stewardship of soils that have low to moderate, near surface actinide contamination. We plan to demonstrate potential benefits of phytosiderophore-producing plants for long-term actinide contaminant stabilization by the plant's prevention of soil erosion and actinide migration through hydraulic control and/or through actinide removal through phytoextraction. We may also show possible harm caused by these plants through increased presence of actinide chelators that could increase actinide mobilization and migration in the subsurface environment. This information can then be directly applied by either removal of harmful plants, or be used to develop plant-based soil stabilization/remediation technologies.

Phytosiderophores are naturally produced by some plants, including most grasses and many crop plants, for the solubilization, mobilization, and uptake of Fe and other essential mineral nutrients from the soil (figure 1). These small natural organic chelators are designed to strongly bind low-solubility Fe, and possibly other metals, in a complex and competitive soil environment and actively deliver the metal to the plant. Phytosiderophores, all derivatives of mugineic acid, form stable complexes with numerous metals. Many of these complexes have been well characterized, including by X-ray crystallography.[1] Phytosiderophores have already been shown to enhance soil mobility of Cu, Fe, Mn, and Zn as much as microbial siderophores and more than some synthetic chelators.[2] They are notably similar to EDTA in structure and metal-binding chemistry. Both have multi-carboxlyate chelating groups and form extremely strong complexes with Fe and also strongly bind a number of transition metal ions (Table 1).

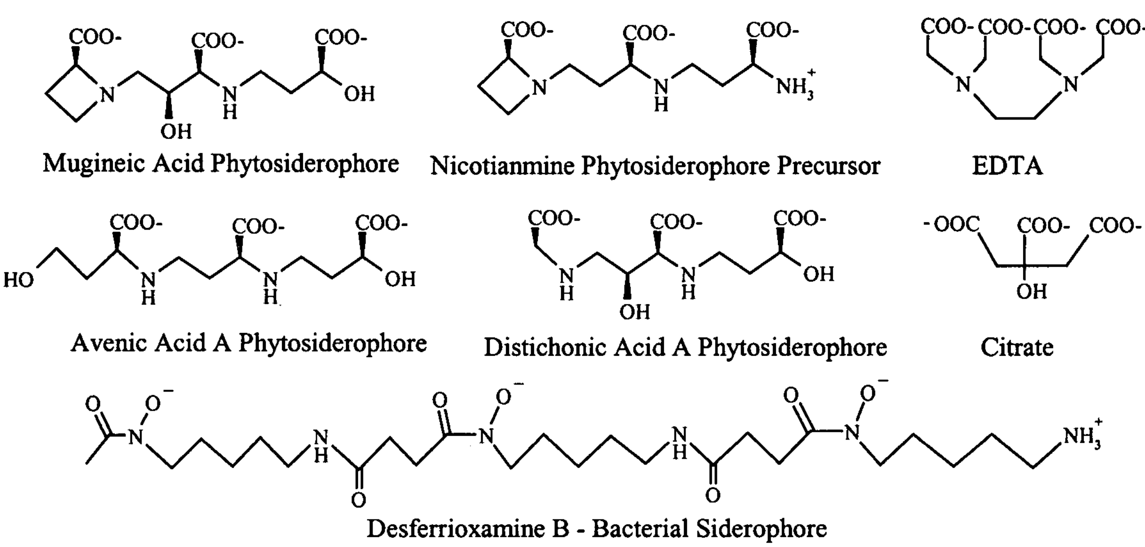


Figure 1: The Mugineic Acid Family Phytosiderophore, Nicotianamine, EDTA, Citrate. DFO

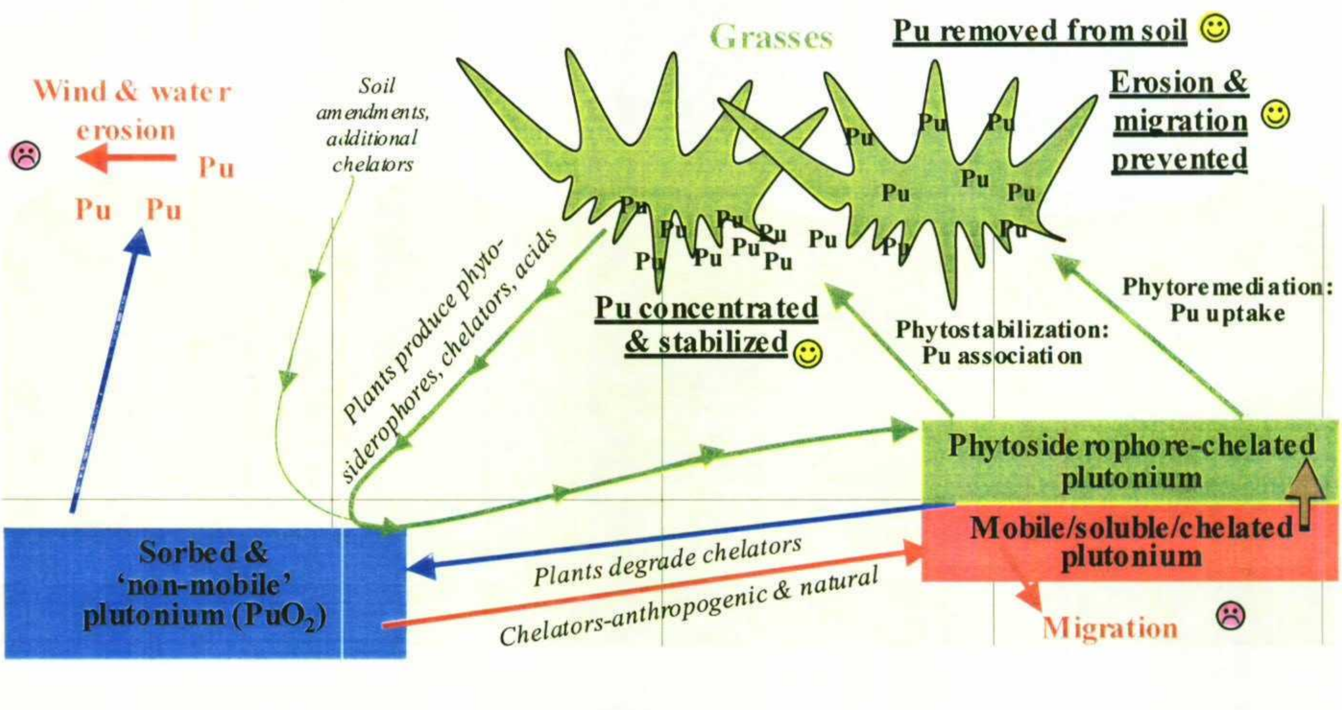
Table 1: Stability constants (log *K*) of Phytosiderophores and other chelators with various metal ions.

Chelator	Mn(II	Fe(II)	Co(II)	Zn(II)	Ni(II)	Cu(II)	Fe(III)	Pu(IV)	U(VI)
Nicotianamine	8.8	~12.4	14.8	~15	16.1	18.6			
Mugineic acid	8.0	8.3		10.7	14.9	~18.4	18.1		
Desferrioxamine B		7.2	10.3	10.1	10.9	14.1	30.6	30.8	18
Citrate	3.8	4.6	5.0	5.0	5.4	5.9	11.4	~12	7.4
EDTA	13.8	14.3	16.3	18.6	16.5	18.8	25.1	25.6	7.4

Phytosiderophore-producing plants are known to uptake uranium and translocate it into above ground parts[3] and may have higher Pu uptake than other plant species.[4] Plutonium uptake and transport in plants seems to mimic nutrient transport, with similarities found to Fe transport.[5] Plutonium and uranium most likely track 'hard' metal nutrient transport systems in plant, such as Fe uptake by phytosiderophores. Phytosiderophores will predictably strongly chelate Pu, U and Th, and increase their solubility and mobility in soils, similar to EDTA and bacterial siderophores. Phytosiderophores-mediated uptake could explain many of the observations made on Pu uptake into plants.

Some phytosiderophores are up to 100 times more efficient than anthropogenic or bacterial Fe chelators for Fe uptake into graminaceous plants.[6] They may be able to enhance Pu uptake by similar amounts. It is likely that applying additional phytosiderophores to these plants would show even greater increases in Pu uptake than seen with applied synthetic chelators. This is due to the fact that phytosiderophores would increase solubility of Pu and increase root translocation rates, whereas synthetic chelators can only increase solubility of Pu. At least for grasses, metal uptake rates will depend on the amount of phytosiderophore available that can outcompete EDTA for the metal; i.e. when solubility of the metal is no longer limiting, root translocation rates are ultimately limited by available transport ligands and the uptake rate of these metal-ligand complexes. This has been directly demonstrated with barley, where application of EDTA to Fe-deficient plants actually decreased xylem concentration of Cu, Fe, Mn, and Zn.[7] Using phytosiderophores directly eliminates this competition/exchange step and insures solubilized metal is balanced with metal uptake ability, eliminating a problem of chelate induced phytoextraction.

Here, we will present our initial research findings on the ability of applied phytosiderophores (synthesized) to chelate, solubilize, and mobilize plutonium from amorphous solids and soil samples, compared to synthetic chelators (such as EDTA) and bacterial siderophores. We will also demonstrate the effect of phytosiderophores on the uptake rate of plutonium in plants by comnparing plutonium uptake amounts in a phytosiderophore producing plant (barley) grown hydroponically in Fe-replete and Fe-depleted conditions and in a non-phytosiderophore producing plant uysed commonly in phytoremediation technologies (Indian Mustard), also grown in Fe-replete and Fe-depleted conditions.



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