Phytoremediation of Pb-Contaminated Soils. S.D. CUNNINGHAM *, W.R. BERTI, J.W. HUANG. DuPont, Newark, DE.
Pb contaminated soils are of concern in many industrial, mining, and urban environments. Currently Pb contaminated soils are largely remediated using engineering excavation, stabilization, and landflling techniques. Phytoremediation seeks to use plant and agronomic techniques to remediate these soils. Phytostabilization of Pb contaminated soils relies on soil amendments to sequester the most biologically and chemically active forms of Pb into the soil matrix. Vegetation management techniques are then employed to prevent erosion and further minimize environmental risks. An overview of the chemical, biological and physical tools that we have employed to measure relative risks will be presented. Phytorextraction is in the research phase and seeks to use plants to extract Pb from contaminated soil. Plants are subsequently harvested and processed. We have screened extensively plant germplasm, altered soil environmental conditions to increase Pb availability (chelates, pH shifts and DC current), conducted basic Pb uptake and transport studies, and, more recently, worked with plant mutants to identify limiting chemical and physiological steps.
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Formation and Dissolution Kinetics of Heavy Metal Surface Precipitates. A.M. SCHEIDEGGER *, and D.L. SPARKS, Univ. of Delaware.
The kinetics of the formation and the dissolution of Ni surface precipitates on pyrophyllite was studied. Ni sorption at pH = 7.5 was initially fast, followed by a gradual decrease in sorption. Based on previous spectroscopic evidence, we attribute the slow reaction stage to nucleation processes on the pyrophyllite surface. The detachment of Ni from surface precipitates at pH = 4 and pH = 6 involves a small amount of Ni being released relatively fast. Thereafter, Ni detachment was extremely slow and the rate depended strongly on the experimental method. Utilizing a conventional batch technique, further Ni release became negligible. The non-removal of reaction products may have caused the formation of secondary precipitates. Under steady-state conditions a constant Ni detachment rate was observed which we attribute to the dissolution of Ni surface precipitates. Surprisingly, the Ni detachment from pyrophyllite was much slower than the dissolution of crystalline Ni(OH)2.
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X-ray absorption fine structure (XAFS) spectroscopy was used to discern the local atomic structure of Ni(II) sorbed on pyrophyllite. The first coordination shell consists of 6 O atoms at 2.02-2.04 Å. For the second shell, XAFS data suggest a single Ni-Al/O site (distance 2.96-3.03 Å), indicative of edge sharing of Ni and Al octahedra and possibly the presence of mixed Ni-Al hydroxides. As Ni surface loading on pyrophyllite increased, the number of Ni second-neighbor atoms at a distance of 2.99-3.00 Å increased from N = 1 to N = 5. The presence of multinuclear surface complexes was depicted at low surface loading and at reaction contact. The Ni concentration with respect to the formation of Ni(OH)2. This observation suggests that the total coverage of surface sites is not necessary for the formation of multinuclear surface complexes and implies that the pyrophyllite surface promotes hydrolysis and multinuclear complex formation.
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Samples from two Vertisols, an Andisol, and an Alfisol were collected from farmers' fields, research station farms, and from uncultivated areas to characterize the organic and inorganic forms of P in the highland plateau soils of Ethiopia using the Hedley P fractionation scheme. Total P values ranged from 226 mg kg^-1 in the Vertisols developed on alluvial deposits to 1570 mg kg^-1 in the Andisols, where the HCl fraction dominates the inorganic soil P pool. The labile inorganic P fractions (Resin Pi and Bicarb Pi) generally accounted for less than 15% of the total P in all soils. The NaOH P fractions, the most prominent in the Alfisol, accounted for 4-15% of total P. The HCl P fraction ranged from 1% in the Alfisol to 46% in the Andisol. Each of the soils showed a loss of P from the residual, and HCl fractions when present in the soil, from the farmers' fields. Addition of fertilizer at the recommended rates to the Debre Zeit Vertisol appears to have resulted in a slight increase in labile P and prevented loss of P from the HCl P and residual P fractions.
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Phosphorus sorption studies were conducted to investigate the effect of pH, ionic strength, and neutral salt cation of the background electrolyte on P sorption by two Vertisols, an Andisol, and an Alfisol from the highland plateau region of Ethiopia. Two of the soil orders sampled (Andisol and Vertisol) contained significant amounts of P in the HCl soluble P fraction such that a decrease in pH resulted in an increase in solution P concentration. Increasing ionic strength increased the amount of sorbed P with P addition. Increasing pH decreased P retention with P addition. The effect of neutral salt cation (CaCl2, KCl, and NaCl; μ=0.03, 0.003) on P sorption was used to evaluate P retention mechanisms for the three soil orders of differing mineralogy (Vertisol, permanent charge; Andisol, variable charge; and Alfisol, both variable and permanent charge).
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Modeling the Interaction Between Aluminum Activity, pH and Ionic Strength in Acid Forest Soils. J.B. NELSON* and W.P. ROBARGE, North Carolina State Univ.
The interaction of acidic deposition with a forest canopy can result in an increase in the ionic strength of throughfall and stemflow which can in turn result in an increase in aluminum activity and a corresponding decrease in pH of the soil solution, without a significant change in base saturation. The interaction between aluminum activity, pH, and ionic strength in acid forest soils is evaluated using a model based on the following equation:

\[ pH = \left( \frac{1}{2a} \right) \log (K_{aq} \cdot K_{d}) - (3/2a) \log (C_{aq} + Mg^{2+}) + (1/2a) \log \left( \frac{C_{aq} + Mg^{2+}}{K_{aq}} \right) \]

where \( K_{aq} \) and \( K_{d} \) are constants. Estimates of \( K_{aq} \) and \( K_{d} \) are obtained from the analyses of soil solution samples collected at sites in the southern Appalachians during the past 7 years. Nonlinear regression analysis is used to determine appropriate values for \( K_{aq} \) and the ratio of \( C_{aq} + Mg^{2+} / K_{aq} \) which this model will be used to predict changes in Al activity during acid precipitation events.
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A convective-dispersive model of soluble P transport is coupled to a model of P phase change in which adsorption-desorption, precipitation-dissolution and ion pairing are explicitly represented as concurrent equilibrium reactions. Simulated P transformations are tested against the distribution of P among resin, NaHCO3, NaOH and HCl extractable fractions in soil following equilibration with different concentrations of soluble H2PO4. This distribution is primarily determined by the model by the effects of precipitation and adsorption reactions on P during equilibration. These effects cause P to be distributed more towards NaOH extractable forms and less towards HCl extractable forms as its concentration in the soil solution increases. Simulated P transport is tested against temporal and spatial patterns of pH and of water-, resin-, NaHCO3-, NaOH- and HCl-extractable P concentrations in soil columns following addition of KH2PO4 as either a surface amendment or in irrigation water. Patterns of P were reproduced in the model from deprotonation of H2PO4 following precipitation of monosite or hydroxyapatite. Reductions in pH from hydroxyapatite precipitation caused solid phase P to be recovered mostly in resin- and NaOH-extractable fractions near the site of P introduction in both simulated and actual soils.