Continuous supply of citric acid and ammonium traces to uranium mine dump soil: A path to acceptable phytoextraction techniques?

Gerhard Gramss, Hans Bergmann

Friedrich-Schiller-University, Institute of Geological Sciences, Burgweg 11, D-07743 Jena, Germany, E-mail: gerhard.gramss@uni-jena.de

Chelate-assisted phytoextraction of soil heavy metals expanding over decades amplifies primarily the leaching problem. In a search for alternative technologies, *Beta vulgaris rapaceae*, *Brassica chinensis*, and *Brassica juncea* plants were potted on the metalliferous soil from uranium mining and daily treated with 14 mg N kg^{-1} soil (applied as NH_4Cl or $(NH_4)H_2PO_4$), and/or citric acid at a common field concentration of 1.62 m*M* over 47 d. In unplanted control soil, degradation of citric acid resulted in pH (+0.36 units) and thus in solubility and leaching rate increases (+52 %) of metal-humic complexes but also in microbial consume of soil NH_4^+ and NO_3^-. Citric acid applied to plant-soil systems reduced thus N_{org} content and DW of *B. chinensis* shoots but increased exclusively shoot concentrations of Co/Mn (3.4/2.9 times). These metals are preferentially chelated by citric anion. Supply of NH_4Cl to, and its nitrification in unplanted soil resulted in pH (-0.4 units) and solubility (leaching) decreases of humic substances (-67 %) and minerals (-12 %). This effect persisted in soil planted to *B. chinensis* (-67/-42 %). Daily N doses were completely taken up. Relative to water-treated plants, shoots of *B. chinensis* attained dry weights of 130 to 150 %, 370 % N_{org}, and 580 % N in free amino acids. N_{org} increases of 370 % attracted a 361-% increase in the concentration of the biocatalytic, protein-associated transition metals, (Cd), Co, Cu, Fe, Mn, Ni, and Zn. Combined application of NH_4Cl and citric acid reduced pH (-0.53 units) and the solubility of humic substances (leaching; -73 %) of unplanted soil in comparison to the water treatment further. Concentrations of Co and Mn in the soil solution, chelated by citric anion, were higher than in the NH_4Cl treatment. The N_{org} content of *B. chinensis*, due to soil microbial competition for N, reached only 319 % and attracted 229 % the concentration of Cu, Fe, Ni, and Zn but the 7.0/9.3-fold concentration of Co/Mn in comparison to water-treated plants. Soil treatment with $(NH_4)H_2PO_4$ failed to reduce leaching of soil minerals significantly. Treated *B. chinensis* plants with the elevated concentrations of 5 % N_{org} and 2.5 % P by DW in the shoot grew depressive. *Brassica juncea* reactions to the treatments resembled those of *B. chinensis*. In *B. vulgaris rapaceae*, however, NH_4Cl/(citric acid) treatments increased selectively the shoot concentrations of Ca, Cd, (Co), (Mn), and Ni. Evaluating the different treatments it is recommended to use *Brassica* sp./NH_4Cl combinations to retrieve the 5-fold quantity of transition metals (calculated from increases in DW x N_{org}) from metalliferous soil with a leaching rate reduced to 50 % in comparison to water-treated plants. Uptake of further elements including uranium increased little more than with the shoot DW of the N-sufficient plants. Trace supplements of citrate stimulated exclusively Co and Mn uptake by all plant species. Treatments should avoid to increase shoot N_{org} concentrations to the toxic threshold of 4 % by DW.