BIOAVAILABILITY OF ELEMENTS FOR EFFECTIVE PHYTOREMEDIATION AND PHYTOMINING: THE ROLE OF RHIZOSPHERE PROCESSES

Oliver Wiche[1], Christin Moschner[1], Balázs Szekely[2,3] and Hermann Heilmeier[1]
[1]*TU Bergakademie Freiberg, Institute for Biosciences, Biologie / Ecology Unit, Freiberg, Germany*
[2]*Department of Geophysics and Space Science, Eötvös University, Budapest, Hungary,*
[3] *Department of Geodesy and Geoinformation, Vienna University of Technology, Austria*
oliver.wiche@ioez.tu-freiberg.de

The success of phytoremediation (especially phytoextraction) and phytomining depends heavily on the bioavailability of target elements, which, among others, is a function of soil mineral phases, soil organic matter, pH and redox potential. The use of soil additives which, e.g., change soil pH or increase the amount of chelating compounds, has been propagated in the past in order to desorb the target elements from the soil matrix. These additives, however, may have negative environmental consequences by causing leaching of toxic elements from the soil due to enhanced mobility in the soil solution. For this reason less dangerous alternatives are necessary which use the natural capacity of plants to increase availability of target elements in their root environment. Here we report on rhizosphere mechanisms of various plant species to increase bioavailability of germanium (Ge), rare earth elements (REEs) and also toxic elements for phytomining and phytoremediation.

Several species of forbs (e.g. *Lupinus albus*, *L. angustifolius*, *Fagopyrum esculentum*, *Brassica napus)* and grasses (e.g. *Hordeum vulgare*, *Panicum miliaceum*, *Phalaris arundinacea*, *Zea mays*, *Phragmites australis, Miscanthus giganteus*) were grown on various substrates, either without or with addition of organic acids, in mono- and mixed cultures both in the greenhouse and in the field. Plants were harvested, and the concentration of metals and metalloids was analyzed in the dried plant material via ICP-MS following micro-wave digestion with concentrated HNO_3 and HF. Germanium and REEs were also determined in different soil fractions after sequential extraction.

The addition of carboxylates (e.g. 1 and 10 mM citric acid) dramatically increased the mobility of Ge in soils (the amount of extractable Ge was increased up to 10-fold) and Ge contents in the plant material (ca. 50%). However it seems that this mobilization is restricted to very acidic conditions (pH < 4). The accumulation of Ge in aboveground plant material was by a factor of 10 higher in grasses than in forbs. In contrast, forbs accumulated higher concentrations of REEs than grasses. For those plants with a high capacity for lowering pH and releasing carboxylates from roots (e.g. genus *Lupinus*), which is a common strategy of plants to mobilize poorly available nutrients such as Fe, Mn and P in the rhizosphere, we could demonstrate that they were able to mobilize Ge and REEs.

Due to the chemical similarity between Si and Ge grass species, which accumulate Si in their shoots, are able to take up higher amounts of Ge than forbs. On the other hand, forbs which can release a high amount of organic acids from their roots and thus mobilize Ge in the soil, show only a limited capacity for Ge uptake, but a high capacity for accumulation of REEs. The mobilization of Ge and REEs seems to be restricted to the rhizosphere with its distinct pH and carboxylate gradients. Due to the higher reactivity of Ge in the soil, plant availability of Ge is lower compared to Si. This demonstrates that mobility of elements in the soil solution *per se* is not necessarily a good indicator for bioavailability of target elements in phytomining and phytoremediation.

Keywords: Bioavailability, Germanium, Rare Earth Elements, Phytoextraction, Rhizosphere