

## Enhanced phytoextraction of germanium and rare earth elements – a rhizosphere-based approach

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Germanium (Ge) and rare earth elements (REEs) are economically valuable raw materials that have become an integral part of our modern high tech society. While most of these elements are not actually rare in terms of general amounts in the earth's crust, they are rarely found in sufficient abundances in single locations for their mining to be economically viable. The average concentration of Ge in soils is estimated at 1.6  $\mu$ g g-1. The REEs comprise a group of 16 elements including La, the group of lanthanides and Y that are abundant in the earth crust with concentrations varying from 35  $\mu$ g g-1 (La), 40  $\mu$ g g-1 (Nd), 6  $\mu$ g g-1 (Gd) and 3.5  $\mu$ g g-1 (Er) to 0.5  $\mu$ g g-1 in Tm. Thus, a promising chance to improve supply of these elements could be phytomining. Unfortunately, bioavailability of Ge and REEs in soils appears to be low, in particular in neutral or alkaline soils. A sequential dissolution analysis of 120 soil samples taken from the A-horizons of soils in the area of Freiberg (Saxony, Germany) revealed that only 0.2% of total Ge and about 0.5% of La, Nd, Gd and Er of bulk concentrations were easily accessible by leaching with NH4-acetate (pH 7). Most of the investigated elements were bound to Fe-/Mn-oxides and silicates and were therefore only poorly available for plant uptake. Here we report an environmentally friendly approach for enhanced phytoextraction of Ge and REEs from soils using mixed cultures of plant species with efficient mechanisms for the acquisition of nutrients in the rhizosphere. The rhizosphere is characterized as the zone in soil sourrounding a plant root that consists of a gradient in chemical, physical and biological soil properties driven by rhizodeposits like carboxylates and protons. Some species like white lupin (Lupinus albus) are able to excrete large amounts of organic acid anions(predominantly citrate and malate) and show a particularly high potential for the acidification of the rhizosphere. In our experiments, mixed cultures with white lupin and cereals like barley (Hordeum vulgare) and millet (Panicum miliaceum) significantly enhanced the uptake of all investigated elements in co-cultured species due to interspecific root interactions. Concentrations of the investigated rare earth elements in shoots were significantly correlated to concentrations of Fe, Mn and P in shoots. Enhanced uptake of the mentioned elements corresponded to a depletion of elements in the rhizosphere soil of white lupin. Accordingly, processes in the rhizosphere of plants seem to play a key role controlling availability of REEs in the soil-plant system, since presence of white lupin clearly increased the uptake of REEs in shoots of barley and millet even to a level comparable with white lupin and this was most probably caused by attacking fractions of elements in soil hardly accessible for barley and millet.

These studies have been carried out in the framework of the PhytoGerm project financed by the Federal Ministry of Education and Research, Germany.