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Bioavailability of heavy metals, germanium and rare earth elements at Davidschacht dump-field in mine affected area of Freiberg (Saxony)

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Bioavailability research presents an essential tool, in modern phytoremediation and phytomining technologies, allowing the estimation of plant available fractions of elements in soils. However, up to date, sufficient interdisciplinary knowledge on the biogeochemically impacted behavior of specific target elements, in particular Ge and REEs in mining affected soils and their uptake into strategically used plants is lacking.

This presented work is focused on a correlation study between the concentrations of selected heavy metals, Ge and REEs in soils formed on the top of the dump-field of Davidschacht and the corresponding their concentrations in 12 vascular plant species. The mine-dump of Davidschacht, situated in the Freiberg (Saxony, Germany) municipality area was chosen as the study area, which has been considered to be a high contaminated enclave, due to the mining history of the region. In total 12 sampling sites with differing composition of plant species were selected. At each sampling site soil samples from a soil depth of 0 – 10 cm and samples of plant material (shoots) were taken. The soil samples were analysed for total concentration of elements, pH (H_2O) and consequently analysed by 4-step sequential extraction (SE) to determine fractions of elements that are mobile (fraction 1), acid soluble (pH 5) (fraction 2), bound to organic and oxidizable matter (fraction 3) and bound to amorphic oxides (fraction 4). The plant material was decomposed by hydrofluoric acid in order to extract the elements. Concentrations of elements in soil extracts and digestion solutions were analysed by ICP-MS. For all species bioconcentration factor (BCF) was calculated of the total concentration of elements in order to investigate the bioaccumulation potential. Arsenic (As), cadmium (Cd) and lead (Pb) were chosen as the representative heavy metals. Within the REEs neodymium (Nd) and cerium (Ce) were selected as representatives for all REEs, since Nd and Ce correlated significant with the other elements from this group.

High amounts of As, Cd, Pb in mould horizons were proved. The surprisingly highest concentrations were determined for As (in average 3328 mg kg^{-1}). The results of the pH measurement indicates acid conditions (in average 4.86, min. 3.89) for whole mine heap. Due to the mobility of Cd and Pb in acid environment, a high mobility of Cd in mobile soil fractions (in average 0.58 mg kg^{-1}) was found, that seems to be responsible for the Cd pollution of Freiberger Mulde river, situated near the dump-field in the East direction from the studied area. The Pb content was in the average 1513 mg kg^{-1}. SE analyses shows, that only the minor amounts of these metals were accounted in fractions I – IV (As: 7.75 %, Pb: 5.48 %, Cd: 26.77 %).

The total Ge content in soil samples was 2.7 mg.kg^{-1}in average. The concentrations of Nd and Ce were 17.7 mg $kg^{-1}$and 38.5 mg kg^{-1}, which is even lower than the average Nd and Ce contents in the Earth crust. However, the concentration of Ge was roughly a factor of two higher, than this average showing a large pool of Ge that could be accessed by phytoextraction. The SE analyses shows, that the average in fractions I – IV is even much lower, than in the case of the above mentioned heavy metals in comparison with Ge (1.75 %), Nd (3.28 %) and Ce (3.12 %).

The BCF calculated for plants shows, that the only element, which could be possibly used as the object of phytoaccumulation is Cd (the BCF $>$ 1) in species *Populus tremula* (3.0, 1.7)*, Spirea douglasii* (1.4, 2.2) *and Tanacetum vulgare* (3.2, 1.3) at the most sampling places. Since these species represent the natural occurring vegetation of the dump, the use of these species together with soil amendments enhancing the plant availability of elements in soil fractions hold promise for phytoextraction of economically valuable metalloids and consequently an in situ bioremediation of the dump field.

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