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Analysis of bioavailable Ge in agricultural and mining-affected-soils in Freiberg area (Saxony, Germany)

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Germanium (Ge) concentrations in different soil fraction were investigated using a sequential selective dissolution analysis and a rhizosphere-based single-step extraction method for the identification of Ge-bearing soil fractions and prediction of bioavailability of Ge in soil to plants. About 50 soil samples were collected from various soil depths (horizons A and B) and study sites with different types of land use (dry and moist grassland, arable land, mine dumps) in Freiberg area (Saxony, Germany).
Ge has been extracted in six soil fractions: mobile fraction, organic matter and sulfides, Mn- and Fe-oxides (amorphous and crystalline), and kaolinite and phytoliths, and residual fraction. The rhizosphere-based method included a 7-day-long extraction sequence with various organic acids like citric acid, malic acid and acetic acid. For the residue the aforementioned sequential extraction has been applied. The Ge-content of the samples have been measured with ICP-MS using rhodium internal standard and two different soil standards.
Total Ge concentrations were found to be in the range of 1.6 to 5.5 ppm with highest concentrations on the tailing site in the mining area of Altenberg.
The mean Ge concentration in agriculturally used soils was 2.6 $\pm$ 0.67 ppm, whereas the maximum values reach 2.9 $\pm$ 0.64 ppm and 3.2 $\pm$ 0.67 ppm in Himmelsfürst and in a grassland by the Mulde river, respectively. With respect to the fractions, the vast majority of Ge is contained in the last three fractions, indicating that the bioavailable Ge is typically low in the samples. On the other hand at the soil horizons A at the aforementioned two sites characterised by high total Ge, together with that of Reiche Zeche mine dump have also the highest concentrations of Ge in the first three fractions, reaching levels of 1.74 and 0.98 ppm which account for approximately 40% of the total Ge content.
Ge concentrations of soil samples extracted with 0.01 or 0.1 M citric acid and malic acid were significantly higher than those extracted with acetic acid or solutions adjusted to pH 3.5 with nitric acid, indicating the formation of Ge-organic acid complexes. Ge eluted with organic acids like citric acid or malic acid closely corresponded to Ge concentrations in the initial fractions indicating that these organic acids are able to mobilize Ge bound to organic matter, crystalline Fe-oxides and silicates.
The results show that bioavailability of Ge in soils of Freiberg area is strongly related to Ge bound to organic matter, Fe-oxides and silicates. Organic acids, exuded by plant roots, might be of particular importance in controlling bioavailability of Ge to plants by attacking resistant soil fractions as an effect of lowering pH in the rhizosphere and complexation.
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