Effect of low-molecular-weight organic acids on thallium mobility in soil – A model rhizosphere solution approach

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The kinetic batch leaching of Tl-bearing mineral soil in 500 µM solutions of citric, oxalic and acetic acid was performed to simulate the release of Tl in the rhizosphere-like environment. The obtained data demonstrate that low-molecular-weight organic acids significantly contribute to soil alteration accompanied by the release of lithogenic Tl (if present). The highest mobilization rates for Tl were observed after 0.5 h of leaching (with maximal values obtained for oxalate) followed by a substantial decrease. Thallium extractability in the organic acid solutions was up to 2.8-fold higher compared to water. Based on the experimental and speciation modeling data, Tl release is mainly pH-driven and can be attributed to acid ion exchange and/or acid leaching, as the formation of Tl-LMWOA complexes is negligible. The main Tl solubility-controlling phases predicted include illite and the identified Mn (III, IV) oxide due to their ability to efficiently sorb Tl^+ on the mineral surfaces from which Tl can be potentially mobilized. The role of primary silicates (i.e. orthoclase and muscovite) in the total process of Tl mobilization seems to be of lesser importance because the supposed alteration/dissolution of these phases during LWMOA leaching was limited.

A geochemical reference (baseline) for the natural geogenic variation in Pb isotope ratios in sedimentary soils

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Given the wide historic to recent use of lead, enhanced Pb concentrations in soils may pose serious problems. The Pb isotopic composition (Pb-ic) can be used to distinguish natural from anthropogenic Pb and to appoint anthropogenic Pb sources. Often, a local reference is used to establish the natural geogenic Pb-ic, with which to compare the observed ratios in contaminated soils. However, Pb-ic is known to depend on soil type and show high spatial variability. Here we go for a regional approach, using as reference a set of 342 samples of sand and clay subsoils in the Netherlands. The combined geogenic Pb isotope ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$) are empirically modelled, through regression with geochemical proxies as predictors.

Total concentrations of Al and Zr, as measured by XRF, were found to be suitable, mutually independent predictors of the geogenic Pb isotope variability. To eliminate the effects of outliers and high variability, we used a robust trimmed least squares regression, based on a core dataset containing the 70% of the data having the smallest absolute regression residuals. For this core dataset, the percentage of variance explained is about 70%. The model grasps the main trends displayed in the measured data: a) an apparent age range within both sands and clays, tending towards higher ^{208}Pb with increasing apparent age, and b) a clear shift towards lower ^{207}Pb from sands to clays. The Zr content is hypothesized to represent the proportion of U-Th containing 'parent' minerals to Pb containing 'daughter' minerals; the Al content represents the proportion of secondary minerals.

The regional reference allows prediction of the baseline Pb-ic where no local reference is avaialble, e.g. in topsoils that differ in lithology from their subsoil or where subsoil Pb contamination is suspected. Otherwise the regional reference is as suitable as a local subsoil reference.