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Evaluation of single extractions for determination of available metals in highly contaminated soils and sediments – thermodynamic and analytical approach

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Environmental samples (forest/tilled soils and stream sediments) from highly polluted mining and smelting district of Příbram (Czech Republic) were submitted to single extraction procedures in order to determine the bioavailable contents of Pb, Cd, Cu and Zn. The results obtained from four single extraction tests were compared: deionised water, 0.01 M $CaCl_2$, 1 M NH_4NO_3 and 0.05 M DTPA. The analytical data were coupled with the measurements of pH and Eh in extracts, speciation modelling using the PHREEQC-2 geochemical code. The mineralogical investigations of solids were carried out using the X-ray diffraction (XRD), voltammetry of microparticles (VMP) and diffuse reflectance spectroscopy (DRS). It was found that DTPA is not suitable extractant for highly organic/acidic forest soils because of a strong re-sorption of negatively charged metal complexes ($MeH(DTPA)^{2-}$ and $Me(DTPA)^{3-}$) on organic matter (and Fe oxyhydroxides) that have protonated surfaces in acidic conditions. The extracts obtained by a 1 M NH_4NO_3 solution have too high ionic strength to calculate correctly the speciation. Furthermore, protons are released through the formation of predominant $Cu(NH_3)^+$ complex, and the NH_4NO_3 extracts become the most acid. The 0.01 M $CaCl_2$ solution seems to be the most suitable extractant for such highly contaminated soils and sediments, as the metals extracted are present in free ionic forms or as $MeCl^+$ complexes that will not be re-adsorbed on positively charged surfaces of soil constituents in acidic to circumneutral conditions (pH = 3-7). Deionised water can be used as the simplest extractant especially for the comparison purposes.