

Isotopic fractionation of Cu and Zn in the soil system

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Different isotopes of an element show distinct behaviour during chemical and physical processes because vibration frequencies of molecules of distinct isotopes differ resulting in different dissociation energies and different reactivity.

Many environmental processes cause detectable fractionation of isotope ratios. Depending on element speciation equilibrium fractionations may occur between two species but also kinetic fractionations during incomplete chemical reactions may result in measurable isotopic fractionation. For heavy elements like Cu and Zn these fractionations are in the range of a few per mil deviations from an arbitrarily defined reference value. Because of the small total variation high precision methods are necessary to detect variations of isotope ratios.

To investigate isotopic fractionation of Cu and Zn stable isotopes in soil samples the samples were measured by multicollector-ICP-MS after acid digestion and ion exchange chromatographic purification. With the used method precision were always better than 0.15‰ (2SD) for Cu and 0.11‰ (2SD) for Zn, respectively, and thus suitable for detecting isotopic fractionation in soil.

The method was applied to different soil types, which have formed under various environmental conditions. In the soils, the fate of Cu is dominated by redox reactions, organic complexation and chemical weathering. Furthermore, Cu and Zn isotopic composition was studied in contaminated soil profiles near a copper smelter to assess the potential use of stable isotope ratios as tracer of metal sources and vertical transport in the soil.

Our results showed isotopic fractionation of up to 1‰ for copper in a well developed Podzol profile. Smaller Cu isotopic variations were found in water-influenced profiles and profiles developed by oxic weathering.

In polluted soils, Zn isotopes showed lightest isotopic composition in organic layers which are most influenced by metal contamination as indicated by metal accumulation in the topsoil. These findings are consistent with Sonke et al. (2008) who described isotopic fractionation of Zn emitted from smelters. With increasing depth and decreasing contamination Zn isotopic composition became heavier and more similar to the isotopic composition of local bedrock the soil developed from. The use of Cu isotopes for pollution tracing was less successful because the isotopic composition of emitted Cu was very close to that of local bedrock.

Altogether stable isotope ratio measurements of metals may offer the opportunity to study long-term chemical processes during soil development and to trace pollution sources and pollutant transport in soil.

Sonke, J.E., Y. Sivry, J. Viers, R. Freydier, L. Dejonghe, L. Andre, J.K. Aggarwal, F. Fontan, and B. Dupre. 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. *Chemical Geology* 252:145-157.