Geophysical Research Abstracts, Vol. 9, 06003, 2007 SRef-ID: 1607-7962/gra/EGU2007-A-06003 © European Geosciences Union 2007



Fractionation of humic acid by cation-induced coagulation

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Humic acids act as important sorbents for metal cations in soils. The mobility of metalhumate complexes can be strongly altered by sorption processes as well as cationinduced coagulation. We investigated the influence of cation-induced coagulation on the chemical composition of dissolved and coagulated fractions of a soil humic acid in batch coagulation experiments for additions of Al at pH 4 and 5, Fe at pH 4, and Ca and Pb at pH 6. The partitioning of organic carbon and metals was determined by measuring total organic carbon and total metal contents of the dissolved phase. Both the dissolved and the coagulated humic acid fractions were characterized by synchrotron scanning transmission X-ray microscopy (STXM) and C-1s near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Intensities of π^* -transitions of carboxylic carbon and σ^* -transitions of alkyl, O-alkyl and carboxylic carbon decreased with increasing metal concentration for the dissolved humic acid fractions. Concurrently, the intensities of these transitions increased in the coagulated fraction as shown for Pb. The intensities of π^* -transitions of aromatic and phenolic carbon were affected to a larger extent only by Al and Fe additions. The changes observed in the C-1s NEXAFS spectra coincided with an increasing removal of organic carbon from the dissolved phase with increasing total metal concentrations. We conclude that the humic acid was chemically fractionated by cation-induced coagulation which preferentially removed functional groups involved in metal-cation binding from the dissolved phase.