TRACE METAL-HUMIC COMPLEXES IN NATURAL WATERS: INSIGHTS FROM SPECIATION EXPERIMENTS

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Introduction

The dissolved organic matter (DOM) cycle is intimately linked to the cycling and bioavailability of trace metals in aqueous environments. The presence or absence of DOM in the water column can determined whether trace elements will be present in limited quantities as a nutrient, or in surplus quantities as a toxicant. Humic substances (HS), which represent the refractory products of DOM degradation, strongly affect the speciation of trace metals in natural waters. To simulate metal-HS interactions in nature, experiments must be carried out using trace metal concentrations. Sensitive detection systems such as ICP-MS make working with small (nanomolar) concentrations possible. Capillary electrophoresis coupled with ICP-MS (CE-ICP-MS) has recently been identified as a rapid and accurate method to separate metal species and calculate conditional binding constants (log K_c) of metal-humic complexes.

Experimental

CE-ICP-MS was used to measure partitioning of metals between humic substances and a competing ligand (EDTA) and calculate binding constants of rare earth element (REE) and Th, Hf, and Zr-humic complexes at pH 3.5-8 and ionic strength of 0.1. Equilibrium dialysis ligand exchange (EDLE) experiments to validate the CE-ICP-MS method were performed to separate the metal-HS and metal-EDTA species by partitioning due to size exclusion via diffusion through a 1000 Da membrane. CE-ICP-MS experiments were also conducted to compare binding constants of REE with humic substances of various origin, including soil, peat, and aquatic DOM.

Results and Discussion

Results of our experiments show an increase in log K_c with decrease in ionic radius for REE-humic complexes (the lanthanide contraction effect). Conditional binding constants of tetravalent metal-humic complexes were found to be several orders of magnitude higher than REE-humic complexes, indicating that tetravalent metals have a very strong affinity for humic substances. Because thorium is often used as a proxy for the tetravalent actinides, Th-HS binding constants can allow us to assess the importance of tetravalent actinide-humic complexes in groundwater transport from nuclear repositories. Our results suggest that tetravalent actinide-humic complexes could be more important to account for in predictive speciation models than previously thought.