



Metal loading levels influence on REE distribution on humic acid: Experimental and Modelling approach

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In natural organic-rich waters, rare earth elements (REE) speciation is mainly controlled by organic colloids such as humic acid (HA). Different series of REE-HA complexation experiments performed at several metal loading (REE/C) displayed two pattern shapes (i) at high metal loading, a middle-REE (MREE) downward concavity, and (ii) at low metal loading, a regular increase from La to Lu (e.g. Sonke and Salters, 2006; Pourret et al., 2007). Both REE patterns might be related to REE binding with different surface sites on HA. To understand REE-HA binding, REE-HA complexation experiments at various metals loading were carried out using ultrafiltration combined with ICP-MS measurements, for the 14 REE simultaneously. The patterns of the apparent coefficients of REE partition between HA and the inorganic solution ($\log K_d$) evolved regularly according to the metal loading. The REE patterns presented a MREE downward concavity at low loading and a regular increase from La to Lu at high loading. The dataset was modelled with Model VI by adjusting two specific parameters, $\log KMA$, the apparent complexation constant of HA low affinity sites and $DLK2$, the parameter increasing high affinity sites binding strength. Experiments and modelling provided evidence that HA high affinity sites controlled the REE binding with HA at low metal loading. The REE-HA complex could be as multidentate complexes with carboxylic or phenolic sites or potentially with sites constituted of N, P or S as donor atoms. Moreover, these high affinity sites could be different for light and heavy REE, because heavy REE have higher affinity for these sites, in low density, and could saturate them. These new Model VI parameter sets allowed the prediction of the REE-HA pattern shape evolution on a large range of pH and metal loading. According to the metal loading, the evolution of the calculated REE patterns was similar to the various REE pattern observed in natural acidic organic-rich waters ($pH < 7$ and $DOC > 10 \text{ mg L}^{-1}$). As a consequence, the metal loading could be the key parameter controlling the REE pattern in organic-rich waters.