Modeling rare earth elements uptake by hydrous manganese oxides: implication for REE mobilization in a groundwater system

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Hydrous manganese oxides (HMO) are ubiquitous in nature and their tendency to be finely dispersed and to coat particles make them one of dominant scavengers of rare earth elements (REE) in hydrosystems. Although many field studies concerning REE aquatic geochemistry note that REEs exhibit the great propensity for sorption onto HMO, quantitative descriptions of this sorption from a basin-scale are apparently nonexistent. A previouslyidentified flow system (i.e., from piedmont to littoral) is used to further study REE surface complexation reaction for HMO using a diffuse double layer model. Results of the modeling study show that REE uptake by HMO strongly depends on manganese concentrations and pH. Proportion of scavenged Nd increases from <1% in recharge zone to 33% in discharge zone with a mean of 7%. This is well consistent with the increasing trends of Mn concentration (0.32~95.06 $\mu\text{g/L})$ and pH (7.1~8.6) along the flow system. However, REE sorption behavior exhibits discrepancy between individual REE with greater binding strength for light REE (LREE) than heavy REE (HREE). Specifically, fraction of sorbed La ranges from <1% to 63% (mean 13%), exhibiting much higher than that of Lu from <1% to 7% (mean 1%). It indicates that preferential uptake of LREE rather than HREE readily occurs during the REE sorption onto HMO, in spite of the changes in pH and Mn concentrations over the flow system. Proportions of HMO-REE complex slowing downward across REE series is further evidence for the REE sorption behavior. Therefore, we propose that HMO uptake is an essential regulator of groundwater HREE enrichment during REE mobilization.