Systematics on the stability constants of REE-humic complexes at various metal loading levels

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The stability constants of rare earth elements (REE) with humic substances (HS) have been widely studied to predict the behavior of REE in natural waters. It is well known that the apparent stability constant ($\beta_{\text{M-HS}}$) of metal cation with HS depends on various parameters such as pH. There are differences in not only the absolute value but also relative shape of REE pattern of the $\beta_{\text{M-HS}}$ among previous studies [1-5]. This difference in the relative shape could be explained by change of the main binding site of REE in HS due to the variation of REE loading in HS. However, it has not been confirmed yet in a series of experiments where relative shape of REE pattern of the $\beta_{\text{M-HS}}$ can change with the variation of REE loading in HS. In order to understand the systematics on the $\beta_{\text{M-HS}}$ of REE-HS complexes with the variation of REE loading, we determined the $\beta_{\text{M-HS}}$ of all REE (except for Pm) at various REE loading levels using solvent extraction, equilibrium dialysis, and ultrafiltration methods.

The $\beta_{\text{M-HS}}$ using solvent extraction has a peak around middle REE part at higher REE loading, while the REE pattern shows a monotonous increase from La to Lu at lower REE loading. On the other hand, the variation of relative shape of the REE pattern is not found in the $\beta_{\text{M-HS}}$ using equilibrium dialysis. By comparison with previous studies, it is suggested that abundance of major multivalent cations originally included in HS such as Fe^{3+} can control the variation of relative shape of REE pattern of the $\beta_{\text{M-HS}}$.

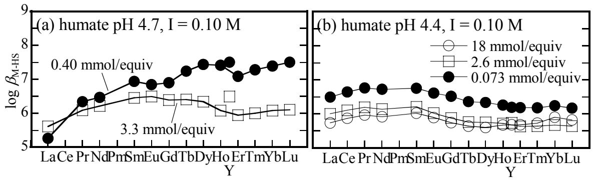

Figure 1: Log $\beta_{\text{M-HS}}$ of humate using (a) solvent extraction and (b) equilibrium dialysis.

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Estimation of recharge water flux into confined aquifer system in northeastern Osaka Basin, Japan

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The objective of this study is to estimate recharge water flux into confined aquifer system in Northeastern Osaka Basin (NEOB), where the system is well developed, by using mass balance method based on cation exchange reaction.

Shallow confined groundwater (above depths of 100m) in the NEOB modified its chemistry from Ca-HCO_3 type through Mg-HCO_3 type to Na-HCO_3 type along the flowpaths. Areas with the water types are expressed as zones A, B, and C, in that order. In addition, exchangeable cation (EXC) in clay layers distributes in concordant with the caition of the groundwater and the NEOB had suffered transgression in the past. These facts indicate that distributional patterns of both cation compositions reflect adsorption affinities of the cations onto clay. Namely, the EXC of clay layers had been fairly enriched in Na and Mg with marine origin right after the regression, and then, had released Na and Mg in turns by cation exchange reaction with Ca-HCO_3 type recharge water. As the consequent of such a displacement chromatography for a long-term period, it is considered that cations of both groundwater and EXC have been spatially distributed in turns of Ca type, Mg type and Na type from the recharge area to down-flow area.

We tried to estimate a necessary amount of natural recharge to differentiate the EXC after the latest regression. It is assumed that Na-X and Mg-X_2 of EXC (X: exchange substrate) have been exchanged by Ca originated from recharge water since the regression. By using the distributional pattern of EXC, the period of the recharge, Ca contents of recharge water and parameters of clay layers such as thickness, bulk density and cation exchange capacity, the flux of recharge water into the confined aquifer system according to this chromatographic model is estimated to be 0.99 mm/day, which is compatible with the average recharge flux to unconfined groundwater in Japan (1 mm/day).