



## **The role of clay minerals and fulvic acid to the complexation of Na, Mg, and Ca in stream flows from adjacent forested head watersheds composed of different vegetation**

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In order to understand the complexation and flow process in metal elements under a fresh water environment, discharges of Na, Mg, and Ca were measured in streams of adjacent forested head watersheds composed of coniferous evergreen- and deciduous broad leaf- trees. Total elements (T-Na, T-Mg, and T-Ca) and ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in stream flows which passed through  $0.45 \mu\text{m}$  filters were measured with an ICP and Ion-chromatograph. The remainders of total elements and ions were equated with complex compounds. Then the discharges of Si and fulvic acid, which respectively are the representatives of ligands by clay minerals and humic substances, provided the relationship between the compound discharges and the complexation process of the above metal elements.

Even if Na, Mg, and Ca are believed to be mostly free ions in fresh water environments, the rates of the compounds to the total elements ranged 10 to 40 % in the coniferous watershed and 20 to 60 % in the deciduous watersheds. The compounds sometimes occupied more than half of the total elements; this was predominant in the deciduous watershed. These mean that the discharge of compounds is not negligible in watershed hydrology. Possible complexation processes in metal elements are #1) Hydration, #2) Adsorption or substitution with clay minerals, #3) Mineral complex, #4) Adsorption with humic substances as represented by fulvic acid, and #5) Chelate with organic acids as oxalate, formic acid, and pyrrole. Under fresh water environments, #2 and #4 must be the most potential processes of the complexation in metal elements.

The relationship between the compounds, Si, and fulvic acid, therefore, supplies useful information to presume the status of the compounds. The compounds-Si relations in both watersheds showed linear correlations ( $r=0.79$  to  $0.99$ ) for a stream base flow and stream flow in a small rainstorm. The linear correlations, however, occurred only for the stream flow in the compounds-Si relations at a big rain storm in the deciduous watershed ( $r=0.89$  to  $1.00$ ) and also for the storm flow in the compound-fulvic acid relations ( $r=0.95$  to  $0.99$ ). These things mean that the metal elements possibly flowed out as organic and/or inorganic complexes and the complexation could have been promoted in the deciduous watershed during rain storms.

Thick organic soil, broadly distributing in the deciduous watershed, seems to be reasonable for promoting such complexation due to subsurface water movement in the soil through the contact of the metal elements with clay minerals and fulvic acid. In contrast, the much rainwater flows down below the surface within the loose litter and root-permeated zone developing predominantly in the coniferous watershed, where small clay minerals and humic substances occurs; which represents the rare contact of the metal elements with the clay minerals and fulvic acid in such flow paths. This would be the reason for the small and restrained complexation in the coniferous watershed at the big rain storm. The hydrochemical process in slope-stream systems can be controlled by the complexation affected by both the flow path of rainwater and the distribution of clay minerals and humic substances in soils.