

Dynamics of dissolved ions inferred from sulfur isotope ratio of sulfate, nitrogen and oxygen isotope ratios of nitrate in Chikusa river watershed, Hyogo

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The Chikusa river watershed is located in the southwestern part of Hyogo prefecture. Recent river improvement in the watershed has posed concerns about changes in water quality and river ecosystem. This study aims to clarify dynamics of dissolved ions using sulfur isotope ratio of sulfate, nitrogen and oxygen isotope ratios of nitrate, and to contribute the evaluation of water environment in the watershed.

Water samples were collected by local residents at total 94 points from headwaters to river mouth in August 6th, 2017. The samples for ion concentrations were filtrated (Advantec 25CS020AN) and measured by ion chromatography (ICS-3000, Dionex) at Research Institute for Humanity and Nature (RIHN). Nitrogen and oxygen stable isotope ratios of nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) were determined by the 'denitrifier' method (Sigman et al., 2001) and measured by GC-IRMS (GasBench/DELTAplusXP, Thermo Fisher Scientific) at RIHN. Water samples for sulfate isotope analysis were filtrated (Advantec C020A047A) and acidified with 6M HCl, and the SO_4^{2-} in acidified samples was collected as BaSO_4 compounds by adding 10% BaCl_2 solutions. BaSO_4 solids were obtained after filtration (Whatman Nucleopore 110609), and measured for sulfur isotope ($\delta^{34}\text{S}$) by an elemental analyzer coupled to the mass spectrometer (DELTA V and Flash2000, Thermo Fisher Scientific) at RIHN.

Sulfate concentration ranged from 1.7 mg l^{-1} to 40 mg l^{-1} and the trend of increase in concentration from upstream to downstream was observed. Also, the nearest point to the river mouth showed topical high concentration (1156 mg l^{-1}). On the other hand, nitrate concentration ranged from 0.06 mg l^{-1} to 13 mg l^{-1} and the trend of decrease in concentration from upstream to downstream was observed. $\delta^{34}\text{S}$ of sulfate at the nearest point to the river mouth was +22‰, which suggests that the origin of sulfate is seawater. Furthermore, change in sulfate concentration and $\delta^{34}\text{S}$ along mainstream suggests the mixing of sulfate originated from headwater and sulfate originated from bedrock (accretionary wedge) in Shifumi-tributary. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate suggest that nitrate in three tributaries (Oobiyama, Egawa, Yano) originated from nitrification of manure and septic waste. Furthermore, changes in nitrate concentration, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ along mainstream suggest that nitrification of manure and septic waste is the major source of nitrate in downstream.

Keywords: sulfate, nitrate, sulfur stable isotope ratio, nitrogen and oxygen stable isotope ratios, Chikusa river, Hyogo