Sulfur isotope constraint on the provenance of salinity in confined aquifer system.

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This study aims to comprehend the provenance of salinity in confined aquifer system in estuarine area of Kiso River, central Japan, by using water quality and sulfur isotopic ratios (d34S) as indicators.

Groundwater samples were collected in July or August in 2002 from 29 wells which have single screen around 50m in depth, and were used for chemical and sulfur isotopic analyses. High Cl content groundwater (over 1000mg/L) is distributed in tongue-shape along Kiso River (where three rivers: Kiso, Ibi and Nagara Rivers flow into sea) and has fairly low SO4/Cl ratios and high d34S values (~79 permil) than those of present seawater.

Assuming that present seawater induces the salinization of confined groundwater, intruded SO4 with Cl is expected to be reduced in confined aquifer where is in anaerobic condition as follows (Barner, 1980):

2CH2O + SO42 - = H2S + 2HCO3 - (1)

The d34S values of the saline groundwater would be well explained by following Rayleigh distillation model, in which initial SO4 has d34S = 21 permit of the seawater (Longinelli, 1989):

 $d34S = 21 + e \ln f$ (2)

where e is the isotopic enrichment factor and f is the fraction of initial SO4 remaining in groundwater. Based on previous field studies of sulfate reduction, -20 permil can be adopted as e for the model. The f is calculated by following equation using SO4/Cl content ratio of present seawater:

f = SO4 / (Cl * 2700/19000) (3)

A part of the saline groundwater along the Ibi-Nagara Rivers can be well explained by this Rayleigh model, in which volume contribution of present seawater in the groundwater is 10.7% as a maximum, whereas most of the saline groundwater plotted on smaller f field than theoretical line of the model on f-d34S diagram. This is caused by overestimation of initial SO4 (Cl * 2700/19000) on Equation (3), strongly indicating another Cl source without SO4 besides present seawater. Fossil seawater trapped in aquiclude layer for hundreds years is the most plausible candidate for the Cl source, since SO4 can be completely reduced in anaerobic stagnant conditions. Based on Equations (2) and (3), it is estimated that the volume contributions of present and fossil seawaters are 10.4%(Cl=1924mg/L) and 9.4% (Cl=1794mg/L) respectively, and the lost SO4 content through sulfate reduction process is 350mg/L as maximums.