



Evidence of bacterial sulfate reduction in oxic soils and groundwater systems determined by isotope analyses on groundwater sulfate, fulvic acid sulfur and S XANES spectroscopy

F. Einsiedl (1), T. Schäfer (2) and P. Northrup (3)

(1) GSF-National Research Center for Environment and Health, Institute of Groundwater Ecology, Neuherberg, Germany (2) Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, Karlsruhe, Germany, (3) Environmental Sciences Department, Brookhaven National Laboratory, Upton, New York 11941, USA (einsiedl@gsf.de/ fax: +49 (0) 89-31873361)

Karst groundwater systems are highly vulnerable to contamination and self-purification is a major challenge. Sulfate-reducing microorganisms contribute extensively to the mineralization of organic contaminants, implying the importance of bacterial sulfate reduction for biodegradation of contaminants in groundwater systems. Moreover, hydrogen sulfide derived from microbial sulfate reduction has also been documented to serve as electron donor during denitrification. In this study sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy on fulvic acid and isotope analyses on karst groundwater sulfate, atmospheric deposition sulfate and fulvic acid sulfur was performed to identify anaerobic microenvironments in otherwise apparent oxygen-rich soil and karst groundwater systems of the Franconian Alb.

$\delta^{34}\text{S}$ values of soil water sulfate are similar to that of atmospheric deposition. However, $\delta^{18}\text{O}$ values of sulfate show an isotopic shift to lower values compared to recent atmospheric deposition. Mineralization of carbon-bonded S in soils has been shown to cause isotopic shifts in $\delta^{18}\text{O}$ of SO_4^{2-} because the newly formed sulfate molecules incorporate water oxygen and atmospheric oxygen as the two potential oxygen sources. However, decreasing $\delta^{34}\text{S}$ values of fulvic acids sulfur compared to that of atmospheric deposition and the XANES data indicate reduced sulfur species in fulvic acids. It is suggested, that sulfide formed by bacterial (dissimilatory) sulfate reduction in mi-

environments of oxic soils of the Franconian Alb karst aquifer is incorporated in fulvic acids. This result is consistent with the hypothesis that $\delta^{18}\text{O}$ of soil water sulfate is influenced by immobilization of seepage water sulfate in soils and subsequent mineralization of carbon-bonded S as well as the formation of sulfate by re-oxidation of sulfide.

In the lower part of the aquifer markedly higher $\delta^{34}\text{S}$ values +7.5‰, compared to those of atmospheric deposition were found. Three potential explanations for increasing $\delta^{34}\text{S}$ values and decreasing sulfate concentrations are discussed. Neither bedrock weathering nor higher $\delta^{34}\text{S}$ values during pre-industrial times provide a fully satisfactory explanation for the observed trend. Therefore our results indicate that in karst systems with matrix porosity, bacterial (dissimilatory) sulfate reduction may occur. Natural attenuation processes of karst groundwater systems including anaerobic microbial degradation of organic contaminants could become increasingly important, in soils before percolating into the deeper parts of the aquifer and in karst systems with matrix porosity, for protecting these groundwater reservoirs as future drinking water resources.