



## Assessing the origin and age of ground water: a link to an understanding of denitrification in a heterogeneous porous aquifer

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Vertical distributions of hydrochemical parameters and tritium as well as isotopic analysis on nitrate, sulfate and dissolved inorganic carbon (DIC) have been used to determine the age of groundwater and to identify denitrification processes in a heterogeneous porous aquifer in South Germany.

A vertical profile of mean transit times was determined using tritium concentrations in precipitation and ground water in different depths. The mean transit times between 10 and 130 years were found by applying the lumped-parameter dispersion model. Shallow groundwater shows a significant contribution of old groundwater with relatively low nitrate concentrations. With increasing depth decreasing water ages and higher nitrate concentrations were found. Considering the flow-paths and hydraulic properties below the water level, the water age distribution determined was explained by a differing thickness of the unsaturated zone at the location of recharge.

Because of the various origins and ages of the water it is difficult to distinguish between hydrodynamic effects and microbial processes governing nitrate concentrations. Therefore chemical and isotope analyses of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and DIC were used to identify denitrification processes.

For old groundwater with mean transit times between 60 and 130 years nitrate concentrations were as high as  $130 \mu\text{mol/l}$  and the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate were around +19‰, and +10‰, respectively. Young groundwater (< 60 years) was characterized by nitrate concentrations up to  $300 \mu\text{mol/l}$ .  $\delta^{15}\text{N}$  of nitrate ranged from +5‰, to +10‰,  $\delta^{18}\text{O}$  from +1‰, to +5‰. The isotope values of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$

indicate sewage or organic fertilizers as a nitrate source. However the additional isotopic measurements of  $\delta^{13}\text{C}$ -DIC and  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  are helpful to detect denitrification processes.

Microbial denitrification requires electrons that can be derived from several energy sources, e.g. organic matter or reduced sulfur species, which are oxidized during the process.

On the one hand the isotopic analysis of  $\delta^{13}\text{C}$ -DIC indicates an oxidation of organic matter in the very upper part of the aquifer ( $\delta^{13}\text{C} = -16\text{\textperthousand}$ ). On the other hand  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  values ranging down to  $-15\text{\textperthousand}$ , in certain layers show a strongly pronounced contribution of sulfate that originates from reduced sulfur species.

Decreasing  $\delta^{13}\text{C}$ -DIC and  $\text{SO}_4^{2-}$  values fit well with increasing  $\delta^{15}\text{N}$  values and decreasing nitrate concentrations. Hence we conclude that denitrification is partially responsible for low nitrate concentrations. Furthermore our results suggest that the predominating electron donors form a variable pattern that depends on geochemical properties of the aquifer. The findings confirm that the microbial activity and the potential of biodegradation depend considerably on geochemical and hydrogeological settings.