

The influence of groundwater mean transit times, oxygen reduction and denitrification on nitrate fluxes in a heterogeneous aquifer

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Nitrate contamination in groundwater has become a concern for many drinking water supplies in Europe and North America. Microorganisms have the potential to self-purify the aquifer by using nitrate (NO_3^-) as an e^- -acceptor to decompose dissolved organic matter (DOC) or oxidize inorganic compounds such as pyrite. The understanding of the spatial distribution of redox reactions in heterogeneous groundwater systems is essential to assess the water quality of groundwater ecosystems. Hence, we determined the extent of O_2 reduction in a nitrate-contaminated groundwater system in Lower Bavaria (Germany) and calculated the denitrification lag-times in the aquifer using $^3\text{H}/^3\text{He}$, ^3H time series and stable isotopes of water ($\delta^2\text{H}$ & $\delta^{18}\text{O}$) and nitrate ($\delta^{15}\text{N}$ & $\delta^{18}\text{O}$). The isotopic composition of nitrate ($\delta^{15}\text{N}$ & $\delta^{18}\text{O}$) revealed that denitrification is not a major N removal process in most of the groundwater system. Therefore, we assessed the controlling and limiting factors, which determine the high nitrate fluxes in the groundwater. We found that O_2 concentrations show a slight decrease with increasing groundwater age, and recharged-derived DOC decreases from $\sim 80 \mu\text{mol/L}$ (median) to $\sim 11 \mu\text{mol/L}$ in the shallow depth of the aquifer with groundwater mean residence times of up to some decades. Under the assumption that $1 \mu\text{mol}$ DOC can reduce $1 \mu\text{mol}$ O_2 , the O_2 reduction can solely be explained by the oxidation of recharge-derived DOC. In addition, no correlation between sulphate concentrations, calculated mean residence times, and nitrate concentrations was observed, suggesting a lack of pyrite oxidation in the system. These findings suggest that the limited availability of recharged-derived DOC and the lack of sulphide oxidation are the controlling factors that result in high nitrate fluxes and a lack of significant denitrification in the aquifer, resulting in very limited natural attenuation of nitrate.