



Influence of environmental factors on dissolved nitrate stable isotopes under denitrifying conditions – carbon sources and water isotopes

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Stable isotopes in dissolved nitrate are regularly used to identify sources of nitrate contamination in aquifers and water bodies. A dual isotope plot of ^{15}N and ^{18}O in nitrate can provide good evidence of the origin of such pollution as various sources have different isotopic signatures. Microbial denitrification changes both isotopic values by removing nitrate with lighter isotopes first, thereby increasing $\delta^{18}\text{O}$ as well as $\delta^{15}\text{N}$. This change can distort the determination of sources but also has the potential to be used to identify and quantify microbial denitrification. Previous studies found a wide range of enrichment factors (ϵ) that did not allow conclusions towards the extent of microbial denitrification. However, it was found that during denitrification at each respective field site or laboratory experiment, there was a constant ratio in increase of the values of $\delta^{18}\text{O}$ in relation to $\delta^{15}\text{N}$. That ratio was, however, not constant across field sites and the values published range from below 0.5 to more than 1.0. The reasons for these variations in enrichment factors and relative enrichment of oxygen compared to nitrogen are yet unknown.

We conducted microcosm experiments with three different bacterial species to elucidate possible influences of environmental factors on these parameters. As a result we conclude that the type of carbon source available to denitrifying bacteria can play a role in the value of the enrichment factors, but not in the relative enrichment of the two isotopes. Specifically we found that complex hydrocarbons (toluene, benzoate) produce significantly different enrichment factors in nitrate than a simple hydrocarbon substrate (acetate). The relative enrichment of $\delta^{18}\text{O}$ compared to $\delta^{15}\text{N}$ was 0.86.

We hypothesise that this influence is based on a variation in process kinetics of cross-membrane nitrate transport in relation to intracellular nitrate reduction. The core of the hypothesis is that nitrate transport into the cell becomes rate limiting as a result of a carbon source induced change in cell membrane composition. The apparent kinetic isotope effect observed outside the cell is then changed as transport-related isotope effects dominate the observations.

In addition, a possible effect of water $\delta^{18}\text{O}$ values on the $\delta^{18}\text{O}$ of dissolved nitrate was researched. Intermediary nitrite is known to exchange oxygen atoms with water; a reverse reaction of the nitrate reducing step could thus influence the oxygen isotope composition of dissolved nitrate without changing the nitrogen isotopic composition in the same way. Such a process was already shown for sulfate reduction. By adding ^{18}O -labelled water to microcosm experiments, we could show that such an exchange exists for selected microorganisms. The environmental implications of this result is discussed.