



Isotopic signatures and concentrations of dissolved NO_3^- , N_2O und N_2 as indicators of denitrification history in aquifers

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In NO_3^- contaminated aquifers containing reduced compounds like organic carbon or sulfides, denitrification is an intense process. Its characterisation is of interest because NO_3^- consumption improves water quality and N_2O production can cause emission of this greenhouse gas to the atmosphere. Spatial distribution of NO_3^- and N_2 produced by denitrification in groundwater (excess N_2) reflects the NO_3^- input as well as cumulative denitrification during aquifer passage. Reaction progress (RP) at a given location, i.e. the relative consumption by denitrification of the NO_3^- that had been leached to the aquifers, characterises the stage of the denitrification process. RP can be derived from the ratio between accumulated gaseous denitrification products and initial NO_3^- concentrations (Weymann et al., 2007). RP is also reflected by isotopic signatures of NO_3^- and N_2 . N_2O concentration in denitrifying aquifers results from the balance between production and reduction of this intermediate of denitrification and it is an indicator of the potential to emit N_2O to the atmosphere when groundwater is discharged to wells, springs or streams. Recently, we found that isotopologue signatures of N_2O ($\delta^{18}\text{O}$ and position-specific $\delta^{15}\text{N}$) in shallow groundwater exhibited values which were extremely high compared to N_2O from other aquatic or terrestrial systems (Well et al., 2005). These values could not be explained by known isotope fractionation factors of denitrification.

In the presented study, we measured the spatial distribution of NO_3^- , N_2O , excess

N₂ and isotopic signatures of these N species in pleistocene sandy aquifers of Northern Germany. This was done to identify heterogeneity of denitrification dynamics and N₂O emission potential. Furthermore, reaction progress was compared to isotopic signatures in order to estimate fractionation factors of the partial steps of denitrification. Finally, we wanted to check if extreme isotopologue signatures of N₂O are a general phenomenon of denitrifying aquifers and how these signatures are related to denitrification dynamics.

Median NO₃⁻ concentrations ranged between 1.3 and 13.9 mg N L⁻¹ and were significantly lower than initial NO₃⁻ as calculated from the sum of NO₃⁻ plus excess N₂ (7.4 to 25.3 mg N L⁻¹). This demonstrates that there was substantial NO₃⁻ consumption within the investigated aquifers. Median RP, excess N₂ and N₂O concentrations ranged between 0.06 and 0.92, 1 and 11 mg N L⁻¹, and 3 and 85 μg N L⁻¹, respectively. In three aquifers, medians of δ¹⁸O (vs. SMOW) and “¹⁵N site preference” (SP = difference between δ¹⁵N of the central and peripheral N-position of the linear N₂O molecule) ranged between 36 and 50 per mil and 29 and 53 per mil, respectively. These high values confirm that extreme isotopologue signatures are indicative for denitrifying aquifers. Finally, δ¹⁸O and SP were significantly correlated with excess N₂ and RP which demonstrates that these quantities reflected denitrification dynamics in the investigated aquifers.

References:

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