

Spatial and temporal variability of N₂O and its influencing factors in the soil/ groundwater system

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Introduction

N₂O is a major greenhouse gas and contributes to the destruction of the ozone layer. In agricultural areas, large amounts of nitrate can be leached into the groundwater and then be denitrified with N₂O as an intermediate product. The upscaling of surface groundwater N₂O concentrations is a prerequisite to assess the risk of indirect emissions from aquifers. Indispensable for that is the knowledge of the spatial and temporal variability of N₂O and denitrification-related factors.

Objectives:

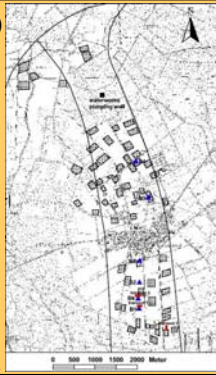
1. Extend of temporal and spatial variability of N₂O concentrations in the surface groundwater?
2. Do denitrification-related factors (O₂, NO₃, SO₄, DOC, CO₂, redox potential, pH) explain the variability of N₂O concentrations?
3. Is N₂O in the surface groundwater produced by autotrophic or heterotrophic denitrification? Is DOC used as electron donor in the heterotrophic denitrification reaction?
4. Which sampling strategy should be used to upscale N₂O concentrations?

Research area: Fuhrberger Feld aquifer (FFA)

The FFA is 30 km north of Hannover and covers 300 km². It's unconfined aquifer extends within 20-30 m thick sands and gravelly sands. Previous research identified intensive denitrification in this aquifer from the groundwater surface to ~8 m below it. Our research focuses mainly on a representative strip of 11 km² which covers a groundwater flow-line (Fig. 1).

Denitrification in the FFA

1. There are indications that heterotrophic denitrification with organic carbon as an electron donor dominates near the groundwater surface (Kölle et al., 1983)
2. Autotrophic denitrification with reduced sulphur as electron donor is the major process in the rest of the aquifer (Böttcher et al., 1992)



Materials and Methods

1. **March 2005: 79 plots** (200 x 200 m) were chosen according to land-use and groundwater level (Fig. 1). They were sampled at 3 sampling sites, 0.5 m below the groundwater surface (N = 237). Analysis: N₂O, CO₂, NO₃, DOC and SO₄
2. **6 multi-level sampling wells** (Fig. 1) were sampled monthly between 0 and 2 m below the groundwater surface in 0.2 m depth intervals from July 05 until June 06. Analysis: N₂O, CO₂, NO₃, DOC, O₂, SO₄, pH and redox potential
3. **multi-level well B1:** (Fig. 1) sampling every 2 days during 1 week, in October 2005 (small N₂O concentrations, Fig. 2) and in May/ June 2006 (high N₂O concentrations, Fig. 2). Analysis: same as under 2.
4. **3 transects** of 12 m (Fig. 1) were sampled every 0.2 m, at 0.3 m below the groundwater surface in September 2006 and March 2007. Analysis: N₂O, CO₂, NO₃, DOC, SO₄ and pH.

Statistical methods:

1. Splitting of the total variance (dispersion variance) of the sampled area (a: plots (see 1.) and b: 3 transects (see 4.)) into variance between and within plots/ transects (Webster and Oliver, 2001)
2. Calculation of a multiple regression analysis of the sampling in March 2005 and of each well.

Fig. 1: The groundwater flow-line strip in the FFA. Dotted squares= plots from March 2005. Blue triangles= multi-level sampling wells. Red dashes= 3 transects.

Results

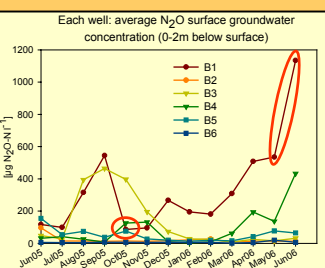


Fig. 2: Monthly N₂O concentrations in the surface groundwater (0-2 m) of 6 multi-level sampling wells

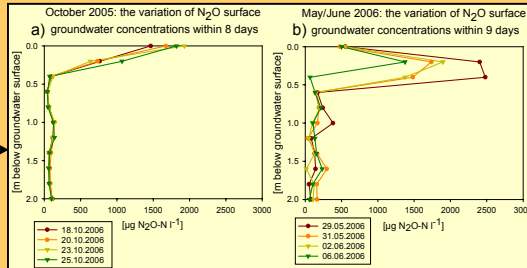


Fig. 3: N₂O concentrations in the surface groundwater (0-2 m) of the multi-level sampling well B1 over a period of one week, the sampling was every 2 days a) in October 2005, b) in May/ June 2006

Temporal variability at the multi-level wells:

The N₂O concentrations of the wells B1, B3 and B4 are highly variable and are highest in late summer/ autumn and in spring (Fig. 2). During periods of variable N₂O concentrations, changes can occur on a day to day-scale (Fig. 3b).

Multiple regression analysis of denitrification related factors at 5 multi-level wells :

The highest r² is 0.72, the smallest is 0.27 and the median of 5 wells is 0.60. Significant variables are, depending on the well, NO₃, CO₂, DOC, redox potential, SO₄ and O₂. **Small distance between soil and groundwater surface:** (B1, B2, B5: 1-2m): CO₂ and DOC significant for N₂O. **Large distance between soil and groundwater surface:** (B3, B4): only SO₄ significant for N₂O.

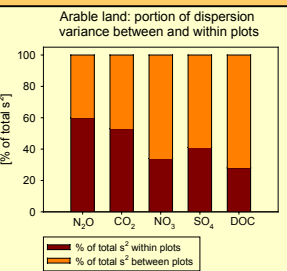


Fig. 4: Portion of dispersion variance (s²) between plots and within plots in March 2005.

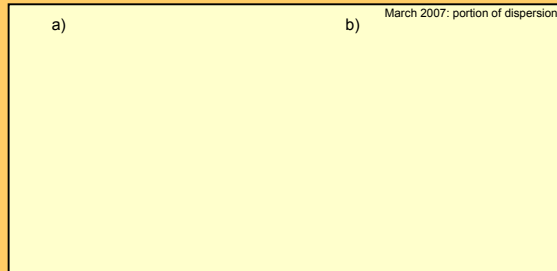


Fig. 5: Portion of dispersion variance (s²) between transects and within transects in a) September 2006 and b) March 2007.

Spatial variability (March 2005, transects) and denitrification-related factors (March 2005):

Sampling in March 2005:

60% of the total variance of N₂O is a consequence of the plot-scale variability (Fig. 4).

NO₃, SO₄ and DOC are better predictable by the selection criteria land-use and groundwater level (Fig. 4).

The r² of the multiple regression analysis is 0.24.

Significant variables are NO₃, DOC and CO₂.

Transects:

The transect-scale variability of N₂O (12 m) is extremely high. September 2006: 68% (Fig. 5a), March 2007: 79% (Fig. 5b).

The variables CO₂, NO₃, DOC and pH show a higher variability between the transects.

Discussion

-The **spatial variability of N₂O is higher than the temporal variability** ⇒ r² of the multiple regression analysis in March 2005 (=spatial) is much smaller than the r² of the wells (=temporal) + the variability is extremely high on the transect-scale (Fig. 5). However, in March 2005, we didn't include O₂ concentrations and redox potential.

-Only some wells show a significant **temporal variability** of N₂O concentrations (Fig. 2+3). High N₂O concentrations in spring and late summer/ autumn are probably caused by seasonally specific dynamics near the groundwater surface.

-The partly small r² of the regression analysis and the high spatial variability indicate that there are **other important small-scale geochemical/ biological factors** influencing the N₂O production.

-**Heterotrophic denitrification with DOC** as electron donor governs the N₂O production at a **high groundwater level** because more bioavailable carbon is leached into the groundwater. Further research is needed to investigate whether DOC or particular organic carbon is more important. At a **deep groundwater level**, **autotrophic denitrification** governs the N₂O production.

-The very high small-scale variability of N₂O (Fig. 4+5) shows that a high sample number on the small transect-scale is sufficient to cover the whole range of N₂O concentrations, which thus enables an **upscaling**. The requirement is, that important N₂O-influencing boundary conditions like groundwater level, land-use and soil type are approximately the same.

Conclusions

1. **Spatial variability**, especially the small-scale variability of N₂O concentrations is extremely high. **Temporal variability** can be very variable in space. Maximum N₂O concentrations occur in autumn/ spring, probably caused by specific dynamics in the surface groundwater during these seasons. **Spatial variability of N₂O is higher than temporal variability**
2. **DOC, CO₂, SO₄, NO₃, O₂ and redox potential** explain in average 60% of the variance of N₂O.
3. **Both denitrification reactions** occur in the surface groundwater, dependent on the distance between the soil and the groundwater surface (small distance= heterotrophic, large distance= autotrophic). **DOC** acts, to a yet unknown extend, as electron donor in the heterotrophic denitrification reaction.
4. Sampling on the transect-scale is appropriate to upscale N₂O concentrations to the catchment scale if plots with catchment-representative groundwater levels, land use and soil conditions are sampled.

References

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- Kölle et al., 1983. Denitrifikation in einem reduzierenden Grundwasserleiter. Vom Wasser 61: 125-147
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