

# Spatial and temporal variability of N<sub>2</sub>O in the surface groundwater: a detailed analysis from a sandy aquifer in northern Germany

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**Abstract** The knowledge of the spatial and temporal variability of N<sub>2</sub>O concentrations in surface groundwater is the first step towards upscaling of potential indirect N<sub>2</sub>O emissions from the scale of localized samples to aquifers. This study aimed to

investigate the spatial and the temporal variability of N<sub>2</sub>O concentrations at different scales in the surface groundwater of a denitrifying aquifer in northern Germany. The spatial variability of N<sub>2</sub>O concentrations in the surface groundwater was analysed at the plot (200 × 200 m) and at the transect scale (12 m). Twenty plots that were distributed across an area of 11 km<sup>2</sup> and 6 transects were sampled. Sixty per cent of the spatial variance of N<sub>2</sub>O was located at the plot scale and 68–79% was located at the transect scale. This indicates that small-scale processes governed the spatial variability of N<sub>2</sub>O in the surface groundwater. A spatial upscaling of N<sub>2</sub>O from the transect to the aquifer scale might be possible with an adequate number of samples that represent important boundary conditions for N<sub>2</sub>O accumulation in the catchment (topography, groundwater level, land use). For the investigation of the temporal variability, 4 multilevel wells were sampled monthly over a period of 13 months. In two periods, a multilevel well was additionally sampled in 2-day intervals over 8 days. At the annual scale, N<sub>2</sub>O concentrations in the surface groundwater were higher during the vegetation period (median 87 μg N<sub>2</sub>O-N l<sup>-1</sup>) and could change rapidly on the day scale whereas the concentrations were smaller in winter (median 21 μg N<sub>2</sub>O-N l<sup>-1</sup>). Groundwater recharge events seemed to be crucial for the day scale variability. Capture of the temporal variations for upscaling might be achieved with a process-based sampling strategy with weekly sampling intervals during the vegetation period, the

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additional sampling after groundwater recharge events and monthly sampling intervals in winter.

**Keywords** Groundwater · N<sub>2</sub>O · Spatial variability · Temporal variability · Upscaling

### Abbreviations

FFA Fuhrberger Feld Aquifer

## Introduction

Nitrous oxide is a major greenhouse gas (Rodhe 1990), that contributes to the destruction of the ozone layer (Crutzen 1976). It is an obligate intermediate product of the denitrification reaction where NO<sub>3</sub><sup>-</sup> is stepwise reduced to N<sub>2</sub>. Denitrification is a well known process in shallow groundwater systems (Böttcher et al. 1992; Gillham and Cherry 1978; Hiscock et al. 1991; Korom 1992; Postma et al. 1991; Smith and Duff 1988; Starr and Gillham 1993; Trudell et al. 1986; Well et al. 2005b) and N<sub>2</sub>O was reported to accumulate in considerable amounts in shallow unconfined aquifers, especially under arable land use (Böhlke et al. 2002; Deurer et al. 2008; Well et al. 2005b). Because N<sub>2</sub>O is subject to vertical and lateral diffusive and convective transport in groundwater it was not necessarily produced at the point where it was sampled. It can be leached from the unsaturated zone where it is produced by nitrification (Mühlherr and Hiscock 1998; Spalding and Parrott 1994) and denitrification (Spalding and Parrott 1994).

Nitrous oxide emissions that originate from NO<sub>3</sub><sup>-</sup> polluted aquifers are defined as indirect emissions (Mosier et al. 1998). Particularly N<sub>2</sub>O that accumulates in shallow aquifers near the groundwater table might be a source of indirect emissions (Deurer et al. 2008; Ronen et al. 1988; Spalding and Parrott 1994). In the following we will use the term 'surface groundwater' for this zone which extends from the groundwater table to about 0.5 m below it (Deurer et al. 2008). Nitrous oxide that was emitted from the groundwater table can rapidly diffuse through the unsaturated zone into the atmosphere (Rice and Rogers 1993; Ueda et al. 1993).

Although shallow aquifers and the occurrence of denitrification with N<sub>2</sub>O accumulation are ubiquitous both in Europe and North America, the significance

of aquifers for indirect N<sub>2</sub>O emissions is still poorly understood (Nevison 2000; Well et al. 2005a). A meaningful spatial upscaling of N<sub>2</sub>O loads in the surface groundwater of shallow aquifers from the local to the regional and finally to the global scale is required to estimate the potential contribution of such aquifers to indirect N<sub>2</sub>O emissions. For upscaling of potential indirect N<sub>2</sub>O emissions, the spatial and temporal variability of N<sub>2</sub>O concentrations in aquifers has to be known. A spatial variability of N<sub>2</sub>O concentrations was indicated by large concentration ranges in aquifers. For example, Well et al. (2005b) measured a concentration range of 11–2,723 µg N<sub>2</sub>O-N l<sup>-1</sup> in shallow groundwater of a hydromorphic soil under arable land use in northwest Germany. In soils, N<sub>2</sub>O emissions are known to be extremely variable with their coefficient of variation typically ranging from 70 to 610% (Ambus and Christensen 1995; Folorunso and Rolston 1984; Mathieu 2006; Parkin 1987; Yanai et al. 2003). Hot-spot like denitrification activity has often been related to a patchy dispersal of soil organic carbon and how these local C pools become available and are invaded by soil microbes (Christensen et al. 1990; Hisset and Gray 1976; Lark et al. 2004; Parkin 1987; Webster and Goulding 1989). However, there is a lack of spatially and temporally resolved data sets on the N<sub>2</sub>O dynamics in the surface groundwater. These data sets would also help to optimize future sampling strategies.

This study was conducted in a denitrifying aquifer of Pleistocene deposits in northern Germany. Previous studies in this aquifer showed that considerable amounts of N<sub>2</sub>O accumulated in the surface groundwater below arable land use (Deurer et al. 2008). This is the first study to analyse the spatial variability of N<sub>2</sub>O in the surface groundwater below arable land use from the transect up to the aquifer scale and to analyse the temporal variability of N<sub>2</sub>O from the day up to the annual scale.

## Methods

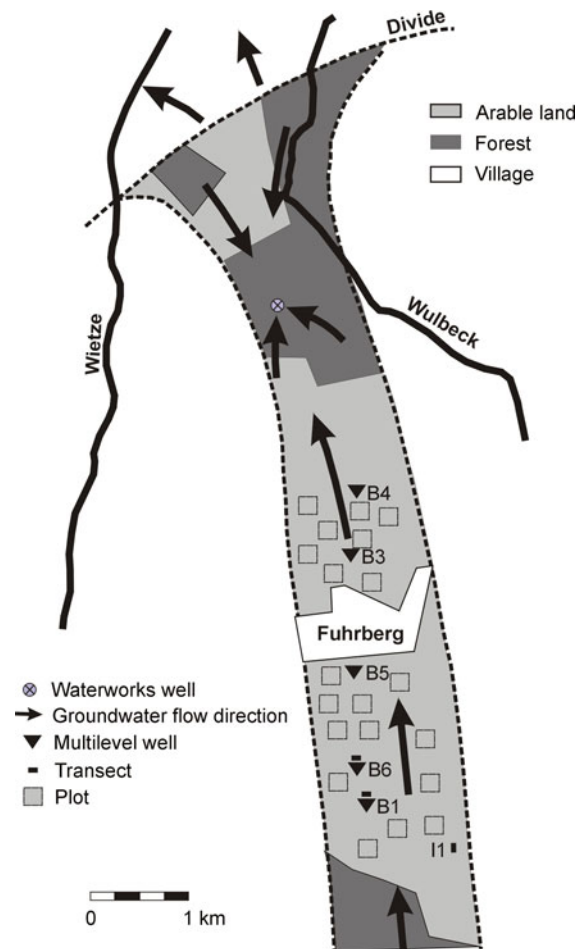
### Research area

The research area was the Fuhrberger Feld Aquifer (FFA) which is situated about 30 km northeast of the city of Hannover in northern Germany. The unconfined aquifer of 316 km<sup>2</sup> extends within 20–40 m

thick sands and gravelly sands with a hydraulic conductivity of 40–150 m day<sup>-1</sup>. The dominant soil types in the area are Podzols and Gleysols which are mainly developed in rather uniform fine to medium sands. The mean precipitation rate is 680 mm year<sup>-1</sup> and the mean annual temperature is 8.9°C. The land use in the FFA is 39% forests, 32% crops, 12% pastures and 15% settlements.

This study focuses on a groundwater flow-line strip of 11 km<sup>2</sup> (Fig. 1). It is representative of the N<sub>2</sub>O dynamics in the surface groundwater below arable land use on the scale of the aquifer because it covers the range of important boundary conditions for N<sub>2</sub>O accumulation in this area (groundwater level,

soil type). The strip extends about 5.5 km from the south towards a waterworks well in the north, and its east-west extension is on average 2 km. The distance from the soil surface to the groundwater table is smallest in the south, fluctuating between 0.7 m in winter to 2.0 m in summer. It increases continuously towards the north and reaches a distance of 4.0–5.0 m at the waterworks well. Previous research identified intensive denitrification reactions in the aquifer. Heterotrophic denitrification with organic carbon as the electron donor dominates in the surface groundwater (Deurer et al. 2008; von der Heide et al. 2008) and indirect N<sub>2</sub>O emissions via the vertical diffusive pathway are only probable from the surface groundwater [groundwater table to 0.55 m (±0.22 m) below (Deurer et al. 2008)]. Autotrophic denitrification with reduced sulphur compounds as the electron donor is the major process deeper than about 2 m below the groundwater table (Böttcher et al. 1992).



**Fig. 1** The groundwater flow-line strip with plots and transects for the investigation of the large and the small scale spatial variability of N<sub>2</sub>O and with multilevel wells for the investigation of the temporal variability of N<sub>2</sub>O

## Spatial variability

### Selection of sampling sites

The spatial variability of N<sub>2</sub>O concentrations was investigated from the transect (12 m), to the plot (200 × 200 m) up to the aquifer scale (11 km<sup>2</sup>). A previous study where the surface groundwater was sampled according to the same method throughout the catchment of the FFA showed that the land use was a significant factor for N<sub>2</sub>O accumulation (von der Heide et al. 2008). Because the lack of NO<sub>3</sub><sup>-</sup> in the surface groundwater below forest and pasture limited the occurrence of denitrification, groundwater only below arable land was sampled in this study.

For the aquifer scale, the surface groundwater was sampled at 20 plots throughout the groundwater flow-line strip (Fig. 1) in March 2007. These plots were chosen from 66 plots below arable land use that were sampled according to the same method in March 2005 (von der Heide et al. 2008). They represented the range of groundwater levels (0.5–2.6 m below soil surface) and N<sub>2</sub>O concentrations below arable land use throughout the catchment area. Each plot was 200 × 200 m (±50 m) and was uniform with respect to the groundwater level, soil type and agricultural management (e.g. crop rotation, fertilizer application).

For the transect scale, we selected three sites with a relatively small distance between the soil surface and the groundwater table. Because of the impact of varying groundwater levels on  $N_2O$  accumulation in the FFA (von der Heide et al. 2008), the results obtained from these sites have to be considered as a first approach towards an understanding of the spatial variability of  $N_2O$  in the surface groundwater. The sites were located next to the multilevel wells B1, B6 and I1 in the south of the groundwater flow-line strip (Fig. 1) and the distance between the soil surface and the groundwater table ranged from 1.55 (I1) to 2.0 m (B6) in September 2006 and from 0.7 (I1) to 1.2 m (B6) in March 2007. B1 and B6 were located on arable fields under intensive arable land use. I1 was under intensive arable land use until July 2005; since then it was unmanaged grassland (*Festuca rubra*) and no fertilizer was applied.

#### *Sampling and analysis*

For the aquifer scale, each plot was sampled at three sampling sites that were evenly distributed over the extend of the plot (see von der Heide et al. 2008). Groundwater samples for the measurement of  $N_2O$  were collected from a depth of 0.5 m below the groundwater table using a slit-probe that was inserted into a hand-augered bore hole (Strebel and Böttcher 1985). The first 20 ml were discarded, then 50 ml of groundwater were collected with a syringe and transferred into gas-tight and partially evacuated (−0.53 bar) serum bottle (118 ml) without air contact. The samples were stored upside down in water at 4°C and were measured within 3 weeks. The preparation of the groundwater samples for the measurement of the  $N_2O$  concentration with a gas chromatograph (Fisons GC 8000) is described in detail in von der Heide et al. (2008). Two replications were measured for each groundwater sample. The gas chromatograph was equipped with a split-injector and an electronic capture detector and a HP-PLOT Q column (30 m length × 0.32 mm ID; Agilent Technologies, Santa Clara, USA) kept at 30°C. The split ratio was 1:8 and Ar-CH<sub>4</sub> (95/5) was used as carrier and make-up gas. Samples of 300 µl were injected using an autosampler (model GC-PAL, CTC-Analytics, Zwingen, Switzerland). The precision as given by the standard deviation obtained from 4 injections of a standard gas was typically 1.5%. The  $N_2O$

concentration in the groundwater samples was calculated according to Henry's law (Well and Myrold 1999; Well et al. 2003) and the final value was the average of the replicated measurements.

For the transect scale, the three transects were aligned with the ploughing direction at the selected sites because a previous study in the FFA showed that the overlapping of fertilizer application strips resulted in a regular oscillation of  $NO_3^-$  concentrations in the surface groundwater perpendicular to the direction of ploughing (Böttcher and Strebel 1988a). Each transect (B1, B6 and I1) was sampled in September 2006 and March 2007 and had a length of 12 m. The groundwater samples for the measurement of  $N_2O$  were collected every 0.2 m at a depth of 0.3 m below the groundwater table. The collection and analysis of the groundwater samples were conducted as described above.

#### Temporal variability

##### *Selection of sampling sites*

For the analysis of the temporal variability of  $N_2O$  concentrations at the time scale of a year with a temporal resolution of a month, four multilevel wells with active denitrification (Deurer et al. 2008) were selected in the groundwater flow-line strip (B1, B3, B4 and B5, Fig. 1). These multilevel wells approximately covered the range of groundwater levels below arable land use in the FFA, with small distances at B1 (about 1.3–2.3 m) and larger distances at B4 (about 2.5–3.5 m).

For the analysis of the temporal variability of  $N_2O$  concentrations at the time scale of a week with a temporal resolution of 2 days, we exemplarily selected the multilevel well B1 in the south of the groundwater flow-line strip (Fig. 1).

##### *Sampling and analysis*

For the temporal variability at the annual scale, the four multilevel wells were sampled monthly from June 2005 to July 2006. Each well was sampled at the depths 0.1–0.7 m below the groundwater table with a depth resolution of 0.2 m. We assumed that the sample, for example, collected in a depth of 0.1 m below the groundwater table ranged from the groundwater table to 0.2 m below. Thus, the groundwater

was sampled from the groundwater table to 0.8 m below.

For the temporal variability on the day scale, the multilevel well B1 was sampled every 2 days over 8 days in October 2005 and June 2006. This well was sampled from the groundwater table to a depth of 2.2 m below. The sampling depths ranged from 0.1 to 2.1 m below the groundwater table with a depth resolution of 0.2 m.

In both sampling campaigns, the first 20 ml of each depth were discarded. Then, 50 ml of groundwater was collected with a plastic syringe that was directly connected to the multilevel well. The sample was transferred into a partially evacuated serum bottle (−0.53 bar) without air contact. The sample preparation and analysis and the calculation of N<sub>2</sub>O concentrations in the groundwater sample was conducted as described above. For both sampling campaigns, a gas chromatograph other than described above was used (Fractovap 400, CARLO ERBA, Milano). It was equipped with an electron capture detector and autosampler (Well et al. 2003) and the measurement precision for N<sub>2</sub>O was 2–3%.

#### *Evaluation of the reason for the temporal variability on the day scale*

There might be two reasons for variations of N<sub>2</sub>O concentrations at the day scale during the 8 day

**Table 1** Overview of the methods used for the investigation of the spatial variability of N<sub>2</sub>O concentrations at the transect and the aquifer scale, the temporal variability of

	Spatial variability		Temporal variability		
	Aquifer scale	Transect scale	Annual scale	Day scale	Evaluation
Sampling time	March 2007	September 2006 & March 2007	June 2005–July 2006	October 2005 & June 2006	May 2006
Number of plots/ transects/mlw	20 plots	3 transects	4 mlw	1 mlw	1 mlw
Size of plots/transects	200 × 200 m	12 m	–	–	–
Sampling depth (m below gwt)	0.5	0.3	0.1–0.7	0.1–2.1	2.3–3.1
Spatial sampling intervals (m)	~140	0.2	0.2	0.2	0.2
Temporal sampling interval	–	–	1 month	Every 2 days over 8 days	<5 min
No. of samples each sampling	60	183	16 (4 depths × 4 mlw)	11 (1 sample each depth)	15 (3 samples each depth)

*mlw* Multilevel well, *gwt* groundwater table

sampling period. Firstly, variations in concentrations at one depth might be due to the sampling procedures, e.g. successive sampling of one depth (see below) and measurement accuracies. Secondly, concentrations in one depth might change because of actual N<sub>2</sub>O processes. We evaluated the reason for varying N<sub>2</sub>O concentrations by successive sampling of the multilevel well B3 (Fig. 1). In May 2006, this well was sampled at five depths ranging from 2.3 to 3.1 m below the groundwater table. Three groundwater samples per depth were collected successively (= time interval < 5 min) and N<sub>2</sub>O concentrations were measured. The sampling and the measurement procedures followed those described in chapter ‘Temporal variability-sampling and analysis’. However, note that for the three successive samples only the first 20 ml were discarded, and then three times 50 ml of groundwater were collected.

An overview of the sampling methods (spatial variability, temporal variability and the evaluation of the reason for the temporal variability on the day scale) is given in Table 1.

#### Estimation of the impact of groundwater sampling on concentration depth profiles

Sampling of 20 ml (discarded) + 50 ml of groundwater at each depth of the multilevel sampling wells (annual scale to day scale) affects an aquifer volume

N<sub>2</sub>O concentrations at the day and the annual scale and the assessment of the reason for the temporal variability on the day scale

of about 230 cm<sup>3</sup>. Presuming a globular volume, the radius is about 4 cm. In the case of the successive sampling the extracted groundwater volume summed to 170 ml. For a globular volume, the affected aquifer volume has a radius of about 5 cm. As samples were taken at depth intervals of 0.2 m, we assume that our groundwater sampling did not affect the concentration depth profiles, at least not in an unacceptable manner. This assumption is supported by the finding of sharp N<sub>2</sub>O concentration changes with depth by Deurer et al. (2008) who used the same sampling procedure as applied in this study. However, because perturbing impact on natural systems by sampling can never be completely excluded; the temporal variability at the day scale, and especially the variability estimated by successive sampling of certain groundwater depths, may be slightly overestimated.

#### Groundwater level

To evaluate the impact of groundwater recharge events on the N<sub>2</sub>O dynamics in the surface groundwater, the groundwater level was monitored at a site that was located about 50 m west of the multilevel well B1. It was recorded every hour from June 2005 to July 2006 using a water depth gauge (Keller Druckmesstechnik GmbH, Germany) that was connected to a data logger (DL2e, Delta-T Devices Ltd., Cambridge).

#### Statistics and calculations

##### *Spatial variability-catchment scale*

From the data collected at the catchment scale in March 2007, we calculated the mean concentration and the coefficient of variation of N<sub>2</sub>O. We tested if the data were normally distributed by using the Kolmogorov–Smirnov Test (Software SPSS 15.0). Because the data were not normally distributed, we additionally calculated the median concentration.

The spatial variability of N<sub>2</sub>O was analysed with a geostatistical approach where the spatial variance (dispersion variance) is partitioned into the variance between blocks and the variance within blocks (Webster and Oliver 2001). Transferred to this study, the variance of all samples within the groundwater flow-line strip was the total variance ( $N = 60$ ). The variance between the plots within the groundwater

flow-line strip was equivalent to the variance between blocks ( $N = 20$ ). The variance of the samples within the plots was the variance within blocks ( $N = 3$ ). The method is described in more in detail by von der Heide et al. (2008) and Webster and Oliver (2001).

##### *Spatial variability-transect scale*

We calculated the mean and median concentration and the coefficient of variation of the N<sub>2</sub>O concentrations for each transect (3 transects, 61 samples per transect) and for both sampling periods (September 2006 and March 2007).

We used the above described geostatistical approach to further analyse the small scale spatial variability. The spatial variance (dispersion variance,  $N = 183$ ) was partitioned into the variance between transects ( $N = 3$ ) and variance within transects ( $N = 61$ ) for each sampling period (September 2006 and March 2007).

To identify spatial ranges of N<sub>2</sub>O, we calculated semivariograms for each transect and for both sampling periods. Prior to the calculation, the data were checked for normality distribution with the Kolmogorov–Smirnov Test (Software SPSS 15.0). Data which were not normally distributed were log-transformed to obtain normally distributed data. Subsequently, the model which best fitted the observed semivariances was identified. We used the range of the fitted semivariogram model to quantify the spatial correlation of N<sub>2</sub>O. The method used for the calculation of variograms and the fitting of spherical models is described in detail by Böttcher and Strebel (1988b) and Webster and Oliver (2001).

##### *Temporal variability-annual scale*

For the investigation of the temporal variability on the annual scale, we calculated the mean N<sub>2</sub>O concentration in the surface groundwater, ranging from the groundwater table to 0.8 m below it for each multilevel well (B1, B5, B3 and B4) and for every monthly sampling (June 2005–July 2006). In order to further analyse the temporal variations, we additionally calculated the mean and median N<sub>2</sub>O concentration of all wells and depths ranging from the groundwater table to 0.8 m below for (1) all months, (2) the vegetation period from March to November and (3) the winter period from December to February.

### Temporal variability-day scale

Firstly, the mean  $N_2O$  concentration of the well B1 was calculated from the groundwater table to a depth of 2.2 m below it, separately for October 2005 and June 2006. For the well B3, the mean  $N_2O$  concentration of the five sampled depths with 3 samples per depth was calculated.

Secondly, we evaluated whether variation in  $N_2O$  concentrations in each depth at the well B1 were due to actual  $N_2O$  transformation processes or due to sampling procedures and proceeded in three steps:

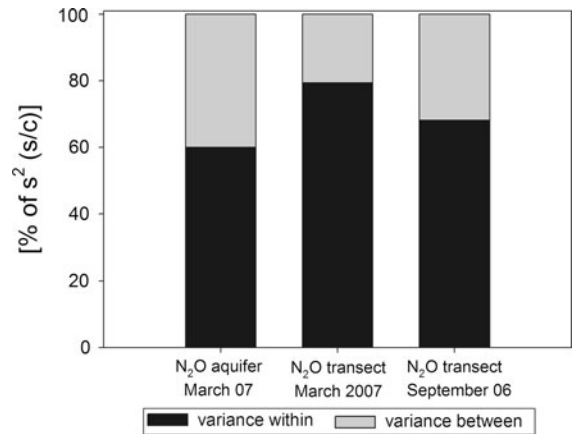
1. At B1 we calculated the variance ( $s^2$ ) of each depth ( $N = 11$ ) with four sampling times per depth within 8 days. We distinguished between October 2005 and June 2006.
2. At B3 we calculated the variance ( $s^2$ ) of each depth ( $N = 5$ ) with the three successively (without time intervals during the collection) collected samples per depth. We selected the maximum variance out of the five calculated variances. This was the reference value which represents the largest possible variation in one depth as a result of the sampling and measurement procedures.
3. We tested the variance of each depth at well B1 against the maximum variance at well B3 using an  $F$ -Test. The hypotheses were  $H_0: B3_{(\max s)}^2 = B1_{(sdepth x)}^2$  and  $H_A: B3_{(\max s)}^2 \neq B1_{(sdepth x)}^2$ . If  $H_0$  is true, the variance at B1 could be due to the sampling strategy (measurement errors, successive sampling of one depth). If  $H_A$  is true, the concentration at B1 varied because of actual  $N_2O$  transformation processes in the course of the 8 days with four sampling times.

## Results

### Spatial variability-aquifer scale

The measurement at the plots yielded a median  $N_2O$  concentration of  $1.61 \mu\text{g } N_2O\text{-N } l^{-1}$  and a mean of  $6.89 \mu\text{g } N_2O\text{-N } l^{-1}$ . The coefficient of variation was 258%.

The partitioning of the spatial variance into the variance between plots and within plots showed that most of the variance of  $N_2O$  (60%) was a consequence of the within-plot scale variability (Fig. 2).



**Fig. 2** Components of the variance between and within plots in March 2007 and between and within transects in March 2007 and September 2006

### Spatial variability-transect scale

Nitrous oxide concentrations were generally low at the three transects in March 2007 and additionally at transect II in September 2006 (median  $< 2.1 \mu\text{g } N_2O\text{-N } l^{-1}$ , Table 2). There was a considerable concentration only at transects B1 and B6 in September (median  $> 6 \mu\text{g } N_2O\text{-N } l^{-1}$ , Table 2).

Although  $N_2O$  concentrations were generally lower in March 2007, most of the spatial variance of  $N_2O$  was located within transects in both sampling periods (68 and 79%, respectively, Fig. 2).

Variograms for  $N_2O$  were calculated for each transect and both sampling periods. The model that fitted best to the observed semivariances was the spherical model. Ranges of  $N_2O$  occurred only at transects with elevated  $N_2O$  concentrations, transect B1 and B6 in September 2006 (Fig. 3a, b). The ranges were 3.28 m at transect B1 and 1.00 m at transect B6.  $N_2O$  did not show a nugget variance indicating that there was no spatial structure smaller than the smallest sampling interval.

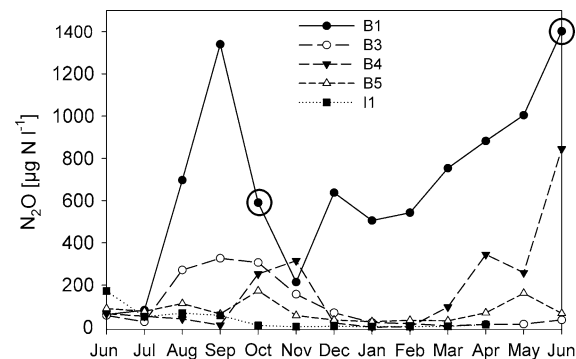
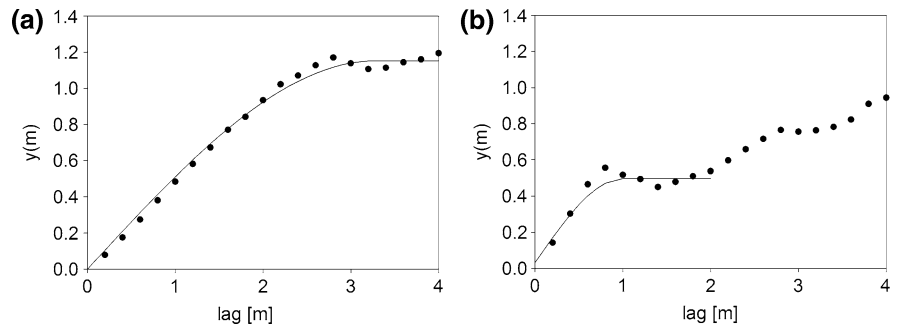
### Temporal variability-annual scale

The annual mean  $N_2O$  concentration in the surface groundwater was  $247.0 \mu\text{g } N_2O\text{-N } l^{-1}$  ( $s = 520.2$ ), the median concentration was  $66.7 \mu\text{g } N_2O\text{-N } l^{-1}$ . Nitrous oxide concentrations in the surface groundwater were generally higher in the vegetation period from March to November (Fig. 4). In this period, the

**Table 2** Median (med) and mean  $\text{N}_2\text{O}$  concentrations and coefficients of variation (cv) at transects B1, B6 and I1 in September 2006 and March 2007 (each transect  $N = 61$ )

	B1			B6			I1		
	Med	Mean	cv	Med	Mean	cv	Med	Mean	cv
$\text{N}_2\text{O}$ [ $\mu\text{g N}_2\text{O-N l}^{-1}$ ] September 2006	32.99	52.38	109	6.00	8.18	89	1.27	1.30	19
$\text{N}_2\text{O}$ [ $\mu\text{g N}_2\text{O-N l}^{-1}$ ] March 2007	1.69	1.62	21	2.06	2.47	41	1.91	1.96	28

The unit of the cv is %

**Fig. 3** Variograms with spatial ranges of  $\text{N}_2\text{O}$  at the transect scale. The dotted lines show the normalized variograms, the solid lines represent the fitted spherical model. **a**  $\text{N}_2\text{O}$ , B1, September 2006; **b**  $\text{N}_2\text{O}$ , B6, September 2006**Fig. 4** Mean  $\text{N}_2\text{O}$  concentrations in the surface groundwater (groundwater table to 0.8 m below it, 4 sampled depths per well and month) of each well from June 2005 to June 2006. The two circles denote the sampling time of B1 for the investigation of the temporal variability at the time scale of a day

mean  $\text{N}_2\text{O}$  concentration of all wells was  $279.1 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 558.0$ ) and the median averaged  $87.3 \mu\text{g N}_2\text{O-N l}^{-1}$ . However, the concentrations of  $\text{N}_2\text{O}$  were considerably smaller in June/July 2005 (mean =  $64.8 \mu\text{g N}_2\text{O-N l}^{-1}$ ,  $s = 38.4$ , median =  $60.4 \mu\text{g N}_2\text{O-N l}^{-1}$ ) compared with June 2006 (mean =  $586.9 \mu\text{g N}_2\text{O-N l}^{-1}$ ,  $s = 835.1$ , median =  $131.8 \mu\text{g N}_2\text{O-N l}^{-1}$ ). In the winter period from December 2005 to February 2006, the mean  $\text{N}_2\text{O}$  concentration was  $134 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 340.1$ ) and the median concentration was  $20.9 \mu\text{g N}_2\text{O-N l}^{-1}$ .

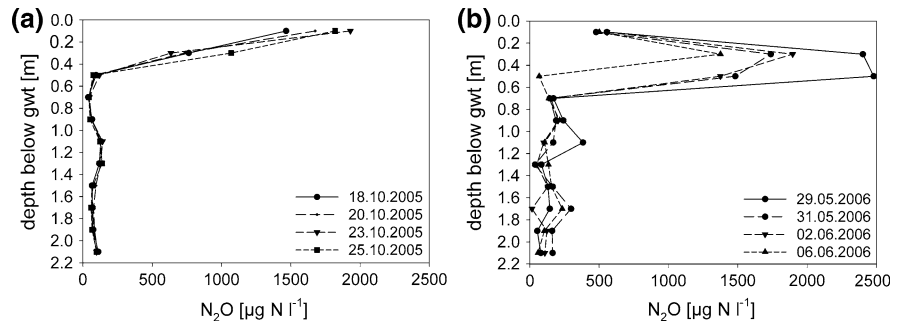
#### Temporal variability-day scale

On the 18th of October 2005, the mean  $\text{N}_2\text{O}$  concentration in the surface groundwater was  $272.4 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 445.9$ ). Concentrations hardly changed over the 8 day sampling period; they averaged  $329.0 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 577.3$ ) at the 25th of October (Fig. 5a). The groundwater level fell continuously from 177 to 183 cm below the soil surface from 1 week prior to sampling to the end of sampling (11th–25th of October, Fig. 6) but the fall during the sampling period (18th–25th of October) was only about 2 cm.

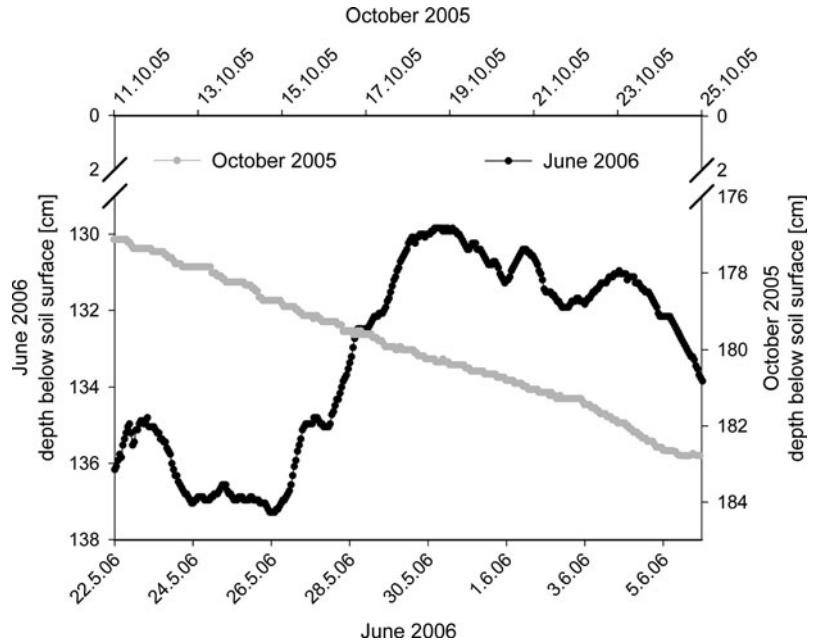
In the second sampling period, the initial (29th of May) mean  $\text{N}_2\text{O}$  concentration averaged  $611.3 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 917.0$ ). The concentrations were much higher than in October and declined considerably over the 8 day sampling period; on average they declined to  $280.9 \mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 383.0$ ) at the 6th of June (Fig. 5b). Thereby, the largest concentration shift was observed in the top 0.6 m of the groundwater (Fig. 5b). From 1 week prior to sampling to the end of sampling (22nd of May–6th of June), the groundwater level showed considerable fluctuations (Fig. 6). Prior to sampling it rose from 137 to 130 cm below the soil surface and during sampling (from 29th of May) it fell with little fluctuations to 134 cm below the soil surface (Fig. 6).



**Fig. 5** N<sub>2</sub>O concentration course at the well B1 over 8 days in **a** October 2005, **b** June 2006. The groundwater table is at 0.0 m



**Fig. 6** The groundwater level near the multilevel well B1 from the 11th to the 25th of October 2005 and from the 22nd of May 2006 to the 6th of June 2006. The soil surface is at 0 cm



*Evaluation of the reason for the temporal variability on the day scale*

The maximum variance (reference value) of the successively sampled well B3 was 117.0 ( $\mu\text{g N}_2\text{O-N l}^{-1}$ )<sup>2</sup> and the mean N<sub>2</sub>O concentration of all samples and depths was 52.3  $\mu\text{g N}_2\text{O-N l}^{-1}$  ( $s = 36.6$ ). The statistical evaluation (*F*-Test) showed that in June 4 out of 11 variances at B1 were significantly higher than the reference variance of the successive sampling at B3, and in October 2 out of 11 variances at B1 were significantly higher. Furthermore, in June the mean variance of all sampled depths was significantly higher than the maximum variance of B3 whereas the mean variance in October was not significantly different from the reference variance of B3 (Table 3). These results indicate that day scale variability of N<sub>2</sub>O concentrations at well B1 in June 2006 (Fig. 5b) was

not caused by sampling and measurement errors but by significant day scale N<sub>2</sub>O transformation processes. However, in October 2005 N<sub>2</sub>O concentrations in depths deeper than 0.4 m below the groundwater table (Fig. 5a) were relatively stable on the day and week scale. This demonstrates that N<sub>2</sub>O concentrations in the surface groundwater may change very rapidly in time.

**Discussion**

N<sub>2</sub>O concentrations

In March 2007, the median aquifer scale N<sub>2</sub>O concentration of 1.6  $\mu\text{g N}_2\text{O-N l}^{-1}$  below arable land was relatively low compared with other aquifers of Pleistocene deposits in northern Germany. For example, Weymann et al. (2008) found median N<sub>2</sub>O

**Table 3** N<sub>2</sub>O variances (s<sup>2</sup>) of four samples per depth (shown in meter below groundwater table) at the well B1 in October 2005 and June 2006 and the mean variance of each sampling period

Depth (m below gwt)	B1, October 2005 [μg N <sub>2</sub> O-N l <sup>-1</sup> ] <sup>2</sup>	B1, June 2006 [μg N <sub>2</sub> O-N l <sup>-1</sup> ] <sup>2</sup>
0.1	40031*	1547
0.3	35317*	181761*
0.5	383	980611*
0.7	14	213
0.9	35	487
1.1	88	17603*
1.3	95	1867
1.5	174	322
1.7	72	14926*
1.9	56	1973
2.1	37	2095
Mean all depths	6,937	109,400*

\* s<sup>2</sup> is significantly higher than the maximum s<sup>2</sup> of the successive sampling at B3 (*P* < 0.05)

concentrations ranging from 3 to 18 μg N<sub>2</sub>O-N l<sup>-1</sup> in three aquifers in northern Germany and a median N<sub>2</sub>O concentration of 89 μg N<sub>2</sub>O-N l<sup>-1</sup> in the FFA. These medians were, however, calculated from different depths and sampling times in the aquifers. In March 2005, the surface groundwater below arable land was sampled at the same plots and according to the same method (von der Heide et al. 2008). At that time, the median N<sub>2</sub>O concentration below arable land use was one order of magnitude higher (10 μg N<sub>2</sub>O-N l<sup>-1</sup>), indicating a temporal variability between years. Because the same sampling time and strategy were used in 2005 and 2007, it can be assumed that the bioavailability of dissolved organic carbon (DOC) in surface groundwater (typically about 20 mg DOC l<sup>-1</sup> in the surface groundwater of this area (Strebel and Böttcher 1989)) was not a crucial factor for *N* transformation processes and thus for different N<sub>2</sub>O concentrations in two sampling periods. Also different levels of NO<sub>3</sub><sup>-</sup> concentrations were not likely to have an impact as the median concentrations were similar (March 2005: 16.4 mg NO<sub>3</sub><sup>-</sup>-N l<sup>-1</sup>, March 2007: 17.7 mg NO<sub>3</sub><sup>-</sup>-N l<sup>-1</sup>). However, different amounts of groundwater recharge could be a reason for the variability of N<sub>2</sub>O concentrations between years. While the cumulative rainfall averaged 278 mm from October 2004 to

April 2005, it was unusually high from October 2006 to April 2007 (401 mm). During rainfall events with high intensity, dissolved O<sub>2</sub> was very probably leached with the infiltrating water, especially in the well drained sandy soils of the research area, and this probably resulted in higher O<sub>2</sub> concentrations in the surface groundwater (Deurer et al. 2008, measured very variable O<sub>2</sub> concentrations up to 8 mg l<sup>-1</sup> in the surface groundwater of the FFA). This could have inhibited the occurrence of heterotrophic denitrification and thus lower net N<sub>2</sub>O accumulation in large parts of the sampled groundwater flow-line strip. However, besides the net N<sub>2</sub>O production, the concentrations of N<sub>2</sub>O in the surface groundwater are also governed by diffusive and convective N<sub>2</sub>O fluxes to other groundwater zones, by diffusive fluxes into the unsaturated zone and, probably more important in this period, by the residence time of the groundwater. The longer the residence time is, the more N<sub>2</sub>O can be produced but the more can also be reduced to N<sub>2</sub>. During periods with high groundwater recharge like in winter 2006/07, the groundwater table rises, and groundwater flow velocity increases. Therefore, the residence time of groundwater close to the groundwater table was comparatively short, and the gross N<sub>2</sub>O production was probably small.

#### Spatial variability

Nitrous oxide concentrations were highly variable at the scale of the aquifer; the coefficient of variation (cv) was 258%. Another sampling at the aquifer scale in the FFA in March 2005 showed a similar cv (219%), although the different land uses arable land, forest and pasture were included in the calculation of this cv (von der Heide et al. 2008). These cv's are comparable to spatial cv's for N<sub>2</sub>O fluxes from arable soils. For example, Yanai et al. (2003) found a cv of 217% on the 100 × 100 m scale, Mathieu (2006) identified cv's of 70–140% on the 20 × 20 m scale and Ambus and Christensen (1995) reported cv's of 282 and 106% along 116 and 58 m transects, respectively. Thus, a high spatial variability of N<sub>2</sub>O seems to be typical not only for soils but also for the surface groundwater of the FFA.

The further analysis of the spatial variance showed that the larger part of the spatial variance was located on the 200 × 200 m plot scale, indicating a mosaic of 'hot' and 'cold' spots with respect to the

accumulation of  $N_2O$ . It is remarkable that although total  $N_2O$  loads in March 2005 (von der Heide et al. 2008) were considerably different from those in March 2007 (e.g. because the infiltration of oxygen-rich water during winter 2006/07 into the surface groundwater might have influenced the overall  $N_2O$  accumulation in the surface groundwater, see above), the general spatial distribution of variability did not change. Therefore, the spatial pattern of  $N_2O$  was obviously governed by other factors on the sub-plot scale.

Because each selected plot was uniform with respect to the soil type, groundwater level, land use and the agricultural management practices like fertilizer application and crop rotation, factors which are known to have an impact on the accumulation of  $N_2O$ , these factors were not crucial for the within-plot variations of  $N_2O$ . Also the impact of the topography that was quoted as an important factor for the spatial variability of  $N_2O$  concentrations in soils (Parkin 1993; Pennock et al. 1992), can be neglected in the flat catchment area of the FFA.

We further analysed the small scale spatial variability of  $N_2O$  concentrations at the transect scale of 12 m. Although the  $N_2O$  concentration levels were different (Table 2), the general spatial distribution of variability was similar in both sampling periods. The largest part of the spatial variance of  $N_2O$  was located within transects. These results indicate that the spatial pattern of  $N_2O$  was governed even by factors on the small sub-transect scale. However, because the transects were all located at sites with a relatively small distance between the soil surface and the groundwater table, these results have to be confirmed by the sampling of more transects at sites with larger distances between the soil surface and the groundwater table.

Spatial ranges of  $N_2O$  (between 1 and 3 m) exclusively occurred at transects where  $N_2O$  accumulated (B1 and B6 in September 2006). At transects with low  $N_2O$  concentrations, a lack of  $NO_3^-$  in the surface groundwater (transect II: median September 2006:  $5.4 \text{ mg } NO_3^- \text{-N l}^{-1}$ , March 2007:  $2.5 \text{ mg } NO_3^- \text{-N l}^{-1}$ ) or the high groundwater recharge in winter 2006/07 (transects B1 and B6 in March 2007) probably inhibited denitrification and thus  $N_2O$  accumulation. At transects with denitrification, the denitrifying microbes obviously created a distinct spatial pattern, a “fingerprint”, with respect to their

denitrifying activity. To our best knowledge, there are no other studies on spatial ranges of  $N_2O$  in groundwater. In soils, spatial ranges were identified at different scales. For example, Yanai et al. (2003) found a moderate spatial dependence of  $N_2O$  fluxes with a range of  $>75 \text{ m}$  and associated this range to variations in topography, organic matter and the pH value. Ambus and Christensen (1994) observed an autocorrelation of  $N_2O$  fluxes at separations  $<1 \text{ m}$  and  $>7 \text{ m}$  and attributed the autocorrelation on the small scale to hot spots of denitrification activity. In many studies, small scale variations of  $N_2O$  in soils were associated with the  $C_{\text{org}}$  content (Hisset and Gray 1976; Lark et al. 2004; Parkin 1987; Webster and Goulding 1989). For example, a study showed that after the addition of particulate organic matter, denitrification hot spots occurred after 2–4 days. First, the  $O_2$  consumption was increased until a denitrification hot spot was formed (Christensen et al. 1990). Jacinthe et al. (1998) assumed that hot spots may be especially important in groundwater because of the low C stock of the aquifer matrix. Potential electron donors for heterotrophic denitrification in the surface groundwater of the FFA were DOC (Deurer et al. 2008; von der Heide et al. 2008) and probably organic matter with a median C content of  $1.02 \text{ g kg}^{-1}$  (range:  $0.01\text{--}7.15 \text{ g kg}^{-1}$ ) in the sampling depth of 0.3 m below groundwater surface at the transects (data not published). Also preferential flow, that was shown to occur in the FFA (Deurer et al. 2003), might have had an impact on small scale variations of  $N_2O$ . Nitrate and DOC rapidly transported to the surface groundwater could have resulted in the formation of hot spots of heterotrophic denitrification with  $N_2O$  accumulation.

#### Temporal variability

Nitrous oxide concentrations in the surface groundwater showed a distinct temporal variability on the annual scale with elevated concentrations in the vegetation period and lower concentrations in winter. This clearly shows that even if the groundwater is often considered to be a slowly reactive system, the topmost layer was highly reactive with respect to  $N_2O$  accumulation. In soils,  $N_2O$  production can also vary considerably with season. Peaks from spring to autumn were related to elevated temperatures, thawing of the frozen soil, high soil moisture and fertilizer

N application (Ambus and Christensen 1995; Flessa et al. 1995; Velthof et al. 1996).

In groundwater, the combined effects of elevated groundwater temperatures and the availability of electron acceptors ( $\text{NO}_3^-$ ) and donors (DOC and  $\text{C}_{\text{org}}$ ) might have promoted the heterotrophic denitrification process in general and also the accumulation of  $\text{N}_2\text{O}$  during the vegetation period from spring to autumn (Firestone et al. 1980; Hutchinson and Davidson 1993; Vinther 1991). In spring, the groundwater table reaches its annual maximum and is, therefore, in contact with a higher amount of bioavailable soil organic carbon in the upper part of the soil profile. This might have initiated intensive denitrification processes that contributed to quickly rising  $\text{N}_2\text{O}$  concentrations (Fig. 4).

In summer, there is usually no groundwater recharge. Owing to the long residence time of the groundwater in the topmost layer of the aquifer,  $\text{NO}_3^-$  and DOC are likely to be used up and a lack of these solutes could temporarily limit the occurrence of heterotrophic denitrification and thus  $\text{N}_2\text{O}$  accumulation in the surface groundwater. This was shown in June/July 2005 (Fig. 4) where the groundwater level fell continuously (data not shown) and median  $\text{N}_2\text{O}$  concentrations were relatively low at the four multilevel wells. In contrast, the groundwater level rose rapidly at about 8 cm 3 days prior to the start of sampling in June 2006. The leaching of much  $\text{NO}_3^-$  and DOC into the surface groundwater might have promoted a heterotrophic denitrification process (Hutchinson and Davidson 1993), resulting in twice as high median  $\text{N}_2\text{O}$  concentrations ( $132 \mu\text{g N}_2\text{O-N l}^{-1}$ ) than the previous year.

In soils of temperate climate, low denitrification rates and little  $\text{N}_2\text{O}$  accumulation in winter were often related to a lack of fertilizer N application and low temperatures (e.g. Bouwman and Boumans 2002; Velthof et al. 1996). Also rates of decomposition and mineralization of organic matter are known to be lowest during this season (Gill et al. 1995; Heumann and Böttcher 2004). In contrast, an increase of  $\text{N}_2\text{O}$  production in soils during winter or spring was reported during freezing and thawing cycles (Burton and Beauchamp 1994; Corre et al. 1996; Flessa et al. 1995; Wagner-Riddle et al. 1997). However, most of these processes are not relevant in aquifers. In this study, only the multilevel well B4 was  $\text{NO}_3^-$  depleted (data not shown). The usage of  $\text{N}_2\text{O}$  as

electron acceptor in the absence of available  $\text{NO}_3^-$  (El-Demerdash and Ottow 1983) or the complete inhibition of the denitrification activity might explain the small  $\text{N}_2\text{O}$  concentrations at this well. However, the groundwater recharge is usually high during winter and the availability of  $\text{NO}_3^-$  was not limited at the wells B3 and B5 (data not shown) where  $\text{N}_2\text{O}$  concentrations were also small (Fig. 4). Also, lower mineralization rates or the lower input of fertilizer N application in winter is not likely to affect the groundwater instantly because the leaching of solutes from the topsoil to the groundwater table takes at least a few months (Duijnsveld et al. 1988; Duijnsveld et al. 1993). A study in coarse sandy soils found that the denitrification activity was low at  $10^\circ\text{C}$  and completely inhibited at 2 and  $5^\circ\text{C}$  (Vinther 1991). We assume that low groundwater temperatures in the FFA, which decreased to  $6^\circ\text{C}$  in February (data not shown), slowed down or even temporarily inhibited the denitrification activity and, therefore, were a crucial factor for low  $\text{N}_2\text{O}$  concentrations in winter.

The sampling with a temporal resolution of a month suggested that  $\text{N}_2\text{O}$  concentrations at the multilevel well B1 declined successively from October to November 2005 (Fig. 4). However, the day scale sampling in October revealed that in the week following ‘October sampling’ concentrations even increased slightly in the uppermost depths (Fig. 5a) and were constant in the depths below (the mean  $\text{N}_2\text{O}$  concentration in the surface groundwater in Fig. 4 and the depth profile of the first day scale sampling at the 18th of October 2005 in Fig. 5a denote the same sampling day).  $\text{N}_2\text{O}$  concentrations declined in the 3 weeks prior to the ‘November sampling’. The day scale sampling in June 2006 showed that such a decline can occur very rapidly. In only 8 days, the mean  $\text{N}_2\text{O}$  concentration in the first 2 m of the aquifer declined about more than a half from  $611 \mu\text{g N}_2\text{O-N l}^{-1}$  down to  $281 \mu\text{g N}_2\text{O-N l}^{-1}$ . It is typical that the largest  $\text{N}_2\text{O}$  concentration shift was located in the topmost layer of the groundwater from the groundwater table to 0.6 m below it (Fig. 5b; Deurer et al. 2008). The monitoring of the groundwater level in both sampling periods support the assumption that the solute input from the unsaturated zone during the recharge of groundwater might be a crucial factor for high  $\text{N}_2\text{O}$  dynamics in the topmost layer of an aquifer. There was no groundwater recharge prior and during the sampling in October and the mean  $\text{N}_2\text{O}$

concentration of  $272 \mu\text{g N}_2\text{O-N l}^{-1}$  was low and relatively constant compared to June 2006 ( $611 \mu\text{g N}_2\text{O-N l}^{-1}$ ) where the groundwater level rose rapidly prior to the start of sampling. Although groundwater recharge events are not typical during summer, these single events can obviously result in strongly varying  $\text{N}_2\text{O}$  concentrations.

In order to accurately estimate and upscale the risk of indirect  $\text{N}_2\text{O}$  emissions from aquifers, it is very important to capture such large variations in the groundwater zone where indirect  $\text{N}_2\text{O}$  emissions into the unsaturated zone are likely to occur from (groundwater table to about 0.6 m below (Deurer et al. 2008)). The variations on the day scale were obtained from a multilevel well (B1) where  $\text{N}_2\text{O}$  concentrations and dynamics were remarkably high (Fig. 4). The temporal variability might be smaller at less reactive sites. To capture the whole width of temporal variability, we recommend the investigation of day scale variations of  $\text{N}_2\text{O}$  at more sites of different reactivity in future research.

## Conclusions

The partitioning of the spatial variance of  $\text{N}_2\text{O}$  concentrations in the surface groundwater indicated that out of three investigated scales (11 km<sup>2</sup> aquifer,  $200 \times 200$  m plot, 12 m transect), the largest part of the spatial variance was located within transects (68–79%). We conclude that an upscaling of  $\text{N}_2\text{O}$  concentrations from the transect scale (12 m with sampling intervals of 0.2 m) to the catchment scale might be possible as long as different sites that represent important boundary conditions for  $\text{N}_2\text{O}$  accumulation (land use, topography, groundwater level) within the catchment are included.

The investigation of the temporal variability of  $\text{N}_2\text{O}$  in the surface groundwater showed that high  $\text{N}_2\text{O}$  concentrations occurred in the vegetation period (March–October) and the concentrations were much smaller in winter (December–February). Sampling on the day scale in the vegetation period showed that  $\text{N}_2\text{O}$  concentrations in the surface groundwater (groundwater table to 0.6 m below) might change rapidly on the day scale. The recharge of groundwater was identified as an important factor for high  $\text{N}_2\text{O}$  dynamics in the surface groundwater. For the assessment and upscaling of indirect  $\text{N}_2\text{O}$  emissions from

the surface groundwater, these variations have to be captured. This might be achieved with a process-based sampling strategy. A minimum sampling interval of a week would probably be adequate to cover most of the variations in the vegetation period. Nitrous oxide peaks might be captured with the additional sampling after groundwater recharge events. In winter, sampling on the time scale of a month might be adequate.

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