

Recovery of groundwater N₂O at the soil surface and its contribution to total N₂O emissions

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Abstract Production and accumulation of the major greenhouse gas nitrous oxide (N₂O) in surface groundwater might contribute to N₂O emissions to the atmosphere. We report on a ¹⁵N tracer study conducted in the Fuhrberger Feld aquifer in northern Germany. A K¹⁵NO₃ tracer solution (60 atom%) was applied to the surface groundwater on an 8 m² measuring plot using 45 injection points in order to stimulate production of ¹⁵N₂O by denitrification and to detect its contribution to emissions at the soil surface. Samples from the surface groundwater, from the unsaturated zone and at the soil surface were collected in regular intervals over a 72-days period. Total N₂O fluxes at the soil surface were low and in a range between -7.6 and 29.1 μg N₂O-N m⁻² h⁻¹. ¹⁵N enrichment of N₂O decreased

considerably upwards in the profile. In the surface groundwater, we found a ¹⁵N enrichment of N₂O between 13 and 42 atom%. In contrast, ¹⁵N enrichment of N₂O in flux chambers at the soil surface was very low, but a detectable ¹⁵N enrichment was found at all sampling events. Fluxes of groundwater-derived ¹⁵N-N₂O were very low and ranged between 0.0002 and 0.0018 kg N₂O-N ha⁻¹ year⁻¹, indicating that indirect N₂O emissions from the surface groundwater of the Fuhrberger Feld aquifer occurring via upward diffusion are hardly significant. Due to these observations we concluded that N₂O dynamics at the soil-atmosphere interface is predominantly governed by topsoil parameters. However, highest ¹⁵N enrichments of N₂O throughout the profile were obtained in the course of a rapid drawdown of the groundwater table. We assume that such fluctuations may enhance diffusive N₂O fluxes from the surface groundwater to the atmosphere for a short time.

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Introduction

The trace gas nitrous oxide (N₂O) is known to contribute to global warming (Mosier et al. 1998) and catalyses the destruction of stratospheric ozone (Crutzen 1981). Its global atmospheric concentration

has increased since pre-industrial times by about 18% (Intergovernmental Panel on Climate Change 2007) and continues to do so. A significant amount of N_2O emissions originates from agricultural ecosystems (Mosier et al. 1998). In aquifers of agricultural catchments, high concentrations of N_2O were found at the groundwater surface (Spalding and Parrott 1994; Well et al. 2005a; Deurer et al. 2008). Thus groundwater N_2O was assumed to be a potential significant source of N_2O emissions to the atmosphere (Mosier et al. 1998; Rice and Rogers 1993; Ronen et al. 1988). These indirect emissions from groundwater are associated with nitrogen that leaves agricultural fields via leaching and runoff to adjacent systems (Nevison 2000; Groffman et al. 2002; Well et al. 2005b). The Intergovernmental Panel on Climate Change (IPCC) methodology provides a concept of N_2O emission factors, containing an emission factor EF5-g for indirect N_2O emissions from groundwater and drainage ditches in order to construct national inventories for these emissions (Mosier et al. 1998). This concept is introduced and discussed in detail by Well et al. (2005b) and Clough et al. (2007). Firstly, the EF5-g default factor was defined as $0.015 \text{ kg } N_2O\text{-N kg}^{-1}$ of N leached (Mosier et al. 1998) and based on very few data which were available for its validation (Groffman et al. 2002). Recent studies have emphasized uncertainties with the magnitude of the EF5-g and suggested a substantial downward revision (Hiscock et al. 2002, 2003; Reay et al. 2005; Sawamoto et al. 2005). Taking the results of these studies into account, the EF5-g default value was corrected to $0.0025 \text{ kg } N_2O\text{-N kg}^{-1}$ of N leached (IPCC 2006). However, the knowledge of indirect N_2O emissions from groundwater is still limited because few studies have tried to relate subsurface N_2O concentrations to N leaching from soils (Clough et al. 2005). Furthermore, the question how much N_2O that was produced in the surface groundwater can finally reach the atmosphere is a subject of uncertainty and the controls governing the balance between N_2O production and consumption are not well understood (Clough et al. 2007). Upward diffusive N_2O fluxes from the aquifer surface have been estimated from concentration gradients (Ronen et al. 1988; Hiscock et al. 2003; Deurer et al. 2008). However, until now these estimations have not been evaluated by direct measurements. So far, emission factors for

groundwater-derived N_2O like the IPCC EF5-g are based on N_2O concentrations assuming that degassing of all dissolved N_2O occurs after convective groundwater flow to wells, springs or streams (Mosier et al. 1998). Principally, the vertical diffusive fluxes from the aquifer surface should be added to the potential total groundwater-derived emission (Deurer et al. 2008; Hiscock et al. 2003). Solid estimates of diffusive fluxes are thus needed in order to check if the inclusion of this path leads to higher emission factors.

Production and consumption of N_2O are simultaneously running reactions during denitrification. This well documented microbiological process occurs in O_2 -depleted layers of aquifers with available electron donors (Korom 1992; Böttcher et al. 1990; Ross 1995). Unfortunately, a number of difficulties in measuring denitrification exist. Diverse approaches to the problem were reviewed by Groffman et al. (2006). In situ tracer tests were conducted in order to study the fate of nitrate (NO_3^-) and potential denitrification rates in subsoils and groundwater using ^{15}N labeled NO_3^- (Tobias et al. 2001; Addy et al. 2002; Well et al. 2003; Kim et al. 2005). For these “push–pull methods”, a test solution containing ^{15}N -labeled NO_3^- is injected (“pushed”) into the soil matrix or groundwater, respectively. After an incubation period, the mixture of test solution and groundwater is extracted (“pulled”) and products of denitrification are determined to quantify the process. However, tracer studies focussing on the analysis of the occurrence of the intermediate denitrification product N_2O are rare. Van Groenigen et al. (2005) applied ^{15}N -labeled fertilizer to a sandy soil and traced soil N_2O concentrations and fluxes over a 1 year period. They concluded that most of the N_2O was formed in the subsoil during the winter, but this did not result in corresponding increases in N_2O fluxes from the topsoil to the atmosphere. Overall, total topsoil N_2O fluxes were very low, and amounted to 0.06% of the applied N fertilizer, suggesting that emissions of N_2O via diffusion upwards through the profile were negligible. However, other authors mentioned the possibility of considerable indirect emissions through supersaturated drainage water (Heincke and Kaupenjohann 1999; Reay et al. 2003).

A study with soil columns and ^{15}N labeled NO_3^- as a tracer was conducted by Clough et al. (1999). After labeling the bottom of the columns, they

observed a decrease in $^{15}\text{N-N}_2\text{O}/^{15}\text{N-N}_2$ ratios during upward diffusion of the labeled gases. Furthermore, they stated that this effect may be caused by dilution of the $^{15}\text{N-N}_2\text{O}$ pool with soil derived N_2O , or by consumption of $^{15}\text{N-N}_2\text{O}$ in the topsoil. To detect the fate of N_2O after its occurrence in subsurface environments, Clough et al. (2007) introduced $^{15}\text{N}_2\text{O}$ enriched groundwater into the groundwater–subsoil matrix of a salt marsh and a forested riparian zone. Whereas added $^{15}\text{N}_2\text{O}$ behaved in a conservative manner at the salt marsh, it was partly and significantly consumed in the saturated zone of the riparian zone. In conclusion, the authors emphasized complexity and variability of the fate of N_2O applied or produced in groundwater and that these quantities should be considered in the development of improved IPCC inventory calculations.

In this study, we examine the occurrence of $^{15}\text{N-N}_2\text{O}$ following the application of a tracer solution containing ^{15}N -labeled NO_3^- directly to the groundwater surface and its emission at the soil surface. To achieve this, we analysed $^{15}\text{N-N}_2\text{O}$ and $^{15}\text{N-NO}_3^-$ in the surface groundwater and $^{15}\text{N-N}_2\text{O}$ in different depths of the unsaturated zone and at the soil surface over a 72 days time period. The objectives in detail are:

1. to initiate $^{15}\text{N-N}_2\text{O}$ production at the groundwater surface stimulated by weekly application of a $^{15}\text{N-NO}_3^-$ tracer solution
2. to evaluate the ^{15}N enrichment of N_2O and to detect groundwater-derived N_2O in the system groundwater/unsaturated zone/atmosphere
3. to measure diffusive fluxes of groundwater-derived N_2O to assess its significance as a component of agricultural N_2O emissions from groundwater.

Materials and methods

Research site

The experimental field plot was located within the catchment of the Fuhrberger Feld aquifer (FFA) in northern Germany, which is situated about 30 km northeast of the city of Hannover. The aquifer is unconfined and consists of 20–40 m of pleistocene, highly permeable carbonate-free sands and gravels

underlain by impermeable cretaceous clays. More information about the research site is given by Frind et al. (1990) and Deurer et al. (2008). In the FFA, substantial microbially mediated processes and reactions like denitrification and desulfurification occur, strongly influencing groundwater chemistry. Autotrophic denitrification with reduced sulphur as an electron donor is the dominant process in the deeper aquifer (Böttcher et al. 1992). In the surface groundwater, heterotrophic denitrification with organic carbon as an electron donor has replaced the autotrophic process due to exhaustion of the reduced sulphur compounds (Kölle et al. 1983; Deurer et al. 2008). The heterotrophic process close to the groundwater table is characterised by low nitrate removal efficiency (Weymann et al. 2008). The organic carbon content of the aquifer sands is typically in a range between 0.5 and 0.8 g kg^{-1} . Dissolved organic carbon (DOC) was found to be between 20 and 70 mg l^{-1} in groundwater samples. Our study was conducted from July–September 2007 on an 8 m^2 measuring field plot situated at the south of the Fuhrberger Feld aquifer (52°32'N, 9°51'E). Until July 2005, tillage has been the dominant land use for years. The last cultivated species was *Festuca rubra*. Afterwards, the field had been kept under fallow for experimental purposes. Despite a stronger influence of denitrification and groundwater-derived N_2O is likely during the winter months, we decided to conduct the experiment in summer in order to study the effects of a groundwater drawdown which could be expected during that time.

Experimental setup

To apply the tracer solution, the plot was divided into a raster of 0.5 by 0.5 m. This yielded 45 raster points, where we installed polyvinyl chloride (PVC) pipes (30 mm inner diameter) with their endings direct above the groundwater table. To assess ^{15}N enrichment gradients of N_2O , we conducted measurements in groundwater, in the unsaturated zone and at the soil surface. Four multilevel sampling wells (Böttcher et al. 1985) were installed at the plot in order to collect samples from near the groundwater surface from defined depths (1.5, 1.6 and 1.7 m below soil surface). The soil atmosphere was sampled using gas probes installed in four replications in the unsaturated zone at depths of 0.3, 0.6 and 0.9 m, respectively.

Surface emissions were monitored using eight static flux chambers. The arrangement of the PVC pipes, the wells, the gas probes and the static flux chambers at the measuring field are represented in Fig. 1.

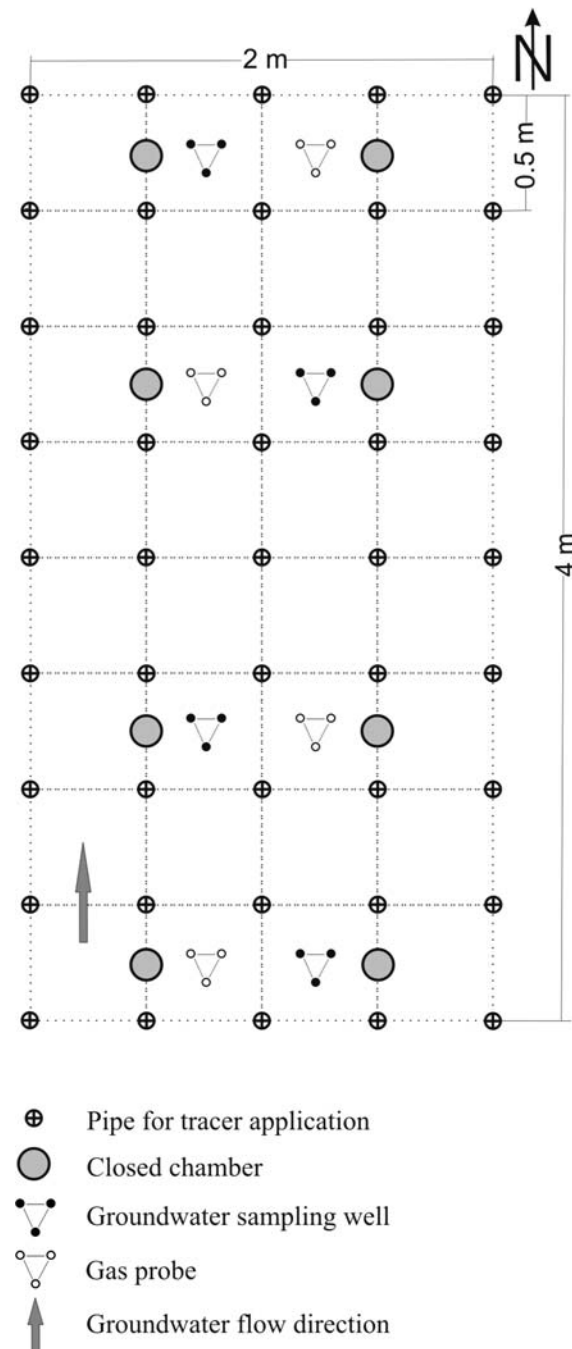


Fig. 1 Measuring field with its elements and dimensions

Tracer application and sampling schedule

We prepared a tracer solution on site using raw water from a drinking water well of the waterwork of the Fuhrberger Feld aquifer. Although parts of the aquifer receive a strong influx of NO_3^- from agricultural activities, the raw water contains only traces of NO_3^- due to intensive denitrification (Duijnsveld et al. 1989). The raw water was filled into two canisters and K^{15}NO_3 (60 atom%) was added. The NO_3^- concentration of the tracer solution was 12.5 mg N l^{-1} , which is close to the mean NO_3^- concentration in seepage water of the arable land. The tracer solution was transferred into 45 plastic buckets (10 l). Afterwards, 10 l of the tracer solution were carefully applied to the groundwater surface via each PVC pipe. Pieces of silicone tubing (diameter of 6 mm, length of 1 m) were used as siphons to transfer the tracer solution from the buckets to the PVC pipes. Great care was taken to exclude contamination of the soil surface with tracer solution in order to avoid labeling of the topsoil. In order to assure a permanent labeling of surface groundwater throughout the experiment, the tracer solution was applied weekly. A single injection was typically completed within 15 min. We conducted the first tracer application on July 4, 2007 and the last on August 29, 2007. Altogether, nine tracer applications took place.

Prior to the first tracer application, we measured NO_3^- -N and N_2O -N concentrations in the surface groundwater. From July 11 to September 14, 2007, the surface groundwater, the soil atmosphere and samples from the flux chambers were collected weekly. Sampling was conducted at the days of labeling while the tracer solution was applied. Total N_2O and its ^{15}N enrichment were analysed in the surface groundwater, in the soil atmosphere and in the samples from the flux chambers. NO_3^- -N and ^{15}N enrichment of N_2 and NO_3^- were analysed in the groundwater samples.

Sampling methods and analytical techniques

Surface groundwater samples for measuring NO_3^- concentrations, N_2O concentrations and the ^{15}N enrichments of NO_3^- , N_2O and N_2 were collected using partially evacuated (-0.53 bar) serum bottles (118 ml) sealed with gas-tight butyl rubber septa and crimp caps. 50-ml samples of groundwater were

collected with a plastic syringe from the multilevel sampling wells and were transferred into the partially evacuated serum bottle without any air contact. The first 20 ml of every depth were discarded. The samples were stored upside down in water at 4°C and were measured within 10 days. Prior to the gas measurements, liquid and gas phase were equilibrated at constant temperature (25°C) by agitating on a horizontal shaker for 3 h. Concentrations of N₂O in the gas phase of the serum bottles were directly analysed using a gas chromatograph (Fisons GC 8000, Milan, Italy) 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-CH₄ (95/5) was used as carrier and make-up gas. Samples of 300 µl were injected using an autosampler (model GC-PAL, CTC-Analytcs, Zwingen, Switzerland). Precision as given by the SD obtained from four injections of a standard gas was typically 1.5%. Dissolved N₂O was calculated from the gas phase concentrations of the water samples using the Bunsen absorption coefficient of N₂O (Weiss and Price 1980). ¹⁵N-N₂ was analysed following the method specified in Well et al. (1998) and (2003). The gas concentrations of the sample solution (dissolved N₂) were calculated according to Henry's law from the headspace concentrations using the Bunsen absorption coefficient of N₂ (Weiss 1970).

NO₃⁻ in the groundwater samples was determined photometrically using a continuous flow analyser (Skalar, Erkelenz, Germany). The measurements precision was 5%.

Gas probes for sampling the soil atmosphere in the unsaturated zone were modified from a soil atmosphere sampling device as described by Schack-Kirchner et al. (1993). PVC pipes were permanently installed in defined soil depths (0.3, 0.6 and 0.9 m below the soil surface), containing an aerated macropore, which was connected with the soil surface using an 1 mm-ID stainless steel tubing. We collected the soil atmosphere by using a plastic syringe, which was connected with the tubing via a plastic three-way luer-lock stop cock (Braun, Melsungen, Germany). Prior to the sample collection we discarded the first 5 ml to flush the volume of the tubing with soil air. Afterwards, the soil atmosphere sample was transferred into evacuated serum bottles (118 ml) sealed with gas-tight butyl rubber septa and crimp

caps. The samples were analysed within 10 days using the gas chromatograph as described above.

Surface N₂O emissions were measured using a static chamber technique. Eight PVC base collars, 24 cm in diameter and covering an area of 0.0434 m², were cut into the soil to a depth of 6 cm and remained in place until the end of the study. Plexiglass covers were prepared with a vent tube to allow pressure equilibration (Mosier 1989) and were covered with aluminium foil to avoid heating during the measurements. Prior to the collection of gas samples, the covers were attached to the PVC-collars using a rubber seal, resulting in a total volume of the static chambers of 14 l. Four gas samples were taken with a syringe at 20 min intervals over a 1 h period (0, 20, 40, 60 min). At 0 and 60 min, gas samples were transferred into evacuated serum bottles (118 ml) sealed with gas-tight butyl rubber septa and crimp caps, in order to allow GC and IRMS analysis. At 20 and 40 min, gas samples were transferred into evacuated gas-tight 12-ml ExetainersTM (LABCO, High Wycombe) for GC-analysis only. The samples were analysed within 1 week.

¹⁵N enrichment of N₂O was analysed using an isotope ratio mass spectrometer (Delta XP IRMS, Thermo-Finnigan, Bremen, Germany). The IRMS was connected to a modified Precon (Thermo-Finnigan, Bremen, Germany) equipped with an autosampler (model Combi-PAL CTC-Analytcs, Zwingen, Switzerland) as described by Casciotti et al. (2002). ¹⁵N enrichments are reported as atom% ¹⁵N or δ¹⁵N versus air-N₂ (in ‰). Typical analytical precision for δ¹⁵N was 0.6‰, the detection limit for N₂O-N was 0.5 nM.

¹⁵N enrichment of NO₃⁻ was determined using the method described by McIlvin and Altabet (2005). This method is based on the reduction of NO₃⁻ to nitrite (NO₂⁻) with spongy cadmium and a further reduction of NO₂⁻ to N₂O using sodium azide in an acetic acid buffer. Both reduction steps are assumed to be complete. ¹⁵N enrichment of N₂O was analysed using the instrumentation as described above.

Groundwater level, precipitation and soil water content

The groundwater level was continuously recorded during the experiment in order to assess the distance between the groundwater surface and the level of the injection pipes. This was done with a water depth

gauge (Keller Druckmesstechnik GmbH, Jestetten, Germany). The measurement accuracy was ± 0.01 m. Precipitation was measured to estimate the occurrence of potential seepage during the experiment which might cause dilution of the ^{15}N tracer by NO_3^- leaching to the groundwater surface. For recording of precipitation, we installed a rain gauge with a tilting balance (Lambrecht, Göttingen, Germany). The rain gauge was connected with a data logger (DL2e, Delta-T Devices Ltd, Cambridge, UK) which recorded the rainfall every hour. The minimal resolution was 0.1 mm m^{-2} . To assess possible effects of soil moisture and soil temperature on N_2O fluxes at the soil surface, these soil properties were measured using time domain reflectometry (TDR) (Easy Test, Poland). We installed two TDR probes in a depth of 0.2 m. The measurement accuracy was 2% for soil moisture and 0.8°C for the temperature. Water filled pore space (WFPS) was subsequently calculated from the bulk density and soil moisture, assuming a particle density of 2.65 g cm^{-3} .

Flux calculations and the mass of groundwater-derived N_2O in surface emissions

Fluxes of total N_2O -N at the soil surface were calculated by linear regression from four samples taken from the flux chambers (atmospheric air before enclosure; samples 20, 40 and 60 min after enclosure). The slope of the temporal change of N_2O concentrations within the closed chamber had to show $r^2 > 0.8$ derived from linear regression analysis to be accepted as significant. Otherwise, fluxes were considered zero. Negative fluxes were counted in the data set, because those fluxes have been measured at the soil surface under a large range of conditions Chapuis-Lardy et al. (2007).

The mass of groundwater-derived N_2O ($c\text{N}_2\text{O}_{\text{gw}}$) [ppmv] in the chamber atmosphere after 1-h enrichments was calculated using a mixing equation for the three components groundwater, unsaturated zone and surface emissions, respectively:

$$\delta_{\text{mix, chamber}} = \frac{\delta_{\text{gw}} \times c\text{N}_2\text{O}_{\text{gw}} + \delta_{\text{soil}} \times c\text{N}_2\text{O}_{\text{soil}} + \delta_{\text{atm}} \times c\text{N}_2\text{O}_{\text{atm}}}{c\text{N}_2\text{O}_{\text{chamber}}} \quad (1)$$

what leads to

$$c\text{N}_2\text{O}_{\text{gw}} = \frac{\delta_{\text{mix, chamber}} \times c\text{N}_2\text{O}_{\text{chamber}} - \delta_{\text{soil}} \times c\text{N}_2\text{O}_{\text{soil}} - \delta_{\text{atm}} \times c\text{N}_2\text{O}_{\text{atm}}}{\delta_{\text{gw}}} \quad (2)$$

where $\delta_{\text{mix, chamber}}$ is the ^{15}N enrichment of N_2O measured in the flux chambers after 60 min. $c\text{N}_2\text{O}_{\text{soil}}$, $c\text{N}_2\text{O}_{\text{atm}}$ and $c\text{N}_2\text{O}_{\text{chamber}}$ are concentrations of N_2O in the soil atmosphere of the unsaturated zone (means of all investigated sampling depths), in atmospheric air and in the flux chambers after 60 min in ppmv, respectively. δ_{gw} , δ_{soil} and δ_{atm} denote the ^{15}N -enrichment of N_2O in the groundwater (means of the investigated sampling depths), in the soil atmosphere of the unsaturated zone and in atmospheric air.

Prior to the calculation of the mass of groundwater-derived N_2O , we compared $\delta_{\text{mix, chamber}}$ with background $\delta^{15}\text{N}$ of N_2O in atmospheric air and in the soil atmosphere of a control plot. The background of $\delta^{15}\text{N}$ of N_2O was between 2 and 8‰, the calculated mean value was 4.4‰ and the SD was 1.2‰, respectively, (data not shown). A confidence interval analysis with 94 samples using a confidence coefficient (α) of 0.001 resulted in an upper interval limit of 4.78‰. We only used samples with $\delta^{15}\text{N}$ of N_2O higher than 4.78‰ for the calculations of the mass of groundwater-derived N_2O and groundwater-derived N_2O fluxes. Otherwise, the mass of groundwater-derived N_2O and groundwater-derived N_2O fluxes were considered zero.

To calculate the flux of groundwater-derived N_2O to the flux chambers, we converted $c\text{N}_2\text{O}_{\text{gw}}$ [ppmv] into the mass of groundwater-derived N_2O in the chamber, $\text{N}_2\text{O}_{\text{gw}}$ [$\mu\text{g N}_2\text{O-N}$] by using molar weight and molar volume of $\text{N}_2\text{O-N}$ and the volume of the flux chambers. Finally, we used the following equation for the calculations of groundwater-derived fluxes:

$$F = \frac{\text{N}_2\text{O}_{\text{gw}}}{A_{\text{chamber}} \times T} \quad (3)$$

where $\text{N}_2\text{O}_{\text{gw}}$ is the mass of groundwater derived N_2O in the surface emission during a 1-h enrichment interval under the flux chamber in $\mu\text{g N h}^{-1}$. A_{chamber} is the area that is covered by the collars in m^2 , T denotes the collection time in h and F is the flux of groundwater derived N_2O in $\mu\text{g N}_2\text{O-N h}^{-1} \text{ m}^{-2}$.

Results

Groundwater level, soil moisture and meteorological conditions

During July and August 2007, the precipitation was 104.3 and 102.9 mm, respectively. The groundwater level varied between 1.09 and 1.42 m below the soil surface (Fig. 2a). If the groundwater levels at the start and at the end of the measuring period in Fig. 2a are compared, it can be seen that no effective decrease of the groundwater level occurred. This was contrary to our expectations, because a decrease of the groundwater level during the summer is representative and has been observed earlier (Deurer et al. 2008).

However, there were two stages with stronger groundwater fluctuation: a drawdown of 0.26 m from day 12 to day 20 after the first application of the tracer solution and a phreatic rise of 0.16 m within 2 days from day 48 to day 50. The drawdown occurred during a dry period between day 9 and day 17. This period was also characterized by lowest WFPS and highest soil temperatures in the topsoil (0.2 m below the soil surface, Fig. 2b). The abrupt phreatic rise from day 48 to day 50 followed a major precipitation event at day 48 with a daily rainfall of 34 mm (Fig. 2a). Correspondingly, we observed a

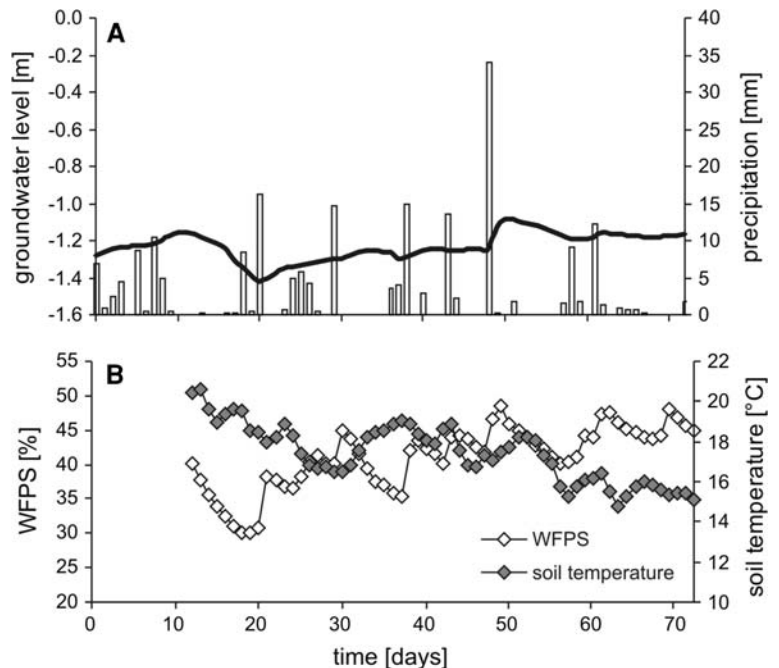
WFPS of 49% at day 49, which was the highest during the measurement period (Fig. 2b).

NO_3^- concentrations and ^{15}N enrichment of NO_3^- in the surface groundwater

The time course of NO_3^- concentrations in the surface groundwater (1.5–1.7 m below soil surface) is represented in Fig. 3a. Prior to the tracer application, NO_3^- concentrations were low, ranging from 0.38 to 0.82 mg N l⁻¹. During the labeling phase with K^{15}NO_3 tracer solution (12.5 mg $\text{NO}_3\text{-N l}^{-1}$), mean NO_3^- concentrations in each depth increased until day 21 to a level of approximately 6–10 mg N l⁻¹. After this NO_3^- concentrations in 1.5 and 1.6 m remained nearly constant until the last sampling event, whereas NO_3^- concentrations in 1.7 m decreased temporarily to 3.5 mg N l⁻¹ and reincreased from day 42 to the last sampling event to the concentration level in 1.5 and 1.6 m depth.

The time course of the ^{15}N enrichment of NO_3^- in the surface groundwater is shown in Fig. 3b. At day 7, the labeling of the surface groundwater decreased rapidly with depth. The ^{15}N enrichment of NO_3^- was 21.1, 14.6 and 4.2 atom% in 1.5, 1.6 and 1.7 m, respectively. In contrast, we observed a substantial and relatively homogenous labeling of the

Fig. 2 Groundwater level below the soil surface, precipitation (a) and water-filled pore space as well as soil temperature at 0.2 m below the soil surface (b) during the measurement period



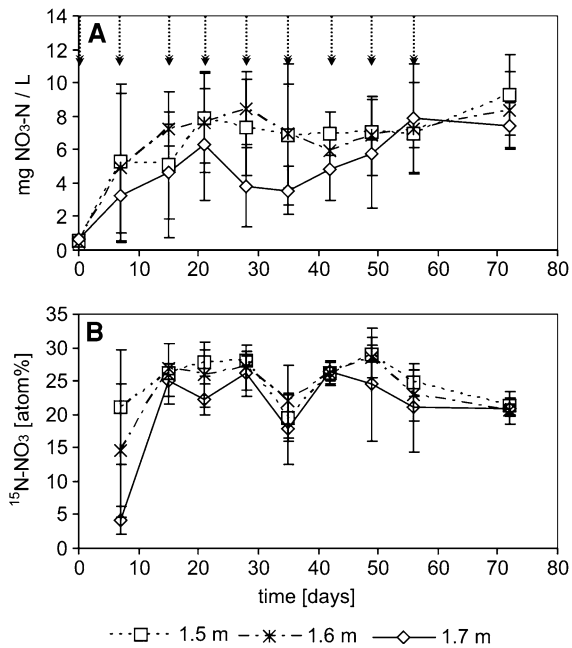


Fig. 3 NO_3^- -N concentrations (a) and ^{15}N enrichment of NO_3^- (b) in the surface groundwater. Error bars denote the SD of four samples collected from multilevel wells. The dates of the tracer applications are indicated by arrows

surface groundwater from day 15 until the end of the measuring period. Both, the increased NO_3^- concentrations as well as the stable labeling of the surface groundwater since day 15 show that the label had been successfully distributed at the groundwater surface.

N_2O and ^{15}N - N_2 concentrations in the surface groundwater, N_2O concentrations in the unsaturated zone and total N_2O fluxes at the soil surface

Time courses of the mean N_2O concentrations and of the N_2O fluxes at the soil surface are represented in Fig. 4. In the surface groundwater (Fig. 4c), highest N_2O concentrations between 14.0 and 15.8 $\mu\text{g N}_2\text{O-N l}^{-1}$ occurred at day 21. At all the other sampling events, N_2O concentrations were comparatively low, ranging between 0.9 and 4.9 $\mu\text{g N}_2\text{O-N l}^{-1}$ with a tendency to lowest concentrations at the beginning and at the end of the labeling time. The lowest value is very close to a concentration of 0.88 $\mu\text{g N}_2\text{O-N l}^{-1}$, which reflects the N_2O concentration in water equilibrated with atmospheric air at groundwater temperature.

Generally, we found no significant differences in N_2O concentrations between the sampling depths at the same sampling day. Mean ^{15}N - N_2 concentrations in the groundwater were 56.14 (± 50.42) $\mu\text{g l}^{-1}$ and within the range of the concentrations that were previously measured in the saturated zone of hydromorphic soils (Well et al. 2003). The mean N_2O -to- N_2 ratio was found to be 0.10 (± 0.11).

In the soil atmosphere of the unsaturated zone (Fig. 4b), N_2O concentration ranged between 297 and 427 ppbv and was thus close to ambient concentration

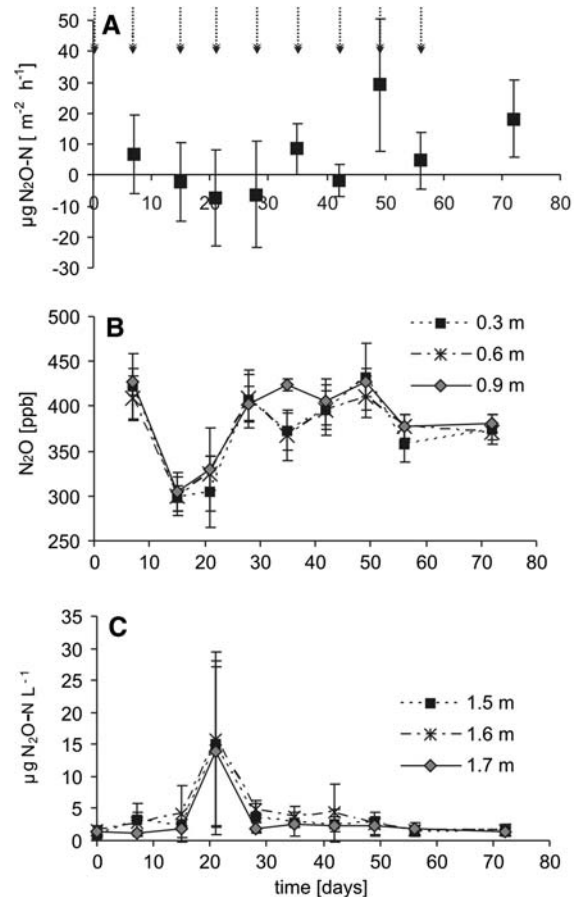


Fig. 4 N_2O fluxes at the soil surface measured in static flux chambers after an enrichment time of 60 min (a), N_2O concentration in the soil atmosphere in 0.3, 0.6 and 0.9 m depth below the soil surface (b) and dissolved N_2O concentration in the surface groundwater in 1.5, 1.6 and 1.7 m depth below soil surface (c). Error bars denote the SD from eight static flux chamber measurements (a) and four samples collected from defined depths in the unsaturated zone (soil atmosphere, b) and from surface groundwater (c), respectively. The arrows indicate the date of the tracer applications

for the entire measurement period. However, highest N_2O concentration levels occurred at day 7 and day 49 after the first tracer application and were connected with significant precipitation rates several days running or a major precipitation event at day 48, respectively. In contrast, we found lowest N_2O concentrations in the soil atmosphere at day 15 during a period of several days without rainfall (Figs. 2, 4b). Significant differences in N_2O concentrations between the three sampling depths were not detected, with the exception of the sampling event at day 35, where we measured a N_2O concentration in 0.9 m depth that was up to 56 ppbv higher than those in 0.3 and 0.6 m depth.

Throughout the study period, we carried out a total of 71 measurements of total N_2O fluxes at the soil surface using the closed chamber method. In 37 cases, fluxes were not significant (r^2 of the slopes <0.8). Furthermore, we observed significant positive fluxes in 25 cases and significant negative fluxes in 9 cases.

Mean N_2O fluxes of the sampling events ranged between -7.6 and $29.1 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ (Fig. 4a). We measured highest fluxes of 29.1 and $18.2 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ at day 49 and day 72, respectively. At the other sampling events, fluxes were very low and close to zero. Low negative fluxes occurred at the days 15, 21, 28 and 42 (Fig. 4a).

^{15}N enrichment of N_2O in the surface groundwater, in the unsaturated zone and at the soil surface

Figure 5 illustrates the time courses of the mean ^{15}N enrichment of N_2O . Generally, ^{15}N enrichment of N_2O in the profile rapidly decreased upwards from the surface groundwater via the unsaturated zone to the soil surface.

In the surface groundwater (Fig. 5c), we observed average $\delta^{15}\text{N}$ between $56,000$ and $207,000\text{‰}$ corresponding to 13 and $42 \text{ atom}\% \text{ }^{15}\text{N}$ (mean of 3 sampling depths per sampling event, respectively), i.e. less than the ^{15}N enrichment of the applied tracer solution of $60 \text{ atom}\%$. At day 7, no significant ^{15}N enrichment of the groundwater in 1.7 m depth occurred suggesting that a single application of the tracer solution caused only substantial labeling of the groundwater in 1.5 and 1.6 m depth. We found similar results for the pattern of the ^{15}N enrichment of NO_3^- in the surface groundwater (Fig. 3b).

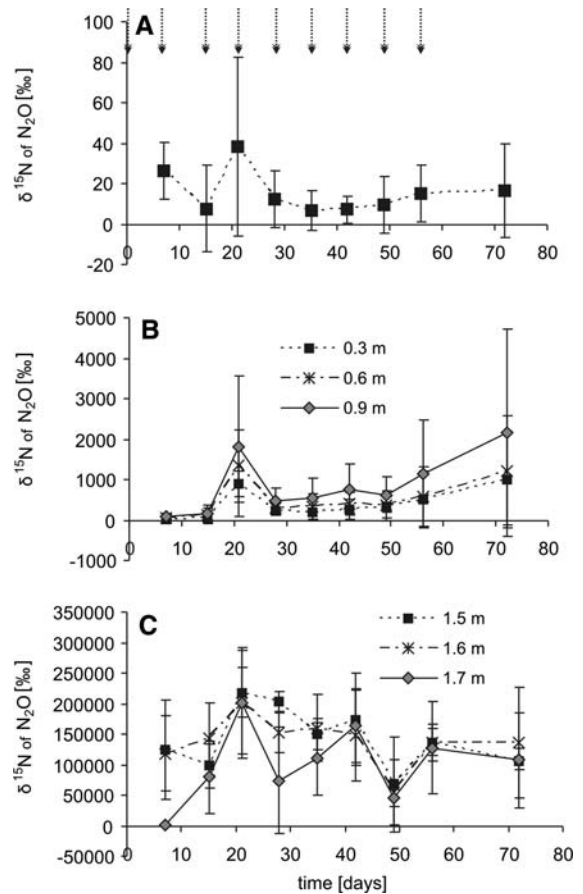


Fig. 5 ^{15}N enrichment of N_2O : (a) at the soil surface measured in flux chambers after an enrichment time of 60 min, (b) in soil atmosphere in 0.3, 0.6 and 0.9 m depth below soil surface and (c) in surface groundwater in 1.5, 1.6 and 1.7 m depth below soil surface. Error bars denote the SD from eight static flux chamber measurements (a) and four samples of each depth in the unsaturated zone (soil atmosphere, b) and four samples of each depth from the surface groundwater (c), respectively. The arrows indicate the date of the tracer applications

In the soil atmosphere of the unsaturated zone (Fig. 5b), N_2O was already significantly enriched with ^{15}N at the first sampling date after the first tracer application. Mean $\delta^{15}\text{N}$ of N_2O was 35 , 63 and 92‰ in 0.3 , 0.6 and 0.9 m depth, respectively. $\delta^{15}\text{N}$ of each sample was significantly higher than the background $\delta^{15}\text{N}$ of N_2O in the soil atmosphere and atmospheric air, which we determined at a control plot giving a range from 2 to 8‰ and a mean value of 4.4‰ (data not shown). At all sampling days, $\delta^{15}\text{N}$ of N_2O in the soil atmosphere depended on sampling depth and followed the order $0.3 \text{ m} < 0.6 \text{ m} < 0.9 \text{ m}$. At

day 21, a clear peak of the mean $\delta^{15}\text{N}$ of N_2O occurred at each depth (Fig. 5b).

At the soil surface, mean $\delta^{15}\text{N}$ of N_2O was substantially lower than in the soil atmosphere. Mean $\delta^{15}\text{N}$ of N_2O was within the range of background $\delta^{15}\text{N}$ of N_2O at four out of nine sampling events (days 15, 35, 42 and 49). In contrast, mean $\delta^{15}\text{N}$ of N_2O was higher and out of the background range at the other five sampling events. The highest mean $\delta^{15}\text{N}$ of N_2O was 38‰ at day 21 (Fig. 5a).

Groundwater derived N_2O in surface emissions

Mass of groundwater derived N_2O in the chambers per sampling event covered an interval between 0.0002 and 0.0009 $\mu\text{g N}_2\text{O-N}$ (Table 1) after an enrichment time of 60 min in the flux chambers. These proportions reflect very low N_2O fluxes from the surface groundwater via the unsaturated zone to the soil surface. We calculated mean fluxes from 0.0022 to 0.0207 $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ per sampling event (Eqs. 1, 2, 3; Table 1) which is equivalent to 0.0002–0.0018 $\text{kg N}_2\text{O-N ha}^{-1} \text{year}^{-1}$. Only 0.04–0.28% (depending on sampling date, averaged 0.13%) of the total positive N_2O fluxes at the soil surface originated from groundwater-derived N_2O (Table 1; Fig. 4a).

Discussion

Groundwater labeling

Was the extent of groundwater labeling sufficient for detecting fluxes of $^{15}\text{N}_2\text{O}$ that was produced in the surface groundwater by denitrification? In contrast to push-and-pull tracer studies carried out at single groundwater wells (Addy et al. 2002; Well et al. 2003; Kim et al. 2005), we performed a tracer experiment with labeling of an extended area of the surface groundwater where an even distribution of the label was approximated by using multiple injection points. Because concentrations of NO_3^- and N_2O in the groundwater were very low before the first tracer application (Figs. 3, 4c) and the NO_3^- concentration of the tracer solution and its ^{15}N enrichment were comparatively high, we achieved a high enrichment of NO_3^- within the groundwater layer which was sampled by the multilevel wells. This was shown by

both, increasing concentrations of NO_3^- as well as the significant ^{15}N enrichment of the groundwater at all multilevel wells. Consequently, the prerequisite for using $\delta^{15}\text{N}$ of N_2O to monitor formation of N_2O and its emission at the soil surface was fulfilled. However, temporal and spatial variation of labeled N_2O and NO_3^- was relatively high at all sampling events, showing that there was variable mixing of the tracer solution with the original groundwater.

Identifying the origin of N_2O

To which extent was the variability of N_2O concentrations in the soil atmosphere of the unsaturated zone and of N_2O fluxes at the soil surface caused by N_2O produced in the surface groundwater? With a few exceptions, the variability of N_2O concentrations in the soil atmosphere of the unsaturated zone and of fluxes at the soil surface was relatively low. Peak N_2O concentrations in the groundwater occurring at day 21 did not enhance N_2O concentrations in the soil atmosphere and surface fluxes, respectively. This is in line with observations of Van Groenigen et al. (2005), who did not find increases in N_2O fluxes from the topsoil as a result of increased N_2O concentrations in the subsoil. Furthermore, highest surface fluxes and concentrations in the soil atmosphere measured at day 49 did not coincide with elevated groundwater N_2O concentration but with the major precipitation event at day 48 and with the highest value for WFPS in the topsoil measured during the study. Our observation of lowest N_2O concentrations in the soil atmosphere and at the soil surface during dry periods with comparatively low values of WFPS and high soil temperatures is in agreement with the frequently reported moisture effect on N_2O emissions, which typically leads to low fluxes under these conditions (Granli and Bøckman 1994; Dobbie et al. 1999). According to these findings and to the results represented in this study, it can be concluded that N_2O concentrations in the soil atmosphere and N_2O fluxes measured at the soil surface were more affected and controlled by factors like precipitation, soil moisture and temperature of the topsoil but obviously less by groundwater N_2O dynamics.

We assume that decreasing ^{15}N enrichment of N_2O upwards from groundwater via the unsaturated zone to the soil surface is mainly caused by dilution of the $^{15}\text{N-N}_2\text{O}$ pool with soil derived and atmospheric

Table 1 Mass of groundwater-derived N₂O emitted at the soil surface and calculated emission rate of groundwater-derived N₂O from the groundwater to the atmosphere

Time [days]	Amount of groundwater-derived N ₂ O [$\mu\text{g N}$]	N ₂ O flux from groundwater [$\mu\text{g N m}^{-2} \text{h}^{-1}$]
7	0.00082 \pm 0.00107	0.01890 \pm 0.02460
15	0.00039 \pm 0.00108	0.00900 \pm 0.02494
21	0.00090 \pm 0.00063	0.02072 \pm 0.01446
28	0.00023 \pm 0.00033	0.00530 \pm 0.00770
35	0.00017 \pm 0.00029	0.00348 \pm 0.00658
42	0.00010 \pm 0.00018	0.00221 \pm 0.00421
49	0.00062 \pm 0.00140	0.01435 \pm 0.03238
56	0.00040 \pm 0.00051	0.00924 \pm 0.01177
72	0.00065 \pm 0.00114	0.01495 \pm 0.02639

The values represent means (\pm SD) of eight flux chamber measurements per sampling event

¹⁴N-N₂O. Clough et al. (1999) also observed a decrease in the ¹⁵N enrichment of N₂O as the gas diffuses upwards through the profile. The authors mentioned dilution as the most likely cause for decreasing ¹⁵N enrichment of N₂O, but their results are also compatible with consumption of ¹⁵N-enriched N₂O in the upper part of the soil. In our study, ¹⁵N enrichment of N₂O in the groundwater was comparatively low at day 49 (Fig. 5). It can be assumed that this phenomenon is also a dilution effect caused by the major precipitation event at day 48.

A clear peak in the time courses of the mean ¹⁵N enrichments of N₂O through the whole profile occurred at day 21 (Fig. 5) and coincided with a substantial drawdown of the groundwater level immediately before sampling. Apparently, a rapid drawdown can cause a rapid release of dissolved N₂O into the unsaturated zone (Well 2002, Grant and Pattey 2003) which might cause also an increased ¹⁵N-enrichment of N₂O near the soil surface. Otherwise, the increasing groundwater level starting with day 48 did not induce dynamics of the ¹⁵N-enrichment in the unsaturated zone and at the soil surface. Aeschbach-Hertig et al. (2002) argued that during a rise of the water table soil air can be trapped in pores and fractionally dissolved under an increasing hydrostatic pressure. Relating this concept to our results, we hypothesize that a release of N₂O is unlikely during a phreatic rise, because dissolution of soil air is the dominant process. Hence, we assume

that dynamics of the ¹⁵N-enrichment within the profile is prevented during a rise of the water table.

Fluxes of total N₂O at the soil surface and of groundwater-derived N₂O to the atmosphere

Compared to other studies reviewed in Chapuis-Lardy et al. (2007), total fluxes of N₂O at the soil surface were low. During the measuring period, a majority of these fluxes were close to zero and not significant (Fig. 4a). Similar low fluxes were found by Butterbach-Bahl et al. (2002) for a sandy cambisol under pine forest in northeastern Germany, ranging between -4.1 and $34.1 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$. This suggests that total fluxes of our study are typical for unfertilized sandy soils.

We observed slightly increased emissions at day 49, following the major precipitation event at day 48. In contrast, highest measured N₂O concentrations in groundwater at day 21 did not affect the surface fluxes. These observations confirm the assumption that surface fluxes were hardly influenced by the dynamics of the groundwater level and N₂O concentrations in groundwater.

The very low groundwater-derived N₂O fluxes to the atmosphere indicate that the importance of groundwater-derived N₂O for atmospheric emissions was negligible at our research site during the measuring period. This is illustrated by the fact that only 0.04–0.28% of the positive N₂O fluxes at the soil surface originated from ¹⁵N₂O-N that was produced in groundwater.

In a previous study conducted in the Fuhrberger Feld aquifer, Deurer et al. (2008) estimated upward N₂O fluxes from the surface groundwater into the unsaturated zone based on measurements of groundwater N₂O concentrations at six multilevel wells. These fluxes ranged from 0.0009 to 0.3 kg N₂O ha⁻¹ year⁻¹ which is equivalent to a range from 0.0006 to 0.2 kg N₂O-N ha⁻¹ year⁻¹. In our study, fluxes of ¹⁵N₂O from groundwater to the atmosphere were found to be in a range from 0.0002 to 0.0018 kg N₂O-N ha⁻¹ year⁻¹, what is similar to the range of the data of Deurer et al. (2008). However, it remains to be determined to what extent potential N₂O consumption in the unsaturated zone and in the topsoil allows a comparison between the different approaches. More research is needed to quantify consumption of N₂O during its transport via

the unsaturated zone to the atmosphere. In contrast to the results presented in this study and in Deurer et al. (2008), Ronen et al. (1988) estimated for the sandy Coastal Plain aquifer of Israel that the N_2O flux from groundwater into the unsaturated zone ranges from 3.4 to 7.8 kg $\text{N}_2\text{O-N ha}^{-1} \text{ year}^{-1}$. This is an extremely high emission rate, although groundwater N_2O concentration was not substantially different from the highest values measured by Deurer et al. (2008). This discrepancy can be explained by a calculation error in Ronen et al. (1988) caused by using an incorrect unit (mg l^{-1} instead of $\mu\text{g l}^{-1}$) for the concentration gradient of N_2O . Thus, the N_2O flux from the surface groundwater to the unsaturated zone is substantially overestimated by three orders of magnitude. If the correct concentration gradients would be incorporated in the flux calculation, the data of Ronen et al. (1988) were within the range of the N_2O fluxes reported by Deurer et al. (2008), but still higher than the N_2O fluxes reported in this study according to the different N_2O concentrations in the groundwater. Other previous studies tend to confirm our result of relatively low diffusive N_2O fluxes from the groundwater to the atmosphere (McMahon et al. 2000; Hiscock et al. 2003). In the light of these studies and of our results, indirect N_2O emissions via the diffusive pathway seem to be hardly significant.

Conclusions

We measured N_2O fluxes from the surface layer of a sandy aquifer through the unsaturated zone to the atmosphere. For the first time, we could prove fluxes of labeled N_2O to the soil surface that was produced in groundwater by denitrification using a ^{15}N tracer in situ approach.

Stable ^{15}N labeling of the surface groundwater for several weeks showed that it was possible to monitor these fluxes over an extended period and thus yielded robust results.

The contribution of groundwater-derived $^{15}\text{N}_2\text{O}$ to surface emissions was very low within the measuring period and not detectable with the conventional closed chamber method. Using the ^{15}N tracer technique, we observed highest N_2O fluxes from groundwater in temporal connection with a rapid decrease of the groundwater table which suggests that diffusive indirect N_2O emissions from groundwater

can be favoured by such dynamics. Generally, our data support previous assumptions that indirect N_2O emissions from groundwater occurring by upward diffusion to the atmosphere are hardly an important part of total N_2O emissions. This shows that the neglect of diffusive emissions in previous estimates of emission factors did not lead to a significant underestimation of total groundwater-derived fluxes.

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