

Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N₂O accumulation

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Abstract. We investigated the dynamics of denitrification and nitrous oxide (N₂O) accumulation in 4 nitrate (NO₃⁻) contaminated denitrifying sand and gravel aquifers of northern Germany (Fuhrberg, Sulingen, Thülsfelde and Göttingen) to quantify their potential N₂O emission and to evaluate existing concepts of N₂O emission factors. Excess N₂ – N₂ produced by denitrification – was determined by using the argon (Ar) concentration in groundwater as a natural inert tracer, assuming that this noble gas functions as a stable component and does not change during denitrification. Furthermore, initial NO₃⁻ concentrations (NO₃⁻ that enters the groundwater) were derived from excess N₂ and actual NO₃⁻ concentrations in groundwater in order to determine potential indirect N₂O emissions as a function of the N input. Median concentrations of N₂O and excess N₂ ranged from 3 to 89 μg NL⁻¹ and from 3 to 10 mg NL⁻¹, respectively. Reaction progress (RP) of denitrification was determined as the ratio between products (N₂O-N + excess N₂) and starting material (initial NO₃⁻ concentration) of the process, characterizing the different stages of denitrification. N₂O concentrations were lowest at RP close to 0 and RP close to 1 but relatively high at a RP between 0.2 and 0.6. For the first time, we report groundwater N₂O emission factors consisting of the ratio between N₂O-N and initial NO₃⁻-N concentrations (EF1). In addition, we determined a groundwater emission factor (EF2) using a previous concept consisting of the ratio between N₂O-N and actual NO₃⁻-N concentrations. Depending on RP, EF(1) resulted in smaller values compared to EF(2), demonstrating (i) the relevance of NO₃⁻

consumption and consequently (ii) the need to take initial NO₃⁻-N concentrations into account. In general, both evaluated emission factors were highly variable within and among the aquifers. The site medians ranged between 0.00043–0.00438 for EF(1) and 0.00092–0.01801 for EF(2), respectively. For the aquifers of Fuhrberg and Sulingen, we found EF(1) median values which are close to the 2006 IPCC default value of 0.0025. In contrast, we determined significant lower EF values for the aquifers of Thülsfelde and Göttingen. Summing the results up, our study supports the substantial downward revision of the IPCC default EF5-g from 0.015 (1997) to 0.0025 (2006).

1 Introduction

The trace gas nitrous oxide (N₂O) is known to contribute to global warming (Duxbury and Mosier, 1993) and to the destruction of stratospheric ozone (Crutzen, 1981). A significant amount of N₂O emissions originates from agricultural soils and aquatic systems (Mosier et al., 1998). In contrast to direct agricultural N₂O emissions arising at the sites of agricultural production, e.g. soils, indirect emissions from ground and surface waters result from nitrogen leaching and runoff to adjacent systems (Well et al., 2005a; Nevison, 2000). The knowledge of these indirect emissions is limited because few studies have tried to relate subsurface N₂O concentrations to N leaching from soils (Clough et al., 2005) and investigations of N₂O in deeper aquifers are rare (Ronen et al., 1988; McMahon et al., 2000; Hiscock et al., 2002).

In the aquifers of unconsolidated pleistocene deposits covering large areas in the northern part of central Europe, agricultural NO₃⁻ contamination often coincides with reducing



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conditions (Walther, 1999), suggesting that this region might be susceptible for relatively high N₂O fluxes from deeper groundwater. However, until now there have been no systematic investigations of N₂O dynamics in these aquifers.

N₂O emissions from groundwater were thought to comprise a significant fraction of total agricultural N₂O emissions (IPCC, 1997), but recent studies show in agreement that their significance is lower (McMahon et al., 2000; Hiscock et al., 2003; Höll et al., 2005; Reay et al., 2005; Well et al., 2005a; Sawamoto et al., 2005). Consequently, the nitrous oxide emission factor from aquifers and agricultural drainage water (EF5-g) was corrected downwards from 0.015 to 0.0025 by the Intergovernmental Panel on Climate Change (IPCC) in 2006, taking the data of Hiscock et al. (2002, 2003), Reay et al. (2004, 2005) and Sawamoto et al. (2005) as a basis.

Typically, the N₂O emission factor of a system is defined by the ratio between N₂O emission and N input (IPCC, 1997). However, the IPCC factor characterizing indirect emissions from aquifers and agricultural drainage water had been derived from the ratio between dissolved N₂O and NO₃⁻ concentrations observed in a small number of studies, because input and emission data had not been available. Consequently, there are uncertainties in the estimate of the EF5-g because both NO₃⁻ and N₂O are subject to reaction during subsurface transport (Dobbie and Smith, 2003). Furthermore, determination of N₂O fluxes from aquifers is connected with experimental difficulties: N₂O as an intermediate product from denitrification is permanently influenced by different enzyme kinetics of various denitrifying communities and groundwater N₂O concentration is the net result of simultaneous production and reduction reactions (Well et al., 2005b). Höll et al. (2005) stated that these transformations are the reason why N₂O concentration in groundwater does not necessarily reflect actual indirect N₂O emission.

N₂O represents an obligate intermediate of the denitrification process. Denitrification is considered the most important reaction for nitrate (NO₃⁻) remediation in aquifers. This process occurs in O₂ depleted layers with available electron donors (Ross, 1995; Böttcher et al., 1990). Especially in agricultural areas with high N inputs via fertilizers considerable NO₃⁻ reduction is possible (Böttcher et al., 1985). Dinitrogen (N₂) is the final product of this process. Thus the quantification of groundwater N₂ arising from denitrification (excess N₂) can facilitate the reconstruction of historical N inputs, because NO₃⁻ loss is derivable from the sum of denitrification products (Heaton, 1983; Böhlke and Denver, 1995). Generally, the concentration of excess N₂ produced by denitrification in groundwater is estimated by comparing the measured concentrations of Ar and N₂ with those expected from atmospheric equilibrium, assuming that the noble gas Ar is a stable component (Blicher-Mathiesen et al., 1998; Böhlke, 2002; Dunkle et al., 1993; Mookherji et al., 2003). However, measuring of excess N₂ is complicated by variations of recharge temperatures and entrapment of air bubbles near the

groundwater surface which leads to varying background concentrations of dissolved N₂ in groundwater due to contact of the water with atmospheric air (Böhlke, 2002). Furthermore, N₂ can be lost by degassing (Blicher-Mathiesen et al., 1998).

As a result of NO₃⁻ consumption in denitrifying aquifers, the NO₃⁻ concentration in the deeper groundwater is lower than the initial NO₃⁻ concentration at the groundwater surface. Thus, the reconstruction of initial NO₃⁻ concentrations by means of measuring excess N₂ could be a tool to determine the N input to aquifers and thus reduce uncertainties connected with determination of EF5-g.

In this study, we measured excess N₂ and N₂O in the groundwater of 4 nitrate-contaminated, denitrifying aquifers in Northwest Germany in order (1) to estimate initial NO₃⁻ that enter the groundwater surface, (2) to assess potential indirect emissions of N₂O, and (3) to compare existing concepts of groundwater N₂O emission factors.

2 Material and methods

2.1 Study sites

Investigations were conducted in the aquifers of 4 drinking water catchments (Fuhrberg, Göttingen, Thülsfelde and Sulingen) located in Northwest Germany, Lower Saxony. These aquifers consist of pleistocene sand and pleistocene gravel and are characterized by NO₃⁻ contamination that results from intensive agricultural N inputs via fertilizers. In all aquifers, NO₃⁻ concentrations in the deeper groundwater are substantially lower compared to the shallow groundwater. In previous studies, denitrification was identified as the natural process for reduction of groundwater NO₃⁻ concentrations in Fuhrberg (Kölle et al., 1985; Böttcher et al., 1990), Thülsfelde (Pätsch, 2006; Walther et al., 2001), and Sulingen (Konrad, 2007). General properties of the aquifers are summarized in Table 1.

2.2 Sampling and laboratory analyses

Groundwater samples (3 or 4 replications per depth, respectively) were collected from groundwater monitoring wells allowing collection of samples from defined depths (Table 1). In Sulingen and Göttingen, we collected groundwater samples during a single sampling event, whereas up to three sampling events took place in Thülsfelde. In Fuhrberg, sampling was conducted 4 times within one year. The Fuhrberg site was equipped with multilevel sampling wells (Böttcher et al., 1985) with a depth resolution of 0.2 m in the first 2 m of the groundwater and 1.0 m for the rest. Samples were collected using a peristaltic pump (Masterflex, COLE-PARMER, Vernon Hills, USA). Because negative pressure in the suction tubing might cause partial outgassing of the water sample during pumping, a low suction rate of approximately 50 ml min⁻¹ was used to minimize this effect

Table 1. General properties for the aquifers of Fuhrberg, Sulingen, Thülsfelde and Göttingen. Further information are available in Kölle et al. (1985), Böttcher et al. (1990), Pätsch (2006), Walther et al. (2001), Konrad (2007) and Schlie (1989).

Site (number of samples/wells); [geographical coordinates]	Thickness of the aquifer body/depth to the groundwater table [m]	Hydraulic active sediment	Sampling depth (m below groundwater surface)	pH	O ₂ [mg L ⁻¹]	Temp [°C]
Fuhrberg (80/7) [52°33' N; 9°50' E]	20–35/1–3	sand	0.1–27.0	3.7–6.6	0–10.2	n.d.
Sulingen (30/2) [52°43' N; 8°41' E]	20–30/6–9	sand	8.5–63.0	4.6–6.7	0.2–13.6	10.3*
Thülsfelde (19/4) [52°57' N; 7°55' E]	150/1–8	sand	1.7–35.4	4.3–5.8	0.1–8.8	10.1*
Göttingen (25/6) [51°30' N; 9°56' E]	5–10/1–2	gravel	4.0–23.5	6.8–7.9	0.6–11.7	9.8*

n.d.: not determined; * median values; Temp: groundwater temperature.

(Blicher-Mathiesen et al., 1998). In Fuhrberg, additional samples from a continuously pumped groundwater stream were collected using taps at the pump outlets of drinking water wells which delivered raw water to the waterworks. The other sites were equipped with regular monitoring wells consisting of PVC-pipes (diameter between 3.81 cm and 10.16 cm) with filter elements of one or two m length. In these wells, samples were collected with a submersible pump (GRUNDFOS MP1, Bjerringbro, Denmark), which prevents outgassing because the water samples are at a positive pressure during pumping. From one of these monitoring wells, replicate groundwater samples were collected from 0.5–2.5 m below the groundwater table using both pump types in order to estimate potential outgassing using the peristaltic pump. Differences between the treatments were non-significant, which implies that outgassing was negligible. For both pump types, groundwater was collected from the outlet through a 4 mm ID PVC tubing by placing its end to the bottom of 115 mL serum bottles. After an overflow of at least 115 ml groundwater, the tubing was carefully removed and the bottles were immediately sealed with grey butyl rubber septa (ALTMANN, Holzkirchen, Germany) and aluminium crimp caps. There were no visible air bubbles in the tubings and the vial during the procedure. The samples were stored at 10°C (approximate groundwater temperature as estimated from mean annual air temperature) and analyzed within one week. Eight mL of helium were injected in each vial in order to replace an equivalent amount of groundwater and to create a gas headspace. Liquid and gas phase were equilibrated at constant temperature (25°C) by agitating on a horizontal shaker for 3 h. To analyse N₂ and Ar, 1 mL headspace gas was injected manually with a gas-tight 1-mL syringe equipped with a valve (SGE, Darmstadt) into a gas chromatograph (Fractovap 400, CARLO ERBA, Milano) equipped with a thermal conductivity detector and a packed column (1.8 m length, 4 mm ID, molecular sieve 5Å) and us-

ing helium as carrier gas. Because retention times of O₂ and Ar are similar on this column, O₂ was completely removed using a heated Cu-column (800°C) which was installed prior to the GC-column. To avoid contamination with atmospheric air during sample injection the following precautions were necessary: the syringe was flushed with helium immediately before penetrating the sample septum. Subsequently, the syringe was “over-filled” by approximately 15%, the syringe valve closed and the plunger adjusted to 1 mL in order to slightly pressurize the sample. The syringe needle was then held directly above the injection port before the valve was opened for a second to release excess pressure and the sample was finally injected. Generally, 3 replicate groundwater samples were analysed. A fourth sample served as reserve in case of failure during analysis. A calibration curve was obtained by injecting 0.2, 0.3, 0.5 and 1.0 mL of atmospheric air (3 replications each), resulting in different Ar and N₂ concentrations per calibration step.

To determine dissolved N₂O and CO₂ concentrations, the headspace volume was augmented to 40 mL by an additional injection of 32 mL of helium and an equivalent amount of groundwater was replaced. After equilibrating liquid and gas phase at constant temperature (25°C), 24 mL of the headspace gas were equally distributed to 2 evacuated septum-capped exetainers[®] (12 mL, Labco, Wycombe, UK). N₂O and CO₂ were analyzed using a gas chromatographer equipped with a thermal conductivity detector (Fractovap 400, CARLO ERBA, Milano), with an electron capture detector and an autosampler as described by Well et al. (2003). NO₃⁻ concentration was determined on 0.45 μm membrane-filtered samples by use of an ion chromatograph (ICS-90, DIONEX, Idstein, Germany) equipped with an IC-AIS column.

Molar fractions of N₂, Ar, CO₂ and N₂O in the headspace of sample vials and the volume of added helium as well as the solubilities of these gases (Weiss, 1970, 1971; Weiss and

Price, 1980) were used to calculate partial pressure and molar fraction in the groundwater for each gas (Blicher-Mathiesen et al., 1998). Total pressure in the headspace after equilibration was obtained from the sum of partial pressures of each gas or by direct measurement using a pressure transducer equipped with a hypodermic needle (Thies Klima, Göttingen, Germany) were in good agreement, i.e. differences between measured and calculated pressure were <9%. We checked the accuracy of estimated molar concentrations of dissolved gases from headspace concentration by adding defined volumes of N₂ (1 and 2 mL, respectively) to samples of demineralised water equilibrated at 10°C. Recovery of N₂ was found to be satisfactory and was 92.91% for 1 and 2 mL added N₂.

2.3 Calculation of excess N₂

N₂ dissolved in groundwater samples includes atmospheric N₂ and N₂ from denitrification (excess N₂) accumulated during the groundwater flow path (Böhlke, 2002). N₂ from denitrification can be determined by subtracting atmospheric N₂ from total N₂ (N_{2T}). Atmospheric N₂ in groundwater consists of two components, (i) N₂ dissolved according to equilibrium solubility (N_{2EQ}), and (ii) N₂ from “excess air” (N_{2EA}, Heaton and Vogel, 1981). Excess air denotes dissolved gas components in excess of equilibrium and other known subsurface gas sources. Excess air originates from entrapment of air bubbles near the groundwater table during recharge which is subject to complete or partial dissolution (Holoher et al., 2002).

Excess N₂ ($X_{\text{excess N}_2}$) can thus be calculated using the following equation:

$$X_{\text{excess N}_2} = X_{\text{N}_2\text{T}} - X_{\text{N}_2\text{EA}} - X_{\text{N}_2\text{EQ}} \quad (1)$$

where X denotes molar concentration of the parameters. $X_{\text{N}_2\text{T}}$ represents the molar concentration of the total dissolved N₂ in the groundwater sample. $X_{\text{N}_2\text{EQ}}$ is the molar concentration of dissolved N₂ in equilibrium with the atmospheric concentration. It depends on the water temperature during equilibration with the atmosphere, i.e. the temperature at the interface between the unsaturated zone and the groundwater surface. For the equilibrium temperature we assumed a constant value of 10°C which was close to mean groundwater temperature. This is also similar to the mean annual temperature which is the best estimate of the mean temperature at the interface between unsaturated zone and the aquifer (Heaton and Vogel, 1981). $X_{\text{N}_2\text{EQ}}$ was thus obtained using N₂ solubility data (Weiss, 1970) for this recharge temperature. N_{2EA} represents N₂ from excess air. For a given recharge temperature, excess air is reflected by noble gas concentrations (Holoher et al., 2002). If excess air results from complete dissolution of gas bubbles, the gas composition of the excess air component is identical to atmospheric air (Heaton et al., 1983; Aeschbach-Hertig et al., 2002). For this case, $X_{\text{N}_2\text{EA}}$

can be calculated from the concentration of only one noble gas, e.g. Argon (Heaton and Vogel, 1981):

$$X_{\text{N}_2\text{EA}} = (X_{\text{ArT}} - X_{\text{ArEQ}}) * \frac{X_{\text{N}_2\text{atm}}}{X_{\text{Aratm}}} \quad (2)$$

where $X_{\text{N}_2\text{atm}}$ and X_{Aratm} denote atmospheric mole fractions of N₂ and Ar, respectively. X_{ArT} represents the molar concentration of the total dissolved Ar in the groundwater sample. X_{ArEQ} is the molar concentration of dissolved Ar in equilibrium with the atmospheric concentration.

If excess air originates from incomplete dissolution of entrapped gas bubbles, then the N₂-to-Ar ratio of excess air is lower than the atmospheric N₂-to-Ar ratio due to fractionation (Holoher et al., 2002). The lowest value of the N₂-to-Ar ratio of excess air is equal to the N₂-to-Ar ratio in water at atmospheric equilibrium (Aeschbach-Hertig et al., 2002) since this lowest value is approximated when the dissolution of entrapped air approaches zero. The lowest estimate of $X_{\text{N}_2\text{EA}}$ is thus given by

$$X_{\text{N}_2\text{EA}} = (X_{\text{ArT}} - X_{\text{ArEQ}}) * \frac{X_{\text{N}_2\text{EQ}}}{X_{\text{ArEQ}}} \quad (3)$$

where $X_{\text{N}_2\text{EQ}}$ and X_{ArEQ} denote equilibrium mole fractions of N₂ and Ar, respectively. The actual fractionation of excess air can only be determined by analysing several noble gases (Aeschbach-Hertig et al., 2002). Because we measured only Ar, our estimate of excess N₂ includes an uncertainty from the unknown N₂-to-Ar ratio of the excess air component. This uncertainty (U) is equal to the difference between $X_{\text{N}_2\text{EA}}$ calculated with Eqs. (2) and (3), and is thus given by

$$U_{\text{N}_2\text{EA}} = (X_{\text{ArT}} - X_{\text{ArEQ}}) * (X_{\text{N}_2\text{atm}}/X_{\text{Aratm}} - X_{\text{N}_2\text{EQ}}/X_{\text{ArEQ}}) \quad (4)$$

It can be seen that $U_{\text{N}_2\text{EA}}$ directly depends on excess Ar, i.e., $X_{\text{ArT}} - X_{\text{ArEQ}}$. We used equations 1 to 3 to calculate lowest and upper estimates of excess air and excess N₂ and to assess the remaining uncertainty of our excess N₂ estimates connected with excess air fractionation. Finally, we calculated means from the lowest and upper estimates which we considered as best estimates of excess N₂.

2.4 Standard deviation and repeatability of excess N₂ analysis

Precision of the method was tested by evaluating standard deviation (σ) and repeatability (R). σ was determined for N₂ and Ar concentrations in atmospheric air samples ($n=20$), giving 0.000069 LL⁻¹ for Ar and 0.006449 LL⁻¹ for N₂, respectively. Repeatability (R) was derived from $R=2\sqrt{2}\sigma$, giving 0.000196 LL⁻¹ for c_{Ar} (R_{Ar}) and 0.018241 LL⁻¹ for c_{N_2} (R_{N_2}). Errors resulting from R_{N_2} and R_{Ar} were obtained using Eqs. (1)–(3), giving 1.59 and 2.05 mg N L⁻¹, respectively. Finally, total error for excess N₂ was determined by Gaussian error propagation (Mölders et al., 2005) giving 2.58 mg N L⁻¹ for excess N₂.

Table 2. Excess N₂, N₂O, NO₃⁻, and NO₃⁻_{t0} concentrations and reaction progress of denitrification (RP) of the investigated aquifers. NO₃⁻_{t0} concentrations were calculated using equation 5, RP was calculated using Eq. (6).

site		excess N ₂ [mg NL ⁻¹]	N ₂ O [μg NL ⁻¹]	NO ₃ ⁻ [mg NL ⁻¹]	NO ₃ ⁻ _{t0} [mg NL ⁻¹]	RP
Fuhrberg	Min	0.13	0.19	0.00	3.14	0.05
	Max	13.14	1271.39	41.67	44.75	1.00
	Median	4.20	89.00	8.51	13.14	0.45
Sulingen	Min	-0.90	0.53	0.00	0.22	0.00
	Max	14.85	254.51	37.12	51.04	1.00
	Median	2.08	8.27	9.26	13.16	0.33
Thülsfelde	Min	0.57	0.16	0.23	1.48	0.00
	Max	28.83	180.86	33.18	40.87	0.99
	Median	7.97	18.39	4.89	17.11	0.68
Göttingen	Min	1.61	0.07	0.45	2.05	0.11
	Max	10.71	18.68	12.64	13.93	0.96
	Median	3.19	3.40	3.84	8.24	0.43

2.5 Initial NO₃⁻ concentration, reaction progress and emission factors

Initial NO₃⁻ concentration ($c\text{NO}_3^-$) at a given location on the aquifer surface is defined by the NO₃⁻ concentration of the recharging water before alteration by denitrification in groundwater (Heaton et al., 1983).

From the assumption that NO₃⁻ consumption on the groundwater flow path between the aquifer surface and a given sampling spot originates from denitrification and results in quantitative accumulation of gaseous denitrification products (N₂O and N₂), it follows that $c\text{NO}_3^-$ can be calculated from the sum of residual substrate and accumulated products (Böhlke, 2002). Thus, $c\text{NO}_3^-$ -N_{t0} is given by the following equation:

$$c\text{NO}_3^- \text{-N}_{t0} = \text{excess N}_2 + c\text{NO}_3^- \text{-N} + c\text{N}_2\text{O-N} \quad (5)$$

Reaction progress (RP) is the ratio between products and starting material of a process and can be used to characterize the extent of NO₃⁻ elimination by denitrification (Böhlke, 2002). RP is calculated as follows:

$$\text{RP} = \frac{\text{excess N}_2 + c\text{N}_2\text{O-N}}{c\text{NO}_3^- \text{-N}_{t0}} \quad (6)$$

Emission factors (EF) for indirect N₂O emission from the aquifer resulting from N-leaching were calculated as described earlier (Well et al., 2005a). Because $c\text{NO}_3^-$ represents the N-input to the aquifer via leaching, our data set is suitable to calculate an EF(1) from the relationship between potential N₂O emission and N input, which is the ideal concept of emission factors (see introduction):

$$\text{EF}(1) = \frac{c\text{N}_2\text{O-N}}{c\text{NO}_3^- \text{-N}_{t0}} \quad (7)$$

Furthermore, we will compare EF(1) with the ratio of $c\text{N}_2\text{O-N}$ to $c\text{NO}_3^- \text{-N}$ (EF(2)), which was used by the IPCC methodology (1997) to derive EF5-g:

$$\text{EF}(2) = \frac{c\text{N}_2\text{O-N}}{c\text{NO}_3^- \text{-N}} \quad (8)$$

This concept was frequently used in recent studies to characterize indirect emissions in agricultural drainage water or groundwater (Reay et al., 2003; Sawamoto et al., 2005;) but it is non-ideal, because it assumes that these aquatic systems act solely as a domain of transport without any processing of NO₃⁻ and N₂O (Well et al. 2005a, see introduction). The comparison between EF(1) and EF(2) will demonstrate potential errors in predicting indirect N₂O emission from denitrifying aquifers using EF(2).

3 Results

3.1 Basic groundwater properties

Basic groundwater properties of the investigated aquifers are shown in Table 1. Groundwater temperatures at these sites were relatively constant at 10°C. The pH and O₂ concentrations of the groundwater were more variable, suggesting heterogeneous conditions for denitrification and N₂O accumulation. The ranges of O₂ concentrations were similar in all aquifers and demonstrate that the investigated wells included both aerobic and anaerobic zones of each aquifer. Most of the sandy aquifers are acidic (Sulingen, Fuhrberg, Thülsfelde) with similar pH ranges, whereas pH of the Göttingen gravel aquifer is close to 7.

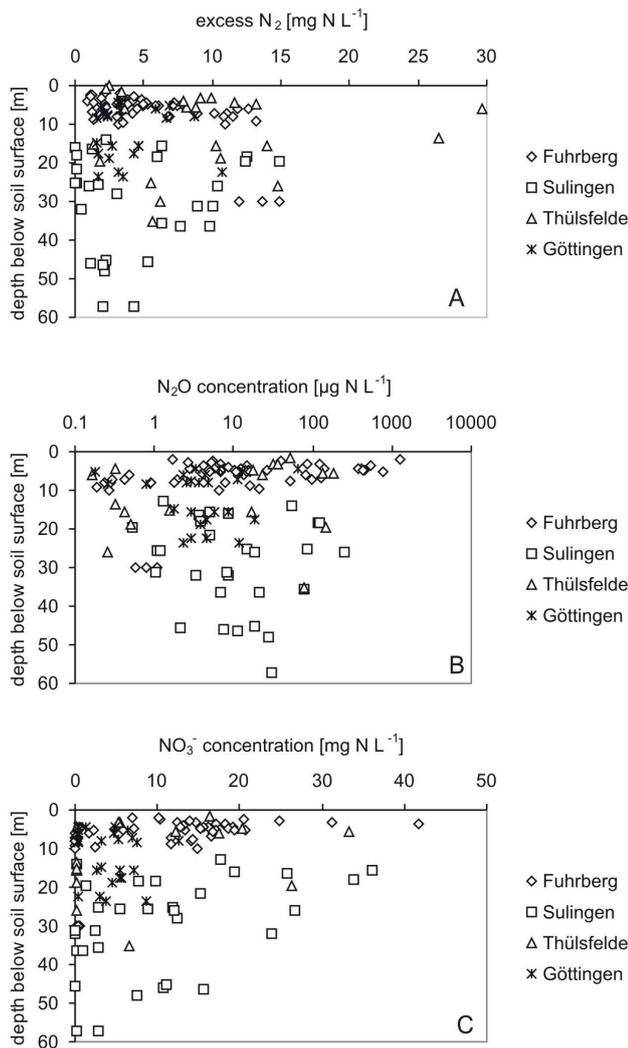


Fig. 1. Vertical distribution of (A) excess N₂, (B) N₂O concentrations (log scaled) and (C) actual NO₃⁻ concentrations in the investigated aquifers.

3.2 Excess N₂, measured and initial NO₃⁻ concentrations

We used the means of lowest and upper estimates for excess N₂ as a possible best estimate which were calculated assuming complete dissolution or maximum fractionation of entrapped gases, respectively (see Sect. 2.3, Eqs. (2) and (3)). The maximum error is thus half the difference between lowest and upper estimates. The uncertainty connected with this procedure is documented in Fig. 3, where excess N₂min and excess N₂max denote lowest and upper estimates for excess N₂, respectively. Derived from the whole data set shown in Fig. 3, the mean difference between lowest and upper estimates for excess N₂ is 1.25 mg N L⁻¹ and the mean of the maximum errors is thus 0.63 mg N L⁻¹ (see Sect. 2.3, Eq. (4)). According to Eq. (5), these error values connected with the uncertainty of excess N₂ are also valid for NO₃⁻_{3r0}.

Using the uncertainty of excess N₂ and NO₃⁻_{3r0} we also estimated the uncertainty of RP (Eq. 6), giving 0.011 for the mean of the maximum errors. From Eq. (7) it follows that the relative error of EF(1) is equal to the relative error in NO₃⁻_{3r0}, giving 4.8 % for the median NO₃⁻_{3r0} of 13.15 mg N L⁻¹.

Ranges and site medians of excess N₂ and reaction progress are given in Table 2. Lowest values for excess N₂ coincided with RP of approximately 0. A RP of approximately 1 was characterized by high values of excess N₂ in all aquifers. In all aquifers, samples cover almost the complete range of RP. Highest excess N₂ values were observed at Thülsfelde, which were twice the values of the other sites (Fig. 1). At a drinking water well of the Fuhrberg catchment, NO₃⁻ and N₂O concentrations were negligible and excess N₂ was 12.9 mg N L⁻¹ in groundwater samples from a depth of 30 m, which results in RP of 1. This shows that denitrification is complete in those deeper parts of the Fuhrberg aquifer.

Measured NO₃⁻ concentrations were highest in the aquifers of Fuhrberg and Sulingen (Fig. 1) with median values of 8.51 and 9.26 mg N L⁻¹, respectively (Table 2). In Thülsfelde and Göttingen measured NO₃⁻ concentrations were significantly lower (Table 2, Fig. 1). We observed the clear tendency that measured NO₃⁻ concentrations decreased with increasing sampling depth (Fig. 1c). Calculated initial NO₃⁻ concentrations (NO₃⁻_{3r0}, Eq. 5) were substantially higher than measured NO₃⁻ concentrations (Table 2), especially in the aquifer of Thülsfelde. The difference between measured NO₃⁻ concentrations and NO₃⁻_{3r0} demonstrates that NO₃⁻ consumption by denitrification was an important process in all investigated aquifers.

3.3 N₂O concentrations and emission factors

Wide ranges of N₂O concentrations were observed in all aquifers (Fig. 1b, Table 2). Highest concentrations up to 1271 µg N₂O-N L⁻¹ were measured in shallow groundwater at the Fuhrberg site at a RP of 0.35 (Fig. 2).

Emission factors EF(1) and EF(2) were highly variable within each site (Table 3). Their medians for the complete data set were 0.00081 and 0.0031, respectively. Thus, EF(2) was in agreement with the 2006 IPCC default value for the EF5-g (IPCC, 2006), which was defined as 0.0025. In contrast, EF(1) was significantly lower than the 2006 IPCC default value. For the whole data set, EF(2) was higher than EF(1). A comparison between EF(1) and EF(2) depending on RP is illustrated in Fig. 4. It can be seen that the difference between the emission factors is relatively small if RP is low. With increasing RP, the difference between EF(1) and EF(2) is also increasing, resulting in substantial discrepancies at RP close to 1. Among the sites, median values for each emission factor covered approximately one order of magnitude (EF(1): 0.00043 to 0.00438, EF(2): 0.00092 to 0.01801) (Table 3). For both emission factors, we determined highest values for the Fuhrberg aquifer and lowest for the aquifer of Göttingen

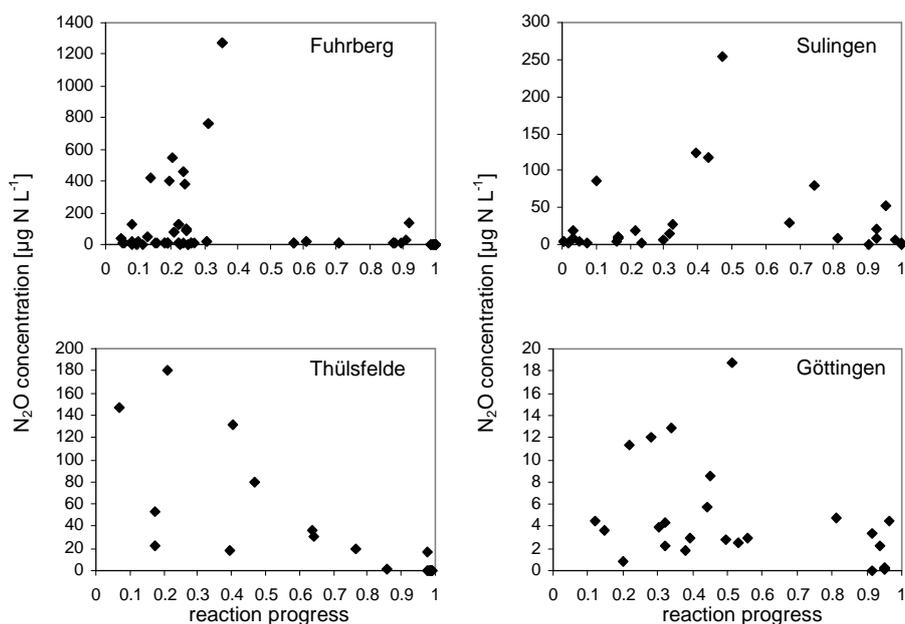


Fig. 2. N₂O in groundwater samples from 4 different aquifers in relation to reaction progress. Reaction progress is the ratio between denitrification products (excess N₂+N₂O) and initial NO₃⁻.

Table 3. Emission factors EF(1) and EF(2) of the investigated aquifers. EF(1) was determined as the ratio of N₂O/NO₃⁻_{t0} concentrations with NO₃⁻_{t0} as initial NO₃⁻ concentration. EF(2) was determined as the ratio of N₂O/NO₃⁻ concentrations with NO₃⁻ as measured NO₃⁻ concentration.

	EF(1)				EF(2)			
	min-max	stand. dev.	mean values	median	min-max	stand. dev.	mean values	median
Fuhrberg	0.00004–0.11834	0.0196	0.01065	0.00438	0.00005–0.23971	0.0409	0.02382	0.01801
Sulingen	0.00004–0.03816	0.0078	0.00380	0.00060	0.00007–0.51012	0.1225	0.04761	0.00248
Thülsfelde	0.00001–0.00643	0.0022	0.00194	0.00103	0.00071–0.07364	0.0167	0.00808	0.00366
Göttingen	0.00001–0.01197	0.0005	0.00058	0.00043	0.00011–0.01038	0.0029	0.00210	0.00092

stand. dev.: standard deviation

(Table 3). For the Fuhrberg and the Sulingen sites, we found EF(1) median values which are close to the 2006 IPCC default value of 0.0025. In contrast, we determined significant lower EFs(1) for the aquifers of Thülsfelde and Göttingen.

N₂O concentrations and EF(1) followed a rough pattern during RP. Values were lowest at the beginning (RP close to 0) and at the end (RP close to 1) of the denitrification process. At a RP close to 1, N₂O concentrations were still slightly above the ambient level, despite NO₃⁻ was completely consumed. It can be concluded that EF(1) and EF(2) would approach zero if N₂O is completely reduced to N₂. In contrast to the lowest values for N₂O concentrations and EF(1) at RP close to 0 and close to 1, N₂O concentrations and EF(1) were relatively high at a RP between 0.2 and 0.6 (Figs. 2 and 4). However, at each RP we observed a relatively wide range of N₂O concentrations and EF(1).

4 Discussion

4.1 Uncertainty of excess N₂ estimates and excess N₂ related parameters

A certain amount of excess air, i.e. dissolved gas components in excess to equilibrium originating from entrapment of air bubbles at the groundwater surface during recharge (see Sect. 2.3), is often found in aquifers (Green et al., 2007). Heaton et al. (1983) found for their data set excess air concentrations between 3.0 and 26.6 ml L⁻¹. In our study, excess air concentrations were lower and ranged between 0 and 7.5 ml L⁻¹. Although Heaton and Vogel (1981) and Heaton et al. (1983) assumed total dissolution of entrapped gas bubbles for their data set, fractionation of excess air (that means partial solution of the bubbles) is a probable phenomenon

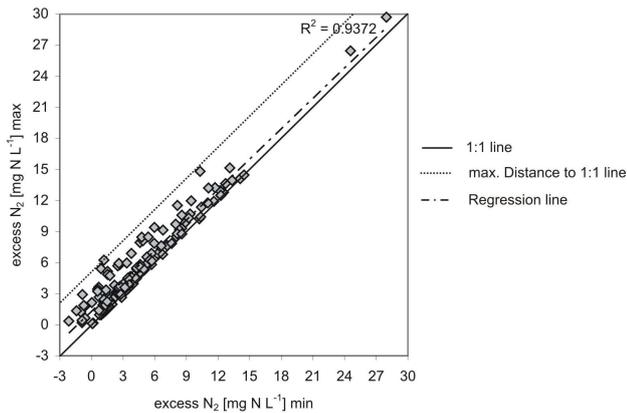


Fig. 3. Lowest (excess N₂ min) and upper (excess N₂ max) estimates of excess N₂ for the whole data set as calculated using eqs. (1) and (2) or (1) and (3), respectively. The maximum distance to the 1:1 line denotes the maximum difference between the lowest and upper estimates. The regression line refers to the mean of the lowest and upper estimates for the whole data set.

(see Sect. 2.3). This was clearly shown by Aeschbach-Hertig et al. (2002) for different aquifers and different environmental conditions. The extent of fractionation of excess air could not be assessed in our data set, because this requires analysing of several noble gases, what was not done in this study. According to this issue, an uncertainty of excess N₂ and of the related parameters was specified in Sects. 2.3 and 3.2.

The uncertainty of RP is small and does not affect our conclusion that maximum N₂O concentrations occurred at RP between 0.2 and 0.6. Thus, this uncertainty hardly affects the relationship between RP and EF(1) shown in Fig. 4. In view of the large range of EF(1) (Table 3), the relative error of EF(1) connected with the uncertainty of NO₃⁻_{t0} is relatively small. Therefore, it can be concluded that the consequences of uncertainties connected with excess N₂ and NO₃⁻_{t0} are negligible for our concept of EF(1).

Significant degassing of groundwater may occur when the sum of partial pressures of dissolved gases (e.g. Ar, N₂, O₂, CO₂, and CH₄) exceeds that of the hydrostatic pressure. This phenomenon was found when high denitrifying activity induced production of excess N₂ in shallow groundwater of riparian ecosystems under the presence of low hydrostatic pressure (Blicher-Mathiesen et al., 1998; Mookherji et al., 2003). In our study, these conditions have not been observed. The sum of partial pressures never exceeded hydrostatic pressure which is due to the fact, that the majority of data originates from deeper groundwater where hydrostatic pressure is higher than in shallow groundwater. These conditions prevent degassing of gaseous denitrification products. Unlike the observations of Blicher-Mathiesen et al. (1998) and Mookherji et al. (2003) excess N₂ in the shallow groundwater measured in this study was low. This shows that hy-

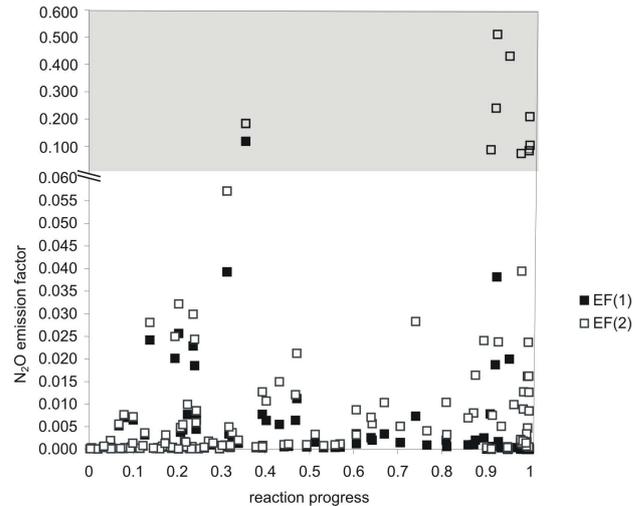


Fig. 4. N₂O emission factors EF(1) and EF(2) of the investigated aquifers in relation to reaction progress (ratio between denitrification products and initial NO₃⁻) and compared to IPCC default EF5-g. EF(1) was determined as the ratio of N₂O-N/NO₃⁻-N_{t0} with NO₃⁻-N_{t0} as initial NO₃⁻ concentration. EF(2) was determined as the ratio of N₂O-N/NO₃⁻-N with NO₃⁻-N as actual NO₃⁻ concentration.

drostatic pressure was not exceeded by accumulation of dissolved gases and that degassing did not occur. Similar observations for comparable conditions were reported previously (Heaton et al., 1983; Dunkle et al., 1993; Böhlke et al., 1995).

4.2 Regulating factors of denitrification and N₂O accumulation

Information on the process dynamics in the investigated aquifers can be obtained from the relationships between parameters of denitrification and N₂O accumulation and their regulating factors. Within the whole data set, sampling depth exhibited significant positive correlations with RP and significant negative correlations with NO₃⁻ (Table 4). Because groundwater residence time generally increases with depth in the upper part of unconfined aquifers, these relationships can be interpreted as a result of ongoing denitrification progress during aquifer passage (Konrad et al., 2007). These relationships and additional significant positive correlations between sampling depth and excess N₂ were mostly pronounced in the data-set of Fuhrberg, whereas the correlations were lower or insignificant for the other aquifers (data not shown). The latter suggests that spatial distribution of denitrification within these aquifers was more heterogeneous. In agreement with the results of Vogel et al. (1981) and Konrad (2007), a significant negative correlation between NO₃⁻ and excess N₂ in the whole data-set ($R_S = -0.37$, Table 4) demonstrates that denitrification was an important factor for NO₃⁻ variability within all aquifers.

Table 4. Spearman rank correlation coefficients between all variables for the full data-set.

	depth	N ₂ O	NO ₃ ⁻	excess N ₂	NO ₃ ⁻ _{t0}	RP	EF(1)	EF(2)	pH
N ₂ O	-0.02 ns								
NO ₃	-0.29***	0.43***							
excess N ₂	0.13 ns	-0.19*	-0.37***						
NO ₃ ⁻ _{t0}	-0.22**	0.25**	0.76***	0.18 ns					
RP	0.25***	-0.39***	-0.86***	0.74***	-0.43***				
EF(1)	-0.03 ns	0.93***	0.19**	-0.28***	-0.08 ns	-0.28***			
EF(2)	0.16*	0.48***	-0.50***	0.27***	-0.34***	0.48***	0.62***		
pH	-0.04	-0.25**	-0.52***	0.37***	-0.36***	0.57***	-0.14 ns	0.25**	
O ₂	0.16*	-0.05 ns	0.21**	-0.34***	0.03 ns	-0.34***	-0.07 ns	-0.42***	0.01 ns

RP: reaction progress of denitrification.

* Correlation significant at the 0.05 probability level.

** Correlation significant at the 0.01 probability level.

*** Correlation significant at the 0.001 probability level.

ns: not significant.

NO₃⁻ usually inhibits N₂O reduction to N₂ (Blackmer and Bremner, 1978; Cho and Mills, 1979). This is confirmed by the positive correlation between N₂O and NO₃⁻ we found in this study (Table 4). A significant negative correlation was found between N₂O and pH, which was mostly pronounced in the aquifer with the widest pH range (Fuhrberg, see Table 1, spearman correlation coefficient (R_S)=-0.33). Stevens et al. (1998) emphasized that pH strongly influences processes that generate N₂O and N₂. N₂O accumulation in aquifers might be supported by increasing groundwater acidity because the reduction step of N₂O to N₂ is much more sensitive to acidic conditions compared to the preceding reduction steps (Granli and Bøckman, 1994; Blicher-Mathiesen and Hoffmann, 1999). The influence of pH on the N₂O-to-N₂ ratio is intensified by high NO₃⁻ concentrations (Blackmer and Bremner, 1978; Firestone et al., 1980). Due to these observations we conclude that conditions were especially favourable for N₂O accumulation and potential N₂O emission in shallow groundwater of the Fuhrberg aquifer, because it is characterized by high NO₃⁻ contamination and comparatively low pH. This is confirmed by our data since N₂O concentrations of these samples were highest within the entire data-set.

4.3 Potential indirect N₂O emissions from groundwater estimated from initial NO₃⁻ concentration

Unlike emission factors determined from measured fluxes across the soil surface, emission factors estimated from groundwater concentration do not reflect the actual N₂O emission from the system because the amount of dissolved N₂O might increase or decrease during further residence time in the aquifer or during the passage of the unsaturated zone before it reaches the atmosphere (Höll et al., 2005; Well et al., 2005a). These dynamics of N₂O in groundwater are

complex and variable and should be considered in the development of improved inventory calculations (Clough et al., 2007). Moreover, diffusive N₂O emission from the aquifer surface to the unsaturated zone and eventually to the atmosphere (Deurer et al., 2008) is not taken into account by EF(1). Therefore, the measured data supply only potential emission factors quantifying the amount of N₂O which could be emitted, if the groundwater was immediately discharged to springs, wells or streams. The determination of an effective emission factor to quantify real N₂O flux from the investigated aquifers requires validated models of reactive N₂O transport. Further research on reaction dynamics and gas transport within the aquifers is needed to achieve this.

However, the comparison of N₂O concentration and EF(1) with RP gives a rough sketch of the principal N₂O pattern during groundwater transport through denitrifying aquifers. Although variations of N₂O and EF(1) at any given level of RP were high, there was a clear tendency of low N₂O concentrations for RP close to zero or close to 1 and highest N₂O concentrations at RP between 0.2 and 0.6. This pattern is consistent with the time course of N₂O during complete denitrification in closed systems observed by modelling (Almeida et al., 1997) as well as laboratory incubations (Well et al., 2005b) and can be explained by the balance between production and reduction of N₂O during a Michaelis-Menten reaction kinetics. It can be concluded that RP can be considered as an important parameter to predict N₂O emission via groundwater discharge. This emission can be expected to be negligible if RP at groundwater discharge is very small or close to 1. However, the occurrence of individual samples with comparatively high N₂O concentrations at RP close to 0 (Fig. 2, Thülsfelde) indicates that the RP range that covers the highest N₂O concentrations might be even more variable. Conversely, relatively high emission can be expected if RP at groundwater discharge is between 0.2 and 0.6. The observed

relationships suggest that emission factors are also related to denitrification rate, groundwater residence time and sampling depth because these quantities determine the reaction progress (Konrad, 2007). This could be helpful to predict or interpret N₂O emission from different types of groundwater systems. For example, low N₂O fluxes observed from tile drainage outlets (Reay et al., 2003) might be explained by relatively low groundwater residence time of this drainage system. The deep wells of the investigated aquifers with low residual NO₃⁻ and low N₂O concentration reflect the typical low emission factors at RP close to 1. Hot spots of N₂O emission from groundwater might be locations where groundwater is discharged to surface waters immediately after partial NO₃⁻ consumption which is known to occur after the subsurface flow through riparian buffers (Hefting et al., 2003).

A downward revision of the EF5-g default value by the IPCC from 0.015 (1997) to 0.0025 (2006) was based on recent findings of Hiscock et al. (2002, 2003), Sawamoto et al. (2005) and Reay et al. (2005). This is supported by site medians of EF(1) of this study (Table 3) which scatter around the revised EF5-g. Obviously, the former 1997 IPCC EF5-g default value of 0.015 substantially overestimated indirect N₂O emissions from groundwater. A comparison of the emission factors EF(1) and EF(2) clearly shows lower values for EF(1) which results from the consideration of initial NO₃⁻ by EF(1). The deviation between EF(1) and EF(2) is highly relevant in aquifers with substantial denitrifying activity and high N inputs like those investigated in this study. Furthermore, Fig. 4 demonstrates that differences between EF(1) and EF(2) are increasing with reaction progress of denitrification. This clearly demonstrates that it is important to take the dynamic turnover of NO₃⁻ during groundwater passage into account. This is also confirmed by Hiscock et al. (2003). The authors stated that future studies are needed which take into account denitrification losses to refine N₂O budgets further. Consequently, potential N₂O emissions from aquifers should be estimated using EF(1) rather than EF(2).

5 Conclusions

In the investigated aquifers, NO₃⁻ consumption by denitrification was estimated from excess N₂ as determined from dissolved N₂ and Ar. This enabled calculation of initial NO₃⁻ concentration at the groundwater surface by adding up concentrations of NO₃⁻, N₂O and excess N₂. Ranges of N₂O concentrations in groundwater were large in all aquifers, covering an interval between 0 and 1271 μg N L⁻¹. The pH was found to be a significant controlling factor for N₂O accumulation. Because initial NO₃⁻ concentration reflects the N input to the groundwater by leaching, it was used to calculate an emission factor EF(1) for indirect agricultural N₂O emissions from groundwater which is for the first time based on the ratio between N₂O concentration and N-input. An uncertainty of excess N₂ estimates according to the excess air

phenomenon was found to be negligible for this concept of EF(1). EF(1) in the investigated denitrifying aquifers was much lower than the values resulting from the earlier concept of groundwater emission factors consisting of N₂O-to-NO₃⁻ mass ratios of groundwater samples (EF(2) in this study). This demonstrates the need to take past NO₃⁻ consumption into account when determining groundwater emission factors. In agreement with recent literature data our observations support the substantial downward revision of the IPCC default EF5-g from 0.015 (1997) to 0.0025 (2006). However, there are still uncertainties with respect to a single emission factor for the effective N₂O flux from the investigated aquifers because spatial and temporal heterogeneity of N₂O concentrations was high and further metabolism of N₂O during transport in the aquifer and through the unsaturated zone before it is emitted is poorly understood.

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