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Assessment of excess N_2 and groundwater N_2O emission factors of nitrate-contaminated aquifers in northern Germany

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Abstract

We investigated the dynamics of denitrification and nitrous oxide (N_2O) accumulation in 4 nitrate (NO_3^-) contaminated denitrifying sand and gravel aquifers of northern Germany (Fuhrberg, Sulingen, Thülsfelde and Göttingen) to quantify their potential N_2O emission and to evaluate existing concepts of N_2O emission factors. Excess N_2-N_2produced 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 NO_3^-concentrations (NO_3^- that enters the groundwater) were derived from excess N_2 and actual NO_3^- concentrations in groundwater in order to determine potential indirect N_2O emissions as a function of the N input. Median concentrations of N_2O and excess N_2 ranged from 3 to 89 μg N L^{-1} and from 3 to 10 mg N L^{-1} respectively. Reaction progress (RP) of denitrification was determined as the ratio between products (N_2O-N + excess N_2) and starting material (initial NO_3^- concentration) of the process, characterizing the different stages of denitrification. N_2O 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 N_2O emission factors consisting of the ratio between N_2O-N and initial NO_3^--N concentrations (EF1). According to denitrification intensity, EF(1) was smaller than the ratio between N_2O-N and actual NO_3^--N concentrations EF(2). In general, these emission factors were highly variable within 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 EFs for the aquifers of Thülsfelde and Göttingen.

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1 Introduction

Denitrification is considered the most important reaction for nitrate (NO_3^-) remediation in aquifers. This process occurs in O_2 depleted layers with available electron donors (Ross, 1995; Böttcher et al., 1990). Especially in agricultural areas with high N inputs via fertilizers considerable NO_3^- reduction is possible (Böttcher et al., 1985). Dinitrogen (N_2) is the final product of this process. Thus the quantification of groundwater N_2 arising from denitrification (excess N_2) can facilitate the reconstruction of historical N inputs, because NO_3^- loss is derivable from the sum of denitrification products (Böhlke and Denver, 1995). Generally, the concentration of excess N_2 produced by denitrification in groundwater is estimated by comparing the measured concentrations of Ar and N_2 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 N_2 is complicated by variations of recharge temperatures and entrapment of air bubbles near the groundwater surface which leads to varying background concentrations of dissolved N_2 in groundwater due to contact of the water with atmospheric air (Böhlke, 2002). Furthermore, N_2 can be lost by degassing (Blicher-Mathiesen et al., 1998). Another aspect of denitrification are potential accumulation and emission of the greenhouse gas nitrous oxide (N_2O) which represents an obligate intermediate of the process. In contrast to direct agricultural N_2O emissions arising at the sites of agricultural production, e.g. soils, indirect emissions from ground and surface waters are associated with 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 N_2O concentrations to N leaching from soils (Clough et al., 2005) and investigations of N_2O 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 NO_3^- contamination often coincides with reducing conditions (Walther, 1999), suggesting that this region might be susceptible for relatively high N_2O fluxes from deeper groundwater. However, until now there have been no systematic investigations of N_2O dynamics in these aquifers.

N_2O emissions from groundwater were thought to comprise a significant fraction of total agricultural N_2O emissions (IPCC, 1997), but recent studies show in agreement that their significance is presumably 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 was corrected downwards from 0.015 to 0.0025 by the 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.

Principally, the N_2O emission factor of a system is defined by the ratio between N_2O emission and N input (IPCC, 1997). However, the IPCC factor characterizing indirect emissions from aquifers and drainage ditches (EF5-g) had been derived from the ratio between dissolved N_2O und NO_3^- 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 EF5-g because both NO_3^- and N_2O are subject to change during subsurface transport (Dobbie and Smith, 2003). Furthermore, determination of N_2O fluxes from aquifers is connected with experimental difficulties: N_2O as an intermediate product from denitrification is permanently influenced by different enzyme kinetics of various denitrifying communities and groundwater N_2O concentration is the net result of simultaneous production and reduction reactions (Well et a. 2005b). Höll et al. (2005) stated that these transformations are the reason why N_2O concentration in groundwater does not necessarily reflect actual indirect N_2O emission. Finally, as a result of NO_3^- consumption in denitrifying aquifers, the NO_3^- concentration in the deeper groundwater is lower than the initial NO_3^- concentration at the groundwater surface. Thus, the reconstruction of initial NO_3^- concentrations by means of measuring excess N_2 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 N_2 and N_2O in groundwater of 4 nitrate-contaminated, denitrifying aquifers in Northwest Germany in order (1) to estimate initial NO_3^- that enter the groundwater surface, (2) to assess potential indirect emissions of N_2O, and (3) to compare existing concepts of groundwater N_2O 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 NO_3^- contamination that results from intensive agricultural N inputs via fertilizers. In all aquifers, NO_3^- 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 NO_3^- 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 during single (Sulingen, Göttingen) or repeated sampling events (Thülsfelde) or 4 times within one year (Fuhrberg), respectively, from groundwater monitoring wells allowing collection of samples from defined depths (Table 1). 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. In Fuhrberg, additional samples were collected from 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 1.5″ and 4″) with filter elements of one or two m length. Here, 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 using both pump types in order to estimate potential outgassing using the peristaltic pump. Differences between the treatments were non-significant, which proves 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 was 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 N_2 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 5 Å) and using helium as carrier gas. Because retention times of O_2 and Ar are similar on this column, O_2 was quantitatively 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 N_2 concentrations per calibration step.

To determine dissolved N_2O 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). Nitrous oxide was analyzed using a gas chromatograph equipped with an electron capture detector and an autosampler as described by Well et al. (2003). NO_3^- 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 N_2, Ar and N_2O in the headspace of sample vials and the volume of added He 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 at 25°C 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 N_2 (1 and 2 mL, respectively) to samples of demineralised water equilibrated at 10°C. Recovery of N_2 was found to be satisfactory and was 92.91% for 1 and 2 mL added N_2.

2.3 Calculation of excess N_2

N_2 dissolved in groundwater samples includes atmospheric N_2 and N_2 from denitrification (excess N_2) accumulated during the groundwater flow path (Boehlke, 2002). Principally, N_2 from denitrification can be determined by subtracting atmospheric N_2 from total N_2 (N_{2T}). Atmospheric N_2 in groundwater consists of two components, (i) N_2 dissolved according to equilibrium solubility (N_{2EQ}), and (ii) N_2 from "excess air" (N_{2EA}, Heaton and Vogel, 1981). Excess air denotes dissolved gas components in excess to equilibrium and other known subsurface gas sources. Excess air originates from entrapment of air bubbles at the groundwater surface during recharge which is subject to complete or partial dissolution (Holocher et al., 2002).

Excess N_2 (X_{excessN2}) can thus be calculated using the following equation:

$$X_{\text{excessN2}} = X_{\text{N2T}} - X_{\text{N2EA}} - X_{\text{N2EQ}} \quad (1)$$

where X denotes molar concentration of the parameters. X_{N2T} represents the molar concentration of the total dissolved N_2 in the groundwater sample. X_{N2EQ} is the molar concentration of dissolved N_2 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_{N2EQ} was thus obtained using N_2 solubility data (Weiss, 1970) for this recharge temperature. N_{2EA} represents N_2 from excess air. For a given recharge temperature, excess air is reflected by noble gas concentrations (Holocher et al., 2002). If excess air results from complete dissolution of gas bubbles, the gas composition of the excess air component is identical to

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atmospheric air. For this case, X_{N2EA} can be calculated from the concentration of only one noble gas, e.g. Argon (Heaton and Vogel, 1981):

$$X_{N2\,EA} = \left(X_{Ar\,T} - X_{Ar\,EQ}\right) \times \frac{X_{N2\,atm}}{X_{Ar\,atm}} \tag{2}$$

where $X_{N2\,atm}$ and $X_{Ar\,atm}$ denote atmospheric mole fractions of N_2 and Ar, respectively. $X_{Ar\,T}$ represents the molar concentration of the total dissolved Ar in the groundwater sample. $X_{Ar\,EQ}$ 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 N_2-to-Ar ratio of excess air is lower than the atmospheric N_2-to-Ar ratio due to fractionation (Holocher et al., 2002). The minimum value of the N_2-to-Ar ratio of excess air is equal to the N_2-to-Ar ratio in water at atmospheric equilibrium (Aeschbach-Hertig et al., 2002) since this value is approximated when the dissolution of entrapped air approaches zero. The minimum estimate of $X_{N2\,EA}$ is thus given by

$$X_{N2\,EA} = \left(X_{Ar\,T} - X_{Ar\,EQ}\right) \times \frac{X_{N2\,EQ}}{X_{Ar\,EQ}} \tag{3}$$

where $X_{N2\,EQ}$ and $X_{Ar\,EQ}$ denote equilibrium mole fractions of N_2 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 N_2 includes an uncertainty from the unknown N_2-to-Ar ratio of the excess air component. This uncertainty (U) is equal to the difference between N_{2EA} calculated with Eqs. (2) and (3), and is thus given by

$$U_{N2\,EA} = \left(X_{Ar\,T} - X_{Ar\,EQ}\right) \times \left(X_{N2\,atm}/X_{Ar\,atm} - X_{N2\,EQ}/X_{Ar\,EQ}\right) \tag{4}$$

It can be seen that $U_{N2\,EA}$ directly depends on excess Ar, i.e. $X_{Ar\,T}-X_{Ar\,EQ}$. We used Eqs. (1) to (3) to calculate minimum and maximum estimates of excess air and excess N_2 and assessed the remaining uncertainty of our excess N_2 estimates connected with excess air fractionation. Finally, we calculated means from the minimum and maximum values which we considered as best estimates of excess N_2.

2.4 Standard deviation and repeatability of excess N_2 analysis

Precision of the method was tested by evaluating standard deviation (σ) and repeatability (R). σ was determined for N_2 and Ar concentrations in atmospheric air samples (n=20), giving 0.000069 for Ar and 0.006449 for N_2, respectively. Repeatability (R) was derived from $R=2\sqrt{2}\,\sigma$, giving 0.000196 for cAr (R_{Ar}) and 0.018241 for cN_2 (R_{N2}). Errors resulting from R_{N2} 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 N_2 was determined by Gaussian error propagation giving 2.58 mg N L^{-1} for excess N_2.

2.5 Initial NO_3^- concentration, reaction progress and emission factors

NO_3^- input to a given spot of the aquifer surface is defined by the NO_3^- concentration of the seepage water or the groundwater directly at the groundwater table which is not yet altered by NO_3^- consumption by denitrification in the groundwater. In the following, this concentration is referred to as "initial NO_3^- concentration" ($cNO_{3\,t0}^-$). From the assumption that NO_3^- consumption on the groundwater flow path between the aquifer surface at a given sampling spot originates from denitrification and results in quantitative accumulation of gaseous denitrification products (N_2O and N_2), it follows that $cNO_{3\,t0}^-$ can be calculated from the sum of residual substrate and accumulated products (Böhlke, 2002). Thus, $cNO_3\text{-}N_{t0}$ is given by the following equation:

$$cNO_3{-}N_{t0} = \text{excess } N_2 + cNO_3^-{-}N + cN_2O{-}N \tag{5}$$

"Reaction progress" (RP) is the ratio between products and starting material of a process and can be used to characterize the extent of NO_3^- elimination by denitrification (Böhlke, 2002). RP is generally correlated with excess N_2 in denitrifying aquifers and is calculated as follows:

$$RP = \frac{\text{excess } N_2 + cN_2O{-}N}{cNO_3{-}N_{t0}} \tag{6}$$

"Emission factors" (EF) for indirect N_2O emission from the aquifer resulting from N-leaching were calculated as described earlier (Well et al., 2005a). Because $cNO^-_{3\,t0}$ represents the N-input to the aquifer via leaching, our data set is suitable to calculate an EF(1) from the relationship between N_2O emission and N input, which is the ideal concept of emission factors (see introduction):

$$EF(1) = \frac{cN_2O{-}N}{cNO_3{-}N_{t0}} \tag{7}$$

Furthermore, we will compare EF(1) with the ratio of cN_2O-N to cNO_3^--N (EF(2)), which was used by the IPPC methodology (1997) to derive EF5-g. 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 NO_3^- and N_2O (Well et al., 2005a, see introduction). The comparison between EF(1) and EF(2) will demonstrate potential errors in predicting indirect N_2O emission from denitrifying aquifers using EF(2).

3 Results

3.1 Basic groundwater properties, controlling factors O_2 and pH

Basic groundwater properties of the investigated aquifers are shown in Table 1. Groundwater temperatures were relatively constant at 10°C. The pH and O_2 concentrations of the groundwater were more variable, suggesting heterogenous conditions for denitrification and N_2O accumulation. The ranges of O_2 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.

3.2 Excess N_2, actual and initial NO_3^- concentrations

Ranges and site medians of reaction progress and excess N_2 are given in Table 2. Lowest values for excess N_2 coincided with RP of approximately 0. A RP of approximately 1 was characterized by high values of excess N_2 in all aquifers. In all aquifers, samples cover almost the complete range of RP. Highest excess N_2 values were observed at Thülsfelde, which were twice the values of the other sites. At the drinking water well of the Fuhrberg catchment, NO_3^- and N_2O concentrations were negligible and excess N_2 was 12.9 mg N L^{-1}, which results in RP of 1. This shows that denitrification is complete within the Fuhrberg aquifer.

Measured NO_3^- concentrations were highest in the aquifers of Fuhrberg and Sulingen with median values of 8.51 and 9.26 mg N L^{-1}, respectively. In Thülsfelde and Göttingen measured NO_3^- concentrations were significantly lower (Table 2). Calculated initial NO_3^- concentrations ($NO^-_{3\,t0}$, Eq. 5) were significantly higher than measured NO_3^- concentrations (Table 2), especially in the aquifer of Thülsfelde. The difference between measured NO_3^- concentrations and $NO^-_{3\,t0}$ demonstrates that NO_3^- consumption by denitrification was an important factor in all investigated aquifers.

3.3 N_2O concentrations and emission factors

Wide ranges of N_2O concentrations were observed in all aquifers (Fig. 1, Table 2). Highest concentrations up to 1271 μg N_2O-N L^{-1} were measured in shallow groundwater at the Fuhrberg site at a RP of 0.3.

Emission factors EF(1) and EF(2) were highly variable (Table 3). Their medians for the complete data set were 0.00081 and 0.0031, respectively. Thus, EF(2) was in very good 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 each aquifer, EF(2) was substantially higher than EF(1). Within 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). For both EFs, we determined highest values for the Fuhrberg aquifer and lowest for the aquifer of Göttingen (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.

N_2O concentrations followed a rough pattern during RP. Values were lowest at the beginning (RP close to 0) and at the end (RP close to 1) but relatively high at a RP between 0.2 and 0.6 (Fig. 1). The same pattern was found for EF(1), which is strongly correlated to N_2O concentrations (Table 4). However, at each RP we observed a relatively wide range of N_2O concentrations and EF(1).

4 Discussion

4.1 Uncertainty of excess N_2 estimates and excess N_2 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., 2008). Although Heaton and Vogel (1981) 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 (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. Therefore, we used the means of minimum and maximum values for excess N_2 as a possible 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 minimum and maximum estimates. The uncertainty connected with this procedure is documented in Fig. 2, where “excess N_2 min” and “excess N_2 max” denote minimum and maximum estimates for excess N_2, respectively. Derived from the whole data set shown in Fig. 2, the mean difference between minimum and maximum estimates for excess N_2 is 1.25 mg N L^{-1} and the mean of the maximum errors is thus 0.63 mg N L^{-1}. According to Eq. (5), these error values are also valid for $NO^-_{3\,t0}$. Using the uncertainty of excess N_2 and $NO^-_{3\,t0}$ we also estimated the uncertainty of RP (Eq. 6), giving 0.008 for the mean of the maximum errors. This shows that the uncertainty of RP has only little implication of our conclusion that maximum N_2O concentrations occured at RP between 0.2 and 0.6 and for the relationship between RP and emission factors shown in Fig. 3. From Eq. (7) it follows that the relative error of EF(1) is equal to the relative error in $NO^-_{3\,t0}$, giving 4.8% for the median $NO^-_{3\,t0}$ of 13.15 mg N L^{-1}. In view of the large range of EF(1) (Table 3) this uncertainty is small. Therefore, it can be concluded that the consequences of uncertainties connected with excess N_2 and $NO^-_3 t_0$ 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, N_2, O_2, CO_2, and CH_4) exceeds that of the hydrostatic pressure. This phenomenon was found when high denitrifying activity induced production of excess N_2 in shallow groundwater of riparian ecosystems (Blicher-Mathiesen et al.,1998; Mookherji et al., 2003). In our study, the sum of partial pressures never exceeded hydrostatic pressure which is in part due to the fact, that the majority of data originates from deeper groundwater (Table 1) where hydrostatic pressure is higher than in upper groundwater. These conditions prevent degassing of gaseous denitrification products. Water samples from shallow groundwater, where the risk of degassing is higher due to lower hydrostatic pressure, were only taken from the Fuhrberg site. Unlike the observations of Blicher-Mathiesen et al. (1998) and Mookherji et al. (2003) excess N_2 in the shallow groundwater measured in this study was relatively low and hydrostatic pressure was thus not exceeded by accumulation of dissolved gases.

The fact that calculation of initial NO^-_3 concentration is based on excess N_2 implies a need for quantitative estimates of excess N_2 in order to determine EF(1) accurately. But it also involves the possibility to validate excess N_2 in cases where $NO^-_{3\,t0}$ is known.

An approximate validation can be obtained for the Fuhrberg aquifer, because average NO_3^- concentration at the groundwater surface had been determined by modeling NO_3^- leaching in the Fuhrberg catchment (Strebel and Böttcher, 1985) giving 13 mg N L^{-1}. Although these data were derived from NO_3^- concentrations approx. 20 to 30 years ago, it can be assumed that they are comparable to mean $NO^-_{3\,t0}$ of the aquifer because the modeled average groundwater residence time for the Fuhrberg aquifer is 40–45 years (Böttcher et al., 1985; Duijnisveld et al., 1993). Furthermore, our recent data indicate that the mean NO_3^- concentrations in the seepage water of the arable soils in the Fuhrberg catchment did not change substantially since the 1980s, because the actual NO_3^- concentration of the uppermost groundwater in the present study was only 8% lower compared to NO_3^- concentrations of the seeapage water of arable soils given by Strebel and Böttcher (1985). Consequently, the average $NO^-_{3\,t0}$ within the whole aquifer should be still close to the 1985 modeled mean NO_3^- concentration of the seepage water. $NO^-_{3\,t0}$ values close to this should therefore be found at the drinking water well which delivers mixed waters of the entire catchment. At the investigated drinking water well, the mean value of $NO^-_{3\,t0}$ was 12.9 mg N L^{-1} (mean value of 4 sampling events). The coincidence of these data with the modeled mean of the past seepage water concentration of 13 mg N L^{-1} further support our assumption that excess N_2 is a valid estimate of denitrification during the groundwater flow path and that $NO^-_{3\,t0}$ and EF(1) were thus reliably estimated.

4.2 Regulating factors of denitrification and N_2O accumulation

Information on the process dynamics in the investigated aquifers can be obtained from the relationships between parameters of denitrification and N_2O accumulation and their regulating factors. Within the whole data set, sampling depth exhibited significant positive correlations with RP and significant negative correlations with NO_3^- (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. These relationships and additional significant positive correlations between sampling depth and excess N_2 were mostly pronounced in the partial 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 which implies that the relationship between reaction progress and residence time was more variable. A significant negative correlation between NO_3^- and excess N_2 in the whole data-set (R_S=−0.37, Table 4) demonstrates that denitrification was an important factor for NO_3^- variability within all aquifers.

With increasing NO_3^- concentration the N_2O-to-N_2 ratio may strongly increase (Kroeze et al., 1989) because NO_3^- usually inhibits N_2O reduction to N_2 (Blackmer and Bremner, 1978; Cho and Mills, 1979). This is confirmed by the positive correlation between N_2O and NO_3^- we evaluated in this study (Table 4). A significant negative correlation was found between N_2O 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). N_2O accumulation in aquifers might be supported by increasing groundwater acidity because the reduction step of N_2O to N_2 is much more sensitive to acidic conditions compared to the preceding reduction steps (Granli and Bøckman, 1994). This regulation is illustrated by the negative correlation between pH and N_2O in our study. The influence of pH on the N_2O/N_2 ratio is intensified by high NO_3^- concentrations (Blackmer and Bremner, 1978; Firestone et al., 1980). Due to these observations we conclude that conditions were especially favourable for N_2O accumulation and potential N_2O emission in shallow groundwater of the Fuhrberg aquifer, because it is characterized by high NO_3^- contamination and comparatively low pH. This is confirmed by our data since N_2O concentrations of these samples were highest within the entire data-set.

4.3 Potential indirect N_2O emissions from groundwater estimated from initial NO_3^- concentration

Unlike emission factors determined from measured fluxes across the soil surface, emission factors estimated from groundwater concentration do not reflect the actual N_2O emission from the system because the amount of dissolved N_2O might increase or decrease during further residence time in the aquifer or during the passage of the unsaturated zone before it reaches the atmosphere. Moreover, diffusive N_2O emission from the aquifer surface to the unsaturated zone and eventually to the atmosphere (Deurer et al., 2007) is not taken into account by EF(1). Therefore, the measured data supply only potential emission factors quantifying the amount of N_2O 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 N_2O flux from the investigated aquifers requires validated models of reactive N_2O transport. Further research on reaction dynamics and gas transport within the aquifers is needed to achieve this.

However, the comparison of N_2O concentration and EF(1) with RP gives a rough sketch of the principal N_2O pattern during groundwater transport through denitrifying aquifers. Although variations of N_2O and EF(1) at any given level of RP was high, there was a clear tendency of low N_2O concentrations for RP close to zero or close to 1 and highest N_2O concentrations at RP between 0.2 and 0.6. This pattern is consistent with the time course of N_2O 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 N_2O during a Michaelis-Menten reaction kinetics. It can be concluded that RP can be considered as an important parameter to predict N_2O emission via groundwater discharge. This emission can be expected to be negligible if RP at groundwater discharge is very small or close to 1. Conversely, relatively high emission can be expected if RP at groundwater discharge is between 0.2 and 0.6. The observed relationship suggests, that emission

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factors are also related to denitrification rate, groundwater residence time and sampling depth because these quantities determine the reaction progress. This could be helpful to predict or interpret N_2O emission from different types of groundwater systems. For example, low N_2O 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 NO_3^- and low N_2O concentration reflect the typical low emission factors at RP close to 1. Hot spots of N_2O emission from groundwater might be locations were groundwater is discharged to surface waters immediately after partial NO_3^- 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 N_2O 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 NO_3^- 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. 3 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 NO_3^- during groundwater passage into account. Consequently, potential N_2O emissions from aquifers should be estimated using EF(1) rather than EF(2).

5 Conclusions

In the investigated aquifers, NO_3^- consumption by denitrification could be estimated from excess N_2 as determined from dissolved N_2 and Ar. This enabled calculation of initial NO_3^- concentration at the groundwater surface by adding up concentrations of NO_3^-, N_2O and excess N_2. Because this initial NO_3^- concentration reflects the N input to the groundwater by leaching it was used to calculate an emission factor EF(1) for indirect agricultural N_2O emissions from groundwater which is for the first time based on the ratio between N_2O concentration and N-input. An uncertainty of excess N_2 estimates according to the excess air phenomenon was found to be negligible for this concept of EF(1). EFs(1) in the investigated denitrifying aquifers were much lower than the values resulting from the earlier concept of groundwater emission factors consisting of N_2O-to-NO_3^- ratios of groundwater samples (EF(2) in this study). This demonstrates the need to take past NO_3^- 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 N_2O flux from the investigated aquifers because spatial und temporal heterogeneity of N_2O concentrations was high and further metabolism of N_2O during transport in the aquifer and through the unsaturated zone before it is emitted is poorly understood.

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Table 1. General properties for the aquifers of Fuhrberg, Wehnsen, Sulingen, Thülsfelde and Göttingen.

Site (number of samples/wells)	Thickness of the aquifer body [m]	Hydraulic active sediment	Sampling depth (m below groundwater surface)	pH	O_2 [mg L^{-1}]	Temp [°C]
Fuhrberg (80/7)	20–35	sand	0.1–27.0	3.7–6.6	0–10.2	n.d.
Sulingen (30/2)	20–30	sand	8.5–63.0	4.6–6.7	0.2–13.6	10.3*
Thülsfelde (19/4)	150	sand	1.7–35.4	4.3–5.8	0.1–8.8	10.1*
Göttingen (25/6)	5–10	gravel	4.0–23.5	6.8–7.9	0.6–11.7	9.8*

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

Table 2. Excess N_2, N_2O, NO_3^-, and $NO^-_{3\,t0}$ concentrations and reaction progress of denitrification (RP) of the investigated aquifers.

site		excess N_2 [mg N L^{-1}]	N_2O [μg N L^{-1}]	NO_3^- [mg N L^{-1}]	$NO^-_{3\,t0}$ [mg N L^{-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

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Table 3. Emission factors EF(1) and EF(2) of the investigated aquifers. EF(1) was determined as the ratio of $N_2O/NO_{3\,t0}^-$ concentrations with $NO_3^- t_0$ as initial NO_3^- concentration. EF(2) was determined as the ratio of N_2O/NO_3^- concentrations with NO_3^- as actual NO_3^- 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.

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

	depth	N_2O	NO_3^-	excess N_2	$NO^-_{3\,t0}$	RP	EF(1)	EF(2)	pH
N_2O	−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.

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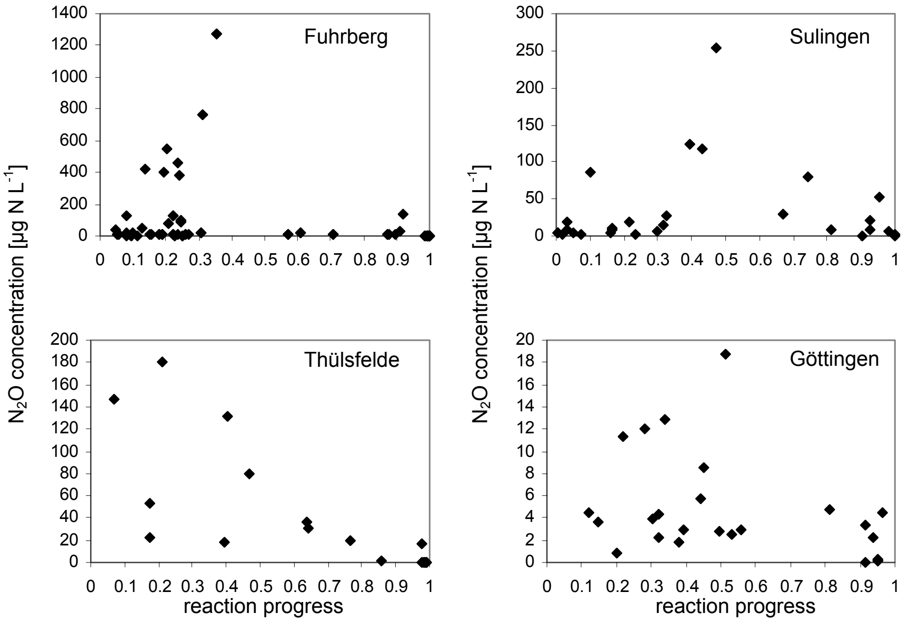

Fig. 1. N_2O in groundwater samples from 4 different aquifers in relation to reaction progress. Reaction progress is the ratio between denitrification products (excess N_2+N_2O) and initial NO_3^-.

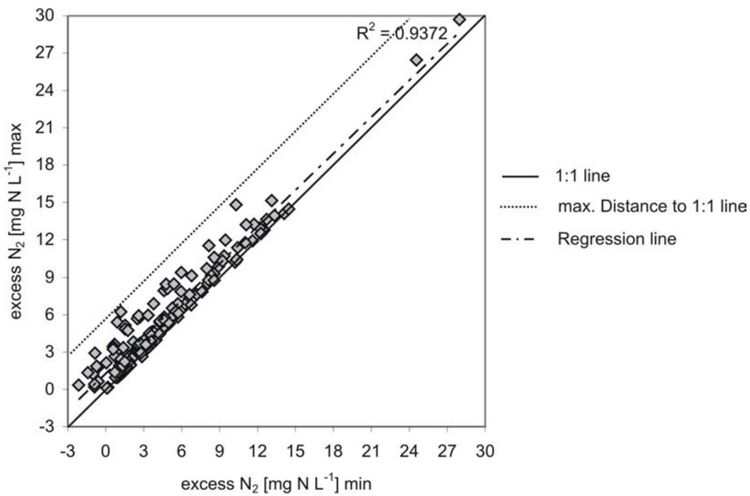

Fig. 2. Minimum and maximum estimates of excess N_2 for the whole data set as calculated using Eqs. (1) and (2) or (1) and (3), respectively.

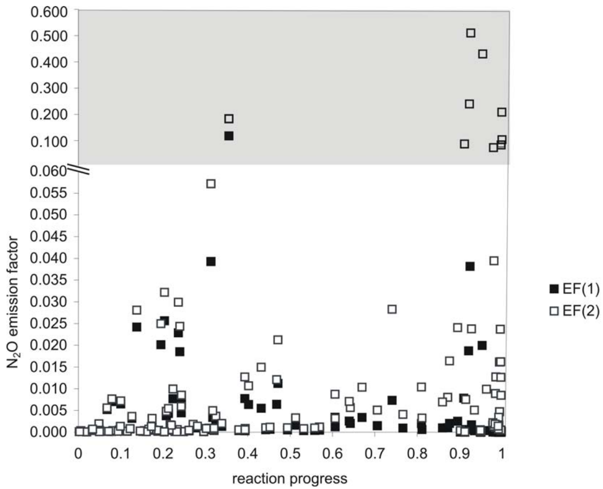

Fig. 3. N_2O emission factors EF(1) and EF(2) of the investigated aquifers in relation to reaction progress (ratio between denitrification products and initial NO_3^-) and compared to IPCC default EF5-g. EF(1) was determined as the ratio of N_2O-N /NO_3^--N_{t0} with NO_3^--N_{t0} as initial NO_3^- concentration. EF(2) was determined as the ratio of N_2O-N/NO_3^--N with NO_3^--N as actual NO_3^- concentration.