

Nitrous Oxide in denitrifying Aquifers:
Reaction Kinetics, Significance of Groundwater-derived Emission
and an improved Concept
for the Groundwater Emission Factor

Dissertation

zur Erlangung des akademischen Grades Doctor of Philosophy (PhD)
der Fakultät für Forstwissenschaften und Waldökologie
der Georg-August-Universität Göttingen

vorgelegt von

Diplom Geoökologe Daniel Weymann

geboren in Erfurt

Göttingen, April 2009

1. Gutachter: Prof. Dr. Heiner Flessa
2. Gutachter: Prof. Dr. Jürgen Böttcher

Tag der mündlichen Prüfung: 25.06.2009

“What becomes of the nitrate? One can hardly assume that the formation of nitrate is a recently acquired trick of nature or that not enough time has elapsed for water in the outcrop to move down to depths of several hundreds of feet. It must necessarily be assumed that something happens to the nitrate in transit.”

(George and Hastings 1951)

Table of contents

Table of contents	i
List of Figures	iii
List of Tables	v
Danksagung	vii
Abstract	ix
Kurzfassung	xi
Preface and Outline	xiii
1 General Introduction	1
1.1 Nitrous oxide as a driver of climate change	1
1.2 Denitrification in groundwater	2
1.3 Emissions of N ₂ O from groundwater	4
1.4 Objectives of this thesis	5
2 Kinetics of N ₂ O production and reduction in a nitrate-contaminated aquifer inferred from laboratory incubation experiments	7
2.1 Introduction	7
2.2 Study site	8
2.3 Materials and methods	10
2.4 Results	14
2.5 Discussion	24
2.6 Interim conclusions	29
2.7 Summary of the chapter	30
3 Recovery of groundwater N ₂ O at the soil surface and its contribution to total N ₂ O emissions	33
3.1 Introduction	33
3.2 Materials and Methods	35
3.3 Results	40
3.4 Discussion	46
3.5 Interim conclusions	49
3.6 Summary of the chapter	49
4 Groundwater N ₂ O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N ₂ O accumulation	51
4.1 Introduction	51
4.2 Materials and Methods	52
4.3 Results	58
4.4 Discussion	64
4.5 Interim conclusions	68
4.6 Summary of the chapter	68

5	Synthesis and general conclusions	71
5.1	Specific characteristics of denitrification and N ₂ O accumulation in the Fuhrberger Feld aquifer	71
5.2	Occurrence of N ₂ O in groundwater	73
5.3	Significance of indirect N ₂ O emissions	73
5.4	Assessment of the groundwater N ₂ O emission factor	75
5.5	Future research and perspectives	76
6	References	79
	Curriculum vitae	91

List of Figures

Figure 1.1:	a: Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO ₂ -eq. (Forestry includes deforestation) and b: Share of anthropogenic GHGs in total emissions in 2004 in terms of CO ₂ -eq. Figure according to IPCC (2007)	1
Figure 1.2:	Turnover of N ₂ O during nitrification and denitrification (“hole-in-the-pipe-model”), according to Davidson (1991).	2
Figure 2.1:	Vertical concentration gradients of N ₂ O, NO ₃ ⁻ and SO ₄ ²⁻ at the wells B1 and I1. The data of well B1 are mean values of three sampling events, the error bars denote the standard deviation.	15
Figure 2.2:	Concentration courses of —◆— N ₂ O —◆— N ₂ O+N ₂ —□— NO ₃ during long-term anaerobic incubation of aquifer material from the heterotrophic denitrification zone.	16
Figure 2.3:	Concentration courses of —◆— N ₂ O —◆— N ₂ O+N ₂ —□— NO ₃ during long-term anaerobic incubation of aquifer material from the autotrophic denitrification zone.	17
Figure 2.4:	Comparison between experimental N ₂ O- (A), (N ₂ O+N ₂)- (B), and NO ₃ ⁻ (C) concentrations (solid circles) and fitting curves (thick solid line: sequential 3-parameter fit; thin solid line: 1-step 3-parameter fit; dashed line: sequential 2-parameter fit) for the data set II-S1 2.0 - 2.5 (heterotrophic denitrification).	23
Figure 3.1:	Measuring field with its elements and dimensions.	36
Figure 3.2:	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.	41
Figure 3.3:	NO ₃ ⁻ -N concentrations (A) and ¹⁵ N enrichment of NO ₃ ⁻ (B) in the surface groundwater.	42
Figure 3.4:	N ₂ O fluxes at the soil surface measured in static flux chambers after an enrichment time of 60 min (A), N ₂ O concentration in the soil atmosphere in 0.3, 0.6 and 0.9 m depth below the soil surface (B) and dissolved N ₂ O concentration in the surface groundwater in 1.5, 1.6 and 1.7 m depth below soil surface (C)	43
Figure 3.5:	¹⁵ N enrichment of N ₂ O: (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.	44
Figure 4.1:	Lowest (<i>excess N₂ min</i>) and upper (<i>excess N₂ max</i>) estimates of excess N ₂ for the whole data set as calculated using eqs. (1) and (2) or (1) and (3), respectively.	59
Figure 4.2:	Vertical distribution of (A) excess N ₂ , (B) N ₂ O concentrations (log scaled) and (C) actual NO ₃ ⁻ concentrations in the investigated aquifers.	61
Figure 4.3:	N ₂ O in groundwater samples from 4 different aquifers in relation to reaction progress. Reaction progress is the ratio between denitrification products (excess N ₂ + N ₂ O) and initial NO ₃ ⁻ .	62
Figure 4.4:	N ₂ O 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.	64

Figure 5.1:	Concentration gradients of N_2O , NO_3^- and SO_4^{2-} reveal the zones of denitrification and N_2O accumulation in the Fuhrberger Feld aquifer.	72
-------------	---	-----------

List of Tables

Table 2.1:	Location and basic properties of the investigated aquifer materials.	10
Table 2.2:	Maximum N_2O concentrations ($c\text{N}_2\text{O}_{\text{max}}$), $c\text{N}_2\text{O}_{\text{max}}$ -to- $(\text{N}_2\text{O}+\text{N}_2)$ ratio and denitrification rates (D_i , D_{max}) during anaerobic incubation	18
Table 2.3:	Spearman rank correlation coefficients between the variables within the heterotrophic and the autotrophic data-set.	20
Table 2.4:	Rate constants for heterotrophic and autotrophic denitrification derived from the sequential 3-parameter fit. $R^2(k_1)$ and $R^2(k_2)$ denote the correlation coefficients for the $(\text{N}_2\text{O}+\text{N}_2)$ -data and the N_2O -data, respectively.	21
Table 2.5:	Rate constants for heterotrophic and autotrophic denitrification derived from the 1-step 3-parameter fit. R^2 denotes the correlation coefficient.	22
Table 3.1:	Mass of groundwater-derived N_2O emitted at the soil surface and calculated emission rate of groundwater-derived N_2O from the groundwater to the atmosphere	46
Table 4.1:	General properties for the aquifers of Fuhrberg, Sulingen, Thülsfelde and Göttingen.	53
Table 4.2:	Excess N_2 , N_2O , NO_3^- , and $\text{NO}_3^-_{10}$ concentrations and reaction progress of denitrification (RP) of the investigated aquifers.	60
Table 4.3:	Emission factors EF(1) and EF(2) of the investigated aquifers.	63
Table 4.4:	Spearman rank correlation coefficients between all variables for the full data-set.	66

Danksagung

Mein besonderer Dank gilt PD Dr. Reinhard Well, der diese Arbeit nicht nur mitinitiiert, sondern auch von Beginn an sehr engagiert betreut hat und mich stets förderte. Einen Großteil meines Wissenszuwachses während der letzten Jahre verdanke ich ihm und seiner wissenschaftlichen Begleitung.

Herrn Prof. Dr. Heiner Flessa danke ich für die Übernahme des ersten Gutachtens und die vielen hervorragenden Ratschläge, die diese Arbeit maßgeblich prägten, aber auch für die Förderung meines wissenschaftlichen Werdeganges.

Für die Übernahme des Koreferates sowie für die engagierte Koordination des DFG-Projektes, in dem diese Arbeit entstand, möchte ich mich ganz herzlich bei Prof. Dr. Jürgen Böttcher bedanken.

Für zahlreiche Diskussionen, Anregungen und die unkompliziert-motivierende Zusammenarbeit danke ich ganz besonders Dr. Carolin von der Heide, weiterhin Dr. Markus Deurer, Dr. Wim Duijnsveld, Prof. Dr. Klaus Schäfer und Dr. Danny Eisermann. Herrn Prof. Dr. Helmut Geistlinger bin ich für seine Anleitung im Bereich der Modellierung zu besonderem Dank verpflichtet.

Ganz besonders herzlich bedanke ich mich bei den MitarbeiterInnen der Abteilung Agrarpedologie des DNPW der Universität Göttingen für die enorme Unterstützung bei den Laborarbeiten und während besonders arbeitsintensiver Phasen sowie für die vielen „täglichen“ Dinge, deren Aufzählung diesen Rahmen sprengen würden. So danke ich dem Leiter der Abteilung, Dr. Christian Ahl, für die unkomplizierte Überlassung vieler Ressourcen. Mit Ingrid Ostermeyer und Karin Schmidt standen mir zwei außergewöhnlich engagierte Kolleginnen zur Seite, deren Unterstützung und Elan ich gar nicht genug würdigen kann. Beiden möchte ich an dieser Stelle sehr herzlich danken.

Den MitarbeiterInnen des Kompetenzzentrums für Stabile Isotope an der Universität Göttingen unter der Leitung von Dr. Jens Dyckmans sei für die vielen Analysen gedankt, ohne die diese Arbeit nicht möglich gewesen wäre.

Weiterhin haben Dr. Peter Gernandt, Bianca Ziehmer, Maria Mundry, Julia-Sophie Obentheuer, Anita Kriegel, Kerstin Jespersen, Florian Trienen, Gunther Klump und Gerhard Benseler an verschiedenen Stellen zu dieser Arbeit beigetragen, wofür ich mich ebenfalls bedanken möchte.

Schließlich möchte ich meinen Eltern für ihre Unterstützung danken. Meiner Freundin Barbara Wagner danke ich ganz besonders für ihr Verständnis, ihre Lebendigkeit und für die Unterstützung und Motivation, die sie mir vor allem in der Endphase dieser Dissertation entgegen gebracht hat.

Abstract

Beside carbon dioxide and methane, the atmospheric trace gas nitrous oxide (N_2O) is a major greenhouse gas. It is predominantly produced in soils and aquatic systems during microbiological processes. Global N_2O emissions have been substantially increased due to the intensification of agricultural practices and the related inputs of nitrogen compounds. High N_2O concentrations were found in the groundwater of agricultural ecosystems. Thus, agricultural groundwater is assumed to be a potential source of N_2O emissions into the atmosphere.

The significance of N_2O emissions from agricultural groundwater is the key question of this thesis. First, this key question is introduced in a preliminary chapter. In the following three chapters, different methods and approaches are described and discussed in order to provide knowledge of different aspects of the topic. Finally, these findings are assessed within the scope of a final synthesis and general conclusions are drawn.

Research activities were conducted within four denitrifying aquifers in Lower Saxony, but the Fuhrberger Feld aquifer situated close to the city of Hannover was the main study site. In all investigated aquifers, the input of nitrate-contaminated agricultural seepage water causes elevated nitrate concentrations at the groundwater table. This nitrate is reduced during denitrification, yielding N_2O as an intermediate and finally dinitrogen.

The kinetics of N_2O production and reduction in the Fuhrberger Feld aquifer was investigated during long-term anaerobic incubations. The results were compared with concentration profiles obtained from multilevel well measurements (chapter 2). It was confirmed that two vertically separated denitrification zones exist within the aquifer, heterotrophic denitrification in the surface groundwater and autotrophic denitrification in the deeper aquifer and both reactions were identified to be a significant source for N_2O . The time courses of the N-species obtained from the laboratory incubations showed that heterotrophic denitrification is kinetically much slower than the autotrophic process. This was quantitatively proven by derived reaction rate constants following first order kinetics and attributed to the different microbial bioavailability of the associated electron donors, i.e. organic carbon and reduced sulfur compounds. The field measurements revealed considerable N_2O accumulation in both denitrification zones, e.g. the mean N_2O concentration close to the water table at one of the investigated wells was $1.84 \text{ mg N}_2\text{O-N L}^{-1}$. The N_2O concentration profiles enabled a further refinement of the existing process model of denitrification in the Fuhrberger Feld aquifer.

Within the scope of a ^{15}N field experiment it was investigated to what extent groundwater-derived N_2O emissions occurring via the vertical emission pathway contribute to total N_2O emissions at the soil surface. This approach was based on stable labeling of the groundwater surface during the entire measuring period with K^{15}NO_3 tracer solution. ^{15}N -labeled N_2O was produced during denitrification and could be measured within the system groundwater / unsaturated zone / soil surface. Fluxes of groundwater-derived N_2O were

very low and found to be between 0.0002 und 0.0018 kg N₂O-N ha⁻¹ year⁻¹. Only 0.13 % of the total positive N₂O fluxes at the soil surface originated from groundwater-derived N₂O. This showed that groundwater N₂O emissions occurring via the vertical pathway are negligible in the Fuhrberger Feld aquifer.

Determination and assessment of emission factors for indirect N₂O emissions from agricultural groundwater was a further main objective of this thesis. A new emission factor basing on reconstructed “initial” nitrate concentrations was introduced. Thus, the concept relates potential N₂O emission to the input of nitrogen to the groundwater surface. The application of this concept yielded emission factors that were considerably lower than conventional emission factors derived from the ratio between N₂O concentrations and measured nitrate concentrations. This showed the necessity to take initial nitrate concentrations for calculating the groundwater N₂O emission factor into account. The reaction kinetics as well as the evaluated rate constants (chapter 2) could be a basis for modeling the reactive transport of N₂O and may contribute to further improve the emission factor for indirect N₂O emissions from agricultural groundwater.

Summarizing the results, it can be underlined for the investigated aquifers that N₂O produced in groundwater is hardly reaching the atmosphere and thus contributes to a very low extent to total emissions of the greenhouse gas.

Kurzfassung

Das atmosphärische Spurengas Distickstoffoxid (N_2O) zählt neben Kohlendioxid und Methan zu den wichtigsten klimarelevanten Gasen. Es wird überwiegend durch mikrobiologische Prozesse in Böden sowie in aquatischen Ökosystemen gebildet. Durch die Intensivierung der landwirtschaftlichen Nutzung und die damit verbundenen Stickstoffeinträge sind die globalen N_2O -Emissionen beträchtlich gestiegen. Im Grundwasser agrarisch genutzter Ökosysteme wurden hohe Konzentrationen an gelöstem N_2O gefunden, weshalb es als potentielle Quelle für N_2O -Emissionen in die Atmosphäre angesehen wird.

Die Bedeutung grundwasserbürtiger N_2O -Emissionen ist die der vorliegenden Arbeit zugrunde liegende zentrale Problemstellung. Diese wird zunächst in einem einleitenden Kapitel konkretisiert. In den folgenden drei Kapiteln werden verschiedene methodische Ansätze beschrieben und diskutiert, die sich der Problematik auf unterschiedliche Weise nähern. Abschließend werden die Einzelergebnisse im Rahmen einer zusammenfassenden Diskussion bewertet und allgemeine Schlussfolgerungen gezogen.

Die Forschungsarbeiten wurden in vier niedersächsischen, reduzierenden Grundwasserleitern durchgeführt, wobei dem Fuhrberger Feld bei Hannover die größte Bedeutung zukam. Allen Untersuchungsgebieten ist gemein, dass als Folge der landwirtschaftlichen Nutzung Nitrat über das Sickerwasser in das Grundwasser eingetragen und über den Prozess der Denitrifikation zu N_2O und elementarem Stickstoff reduziert wird.

Um die Kinetik des N_2O -Umsatzes im Grundwasser des Fuhrberger Feldes zu erfassen, wurden im Labor Langzeit-Inkubationsversuche durchgeführt, deren Ergebnisse mit im Feld gemessenen Konzentrationsprofilen verglichen wurden (Kapitel 2). Es wurde bestätigt, dass im Aquifer - scharf vertikal voneinander abgegrenzt - heterotrophe Denitrifikation im oberflächennahen Grundwasser abläuft und autotrophe Denitrifikation im tieferen Grundwasser dominiert, wobei beide Reaktionen als N_2O -Quelle identifiziert wurden. Die im Zuge der Laboruntersuchungen ermittelten Zeitverläufe der N-species zeigten, dass die heterotrophe Denitrifikation kinetisch gesehen der deutlich langsamere Prozess ist. Dies wurde durch die Ableitung von Ratenkonstanten quantitativ untermauert und auf die unterschiedliche mikrobielle Verfügbarkeit der jeweiligen Elektronendonatoren, organischer Kohlenstoff und reduzierte Schwefelverbindungen, zurückgeführt. Die Feldmessungen zeigten, dass in beiden Prozesszonen N_2O in beträchtlichem Umfang akkumuliert wurde. So betrug beispielsweise die mittlere Konzentration nahe der Grundwasseroberfläche an einer der untersuchten Messstellen $1.84 \text{ mg } \text{N}_2\text{O-N L}^{-1}$. Durch die Berücksichtigung der N_2O -Konzentrationsprofile konnte das bestehende Prozessmodell der Denitrifikation im Fuhrberger Feld konkretisiert werden.

Im Rahmen eines ^{15}N -Feldexperimentes wurde untersucht, inwieweit grundwasserbürtiges N_2O über den vertikalen Emissionspfad zur an der Bodenoberfläche gemessenen

Gesamtemission beiträgt. Grundlage des Versuchs war die über den gesamten Versuchszeitraum hinweg stabile Markierung der Grundwasseroberfläche mit K^{15}NO_3 -Lösung. Das durch Denitrifikation gebildete markierte N_2O konnte im System Grundwasser / ungesättigte Zone / Bodenoberfläche gemessen werden. Die ermittelten Flüsse des grundwasserbürtigen N_2O waren sehr gering und lagen zwischen 0.0002 und 0.0018 $\text{kg N}_2\text{O-N ha}^{-1} \text{ a}^{-1}$. Dies entspricht einem Anteil von durchschnittlich 0.13 % an der Gesamtemission von N_2O in die Atmosphäre und macht deutlich, dass N_2O -Emissionen aus dem oberflächennahen Grundwasser des Fuhrberger Feldes über den vertikalen Transportpfad vernachlässigbar klein sind.

Die Bestimmung und Bewertung von Emissionsfaktoren für indirekte N_2O -Emissionen aus dem Grundwasser war ein weiterer Schwerpunkt dieser Arbeit. Es wurde ein neuer Emissionsfaktor vorgestellt, dessen Konzept durch die Einbeziehung rekonstruierter, „initialer“ Nitratkonzentrationen potentielle N_2O -Emissionen auf den Stickstoffeintrag bezieht. Die Anwendung dieses Konzeptes lieferte für die vier Untersuchungsgebiete Emissionsfaktoren, die deutlich geringer waren als herkömmliche, auf der Grundlage gemessener Nitratkonzentrationen berechnete Emissionsfaktoren. Die in Kapitel 2 untersuchte Reaktionskinetik und die ermittelten Ratenkonstanten können als Basis für eine reaktive Transportmodellierung dienen, die zur weiteren Verbesserung der Aussagekraft von Emissionsfaktoren beitragen kann.

Zusammenfassend kann für die hier untersuchten norddeutschen Aquifere festgehalten werden, dass grundwasserbürtiges N_2O nur in sehr geringem Maße in die Atmosphäre gelangt und somit kaum zur Gesamtemission des klimarelevanten Spurengases beiträgt.

Preface and Outline

This thesis was composed at the department of Soil Science of Temperate and Boreal Ecosystems of the University of Göttingen within the sub-project “Nitrous oxide transformations, fluxes and its controlling factors with respect to controlled and natural aquifer conditions”. The research was embedded in the joint project “Transport and transformation processes of nitrous oxide in the system groundwater / unsaturated zone / atmosphere” and was funded by the German Research Foundation (DFG). Beside the group of the University of Göttingen, further participants were researchers from the Leibniz University of Hannover (group leader: Prof. Dr. Jürgen Böttcher), the Helmholtz Centre for Environmental Research in Halle (group leader: Prof. Dr. Helmut Geistlinger) and - associated - the Forschungszentrum Karlsruhe, Institute for Meteorology and Climate Research in Garmisch-Partenkirchen (group leader: Prof. Dr. Klaus Schäfer).

Research activities were conducted within the Fuhrberger Feld aquifer in Lower Saxony, Germany. Moreover, three further aquifers of Lower Saxony were investigated by the Göttingen group and the cooperation partners Gerres Ingenieure GmbH (Dr. Knut Meyer) and the Dresden Technical University (Prof. Dr.-Ing. em. Wolfgang Walther).

The thesis starts with a general introduction (chapter 1) that will impart knowledge of the climate-relevant trace gas nitrous oxide and its main source process in groundwater, the denitrification. Furthermore, the reader will gain insight into indirect emission of nitrous oxide and will finally get information about the objectives of the thesis. In chapter 2, a laboratory approach is introduced, focusing on the kinetics of production and reduction of nitrous oxide during heterotrophic and autotrophic denitrification in the Fuhrberger Feld aquifer. This chapter also includes an introduction of the study site and gives a survey about recent research progress in denitrification and nitrous oxide in the groundwater of the research area. An in-situ tracer experiment is described in chapter 3. The approach enables tracing nitrous oxide that was produced in the surface groundwater throughout the system groundwater / unsaturated zone / soil surface and reveals the contribution of groundwater-derived nitrous oxide to the total nitrous oxide emission into the atmosphere. Chapter 4 includes investigations into all of the four denitrifying aquifers. It focuses on accumulation of nitrous oxide during different stages of the denitrification progress. Moreover, it suggests an improved method for calculating the emission factor for indirect nitrous oxide emission from groundwater by taking the initial nitrate concentration at the groundwater surface into account. Finally, against the background of the results achieved within the previous chapters, general conclusions are derived forming a synthesis.

1 General Introduction

1.1 Nitrous oxide as a driver of climate change

As the Intergovernmental Panel on Climate Change (IPCC) stated forcefully in the 2007 Climate Change Synthesis Report, warming of our climate system is unequivocal. This has been proven by numerous of scientific studies revealing increases in global average air and ocean temperatures, widespread melting of snow and ice and rising of the global average sea level (IPCC 2007). A crucial parameter governing climate changes is the balance of incoming and outgoing energy in the Earth-atmosphere system. This balance is again affected by the major long-lived greenhouse gases (GHGs) carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), because they are known to absorb outgoing radiation. Since global anthropogenic GHG emissions have increased by 70 % between 1970 and 2004, GHGs are considered to cause a positive radiative forcing of the climate system what tends to warm the atmosphere (IPCC 2007). The sectoral sources of GHGs are shown in Figure 1.1a.

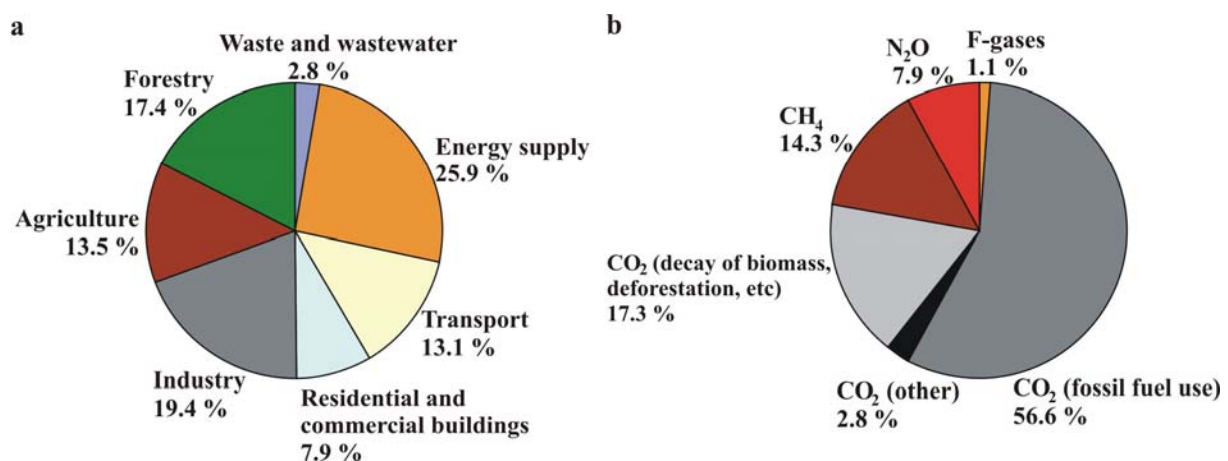


Figure 1.1: a: Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO_2 -eq. (Forestry includes deforestation) and b: Share of anthropogenic GHGs in total emissions in 2004 in terms of CO_2 -eq. Figure according to IPCC (2007).

N_2O as one of the major GHGs contributes by 7.9 % to anthropogenic GHG emissions (IPCC 2007; Figure 1.1b). Its global atmospheric concentration increased since preindustrial times (i.e. 1750) from about 270 ppb to 319 ppb in 2005 (World Meteorological Organization 2006). During the past few decades, the increase of atmospheric N_2O concentrations was nearly linear and estimated to be between 0.2 and 0.3 % per year (IPCC 2007). Although N_2O is the least abundant of the three major greenhouse gases (about 1000 times less abundant than CO_2), its ability to trap heat within the Earth's atmosphere, i.e. its net greenhouse effect per unit mass, is about 320 times greater than that of CO_2 on a 100-year time span (Rodhe 1990).

Whereas global increases in atmospheric CO₂ concentrations are primarily a result of fossil fuel use, the increase in atmospheric N₂O concentration is predominantly attributed to agriculture (IPCC 2007). Agricultural activities are considered the main source of nutrient inputs, such as nitrogen (N), to terrestrial and aquatic ecosystems. These inputs increased fundamentally during the last decades, because increasing amounts of organic and inorganic fertilisers have been applied to agricultural fields. Thus, the intensification of agriculture enhanced the supply of N, what is a prerequisite for the major N₂O-sources, the microbial mediated processes nitrification and denitrification in soils and aquatic systems (Mosier 1998, Mosier et al. 1998). A simplified model illustrating the N₂O turnover (i.e. production, release and consumption of N₂O) was developed by Davidson (1991):

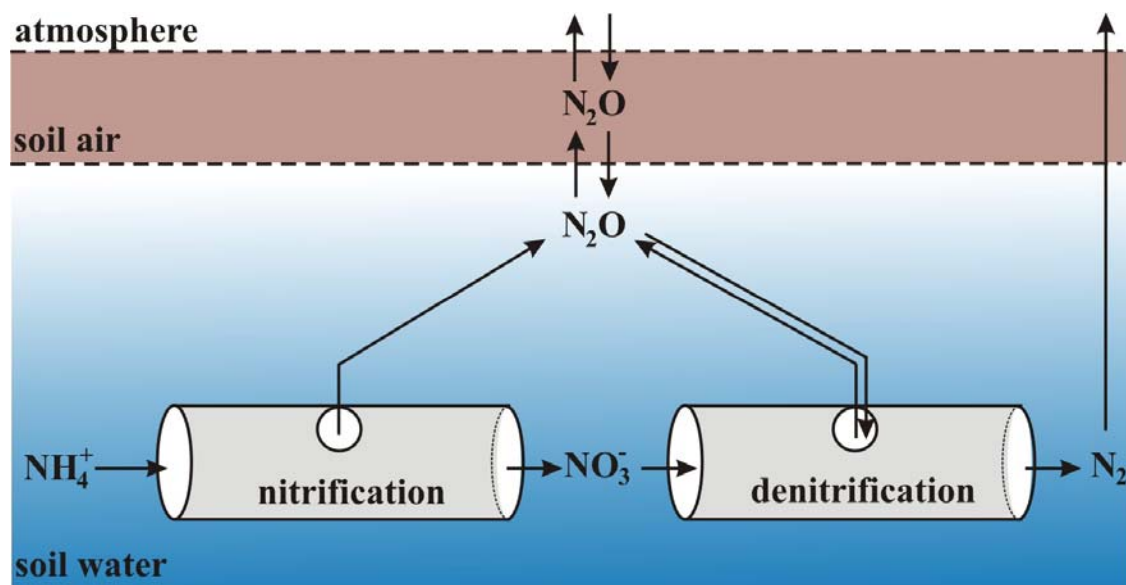


Figure 1.2: Turnover of N₂O during nitrification and denitrification (“hole-in-the-pipe-model”), according to Davidson (1991).

Nitrification of ammonium (NH₄⁺) to nitrate (NO₃⁻) occurs in soils under well-aerated, yet moist conditions, typically at 40-60 % water filled pore space (WFPS). Denitrification is favoured by anaerobic and wet conditions (WFPS greater than 80 %). Therefore, the process is the major source of N₂O in aquatic systems such as aquifers.

1.2 Denitrification in groundwater

As reported by Firestone (1982), denitrification involves the stepwise reduction of NO₃⁻ through nitrite (NO₂⁻), nitric oxide (NO) and N₂O, yielding gaseous dinitrogen (N₂). The complete reaction chain with the oxidation state of the N atoms is as follows:



The ability to eliminate or to reduce NO_3^- in groundwater is the reason why denitrification is considered a highly significant process in groundwater ecology. In many aquifers, denitrification is the beneficial and partly essential process for drinking water production, because NO_3^- concentrations in groundwater often exceed quality standards due to high N-inputs via seepage water.

A number of environmental conditions are needed for denitrification to take place. Firestone (1982) mentioned four general requirements: (1) N-oxides as electron acceptors, (2) the presence of adequate microbial communities, (3) anaerobic conditions or at least restricted availability of oxygen, and (4) availability of suitable electron donors. Since denitrification is an energy-demanding process, microorganisms derive the required energy from oxidation of the electron donors. If organic matter, i.e. bioavailable organic carbon, functions as an electron donor, the reaction is denoted as “heterotrophic”. In contrast, reduced inorganic species like sulfides and Fe^{2+} enable autotrophic denitrification mediated by *Thiobacillus denitrificans* and *Gallionella ferruginea*, respectively (Böttcher et al. 1992, Korom 1992). Further denitrification-related factors, e.g. pH, temperature, NO_3^- , and dissolved as well as particulate organic carbon that regulate the process and thus the occurrence of N_2O , were described in several studies (Granli and Bøckmann 1994, Well et al. 2005b) and - related to the Fuhrberger Feld aquifer - analysed by von der Heide et al. (2008) and Deurer et al. (2008). In case of pH, this factor has often been called a “master variable”, because it affects several soil processes (Brady and Weil 1999, pp. 343-377). Its optimum for denitrification seems to be in a range between 6 and 8 (Šimek and Cooper 2002). However, Šimek and Cooper (2002) also stressed that the microorganisms’ ability to adapt to pH that deviates from the optimum is the reason for considerable denitrification activity at pH down to 4. Beside pH, dissolved organic carbon (DOC) is a governing factor that is still under debate. More precisely, it is questionable whether it may serve as an electron donor for heterotrophic denitrification (Siemens et al. 2003, Deurer et al. 2008, von der Heide et al. 2008, von der Heide et al. 2009b) or particulate organic carbon dominates as the bioavailable electron donor (Jacinthe et al. 1998, Böttcher et al. 1991). With regard to this context it becomes obvious that denitrification is a variable and complex process, because it depends on impact and coaction of several regulating factors and microbial communities.

However, it was definitely shown that groundwater denitrification is able to generate considerable N_2O accumulation at least in the shallow groundwater of the Fuhrberger Feld aquifer (Deurer et al. 2008) and in other aquifers (Spalding and Parrott 1994, Well et al. 2005a). Reported dissolved N_2O concentrations were up to four orders of magnitude higher than the concentration expected as a result of equilibrium with the atmosphere. Thus, the question arises to which extent groundwater N_2O can degas and finally contribute to total emissions into the atmosphere.

1.3 Emissions of N₂O from groundwater

The majority of previous studies on N₂O have focused directly on measuring fluxes of N₂O from the soil surface. As Clough et al. (2006) concisely stated, the fate of N₂O in the subsoil “has often been placed in the ‘too hard’ basket”. Without doubt, this statement can be generalized to the fate of N₂O in subsurface environments, e.g. groundwater. But what are the reasons for this lack of knowledge? In short, there is a lot of what can happen to N₂O from initial production in groundwater to the possible ultimate emission. First, N₂O in groundwater is subject to simultaneously running production and reduction during denitrification, i.e. the amount of N₂O once produced will not be fully emitted. Second, there are different pathways of transport to the atmosphere, i.e. N₂O can be emitted after vertical diffusion within the saturated and through the unsaturated zone or may spontaneously degas when it comes in contact with the atmosphere after convective transport in groundwater while discharging to ditches, streams or rivers. Third, there is strong evidence that N₂O consumption plays an important role in various soils (Chapuis-Lardy et al. 2007, Vieten et al. 2007, Wagner-Riddle et al. 2008, Goldberg and Gebauer 2009, Kellman and Kavanaugh 2009), i.e. conservative transport of groundwater-derived N₂O in the unsaturated zone is unlikely. Fourth, all these processes are highly variable in time and space. Against this background, it becomes clear that assessing N₂O emissions from groundwater is challenging. However, determining the production, movement and fate of N₂O in subsurface environments is a requirement for fully understanding the sources of surface fluxes and for compiling accurate inventories for N₂O emissions.

Emissions of N₂O from groundwater are attributed to indirect emissions, arising from leaching and runoff of nitrogen from agricultural soils (principally NO₃⁻) into adjacent systems (Mosier et al. 1998, Well et al. 2005c). These indirect emissions are accounted for within the IPCC methodology using the emission factor EF₅. The EF₅ is subclassified in the single emission factors EF_{5-g}, EF_{5-r} and EF_{5-e}, which are the emission factors for groundwater and surface drainage, rivers, and estuaries, respectively. The default value for the EF₅ currently stands at 0.0075, i.e. it assumes that 7.5 g N₂O per kilogram N applied to agricultural fields will be finally emitted into the atmosphere. If we take the complexity of N₂O turnover and the highly transient and non-linear N₂O transport into account, it is not surprising that considerable uncertainty surrounds indirect N₂O emissions and the related emission factors which were, in case of the EF_{5-g}, frequently estimated on the basis of average N₂O-to-NO₃⁻ ratios. Hence, the uncertainty range for the EF₅ is 0.0005-to-0.025 and covers three orders of magnitude (IPCC 2006). Beside this, recent studies emphasized that indirect gas emission has to be described by conceptual models including the realistic flow and mass transfer and reactive transport modeling to improve quantification and predictability of indirect N₂O emissions (Grant and Pattey 2003, Chapuis-Lardy et al. 2007, Geistlinger et al. 2009).

1.4 Objectives of this thesis

As introduced above, occurrence of N_2O in denitrifying aquifers and indirect N_2O emissions are underlying complex, multifaceted mechanisms governed by highly variable factors. This thesis will not claim to solve all difficulties connected with the topic, but it will suggest and discuss methods and results that may contribute to improve our understanding of some key processes.

The first objective was to study the process kinetics of N_2O production and reduction during heterotrophic and autotrophic denitrification, respectively. Thus, the balance between N_2O production and reduction can be identified in order to characterise to what extend N_2O tends to accumulate in groundwater. The underlying laboratory approach also enabled the application of a conventional first-order-kinetics modeling approach in order to calculate kinetic rate constants. Therefore, one aim was to assess whether this kinetics is able to describe the experimental data and - further - whether the results of the laboratory experiments are capable to reflect in-situ conditions. These objectives were met in the course chapter 2.

The main objective of the ^{15}N tracer study introduced in chapter 3 was the detection of groundwater-derived N_2O at the soil surface. To achieve this, stable labeling of the groundwater surface with ^{15}N -labeled NO_3^- was required, because a particular aim was to initiate denitrification and N_2O production in the surface groundwater. The final objective met in this chapter was to assess the significance of indirect N_2O emissions occurring via upward diffusion through the soil profile.

In chapter 4, investigations into four aquifers aimed to develop an improved concept for calculating the emission factor $\text{EF}_{5\text{-g}}$. The novelty of this concept was to relate for the first time groundwater N_2O to reconstructed “initial” NO_3^- concentrations, i.e. to the input of leached N that actually met the groundwater surface. Finally, research aimed to reveal factors that regulate denitrification and N_2O accumulation within the investigated aquifers.

2 Kinetics of N₂O production and reduction in a nitrate-contaminated aquifer inferred from laboratory incubation experiments

2.1 Introduction

The atmospheric concentration of nitrous oxide (N₂O), a trace gas contributing to global warming and to the depletion of stratospheric ozone, has increased substantially since preindustrial times and continues to do so (IPCC 2006). Agricultural ecosystems are considered to be a significant source of N₂O emissions due to the prevalent application of mineral and organic fertilisers (Mosier et al. 1998). In aquifers of these ecosystems, elevated N₂O concentrations of up to more than three orders of magnitude above the concentration in water equilibrated air were found in the surface groundwater (Spalding and Parrott 1994, Well et al. 2005a, von der Heide et al. 2008). Thus, N₂O in groundwater was assumed to be a potential source contributing to atmospheric N₂O emissions (Rice and Rogers 1993, Mosier et al. 1998, Hefting et al. 2003). Despite numerous recent studies on N₂O emissions originating from groundwater and agricultural drainage water (Groffman et al. 1998, Heincke and Kaupenjohann 1999, Hiscock et al. 2003, Reay et al. 2003, Weymann et al. 2008), the significance of these indirect emissions is still uncertain. By and large, this could be attributed to two crucial subjects: firstly, N₂O accumulation in groundwater is complexly controlled. N₂O is an intermediate product of denitrification, the major process yielding to the occurrence of N₂O in oxygen depleted groundwater. Thus, N₂O emissions are a net result of the balance between simultaneously running N₂O production and reduction to N₂. This balance is permanently influenced by different enzyme kinetics of various denitrifying communities according to a number of regulating factors. The complex reaction kinetics may lead to a high variability of N₂O concentrations in groundwater (von der Heide et al. 2008) and to wide ranges of groundwater N₂O emission factors (Hack and Kaupenjohann 2002, Weymann et al. 2008). Secondly, it is a challenge to combine research on the reaction kinetics of N₂O with transport parameters. Clough et al. (2005) stated that the movement and the ultimate fate of N₂O in subsurface environments are still poorly understood. For example, knowledge of the consumption of N₂O in groundwater is scarce (Clough et al. 2007). Moreover, the fate of groundwater-derived N₂O passing the unsaturated zone has not been successfully investigated (Weymann et al. 2009).

Denitrification has been frequently investigated during laboratory incubation studies using the ¹⁵N tracer or the acetylene blockage technique, mainly to determine the denitrification capacity of soils and aquifer sediments (Smith and Duff 1988, Ambus and Lowrance 1991, Paramasivam et al. 1999, Well et al. 2005b). However, laboratory experiments to study the occurrence of N₂O and its reaction kinetics in groundwater are comparatively rare. Obenhuber and Lowrance (1991) observed NO₃⁻ removal and an accumulation of N₂O in

flow-through microcosms within a period of 302 days, especially in the treatments with glucose amendment. Jacinthe et al. (1998) designed a similar experiment with two types of aquifer material over 132 days. The authors reported that heterogeneously distributed “patches” of organic matter induced denitrification in the poorly drained aquifer material, whereas the second type of aquifer material - without these patches - showed no denitrification activity. Furthermore, added dissolved organic carbon (DOC) was obviously not an electron donor for the reduction of NO_3^- . N_2O production rates of the poorly drained aquifer material were highest between days 20 and 30 in the NO_3^- amended treatments and substantially higher than the production rates of N_2 . Blicher-Mathiesen and Hoffmann (1999) conducted an experiment with continuously permeated columns as well as static incubations. In both cases, they observed considerable NO_3^- removal and net N_2O production, but they also questioned the transferability of these results to parallel investigated field conditions which did not exhibit N_2O accumulation due to an efficient reduction of N_2O to N_2 . Differences in net N_2O production between field and laboratory studies were also observed and discussed by Well et al. (2003). By comparing the N_2O fractions of total denitrification, the laboratory incubation yielded substantially higher values than the field study. Thus, this result confirms the observation of Blicher-Mathiesen and Hoffmann (1999). In contrast, other studies reported a good agreement of laboratory experiments and field methods related to the occurrence of N_2O (Obenhuber and Lowrance 1991, Hénault et al. 2001). As becomes clear at this point, it is uncertain whether laboratory investigations of the kinetics of N_2O production and reduction are applicable to field conditions.

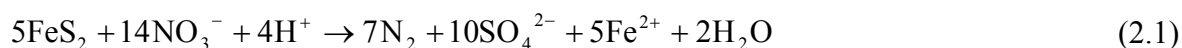
In this study, we investigated the kinetics of N_2O production and reduction in an unconsolidated sandy aquifer in northern Germany. This aquifer consists of vertically separated denitrification zones according to the availability of electron donors, i.e. organic carbon and reduced sulfur (von der Heide et al. 2008). This provides the opportunity to investigate not only the kinetics of N_2O production and reduction during heterotrophic denitrification as it was done in previous studies, but also during the autotrophic pathway.

The specific objectives of this study are (i) to determine the time courses of NO_3^- , N_2O and N_2 during long-term laboratory incubation of aquifer material samples, (ii) to evaluate kinetic rate constants of N_2O production and reduction during heterotrophic and autotrophic denitrification using a conventional k_1 - k_2 -model that follows first-order-kinetics and (iii) to assess the validity of the laboratory experiments for the relevant in situ processes.

2.2 Study site

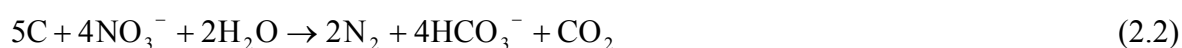
The Fuhrberger Feld aquifer (FFA) in northern Germany is located about 30 km northeast of the city of Hannover. The unconfined aquifer consists of pleistocene, highly permeable carbonate-free sands and gravels with a thickness of 20 - 40 m underlain by impermeable cretaceous clays. More information about the soils, the hydrology and the land use of the research site is given by Frind et al. (1990), Deurer et al. (2008) and von der Heide et al.

(2008). The FFA has been a subject of extensive research activities since the 1980s (reviewed in Korom 1992). This could be due to the fact that the catchment is in an area of conflict between its key function for drinking water supply on the one hand and agricultural activities causing considerable inputs of pollutants via seepage, especially of nitrate, on the other (Kölle et al. 1985, Frind et al. 1990). In the FFA, substantial microbially mediated processes and reactions like denitrification and desulfurication occur, strongly influencing groundwater geochemistry. Autotrophic denitrification with reduced sulfur compounds as an electron donor was identified as the dominant microbial reaction for NO_3^- elimination in the deeper aquifer (Kölle et al. 1985) in depths beyond 2-3 m below the groundwater table (Böttcher et al. 1992). The process was stoichiometrically described by Kölle et al. (1985) and Böttcher et al. (1990) as a reaction mediated by the bacteria *Thiobacillus denitrificans*:



Kölle et al. (1985) conducted an incubation experiment in order to evaluate the sulfate formation capacity of nitrate amended aquifer slurries from different depths. They found an ongoing sulfate formation during a 284-days-period and calculated schematically the potential of autotrophic denitrification on the basis of pyrite oxidation.

In case of the surface groundwater, von der Heide et al. (2008) confirmed former assumptions, that heterotrophic denitrification with organic carbon as an electron donor replaced autotrophic denitrification due to an exhaustion of the reduced sulfur compounds (Kölle et al. 1983, Böttcher et al. 1991):



Autotrophic denitrification in the deeper aquifer is much more efficient for NO_3^- reduction than heterotrophic denitrification in the surface groundwater. With respect to denitrification efficiency, Weymann et al. (2008) revealed the considerable difference between heterotrophic and autotrophic denitrification by determination of “excess nitrogen” in groundwater samples. Hence, high NO_3^- concentrations are limited to the top few metres of the aquifer, but the deeper groundwater is almost NO_3^- -free (Frind et al. 1990, von der Heide et al. 2009a).

Recently, research activities in the FFA focused on the occurrence of N_2O in the groundwater. Deurer et al. (2008) investigated the accumulation and dynamics of N_2O near the groundwater table and its transfer into the unsaturated zone from an exchange zone extending 0.55 ± 0.22 m below the groundwater table. They reported that this zone may also act as a sink for N_2O . An extremely high spatial variability of N_2O concentrations in

the surface groundwater of the FFA was postulated by von der Heide et al. (2008). They identified the land use and the distance of the groundwater level to the soil surface as factors governing the magnitude of N_2O concentrations in the surface groundwater. Weymann et al. (2008) determined groundwater N_2O emission factors with respect to initial NO_3^- concentrations and assessed these factors related to N_2O accumulation during different stages of the denitrification progress. All recent studies were conducted within a groundwater flowpath strip equipped with multilevel sampling wells (Deurer et al. 2008). Within this chapter, the groundwater and the aquifer material of the multilevel sampling wells B1 and I1 (von der Heide et al. 2009a) were investigated. The main characteristics of the aquifer material are shown in Table 2.1.

Table 2.1: Location and basic properties of the investigated aquifer materials.

Sample location	Depth interval	Denitrification	Organic C	Nt	C-to-N ratio	DOC ¹	C _{hws} ²	Sulfur	Clay
	[m]	zone	[mg kg ⁻¹]						%
B1	2.0 - 2.6	heterotrophic	539.62	17.22	31.34	28.13	n.d.	47.35	0.00
B1	2.6 - 3.0		587.66	40.94	14.35	16.37	n.d.	45.79	0.00
B1	3.4 - 4.0		658.61	39.46	16.69	13.27	n.d.	39.65	0.00
I1 - S1	1.5 - 2.0	autotrophic	816.12	53.43	15.27	19.27	167.25	44.61	0.00
I1 - S1	2.0 - 2.5		609.26	40.22	15.15	16.28	111.80	75.78	0.00
I1 - S1	2.5 - 3.0		485.18	67.82	7.15	12.69	109.66	91.55	0.00
I1 - S2	1.5 - 2.0		536.64	23.78	22.57	16.40	91.59	24.76	0.00
I1 - S2	2.0 - 2.5		506.05	32.39	15.62	17.82	101.66	13.57	0.00
I1 - S3	1.5 - 2.0		729.46	42.06	17.34	21.09	113.56	33.72	0.00
I1 - S3	2.0 - 2.5		584.57	36.82	15.88	17.73	103.55	41.67	0.00
I1 - S3	2.5 - 3.0		527.99	41.40	12.75	13.45	94.90	64.33	0.00
I1 - 1	6.5 - 7.0		556.00	30.00	18.53	8.77	330.20	302.45	0.70
I1 - 2	6.5 - 7.0		437.95	129.84	3.37	7.65	338.39	265.47	0.95
I1 - 3	6.5 - 7.0		469.38	52.62	8.92	6.85	351.00	457.96	1.99
I1 - 4	6.5 - 7.0		714.68	65.07	10.98	9.88	390.00	430.86	2.22
I1 - 5	6.5 - 7.0		1293.73	94.97	13.62	8.46	258.70	379.89	3.44
I1 - 6	6.5 - 7.0		1488.87	123.58	12.05	11.87	267.15	396.13	5.09
I1 - 7	6.5 - 7.0		685.32	39.72	17.25	10.37	284.05	253.24	1.95
I1 - 8	6.5 - 7.0		461.45	45.33	10.18	8.27	247.00	361.88	1.50
I1 - 9	6.5 - 7.0		894.72	70.58	12.68	12.27	253.50	376.33	3.55
I1 - 10	6.5 - 7.0		545.91	41.64	13.11	7.25	318.50	436.03	2.26
I1 - 11	6.5 - 7.0		720.72	55.23	13.05	7.00	278.20	361.84	3.11

¹ extractable dissolved organic carbon

² extractable hot-water soluble carbon

n.d. = not determined

2.3 Materials and Methods

Sampling procedures

Groundwater was collected from the multilevel sampling wells (Böttcher et al. 1985) in order to measure the denitrification related parameters N_2O , NO_3^- and SO_4^{2-} . The groundwater samples were collected in September 2005, December 2005 and March 2006

from the multilevel sampling well B1 using a peristaltic pump (Masterflex, COLE-PARMER, Vernon Hills, USA) as described in detail by Weymann et al. (2008). At the multilevel sampling well I1, a single sampling event was conducted in March 2006. Here, we collected the groundwater for N_2O , NO_3^- and SO_4^{2-} analysis with a plastic syringe, applying the method introduced by Deurer et al. (2008). At both wells, the depth resolution was 0.2 m in the surface groundwater (0.1 m - 2.1 m below the groundwater table) and 1.0 m in the deeper groundwater down to a depth of 10 m below the soil surface.

Aquifer material was collected at the well B1 and at the plot appendant to well I1 for laboratory incubations to derive the parameters of the N_2O reaction kinetics. This was done using a hand-operated bailer boring auger set (EIJKELKAMP, Giesbeek, The Netherlands) consisting of a stainless steel bailer, casing tubes (OD of 10 cm) and a tube clamp. At the multilevel sampling well B1, we collected aquifer material in October 2005 from three depth intervals in the zone of heterotrophic denitrification: 2.0 - 2.6 m, 2.6 - 3.0 m and 3.4 - 4.0 m below the soil surface. At the plot of the multilevel sampling well I1, the aquifer material was sampled at three spots that were spatially arranged as described by von der Heide et al. (2008). Sampling took place in October 2005 from the depth intervals 1.5 m - 2.0 m, 2.0 m - 2.5 m and 2.5 m - 3.0 m below the soil surface (heterotrophic denitrification zone). To sample the autotrophic zone, a PVC pipe (OD of 100 mm) was installed at 6.5 m depth at one spot very close to the well using a drilling rig (WELLCO-DRILL, WD 500, Beedenbostel, Germany) with a hollow-stem auger (OD of 205 mm, ID of 106 mm). Samples were collected using the bailer. During sampling, the bottom part of the PVC pipe was continuously refilled with surrounding aquifer material. Samples thus originated from an undefined area in the vicinity of the pipe bottom. Hence, we were able to collect samples differing in texture and chemical composition from a single spot. The sampling of the autotrophic zone was conducted in December 2005.

The collected aquifer material was transferred from the bailer to 16 L plastic buckets. We filled the buckets until the supernatant groundwater overflowed. Subsequently, the buckets were closed airtight with a lid. From the heterotrophic denitrification zone, we filled one bucket per depth interval. From the autotrophic denitrification zone, 11 buckets were collected from the same depth interval. The aquifer material was stored at groundwater temperature (10°C) and batched for laboratory incubations within four weeks.

Laboratory incubations

We performed a laboratory method using the ^{15}N tracer technique that reaches back to the seminal study of Nömmik (1956) who quantified the gaseous denitrification products from soils receiving K^{15}NO_3 by mass spectrometry. The approach of anaerobic incubation of NO_3^- amended slurries has been extensively used for measuring denitrification and N_2O production (Tiedje 1994, Hénault et al. 2001, Well et al. 2003, Well et al. 2005a). In detail, 500 g of each aquifer material were transferred as slurries in 4 replications to 1125-mL transfusion bottles and amended with 400 mL of a K^{15}NO_3 test solution (10 mg N L^{-1} ; 60 atom% ^{15}N). The transfusion bottles were sealed with rubber septa and aluminium screw

caps. The gravimetric water content of the slurries was 0.19 g g^{-1} , resulting in a dry weight of 405 g. The volume of the solid matter was 153 mL, assuming a particle density of 2.65 g cm^{-3} . Taking the water content of the slurries into account, we determined the liquid volume in the bottles as 495 mL. Consequently, the headspace volume was 477 mL. We established anaerobic conditions by three cycles of evacuation and refilling with N_2 , respectively. Subsequently, the samples were incubated at 10°C , which is the approximate groundwater temperature as estimated from the mean annual air temperature. Gas and water samples were collected following a flexible sampling schedule according to the progress of denitrification. Prior to each sampling, the liquid and the gas phase were equilibrated by vigorous shaking for 3 hours. 24 mL of the headspace gas were sampled using a double syringe system consisting of two 30-mL plastic syringes equipped with 3-way Luer-lock stop cocks (BRAUN, Melsungen, Germany) which were connected to each other. After mixing the gas sample within the syringe system, 12 mL from each of the separate syringes were transferred into fully evacuated ExetainersTM (LABCO, High Wycombe, UK). One ExetainerTM was stored for the measurement of N_2O by gas chromatography, the other for the $^{15}(\text{N}_2\text{O}+\text{N}_2)$ analysis by mass spectrometry and both were analysed within 3 weeks. To retain normal pressure in the serum bottles, we re-injected an equivalent volume of pure N_2 after sampling. The resulting dilution of the headspace gas was taken into account in the calculation of the $^{15}(\text{N}_2\text{O}+\text{N}_2)$ concentrations. Water samples were collected with a syringe. Routinely, we withdrew an 15-mL aliquot for NO_3^- analysis. Subsequently, an equivalent amount of the oxygen-free K^{15}NO_3 test solution was re-injected. The NO_3^- concentration of the test solution was adjusted according the actual NO_3^- concentration.

Analytical techniques

The particle size distribution was determined gravimetrically after separating the fractions by sieving and sedimentation following the Atterberg-method (Schlichting et al. 1995). Total organic carbon (C_{org}) and total N of the pulverised and carbonate-free aquifer material was measured using the elemental analyser vario MAX CN (ELEMENTAR ANALYSENSYSTEME GmbH, Hanau, Germany) equipped with a thermal conductivity detector. The precision of the analysis was 0.5 %. Sulfur in the identical samples was analysed with a vario EL III elemental analyser (ELEMENTAR ANALYSENSYSTEME GmbH, Hanau, Germany) equipped with a thermal conductivity detector and an UV-absorption photometer. The precision of the analysis was 0.1 %. DOC in cold-water extracts and hot-water soluble organic carbon (C_{hws}) were analysed as described by Well et al. (2005b). NO_3^- and SO_4^{2-} in the groundwater samples collected from the multilevel sampling wells were determined by ion chromatography (ICS-90, DIONEX, Idstein, Germany) with a precision of 5 %. NO_3^- of the water samples from the laboratory incubations was analysed photometricly using a continuous flow analyser (Skalar, Erkelenz, Germany). The measurement precision was 5 %.

N₂O was measured using a gas chromatographer equipped with an electron capture detector and an auto sampler that was described earlier (Well et al. 2003). The ¹⁵N analysis of (N₂O+N₂) in the headspace gas was conducted following the method specified in Well et al. (1998) and Well et al. (2003). The gas concentrations of the sample solutions (dissolved N₂O and N₂) were calculated according to Henry's laws from the headspace concentrations using the Bunsen absorption coefficients of N₂O and N₂, respectively (Weiss 1970, Weiss and Price 1980). The calculation was described in detail by Well and Myrold (1999) and Well et al. (2003).

Reaction kinetics

First-order kinetics is frequently used to model processes in the field of groundwater biogeochemistry. For example, Böttcher et al. (1989) applied this kinetics and estimated field denitrification rates in the FFA. In case of our laboratory approach, we consider a two-step reaction chain for N₂O-production and N₂O-reduction in order to characterise the heterotrophic and autotrophic denitrification process:



Hoehener et al. (2003) presented an analytical solution following first-order kinetics. This k₁-k₂-standard model is described by the following differential equations for NO₃⁻ and N₂O, respectively:

$$\frac{dC_{\text{NO}_3}}{dt} = -k_1 \cdot C_{\text{NO}_3} , \quad (2.4)$$

$$\frac{dC_{\text{N}_2\text{O}}}{dt} = F \cdot k_1 \cdot C_{\text{NO}_3} - k_2 \cdot C_{\text{N}_2\text{O}} \quad (2.5)$$

The analytical solutions are:

$$C_{\text{NO}_3}(t) = C_0 \cdot \exp(-k_1 \cdot t) , \quad (2.6)$$

$$(\mathbf{k}_1 \neq \mathbf{k}_2): C_{\text{N}_2\text{O}}(t) = F \cdot C_0 \cdot \frac{k_1}{(k_2 - k_1)} \cdot [\exp(-k_1 \cdot t) - \exp(-k_2 \cdot t)] , \quad (2.7)$$

$$(\mathbf{k}_1 = \mathbf{k}_2): C_{N_2O}(t) = F \cdot C_0 \cdot k_1 \cdot t \cdot \exp(-k_1 \cdot t), \quad (2.8)$$

where F is the stoichiometric factor and C_0 is the initial nitrate concentration. We note that the sum of N_2 and N_2O is only a function of k_1 and the analytical solution follows by mass balance considerations:

$$C_{sum}(t) = C_{N_2}(t) + C_{N_2O}(t) = F \cdot (C_0 - C_{NO_3}(t)). \quad (2.9)$$

A Marquardt-Levenberg fit was conducted to all heterotrophic and autotrophic data sets, where the analytical solutions are used as fitting function. All calculations were carried out with the mathematical software Mathematica 6.0. For each data set three different fits were conducted: (i) a 1-step 3-parameter fit, (ii) a sequential (or 2-step) 3-parameter fit, and (iii) a sequential 2-parameter fit. These fits are indicated in Figures 1 - 3. The fitting parameters for the 3-parameter fits were C_0 , k_1 and k_2 , respectively.

To further evaluate the control of NO_3^- reduction by denitrification we also used a simpler approach which did not include the distinction between N_2O production and reduction and was based on zero-order-kinetics. Reaction rates (D) were derived from the slope of (N_2O+N_2) over time in order to correlate denitrification with the independent parameters of the aquifer material. Initial values of D (D_i) were obtained from the first 7 days of incubation. Maximum values of D (D_{max}) were calculated from the maximum slopes of the (N_2O+N_2) -curve. Finally, we used the maximum N_2O concentration during incubation ($c_{N_2O_{max}}$) and the ratio between N_2O and (N_2O+N_2) at maximum N_2O concentration ($c_{N_2O_{max}}\text{-to-}[N_2O+N_2]$) as qualitative indicators for the balance between production and reduction of N_2O .

2.4 Results

Multilevel well measurements

At the investigated wells, each of the vertical concentration gradients of NO_3^- and N_2O showed a similar pattern. In the surface groundwater, NO_3^- concentrations initially increased downwards in both profiles to a mean value of 34 mg N L⁻¹ in a depth of 3.8 m below the soil surface at B1 and to 30 mg N L⁻¹ in a depth of 3.2 m below the soil surface at I1, respectively (Figure 2.1). Below 4 m, where the autotrophic denitrification mainly governs NO_3^- reduction, NO_3^- concentrations decreased continuously and reached zero in a depth of 7 m at both wells. In the case of N_2O , we identified two layers where the concentrations were highest: first, there is an obvious zone of N_2O accumulation in the uppermost groundwater coinciding with an “exchange zone” that was recently reported by

Deurer et al. (2008). We observed N_2O concentrations up to 1.84 mg N L^{-1} in a depth of 2.0 m below the soil surface at B1 and 1.63 mg N L^{-1} in a depth of 1.6 m below the soil surface (0.54 m below the groundwater table) at I1.

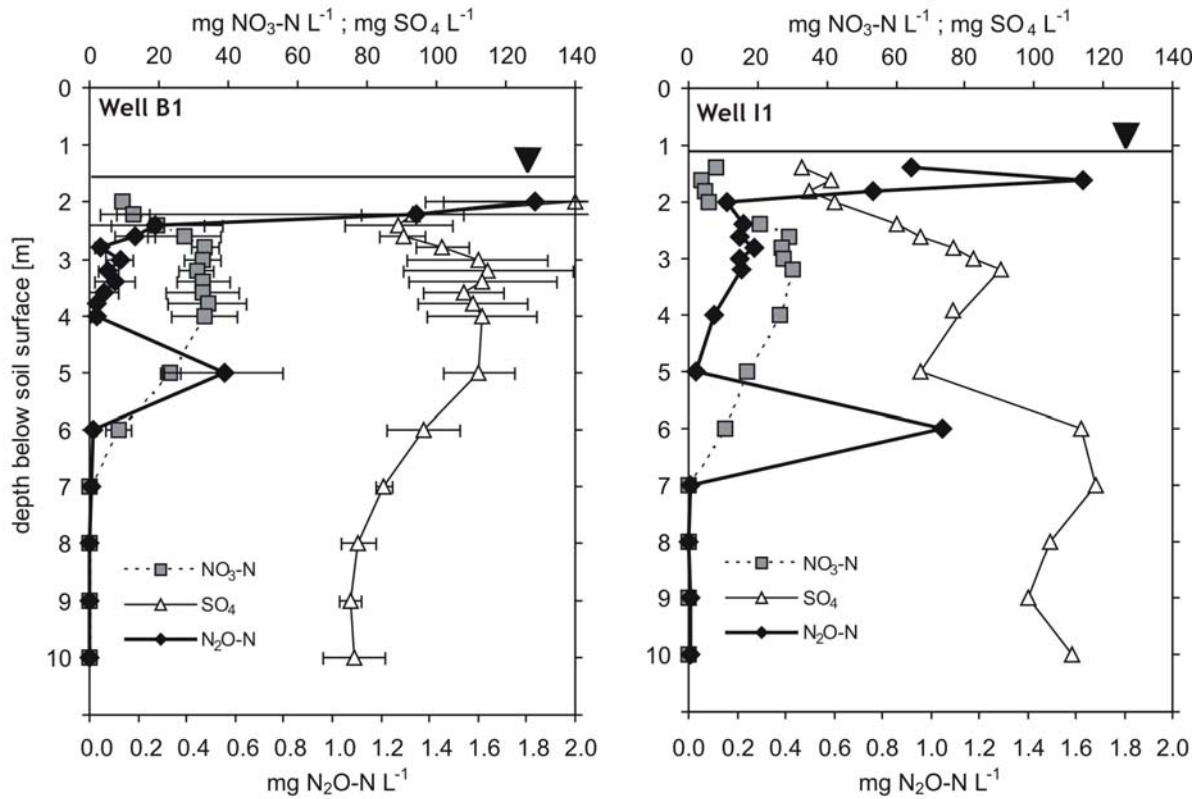


Figure 2.1: Vertical concentration gradients of N_2O , NO_3^- and SO_4^{2-} at the wells B1 and I1. The data of well B1 are mean values of three sampling events, the error bars denote the standard deviation.

Second, Figure 2.1 shows a sharp-cut concentration peak in both profiles, consisting of an outstanding value in 5 m and 6 m depth, respectively. Between these layers, N_2O concentrations in the groundwater were substantially lower at both wells, but still up to three orders of magnitude higher than the N_2O concentration in water equilibrated air. In the deeper groundwater, N_2O concentrations declined rapidly after the sharp-cut peak and were undetectable in 6 m at B1 and 7 m at I1, respectively. In contrast to the vertical concentration gradients of NO_3^- and N_2O , the SO_4^{2-} concentration pattern was different at the investigated wells. At I1, we observed an abrupt increase from 67 mg L^{-1} in a depth of 5 m to 113 mg L^{-1} in a depth of 6 m coinciding with the concentration peak of N_2O . Furthermore, the SO_4^{2-} concentrations remained elevated in the deeper groundwater compared to the surface groundwater. At B1, these phenomena did not occur during all sampling events (further details will be given in the discussion section).

Denitrification rates and time courses of the N-species during long-term laboratory incubation

The concentration courses of N_2O , of the total denitrification products ($\text{N}_2\text{O}+\text{N}_2$) and of NO_3^- are represented in Figure 2.2 and Figure 2.3, respectively. Whereas Figure 2.2 refers to heterotrophic denitrification in the surface groundwater, Figure 2.3 shows the results for the autotrophic case that is dominant in the deeper groundwater.

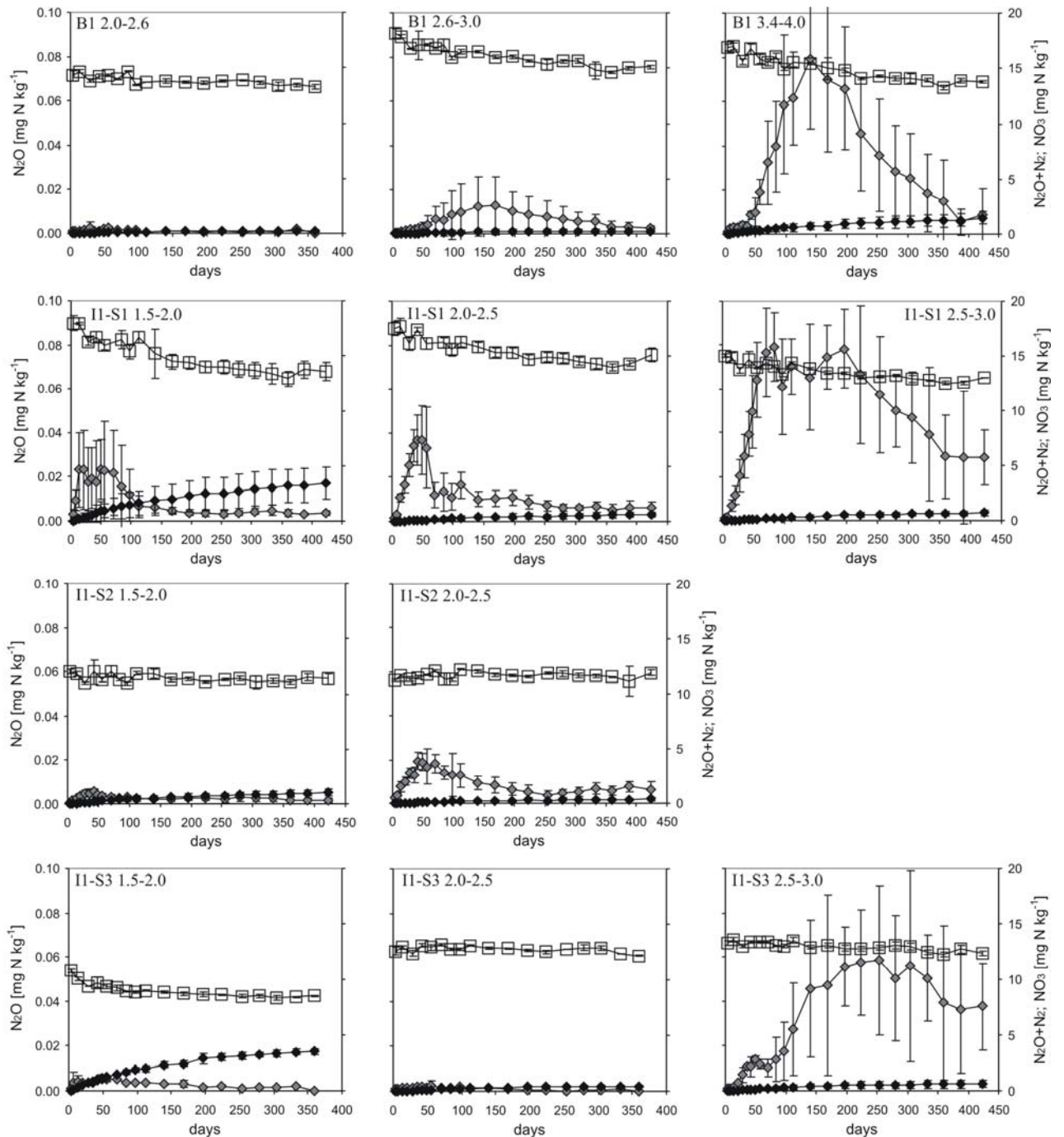


Figure 2.2: Concentration courses of N_2O $\text{N}_2\text{O}+\text{N}_2$ NO_3 during long-term anaerobic incubation of aquifer material from the heterotrophic denitrification zone. The symbols denote the means of 4 replications and the error bars represent the standard deviation.

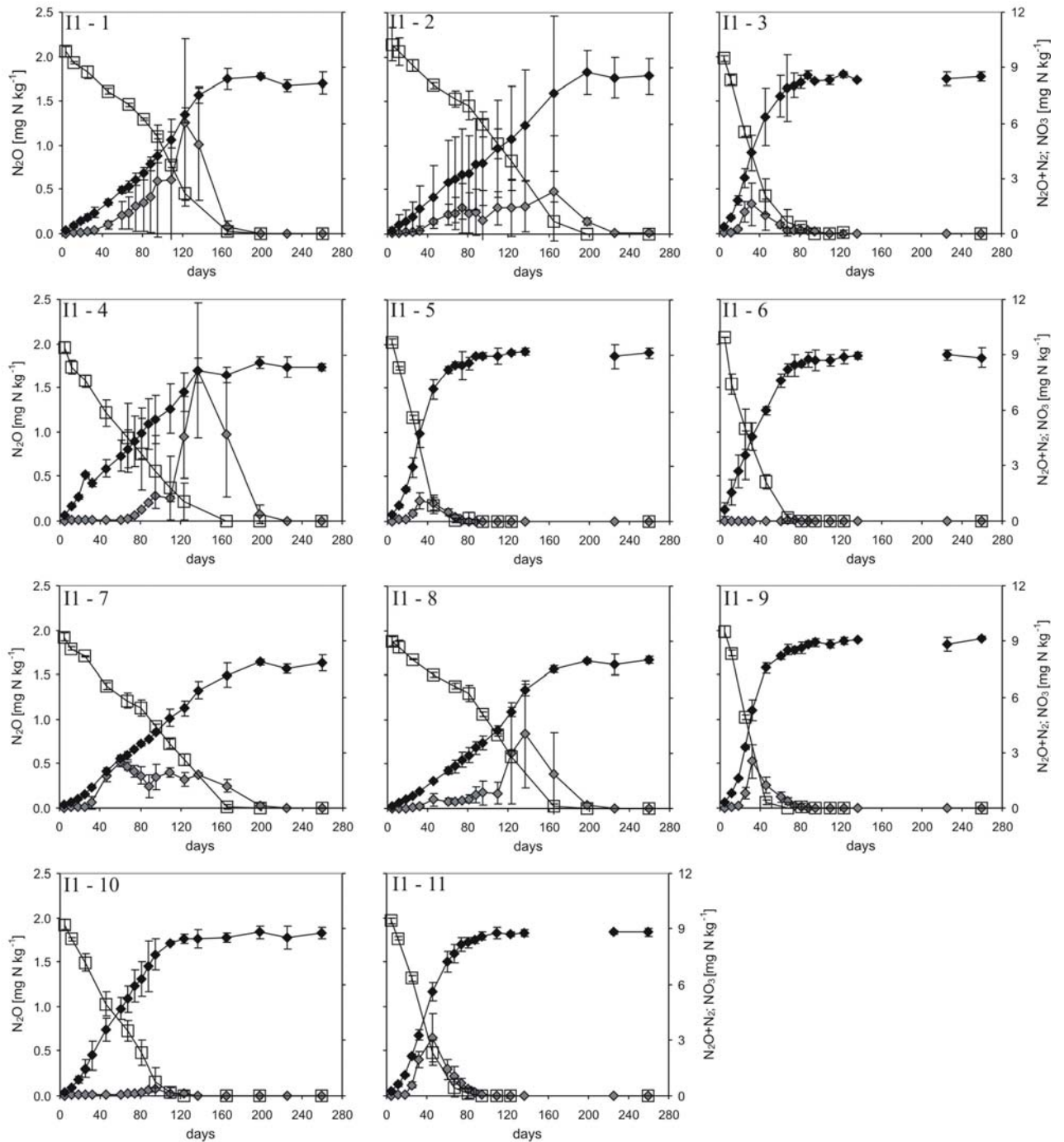


Figure 2.3: Concentration courses of N_2O , $\text{N}_2\text{O}+\text{N}_2$, and NO_3 during long-term anaerobic incubation of aquifer material from the autotrophic denitrification zone. The symbols denote the means of 4 replications and the error bars represent the standard deviation.

N_2O and $(\text{N}_2\text{O}+\text{N}_2)$ were detectable in all samples proving the general occurrence of denitrification. However, there were substantial differences in denitrification activity and the kinetics of N_2O production and reduction between heterotrophic and autotrophic denitrification, but also within these two groups. Calculated rates of autotrophic denitrification (D_i , D_{\max} , Table 2.2), symbolised by the slopes of the $(\text{N}_2\text{O} + \text{N}_2)$ curves (Figure 2.3), were typically one order of magnitude higher than the rates of heterotrophic

denitrification. The coincidence of NO_3^- reduction and $(\text{N}_2\text{O}+\text{N}_2)$ production indicate that the mass balance was satisfactory (Figure 2.2, Figure 2.3). Consequently, NO_3^- concentrations decreased continuously until complete elimination of NO_3^- during autotrophic denitrification (Figure 2.3), whereas the decrease of NO_3^- concentrations during heterotrophic denitrification was marginal and the residual NO_3^- pool was much greater than the reduced one (Figure 2.2).

Table 2.2: Maximum N_2O concentrations ($\text{cN}_2\text{O}_{\text{max}}$), $\text{cN}_2\text{O}_{\text{max}}$ -to- $(\text{N}_2\text{O}+\text{N}_2)$ ratio and denitrification rates (D_i , D_{max}) during anaerobic incubation. D_i denotes the initial denitrification rate calculated at day 7. D_{max} is the maximum denitrification rate calculated for the time interval with the steepest increase of the $(\text{N}_2\text{O}+\text{N}_2)$ curve.

Sample location	Depth interval	Denitrification	$\text{cN}_2\text{O}_{\text{max}}$	$\text{cN}_2\text{O}_{\text{max}}$ -to- $(\text{N}_2\text{O}+\text{N}_2)$	D_i	D_{max}
	[m]	zone	[mg N kg ⁻¹]	ratio	[mg N kg ⁻¹ d ⁻¹]	
B1	2.0 - 2.6	heterotrophic	0.0024	0.0270	0.0005	0.0027
B1	2.6 - 3.0		0.0128	0.0695	0.0006	0.0025
B1	3.4 - 4.0		0.0793	0.1096	0.0034	0.0133
I1 - S1	1.5 - 2.0	autotrophic	0.0233	0.0259	0.0086	0.0352
I1 - S1	2.0 - 2.5		0.0368	0.3794	0.0011	0.0040
I1 - S1	2.5 - 3.0		0.0793	0.4148	0.0007	0.0046
I1 - S2	1.5 - 2.0		0.0055	0.0264	0.0016	0.0119
I1 - S2	2.0 - 2.5		0.0194	0.2581	0.0009	0.0047
I1 - S3	1.5 - 2.0		0.0053	0.0041	0.0133	0.0306
I1 - S3	2.0 - 2.5		0.0025	0.0177	0.0004	0.0035
I1 - S3	2.5 - 3.0		0.0585	0.1182	0.0002	0.0065
I1 - 1	6.5 - 7.0		1.2579	0.1951	0.0432	0.0770
I1 - 2	6.5 - 7.0		0.4827	0.0634	0.0509	0.0612
I1 - 3	6.5 - 7.0		0.3305	0.0754	0.0846	0.1776
I1 - 4	6.5 - 7.0		1.6980	0.2083	0.0784	0.1665
I1 - 5	6.5 - 7.0		0.2391	0.0506	0.0865	0.2577
I1 - 6	6.5 - 7.0		0.0111	0.0013	0.1480	0.1566
I1 - 7	6.5 - 7.0		0.5202	0.1923	0.0344	0.0613
I1 - 8	6.5 - 7.0		0.8362	0.1307	0.0303	0.0397
I1 - 9	6.5 - 7.0		0.5256	0.0997	0.0777	0.2836
I1 - 10	6.5 - 7.0		0.0773	0.0102	0.0415	0.1004
I1 - 11	6.5 - 7.0		0.6470	0.1153	0.0572	0.1685

The balance of N_2O production and reduction yielded a characteristic course of the N_2O concentration curve as it has been reported by Holtan-Hartwig et al. (2000) and Well et al. (2005a): the majority of samples showed an increase to a maximum concentration ($\text{cN}_2\text{O}_{\text{max}}$) followed by a decrease that resulted in complete N_2O reduction in the case of autotrophic denitrification. However, the N_2O concentration courses and $\text{cN}_2\text{O}_{\text{max}}$ values were highly variable and the standard deviations partially indicate an uncertainty.

In the heterotrophic denitrification zone, our sampling method enabled collection and laboratory incubation of slurries from different depth intervals (Table 2.1). The time courses of N_2O showed an increase of $\text{cN}_2\text{O}_{\text{max}}$ with depth (Figure 2.2, Table 2.2). Consequently, $\text{cN}_2\text{O}_{\text{max}}$ was highest in 2.5 - 3.0 m at I1-S1, in 2.5 - 3.0 m at I1-S3 and in

3.4 - 4.0 m at B1 with 0.08, 0.08 and 0.06 mg N₂O-N kg⁻¹, respectively. In contrast, cN₂O_{max} was lowest in the topmost depth intervals where it ranged between 0.0024 and 0.023 N₂O-N kg⁻¹. The results showed that N₂O concentrations were close to the cN₂O_{max} values for a period > 100 days in the majority of cases and decreased slowly towards the end of the incubation period.

Despite the slurries from the autotrophic denitrification zone were collected from the same depth interval, these samples exhibited not only a large variation of N₂O concentrations during anaerobic incubation, but also distinct differences in organic carbon, total sulfur and texture. This demonstrates that the aquifer material obtained by the applied sampling procedure was characterised by heterogeneous properties. For example, sample I1-6, the sample with the highest content of organic carbon and clay in the data-set (Table 2.1), did not show considerable accumulation of N₂O during the entire experiment and exhibited the lowest cN₂O_{max}-to-(N₂O+N₂) ratio (Figure 2.3, Table 2.2). Furthermore, this sample showed by far the highest D_i. cN₂O_{max} of the sample I1-10 was 0.08 mg N₂O-N kg⁻¹ and thus comparable with the highest cN₂O_{max} values we observed in the samples of the heterotrophic denitrification zone. Apart from these two samples, all the other ones were characterised by considerably higher cN₂O_{max} values (Figure 2.3, Table 2.2) between 0.24 mg N₂O-N kg⁻¹ (sample I1-5) and 1.70 mg N₂O-N kg⁻¹ (sample I1-4).

Correlations

We conducted Spearman rank tests for the partial data-sets of the heterotrophic and the autotrophic zone in order to evaluate correlations between the parameters that were introduced in Table 2.1 and Table 2.2, respectively. The correlation coefficients (R_S) for the relationships between cN₂O_{max}, the cN₂O_{max}-to-(N₂O+N₂) ratio, D_i, D_{max} and the independent soil properties are shown in Table 2.3. In the case of heterotrophic denitrification, a significant correlation at the 0.05 probability level was found between organic carbon and D_i. The relationship between the water-extractable C-species (DOC, C_{hws}) and the denitrification rates (D_i, D_{max}) did not reveal a significant correlation. However, the correlation coefficient for the relationship between D_i and C_{hws} was comparatively high (R_S = 0.55). In contrast, DOC was negatively correlated with cN₂O_{max} at the 0.01 probability level. In the case of autotrophic denitrification, the denitrification rates (D_i, D_{max}) were found to be significantly correlated with the potential reductant sulfur, but also with organic carbon. Organic carbon was highly correlated with the clay content, but not with sulfur. DOC and C_{hws} did not correlate with D_i and D_{max}, respectively. Furthermore, we found no significant relations between cN₂O_{max} and the other parameters of the “autotrophic” data set.

Table 2.3: Spearman rank correlation coefficients between the variables within the heterotrophic and the autotrophic data-set. Clay was not detectable in the case of heterotrophic denitrification and was thus excluded from the correlation analysis.

	C _{org}	N _t	C-to-N ratio	DOC	C _{hws}	Sulfur	Clay	cN ₂ O _{max}	cN ₂ O _{max} -to- (N ₂ O+N ₂) ratio	D _i
correlation coefficients between parameters of heterotrophic denitrification										
N _t	0.22ns									
C-to-N ratio	0.27ns	-0.69**								
DOC	0.32ns	-0.34ns	0.65*							
C _{hws}	0.67*	0.69*	-0.17ns	0.45ns						
Sulfur	-0.15ns	0.44ns	-0.62*	-0.44ns	0.33ns					
cN ₂ O _{max}	-0.08ns	0.51ns	-0.64*	-0.82**	0.02ns	0.34ns				
cN ₂ O _{max} -to- (N ₂ O+N ₂) ratio	-0.56*	0.12ns	-0.62*	-0.68*	-0.21ns	0.50ns		0.69**		
D _i	0.62*	0.24ns	0.32ns	0.19ns	0.55ns	-0.45ns		0.15ns	-0.23ns	
D _{max}	0.39ns	0.35ns	0.16ns	0.06ns	0.24ns	-0.42ns		0.33ns	-0.28ns	0.74**
correlation coefficients between parameters of autotrophic denitrification										
N _t	0.33ns									
C-to-N ratio	0.43ns	0.54*								
DOC	0.57*	0.15ns	0.29ns							
C _{hws}	-0.38ns	-0.11ns	-0.20ns	-0.33ns						
Sulfur	0.15ns	0.13ns	-0.28ns	-0.22ns	0.19ns					
Clay	0.82***	0.49ns	0.07ns	0.31ns	-0.43ns	0.47ns				
cN ₂ O _{max}	-0.20ns	-0.35ns	0.04ns	0.11ns	0.15ns	-0.35ns	-0.48ns			
cN ₂ O _{max} -to- (N ₂ O+N ₂) ratio	-0.19ns	-0.52ns	0.17ns	0.16ns	0.25ns	-0.38ns	-0.54*	0.94***		
D _i	0.64*	0.66*	0.66*	0.15ns	0.10ns	0.53*	0.65*	-0.38ns	-0.42ns	
D _{max}	0.65*	0.32ns	0.32ns	0.08ns	-0.08ns	0.52*	0.72**	-0.17ns	-0.21ns	0.73**

* correlation significant at the 0.05 probability level

** correlation significant at the 0.01 probability level

***correlation significant at the 0.001 probability level

Kinetic rate constants of N₂O production and reduction

All data sets with the calculated rate constants and the corresponding fitting parameters are listed in Table 2.4 (1-step 3-parameter fit) and Table 2.5 (sequential 3-parameter fit). As expected from the time courses of the NO₃⁻ and the (N₂O+N₂) concentrations, the obtained rate constants were higher for autotrophic denitrification. The means for k_1 and k_2 showed a difference of about one order of magnitude, when the heterotrophic and the autotrophic process are compared (Table 2.4). The rate constants of autotrophic denitrification exhibited a larger variability (Table 2.4, Table 2.5). For example I1 - 6, the sample with the highest D_i and practically no N₂O accumulation, yielded an outstanding high value for k_2 , indicating intensive N₂O reduction.

Table 2.4: Rate constants for heterotrophic and autotrophic denitrification derived from the sequential 3-parameter fit. $R^2(k_1)$ and $R^2(k_2)$ denote the correlation coefficients for the (N₂O+N₂)-data and the N₂O-data, respectively. The initial nitrate concentration C_0 was used as the third fitting parameter. The ratio of the fitting value and the experimental value is given in the last column and SD denotes the standard deviation.

Sample location	Depth interval	k_1	k_2	$R^2(k_1)$	$R^2(k_2)$	$C_{0\text{fit}}$	$C_{0\text{fit}}/C_{0\text{exp}}$
	[m]	[days ⁻¹]				[mg N kg ⁻¹]	
B1	2.0 - 2.6	0.007	0.977	1.000	0.740	0.263	0.018
B1	2.6 - 3.0	0.008	0.263	1.000	0.270	0.226	0.012
B1	3.4 - 4.0	0.004	0.162	1.000	0.430	1.698	0.101
I1 - S1	1.5 - 2.0	0.005	0.920	1.000	0.844	3.826	0.213
I1 - S1	2.0 - 2.5	0.004	0.115	1.000	0.840	0.714	0.041
I1 - S1	2.5 - 3.0	0.003	0.031	1.000	0.910	0.945	0.063
I1 - S2	1.5 - 2.0	0.004	1.172	1.000	0.830	1.174	0.098
I1 - S2	2.0 - 2.5	0.006	0.103	1.000	0.910	0.364	0.032
I1 - S3	1.5 - 2.0	0.007	4.881	1.000	0.850	3.768	0.350
I1 - S3	2.0 - 2.5	0.005	1.435	1.000	0.900	0.550	0.044
I1 - S3	2.5 - 3.0	0.005	0.100	1.000	0.270	0.687	0.052
mean		0.005	0.924	1.000	0.709	1.292	0.093
SD		0.001	1.407	0.000	0.255	1.310	0.102
I1 - 1	6.5 - 7.0	0.004	0.135	0.980	0.370	15.340	1.550
I1 - 2	6.5 - 7.0	0.003	0.230	1.000	0.580	18.880	1.840
I1 - 3	6.5 - 7.0	0.020	1.145	0.990	0.390	9.680	1.020
I1 - 4	6.5 - 7.0	0.008	0.289	0.990	0.100	10.120	1.080
I1 - 5	6.5 - 7.0	0.019	1.824	0.990	0.330	10.490	1.080
I1 - 6	6.5 - 7.0	0.021	35.320	1.000	0.400	9.950	1.000
I1 - 7	6.5 - 7.0	0.004	0.154	1.000	0.610	12.860	1.390
I1 - 8	6.5 - 7.0	0.002	0.239	0.980	0.300	22.140	2.460
I1 - 9	6.5 - 7.0	0.021	1.157	0.990	0.270	10.140	1.060
I1 - 10	6.5 - 7.0	0.012	3.578	0.990	0.320	9.799	1.060
I1 - 11	6.5 - 7.0	0.014	0.621	0.990	0.330	11.250	1.190
mean		0.012	4.063	0.991	0.364	12.786	1.339
SD		0.008	10.418	0.007	0.140	4.237	0.456

Table 2.5: Rate constants for heterotrophic and autotrophic denitrification derived from the 1-step 3-parameter fit. R^2 denotes the correlation coefficient. The initial nitrate concentration C_0 was used as third fitting parameter. The initial nitrate concentration C_0 was used as the third fitting parameter. The ratio of the fitting value and the experimental value is given in the last column and SD denotes the standard deviation.

Sample location	Depth interval	k_1	k_2	R^2	$C_{0,fit}$	$C_{0,fit}/C_{0,exp}$
	[m]	[days ⁻¹]			[mg N kg ⁻¹]	
B1	2.0 - 2.6	0.003	0.113	0.860	0.063	0.004
B1	2.6 - 3.0	0.006	0.006	0.920	0.023	0.001
B1	3.4 - 4.0	0.007	0.007	0.830	0.127	0.008
I1 - S1	1.5 - 2.0	0.010	0.070	0.950	0.206	0.011
I1 - S1	2.0 - 2.5	0.008	0.050	0.880	0.230	0.013
I1 - S1	2.5 - 3.0	0.007	0.007	0.970	0.195	0.013
I1 - S2	1.5 - 2.0	0.003	0.091	0.950	0.154	0.013
I1 - S2	2.0 - 2.5	0.005	0.044	0.960	0.175	0.016
I1 - S3	1.5 - 2.0	0.005	0.078	0.960	0.087	0.008
I1 - S3	2.0 - 2.5	0.006	0.061	0.960	0.025	0.002
I1 - S3	2.5 - 3.0	0.003	0.003	0.950	0.130	0.010
mean		0.006	0.048	0.926	0.129	0.009
SD		0.002	0.038	0.048	0.072	0.005
I1 - 1	6.5 - 7.0	0.010	0.010	0.560	1.140	0.120
I1 - 2	6.5 - 7.0	0.009	0.009	0.810	0.660	0.060
I1 - 3	6.5 - 7.0	0.038	0.038	0.690	0.460	0.050
I1 - 4	6.5 - 7.0	0.006	0.006	0.370	1.110	0.120
I1 - 5	6.5 - 7.0	0.036	0.036	0.610	0.310	0.030
I1 - 6	6.5 - 7.0	0.006	87.010	0.500	57.710	5.800
I1 - 7	6.5 - 7.0	0.013	0.013	0.830	0.920	0.100
I1 - 8	6.5 - 7.0	0.007	0.007	0.470	0.630	0.070
I1 - 9	6.5 - 7.0	0.038	0.038	0.530	0.520	0.050
I1 - 10	6.5 - 7.0	0.015	0.015	0.650	0.080	0.010
I1 - 11	6.5 - 7.0	0.029	0.029	0.580	0.690	0.070
mean		0.019	7.928	0.600	5.839	0.589
SD		0.014	26.228	0.139	17.207	1.729

To analyse the fitting results, we chose the data set “I1-S1 2.0 - 2.5” as a representative example that is shown in Figure 2.4. Since the time courses of N_2O concentration result from the competition between production (k_1) and reduction of N_2O (k_2), i.e. between nitrate reduction and di-nitrogen production, one would expect that the rate constants describe consistently both the time course of nitrate (Equ.(2.6)) and the time course of (N_2O+N_2) (Equ.(2.9)). As shown in Figure 2.4B, the 1-step 3-parameter fit underestimated the total concentration of the gaseous species. This clearly demonstrates the necessity of an independent measurement in order to prove the rate constants obtained by the kinetics describing the N_2O -curve. We emphasize that fitting for best agreement of measured and modeled N_2O curves (compare 1-step 3-parameter fit in Fig. 4 with experimental data) did not yield a satisfactory agreement for the NO_3^- and (N_2O+N_2) curves, respectively.

In order to ensure that the cumulative curve of (N_2O+N_2) is reproduced reasonable well, we used a second fitting procedure, namely the sequential fit, i.e. in a first fitting step we determined k_1 by the cumulative curve of $N_2O + N_2$ and in a second step we determined k_2 by the N_2O -curve. As can be seen in Figure 2.4B, we then obtained an excellent fit to the

time course of ($\text{N}_2\text{O}+\text{N}_2$). However, the goodness of fit of the N_2O -data deteriorated (Figure 2.4A), i.e. the early-time behaviour exhibits an increase that is too steep. Nevertheless, the profile in its entirety is still reasonably satisfactory.

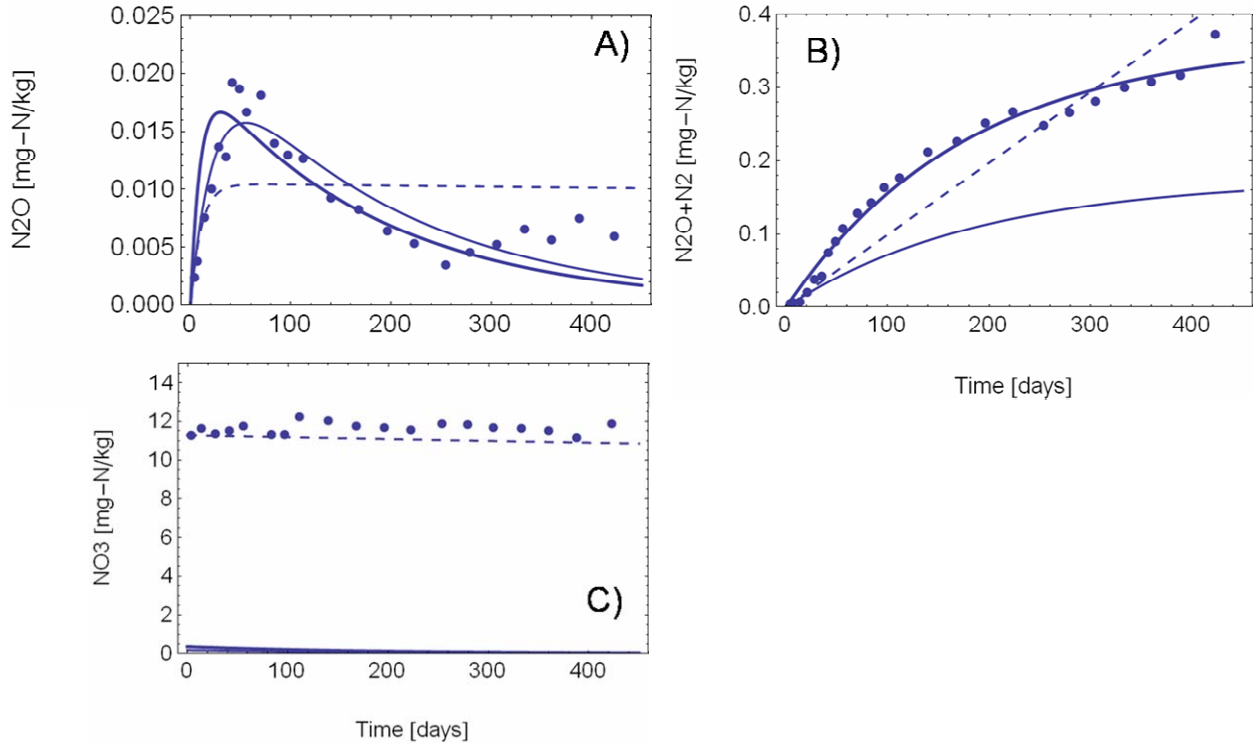


Figure 2.4: Comparison between experimental N_2O - (A), $(\text{N}_2\text{O}+\text{N}_2)$ - (B), and NO_3^- (C) concentrations (solid circles) and fitting curves (thick solid line: sequential 3-parameter fit; thin solid line: 1-step 3-parameter fit; dashed line: sequential 2-parameter fit) for the data set I1-S1 2.0 - 2.5 (heterotrophic denitrification). The rate constants k_1 and k_2 as well as the initial nitrate concentration C_0 were used as fitting parameters for the 3-parameter fits.

As shown in Figure 2.4C, both fitting approaches yielded a very low initial nitrate concentration which deviated considerably from the experimental data. The ratio of the theoretical and experimental initial concentration for the sample I1-S1 2.0 - 2.5 is 0.02 and 0.03, respectively (Table 2.4, Table 2.5). In principle, one would use only the rate constants as fitting parameters, and vary the initial nitrate concentration. This was used as the starting point here. For the sequential 2-parameter fit, the best fits are shown as dashed curves in Figure 2.4. The agreement both to the N_2O - and to the $(\text{N}_2\text{O}+\text{N}_2)$ curves was insufficient, indicating that the constant C_0 (Eqs. 2.7 - 2.9) is not given by the initial nitrate concentration. This is also indicated by the magnitude of the deviation between the experimental data and the theoretical curve (Figure 2.4C).

2.5 Discussion

Field measurements reveal the zones of denitrification and N₂O accumulation

The special characteristic of the studied aquifer is the occurrence of the vertically separated process zones of heterotrophic and autotrophic denitrification. The results of the laboratory incubations showed that these processes generate a different nitrate removal efficiency and thus reaction kinetics. This was also confirmed in a recent study of Weymann et al. (2008) in the FFA by determining excess N₂ dependent upon the depth. Whereas excess N₂ from denitrification was found to be low in the shallow groundwater, i.e. in the heterotrophic zone, the authors reported highest values for excess N₂ (predominantly between 10 and 15 mg N L⁻¹) in depths beyond 5 m below the soil surface, i.e. in the autotrophic zone. Against this background, the question arises to what extent the different nitrate removal efficiencies influence the accumulation of N₂O under field conditions. As the multilevel well measurements indicate, the different reaction kinetics of heterotrophic and autotrophic denitrification yielded a large range and a huge variability of N₂O concentrations in the investigated in-situ profiles at the wells B1 and I1 (Figure 2.1). More precisely, we identified a zone of considerable N₂O accumulation close to the groundwater surface which has been already reported by Deurer et al. (2008). Elevated N₂O concentrations were also found up to 2 to 3 m below the water table. A previous study has shown that this layer probably equates with the zone of heterotrophic denitrification (von der Heide et al. 2008). As the laboratory incubations indicate and Weymann et al. (2008) confirmed, this zone is characterised by low nitrate removal efficiency. The occurrence of N₂O accumulation or N₂O emission combined with low nitrate removal efficiency has also been described in other studies. Hefting et al. (2006) found significant N₂O emissions along a flowpath with low nitrate removal efficiency in a riparian buffer zone. Van Cleemput (1998) stated that conditions causing an inhibition of denitrification, i.e. causing a low nitrate removal efficiency, are favourable for N₂O accumulation. In this context, a key factor for heterotrophic denitrification is the availability of organic carbon. The sandy aquifer material of the FFA contains low amounts of organic carbon (Table 2.1) and the microbial bioavailability can be strongly assumed to be poor (Böttcher et al. 1991). Beside this, it is known that low pH and high NO₃⁻ levels favour N₂O accumulation due to inhibited N₂O reduction to N₂ (Šimek and Cooper 2002, Blackmer and Bremner 1978, van Cleemput 1998). In the case of the FFA, it has been previously assumed that the pH of < 5.5 (Deurer et al. 2008) and the high NO₃⁻ concentrations (von der Heide et al. 2008) are further factors supporting the accumulation of N₂O in the surface groundwater of the FFA in addition to the low availability of organic organic carbon. Confirming the results of Hefting et al. (2006) and van Cleemput (1998), we can thus conclude that the combination of (i) the limited carbon (bio)availability, (ii) the low pH and (iii) high NO₃⁻ concentrations explains the low nitrate removal efficiency in the surface groundwater as well as the considerable N₂O accumulation.

As mentioned in section 2.4, we observed a sharp-cut N_2O concentration peak in both profiles in the deeper groundwater (Figure 2.1). Here, in depths of 5 m and 6 m, respectively, the autotrophic process governs the production and reduction of N_2O . In contrast to heterotrophic denitrification, the nitrate removal in the autotrophic process zone is much more intensive. This has been revealed by the results of the laboratory incubations and was shown previously (Frind et al. 1990, Weymann et al. 2008). Due to the low nitrate removal efficiency in the heterotrophic denitrification zone, the NO_3^- load of the groundwater was still high (concentrations between 11 and 23 mg N L^{-1}) when it came in contact with the reduced sulfur compounds of the deeper aquifer. Accordingly, N_2O was produced within an intensive nitrate removal caused by autotrophic denitrification. But, in contrast to the N_2O accumulation in the surface groundwater, we conclude that the sharp-cut N_2O concentration peak in both profiles is an indicator for rapid N_2O reduction which hampered an accumulation of N_2O in the sense of the heterotrophic denitrification zone. Finally, the high nitrate removal efficiency in the autotrophic denitrification zone resulted in a complete reduction of NO_3^- and N_2O in the deeper groundwater in depths below 5 m and 6 m, respectively. Thus, the deeper aquifer clearly functioned as a sink for N_2O . This is comparable with the findings of Blicher-Mathiesen and Hoffmann (1999) who reported an effective nitrate removal in a riparian fen without N_2O accumulation.

In summary, the vertical courses of NO_3^- and N_2O concentrations at the investigated wells plausibly reflect the occurrence of the separated denitrification zones in the aquifer. Taking the SO_4^{2-} concentrations into account (Figure 2.1), this conception is only confirmed by the gradient of I1. At this well, the increase of the SO_4^{2-} concentrations reflect the considerable sulfate formation capacity of the autotrophic zone (Kölle et al. 1985). This was not observed at well B1. Low potassium concentrations (data not shown) indicate that the deeper groundwater at this well is charged with groundwater that originated from forest or pasture. This groundwater is characterised by significantly lower concentrations of SO_4^{2-} , N_2O and NO_3^- than groundwater under arable land (von der Heide et al. 2008). Hence, we assume that dilution attenuated the concentrations of the investigated parameters in the deeper groundwater at well B1.

Kinetics of N_2O production and reduction during long-term laboratory incubation

The results convincingly showed the substantial difference between the N_2O kinetics of heterotrophic and autotrophic denitrification. Among the factors governing denitrification, the initial NO_3^- concentration, O_2 , and pH had been kept constant by our set-up of anaerobic incubation. Variation in process dynamics was thus mainly caused by the differences in the electron donors, i.e. organic carbon and reduced sulfur and their microbial availability.

We attribute the low activity of heterotrophic denitrification to the limited supply of organic carbon and to its poor microbial availability. This is supported by NO_3^- concentrations that remained close to initial concentrations during the incubation period, indicating that the electron acceptor was not a limiting factor for the process. Carbon

limitation in sand and gravel aquifers was also demonstrated by Smith and Duff (1988), Obenhuber and Lowrance (1991) and Paramasivam et al. (1999). In fact, the organic carbon content in the samples of the heterotrophic zone was very low (Table 2.1) compared to the results of other incubation studies (Paramasivam et al. 1999, Well et al. 2005a). Besides the NO_3^- analyses, we regularly measured DOC concentrations in the “heterotrophic” water samples (data not shown). Initial concentrations were found to be between 6 and 25 mg C L⁻¹ and were predominantly higher than the critical lower threshold of about 2 - 7 mg C L⁻¹ that was reported to be necessary to promote denitrification (Spalding et al. 1978, Groffman et al. 1996). We did not observe significant DOC consumption within the whole incubation period in any sample of the heterotrophic zone. Furthermore, the correlation analysis yielded no significant relationships between extractable DOC and the denitrification rates (Table 2.3). Both findings indicate a poor bioavailability of DOC for denitrification in the heterotrophic zone, supporting the results of a previous field study in the FFA (Deurer et al. 2008) as well as the results of Jacinthe et al. (1998) and Siemens et al. (2003). However, von der Heide et al. (2009b) reported significant negative correlations between DOC and N_2O concentrations in the surface groundwater of the FFA, a relationship that was also observed in this study (Table 2.3). The authors attributed this relationship to a promotion of N_2O accumulation by decreasing bioavailability of DOC. This would require that DOC functions as an electron donor for the NO_3^- -to- N_2O step of denitrification, but to lesser extent for the N_2O -to- N_2 step. As our data supply no evidence to confirm or contradict this, further research into the effect of DOC on N_2O accumulation in groundwater is needed.

In contrast to heterotrophic denitrification, the autotrophic process was not limited by its electron donor reduced sulfur, but by its electron acceptor NO_3^- . The availability of reduced sulfur was sufficient to eliminate NO_3^- and N_2O completely in all samples. Hence, we stress that the laboratory incubations also confirm the role of autotrophic denitrification to function as a sink for NO_3^- and N_2O .

The aquifer material of the autotrophic zone was more variable in texture and organic carbon than the homogeneous sands of the heterotrophic zone (Table 2.1). The samples with the highest contents of organic carbon and clay, i.e. I1 - 5, I1 - 6 and I1 - 9, respectively, showed the highest denitrification activity (Figure 2.3). These observations and the positive correlation between organic carbon and the “autotrophic” denitrification rates (Table 2.3) indicate that the kinetics of denitrification was apparently governed by these parameters. Against this background, the question arises whether heterotrophic denitrification also occurs in the deeper aquifer. On the one hand, lignitic pebbles which are nonuniformly distributed throughout the deeper aquifer (Frind et al. 1990), could function as “patchy” hot spots (Parkin 1987, Jacinthe et al. 1998, Gold et al. 1998) providing organic carbon serving as the electron donor and probably causing the small scale spatial variability of denitrification activity and N_2O accumulation (von der Heide et al. 2009b). This organic carbon is also used as an electron donor to reduce sulfate in the deeper groundwater of the FFA (Böttcher et al. 1989, Frind et al. 1990). Korom (1991) showed thermodynamically, that organic carbon used as an electron donor in the sulfate-

reducing zone of the FFA would preferentially be used by bacteria for heterotrophic denitrification. On the other hand, Böttcher et al. (1991) stated that as long as reduced sulfur compounds are available in the FFA, simultaneous heterotrophic denitrification is unlikely for several reasons. For example, the authors emphasized that the microbial availability of the organic lignitic pebbles is probably poor and might superimpose the thermodynamic “advantage” of heterotrophic denitrification. However, this has not been proven until now. The reactivity of the lignitic pebbles and the question, to what extent a possible heterotrophic process in the deeper aquifer potentially contributes to total denitrification, remain subjects of uncertainty. Further investigations into the deeper groundwater will be necessary to overcome this lack of knowledge.

Kinetic constants k_1 and k_2 of the first-order approach roughly reflected the different reaction rates of heterotrophic and autotrophic denitrification, as a comparison of their mean values revealed (Table 2.4, Table 2.5). The outstanding high k_2 -value in the case of the sample I1 - 6 reflects the fact that the balance between N_2O production and reduction was clearly at the reduction side, yielding negligible N_2O accumulation. Here, the rate constants also described the experimental data plausibly. However, in most cases the goodness of fit as given by R^2 of k_2 was not satisfactory. This can also be seen from the strong deviation between fitted and measured initial NO_3^- concentration (Table 2.4, Table 2.5). The initial nitrate concentration fitted by the 3-parameter fits (C_0 , Table 2.4, Table 2.5) was much too low and not in agreement with the experimental data for the samples of heterotrophic denitrification (example in Figure 2.4C). We assume that the exhaustion of available organic carbon is the reason for this deviation, because organic carbon was not taken into account by the model as a factor that limited the reaction. Instead, the first-order model assumed that process rates were controlled by the decreasing availability of NO_3^- which did not occur during our experiments due to the poor nitrate removing efficiency of heterotrophic denitrification. Furthermore, the predominantly linear time courses of NO_3^- and (N_2O+N_2) during autotrophic denitrification (Figure 2.3) indicate that the reaction kinetics is rather described by a zero-order than by a first-order model. Pätsch (2006) and Konrad (2007) reported in agreement that both kinetics can occur in one aquifer. Therefore, using only one modeling approach may include uncertainties (Pätsch 2006) and an improved model should be flexible enough to include both reaction types.

These considerations reveal that for an improved modeling approach (i) the electron donors have to be taken into account and (ii) zero-order and Michaelis-Menten kinetics should also be applied in order to describe production and reduction of N_2O more precisely.

Transferability of laboratory incubations to field conditions

Did the laboratory experiments and the respective kinetic constants reflect the process kinetics that are present in groundwater of the FFA? Generally, this question is subject to an ongoing controversy in groundwater literature about whether or not batch experiments effectively describe field scale reactions (Dykaar and Kitanides 1996, Ginn et al. 2002, McQuarrie and Sudicky 2001). As Kelly et al. (1996) showed by a comparison between

derived kinetic parameters from batch experiments and column experiments, respectively, the derived kinetic constants deviated significantly. For example, column experiments yielded V_{\max} -values for Benzene between 0.037 and 0.219 1/h, but a batch-experiment revealed a V_{\max} -value that was 0.049 1/h. On the other hand, Schirmer et al. (2000) had shown that kinetics derived from batch experiments can describe an in-situ tracer test. As already mentioned in the introduction section, the question of transferability led also to conflicting statements related to denitrification and to the occurrence of N_2O (Hénault et al. 2001, Obenhuber and Lowrance 1991, Blicher-Mathiesen and Hoffmann 1999, Well et al. 2003). Thus, to find an unambiguous and general answer seems to be impossible. Rather, we should assess the question as the case arises. Taking the present results of this study into account, it becomes obvious that we have to distinguish between heterotrophic and autotrophic denitrification if the transferability of the laboratory incubations should be assessed.

The different denitrification capacities of the heterotrophic and autotrophic zones in the FFA were reflected by the incubation experiments. The anaerobic incubations showed only marginal nitrate removal efficiency in the heterotrophic zone. In contrast, the rapid nitrate removal related to autotrophic denitrification yielded a capacity that is about one order of magnitude higher. Both observations are in agreement with the field data (Figure 2.1) and with a previous field study (Weymann et al. 2008). Hence, this finding confirms the results of Well et al. (2003) who also reported a satisfactory agreement of laboratory and in situ measurements of denitrification.

If we regard the occurrence of N_2O , the subject of transferability has to be considered more differentially. For the autotrophic zone that was investigated at well I1, the field measurements yielded a maximum N_2O concentration of 1.05 mg N L^{-1} at a depth of 6 m (Figure 2.1) which equates to $0.26 \text{ mg N kg}^{-1}$ assuming a pore volume of 40 %. The median of the cN_2O_{\max} values measured during laboratory incubation (Table 2.2) was $0.52 \text{ mg N kg}^{-1}$. This comparison shows that laboratory and field data were in one order of magnitude and thus in satisfactory agreement. Furthermore, laboratory and field investigations showed correspondingly that the autotrophic zone functions as a sink for N_2O if the NO_3^- pool is exhausted, since N_2O was completely consumed during the last stage of denitrification progress (Figure 2.1, Figure 2.3). On the other hand, cN_2O_{\max} measured during laboratory incubation of the heterotrophic aquifer material were considerably lower than the maximum N_2O concentrations we evaluated in the field. Whereas the median of the cN_2O_{\max} values measured during laboratory incubation (Table 2.2) was $0.02 \text{ mg N kg}^{-1}$, the averaged maximum N_2O concentrations at B1 and I1 were 1.74 mg N L^{-1} (Figure 2.1), which equates to $0.43 \text{ mg N kg}^{-1}$. This observation is in contrast to the findings of Well et al. (2003) who reported greater N_2O -fractions as a result of laboratory incubation in most of the investigated soils. Blicher-Mathiesen and Hoffmann (1999) also observed higher N_2O concentrations during their laboratory experiments due to a differing reduction pattern that supported N_2O accumulation. Another disagreement between laboratory and field data is exhibited by the increasing cN_2O_{\max} values of N_2O

with depth during laboratory incubation (Figure 2.2), whereas the field data indicate the highest N₂O accumulation in the uppermost groundwater (Figure 2.1, Deurer et al. 2008).

What are the reasons causing the poorer transferability of the “heterotrophic” incubations to the field scale related to the kinetics of N₂O production and reduction? One explanation could be that the aquifer slurries are subject to a certain disturbance for a short time according to the laboratory method, i.e. physical disruption and aerobic conditions during collection. This may alter the composition of the microbial communities. In fact, the influence of these processes seemed to be negligible in the case of autotrophic denitrification, because the laboratory incubations reflected the field data. This might be explained by the high abundance of reduced sulfur that seems to be easily accessible to the autotrophic denitrifier *Thiobacillus denitrificans* (Böttcher et al. 1991) and by the fact that the electron donor was not sustainably altered by temporal contamination with atmospheric oxygen and physical disturbances during sampling. To the contrary, we assume that the small pool of available organic carbon in the heterotrophic zone might be sensitive to disturbances, e.g. by oxidation with atmospheric oxygen. This could lead to some loss of denitrification capacity and might explain the observed deviations in N₂O accumulation. Another reason for the discrepancy between laboratory and field-based studies was reported by Smith et al. (1996). The authors identified the differences between spatial and temporal scales as a reason for this discrepancy. Furthermore, sampling of a small amount of aquifer slurry for laboratory incubations may miss patches and hotspots of available organic carbon and heterotrophic denitrification activity (Jacinthe et al. 1998). Finally, in-situ N₂O accumulation in the heterotrophic zone is affected by the fluctuating groundwater level and day-scale infiltration events. These dynamics are not provided by static incubation experiments. To sum up, we note that the kinetics of N₂O production and reduction in the heterotrophic denitrification zone tends to be susceptible to effects connected with the static laboratory approach conducted at the microscale and sampling. In contrast, the autotrophic denitrification seems to be a more robust process. The availability of its uniformly distributed electron donor induces high denitrification activity which hampers changes of in situ processes and reaction kinetics during laboratory investigations, yielding a good agreement of field and laboratory results.

2.6 Interim conclusions

N₂O is produced in the surface groundwater of the FFA as an intermediate of heterotrophic denitrification as well as in the deeper groundwater due to autotrophic denitrification. The heterotrophic process is limited by the availability of the electron donor organic carbon yielding a low denitrification capacity. Field measurements indicated considerable N₂O accumulation especially in the uppermost groundwater. In contrast, laboratory incubations of aquifer material yielded substantially lower N₂O concentrations than measured in the field. Thus, the laboratory results are hardly transferable to the field scale. We conclude that the discrepancy is due to the susceptibility of the sensitive heterotrophic process to sampling activities and differences in spatial scales between field and laboratory

conditions. The autotrophic process is characterised by a high denitrification capacity and not limited by its electron donor, reduced sulfur. Laboratory and field data were found to be in good agreement showing that the autotrophic zone functions as a sink for N_2O . The application of a conventional k_1 - k_2 -model following first-order-kinetics revealed rate constants that roughly confirmed the experimental data, i.e. for example the difference between the reaction rates of heterotrophic and autotrophic denitrification. However, the fitting results to the experimental time courses of the N-species were partly unsatisfactory. In conclusion, we note that a more sophisticated approach will be necessary to describe the kinetics of N_2O production and reduction successfully.

2.7 Summary of the chapter

Knowledge of the kinetics of N_2O production and reduction in groundwater is essential for the assessment of potential indirect emissions of the greenhouse gas. In this study, we investigated this kinetics using a laboratory approach. The results were compared to field measurements in order to examine their transferability to the in situ conditions. The study site was the unconfined, predominantly sandy Fuhrberger Feld aquifer in northern Germany. A special characteristic of the aquifer is the occurrence of the vertically separated process zones of heterotrophic denitrification in the surface groundwater and of autotrophic denitrification in the deeper groundwater, respectively. The kinetics of N_2O production and reduction in both process zones was studied during long-term anaerobic laboratory incubations of aquifer slurries using the ^{15}N tracer technique by adding a $\text{K}^{15}\text{NO}_3^-$ solution. We measured N_2O , N_2 and NO_3^- concentrations as well as parameters of the aquifer material that were related to the relevant electron donors, i.e. organic carbon and sulfur. Field measurements of N_2O , NO_3^- and SO_4^{2-} concentrations in the groundwater were conducted at two multilevel sampling wells in depths up to 9 m below the water table. N_2O accumulated considerably in the entire heterotrophic denitrification zone, especially in the uppermost groundwater, where N_2O concentrations up to 1.84 mg N L^{-1} occurred. In the autotrophic denitrification zone, we observed a transient N_2O accumulation followed by a rapid and complete reduction of NO_3^- and N_2O , indicating that the autotrophic zone functioned as a sink for both N-species. The anaerobic incubations showed a low denitrification activity of heterotrophic denitrification with initial rates between 0.0002 and $0.0133 \text{ mg N kg}^{-1} \text{ d}^{-1}$. The process was carbon limited due to the poor availability of its electron donor. In the autotrophic denitrification zone, initial denitrification rates were considerably higher, ranging between 0.0303 and $0.1480 \text{ mg N kg}^{-1} \text{ d}^{-1}$ and NO_3^- as well as N_2O were completely removed within 60 - 198 days. N_2O accumulated during heterotrophic and autotrophic denitrification, but maximum concentrations were substantially higher during the autotrophic process. The results revealed a satisfactory transferability of the laboratory incubations to the field scale for autotrophic denitrification, whereas the heterotrophic process less reflected the field conditions due to considerable lower N_2O accumulation during laboratory incubation. Finally, we applied a conventional model to determine the reaction rates of the NO_3^- -to- N_2O step (k_1) and the N_2O -to- N_2 step (k_2) using first-order-kinetics and evaluated the

reaction rate constants for both steps. The model yielded fits to the experimental data that were of limited goodness, indicating that a more sophisticated approach is essential to describe the investigated reaction kinetics satisfactorily.

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

3.1 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 N₂O emissions originates from agricultural ecosystems (Mosier et al. 1998). In aquifers of agricultural catchments, high concentrations of N₂O were found at the groundwater surface (Spalding and Parrott 1994; Well et al. 2005a; Deurer et al. 2008). Thus groundwater N₂O was assumed to be a potential significant source of N₂O 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. 2005c). The Intergovernmental Panel on Climate Change (IPCC) methodology provides a concept of N₂O emission factors, containing an emission factor EF5-g for indirect N₂O 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. (2005c) and Clough et al. (2007). Firstly, the EF5-g default factor was defined as 0.015 kg N₂O-N per kg 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 kg N₂O-N per kg of N leached (IPCC 2006). However, the knowledge of indirect N₂O emissions from groundwater is still limited because few studies have tried to relate subsurface N₂O concentrations to N leaching from soils (Clough et al. 2005). Furthermore, the question how much N₂O that was produced in the surface groundwater can finally reach the atmosphere is a subject of uncertainty and the controls governing the balance between N₂O production and consumption are not well understood (Clough et al. 2007). Upward diffusive N₂O 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 N₂O like the IPCC EF5-g are based on N₂O concentrations assuming that degassing of all dissolved N₂O 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 one 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 $^{15}\text{N}\text{-N}_2\text{O}/^{15}\text{N}\text{-N}_2$ ratios during upward diffusion of the labeled gases. Furthermore, they stated that this effect may be caused by dilution of the $^{15}\text{N}\text{-N}_2\text{O}$ pool with soil derived N_2O , or by consumption of $^{15}\text{N}\text{-N}_2\text{O}$ 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 $^{15}\text{N}\text{-N}_2\text{O}$ 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 $^{15}\text{N}\text{-N}_2\text{O}$ and $^{15}\text{N}\text{-NO}_3^-$ in the surface groundwater and $^{15}\text{N}\text{-N}_2\text{O}$ 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 $^{15}\text{N}\text{-N}_2\text{O}$ production at the groundwater surface stimulated by weekly application of a $^{15}\text{N}\text{-NO}_3^-$ 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.

3.2 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 to 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 desulfurication 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 m² 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 to 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 Figure 3.1.

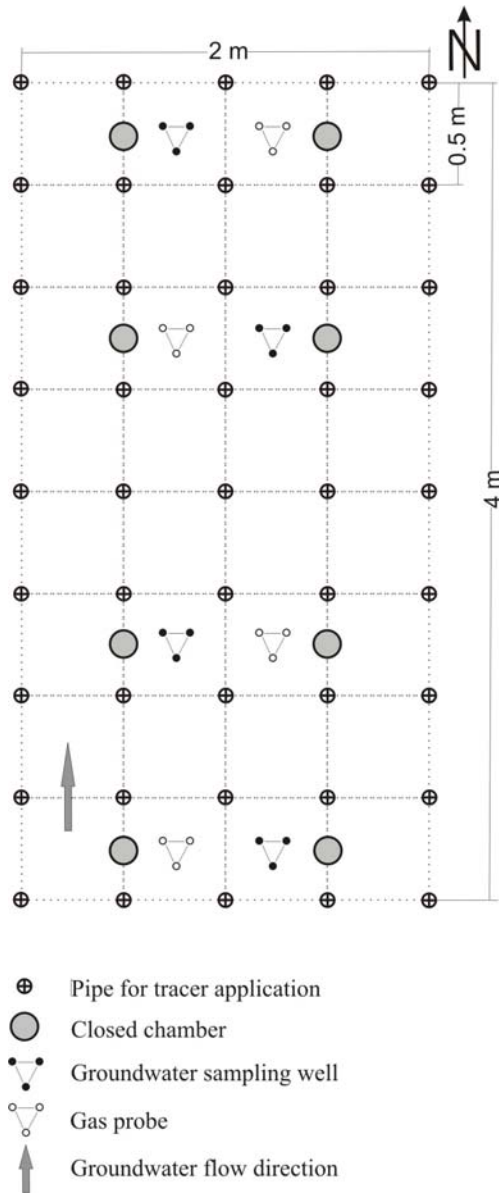


Figure 3.1: Measuring field with its elements and dimensions.

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 minutes. 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 hours. Concentrations of N_2O 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 \times 0.32 mm ID; Agilent Technologies, Santa Clara, USA) kept at 30 °C. The split ratio was 1:8 and Ar- CH_4 (95/5) was used as carrier and make-up gas. Samples of 300 μL were injected using an autosampler (model GC-PAL, CTC-Analytics, Zwingen, Switzerland). Precision as given by the standard deviation obtained from 4 injections of a standard gas was typically 1.5 %. Dissolved N_2O was calculated from the gas phase concentrations of the water samples using the Bunsen absorption coefficient of N_2O (Weiss and Price 1980). ^{15}N - N_2 was analysed following the method specified in Well et al. (1998) and Well et al. (2003). The gas concentrations of the sample solution (dissolved N_2) were calculated according to Henry's law from the headspace concentrations using the Bunsen absorption coefficient of N_2 (Weiss 1970).

NO_3^- 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 3-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 the closed 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 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 one 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-Analytics, Zwingen, Switzerland) as described by Casciotti et al. (2002). ¹⁵N enrichments are reported as atom% ¹⁵N or δ¹⁵N vs. 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 ¹⁵N tracer by NO₃⁻ 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 N₂O fluxes at the soil surface, these soil properties were measured using time domain reflectrometry (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 N₂O in surface emissions

Fluxes of total N₂O-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 minutes after enclosure). The slope of the temporal change of N₂O 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 N₂O (cN₂O_{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:

$$\delta_{\text{mix, chamber}} = \frac{\delta_{\text{gw}} \times \text{cN}_2\text{O}_{\text{gw}} + \delta_{\text{soil}} \times \text{cN}_2\text{O}_{\text{soil}} + \delta_{\text{atm}} \times \text{cN}_2\text{O}_{\text{atm}}}{\text{cN}_2\text{O}_{\text{chamber}}} \quad (3.1)$$

what leads to

$$\text{cN}_2\text{O}_{\text{gw}} = \frac{\delta_{\text{mix, chamber}} \times \text{cN}_2\text{O}_{\text{chamber}} - \delta_{\text{soil}} \times \text{cN}_2\text{O}_{\text{soil}} - \delta_{\text{atm}} \times \text{cN}_2\text{O}_{\text{atm}}}{\delta_{\text{gw}}} \quad (3.2)$$

where $\delta_{\text{mix, chamber}}$ is the ¹⁵N enrichment of N₂O measured in the flux chambers after 60 min. $\text{cN}_2\text{O}_{\text{soil}}$, $\text{cN}_2\text{O}_{\text{atm}}$ and $\text{cN}_2\text{O}_{\text{chamber}}$ are concentrations of N₂O 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 ¹⁵N-enrichment of N₂O 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 N₂O, we compared $\delta_{\text{mix, chamber}}$ with background $\delta^{15}\text{N}$ of N₂O in atmospheric air and in the soil atmosphere of a control plot. The background of $\delta^{15}\text{N}$ of N₂O was between 2 and 8 ‰, the calculated mean value

was 4.4 ‰ and the standard deviation 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 $\text{cN}_2\text{O}_{\text{gw}}$ [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:

$$F = \frac{\text{N}_2\text{O}_{\text{gw}}}{A_{\text{chamber}} \times T} \quad (3.3)$$

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 $\mu\text{g N}_2\text{O-N h}^{-1} \text{m}^{-2}$.

3.3 Results

Groundwater level, soil moisture and meteorological conditions

During July and August 2007, the precipitation was 104.3 mm and 102.9 mm, respectively. The groundwater level varied between 1.09 m and 1.42 m below the soil surface (Figure 3.2 A).

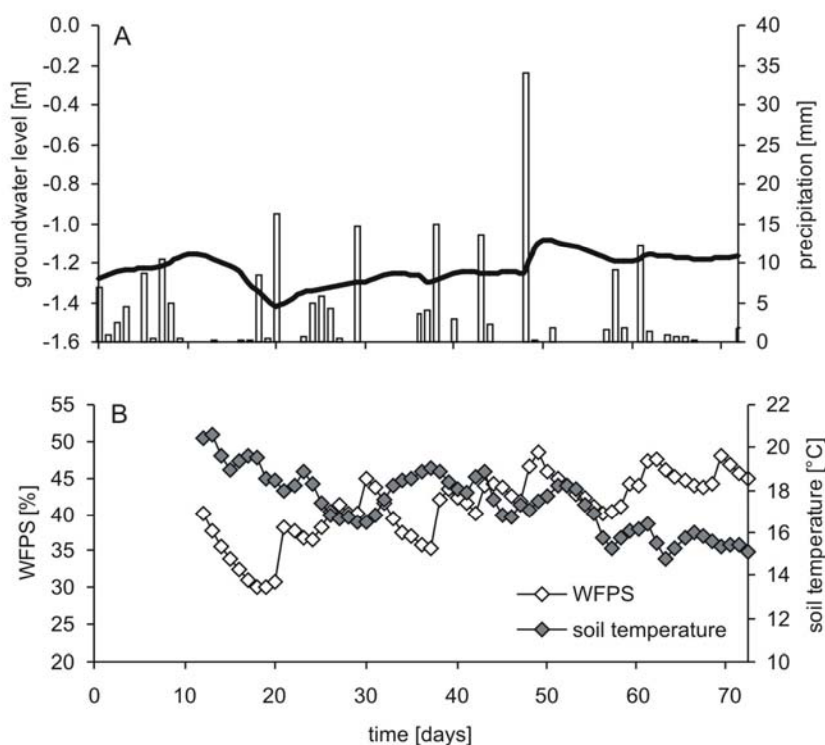


Figure 3.2: Groundwater level below the soil surface, precipitation (A) and water-filled pore space as well as soil temperature at 0.2 m below the soil surface (B) during the measurement period.

If the groundwater levels at the start and at the end of the measuring period in Figure 3.2 A 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; von der Heide 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, Figure 3.2 B). 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 (Figure 3.2 A). Correspondingly, we observed a WFPS of 49 % at day 49, which was the highest during the measurement period (Figure 3.2 B).

NO₃⁻ concentrations and ¹⁵N enrichment of NO₃⁻ in the surface groundwater

The time course of NO₃⁻ concentrations in the surface groundwater (1.5 - 1.7 m below soil surface) is represented in Figure 3.3 A. Prior to the tracer application, NO₃⁻ concentrations were low, ranging from 0.38 to 0.82 mg N L⁻¹. During the labeling phase with K¹⁵NO₃ tracer solution (12.5 mg NO₃⁻-N L⁻¹), mean NO₃⁻ concentrations in each depth increased until day 21 to a level of approximately 6 to 10 mg N L⁻¹. After this NO₃⁻ concentrations in

1.5 m 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 m and 1.6 m depth.

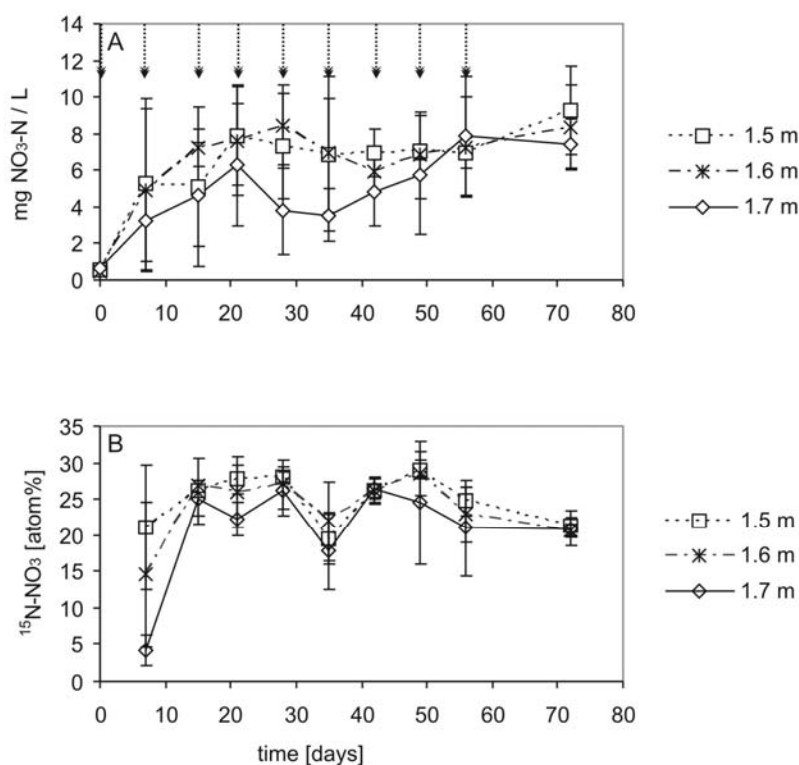


Figure 3.3: NO_3^- -N concentrations (A) and ^{15}N enrichment of NO_3^- (B) in the surface groundwater. Error bars denote the standard deviation of 4 samples collected from multilevel wells. The dates of the tracer applications are indicated by arrows.

The time course of the ^{15}N enrichment of NO_3^- in the surface groundwater is shown in Figure 3.3 B. 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 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 $^{15}\text{N-}\text{N}_2$ 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 the soil surface are represented in Figure 3.4. In the surface groundwater (Figure 3.4 C), highest N_2O concentrations between 14.0 and $15.8 \text{ } \mu\text{g N}_2\text{O-N L}^{-1}$ occurred at day 21. At all the other sampling events, N_2O concentrations were comparatively low, ranging between 0.9 and $4.9 \text{ } \mu\text{g N}_2\text{O-N L}^{-1}$ 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 $0.88 \text{ } \mu\text{g N}_2\text{O-N L}^{-1}$, 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 $^{15}\text{N}\text{-N}_2$ concentrations in the groundwater were $56.14 (\pm 50.42) \mu\text{g L}^{-1}$ 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 $0.10 (\pm 0.11)$.

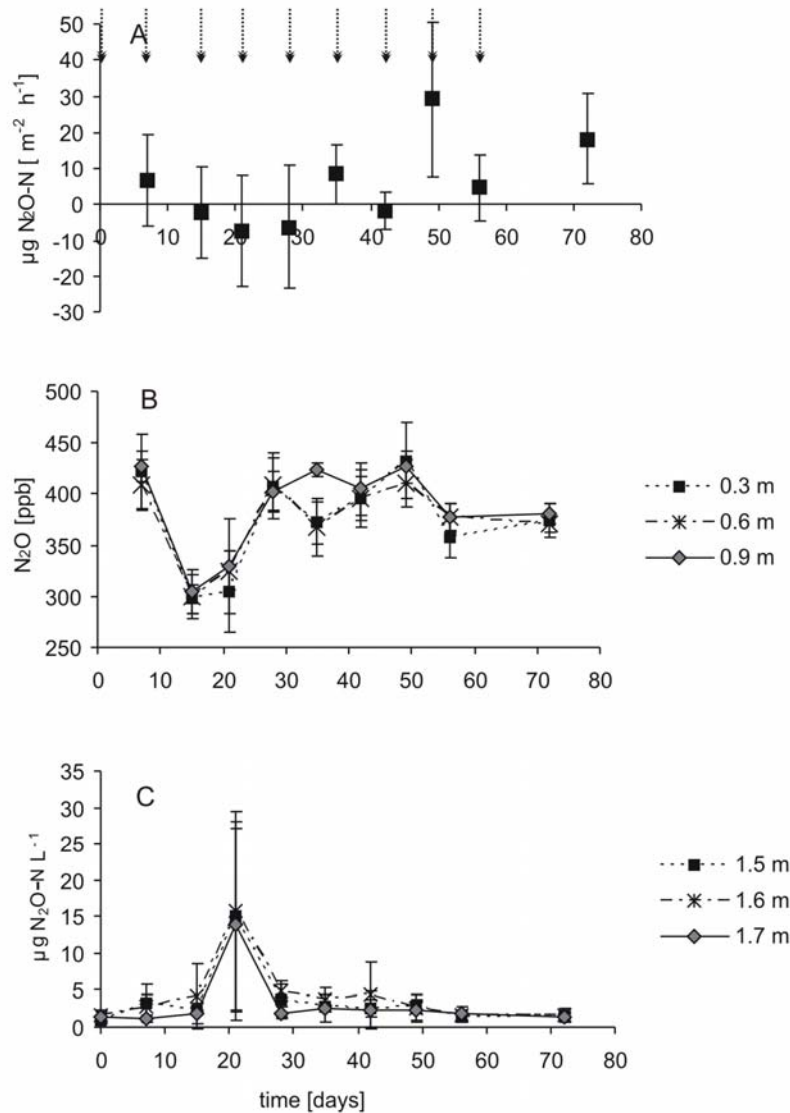


Figure 3.4: N_2O fluxes at the soil surface measured in static flux chambers after an enrichment time of 60 min (A), N_2O concentration in the soil atmosphere in 0.3, 0.6 and 0.9 m depth below the soil surface (B) and dissolved N_2O concentration in the surface groundwater in 1.5, 1.6 and 1.7 m depth below soil surface (C). Error bars denote the standard deviation from 8 static flux chamber measurements (A) and 4 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.

In the soil atmosphere of the unsaturated zone (Figure 3.4 B), N_2O concentration ranged between 297 and 427 ppbv and was thus close to ambient concentration 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 N₂O concentrations in the soil atmosphere at day 15 during a period of several days without rainfall (Figure 3.2, Figure 3.4 B). Significant differences in N₂O concentrations between the 3 sampling depths were not detected, with the exception of the sampling event at day 35, where we measured a N₂O 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 N₂O 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 N₂O fluxes of the sampling events ranged between -7.6 and 29.1 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ (Figure 3.4 A). 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 (Figure 3.4 A).

¹⁵N enrichment of N₂O in the surface groundwater, in the unsaturated zone and at the soil surface

Figure 3.5 illustrates the time courses of the mean ¹⁵N enrichment of N₂O. Generally, ¹⁵N enrichment of N₂O in the profile rapidly decreased upwards from the surface groundwater via the unsaturated zone to the soil surface.

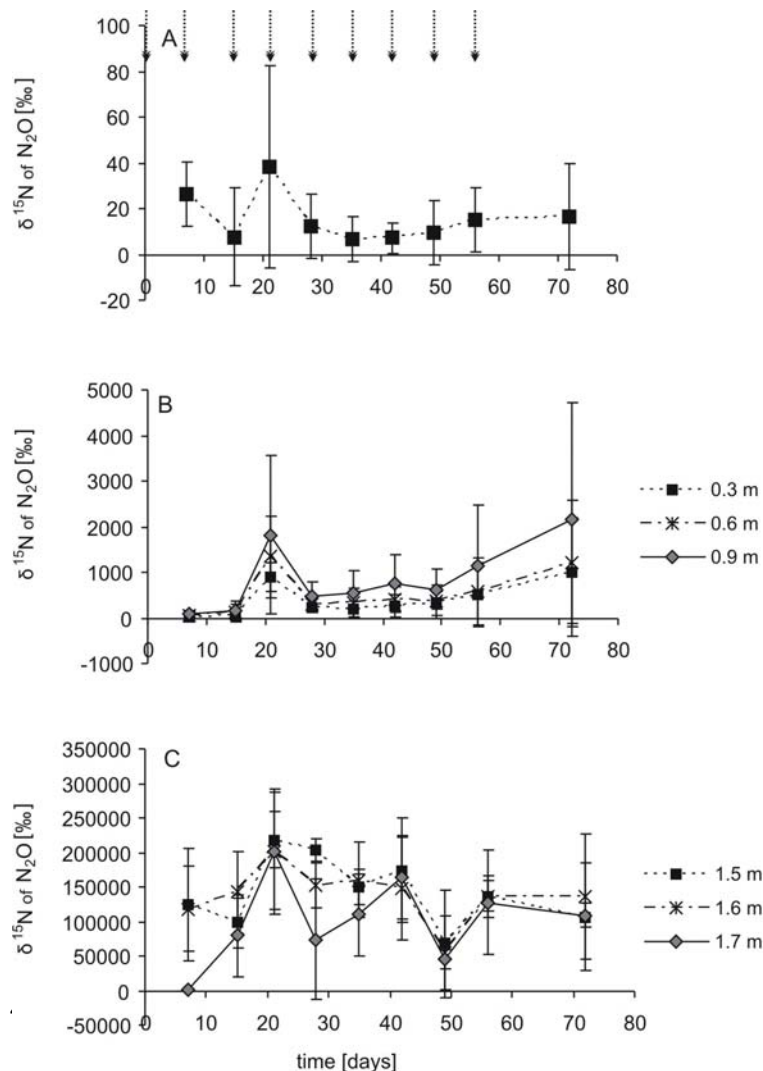


Figure 3.5: ¹⁵N enrichment of N₂O: (A) at the soil surface measured in flux chambers after an enrichment time of 60 min, (B) in soil atmosphere in 0.3, 0.6 and 0.9 m depth below soil surface and (C) in surface groundwater in 1.5, 1.6 and 1.7 m depth below soil surface. Error bars denote the standard deviation from 8 static flux chamber measurements (A) and 4 samples of each depth in the unsaturated zone (soil atmosphere, B) and 4 samples of each depth from the surface groundwater (C), respectively. The arrows indicate the date of the tracer applications.

In the surface groundwater (Figure 3.5 C), we observed average $\delta^{15}\text{N}$ between 56000 and 207000 ‰ corresponding to 13 and 42 atom% ^{15}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 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 (Figure 3.3 B).

In the soil atmosphere of the unsaturated zone (Figure 3.5 B), 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 (Figure 3.5 B).

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 (Figure 3.5 A).

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 3.1) 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 to 3, Table 3.1) which is equivalent to 0.0002 to 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 3.1, Figure 3.4A).

Table 3.1: Mass of groundwater-derived N₂O emitted at the soil surface and calculated emission rate of groundwater-derived N₂O from the groundwater to the atmosphere. The values represent means (\pm standard deviation) of 8 flux chamber measurements per sampling event.

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

3.4 Discussion

Groundwater labeling

Was the extent of groundwater labeling sufficient for detecting fluxes of ¹⁵N₂O 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 NO₃⁻ and N₂O in the groundwater were very low before the first tracer application (Figure 3.3, Figure 3.4 C) and the NO₃⁻ concentration of the tracer solution and its ¹⁵N enrichment were comparatively high, we achieved a high enrichment of NO₃⁻ within the groundwater layer which was sampled by the the multilevel wells. This was shown by both, increasing concentrations of NO₃⁻ as well as the significant ¹⁵N enrichment of the groundwater at all multilevel wells. Consequently, the prerequisite for using $\delta^{15}\text{N}$ of N₂O to monitor formation of N₂O and its emission at the soil surface was fulfilled. However, temporal and spatial variation of labeled N₂O and NO₃⁻ 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 N₂O

To which extent was the variability of N₂O concentrations in the soil atmosphere of the unsaturated zone and of N₂O fluxes at the soil surface caused by N₂O produced in the surface groundwater? With a few exceptions, the variability of N₂O concentrations in the soil atmosphere of the unsaturated zone and of fluxes at the soil surface was relatively low. Peak N₂O concentrations in the groundwater occurring at day 21 did not enhance N₂O

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}N - N_2O pool with soil derived and atmospheric ^{14}N - N_2O . Clough et al. (1999) also observed a decrease in the ^{15}N enrichment of N_2O as the gas diffuses upwards through the profile. The authors mentioned dilution as the most likely cause for decreasing ^{15}N enrichment of N_2O , but their results are also compatible with consumption of ^{15}N -enriched N_2O in the upper part of the soil. In our study, ^{15}N enrichment of N_2O in the groundwater was comparatively low at day 49 (Figure 3.5). 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 ^{15}N enrichments of N_2O through the whole profile occurred at day 21 (Figure 3.5) and coincided with a substantial drawdown of the groundwater level immediately before sampling. Apparently, a rapid drawdown can cause a rapid release of dissolved N_2O into the unsaturated zone (Well 2002, Grant and Pattey 2003) which might cause also an increased ^{15}N -enrichment of N_2O near the soil surface. Otherwise, the increasing groundwater level starting with day 48 did not induce dynamics of the ^{15}N -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 N_2O is unlikely during a phreatic rise, because dissolution of soil air is the dominant process. Hence, we assume that dynamics of the ^{15}N -enrichment within the profile is prevented during a rise of the water table.

Fluxes of total N_2O at the soil surface and of groundwater-derived N_2O to the atmosphere

Compared to other studies reviewed in Chapuis-Lardy et al. (2007), total fluxes of N_2O at the soil surface were low. During the measuring period, a majority of these fluxes were close to zero and not significant (Figure 3.4 A). 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 N_2O 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 N_2O concentrations in groundwater.

The very low groundwater-derived N_2O fluxes to the atmosphere indicate that the importance of groundwater-derived N_2O for atmospheric emissions was negligible at our research site during the measuring period. This is illustrated by the fact that only 0.04 to 0.28 % of the positive N_2O fluxes at the soil surface originated from $^{15}\text{N}_2\text{O-N}$ that was produced in groundwater.

In a previous study conducted in the Fuhrberger Feld aquifer, Deurer et al. (2008) estimated upward N_2O fluxes from the surface groundwater into the unsaturated zone based on measurements of groundwater N_2O concentrations at 6 multilevel wells. These fluxes ranged from 0.0009 to $0.3 \text{ kg N}_2\text{O ha}^{-1}\text{year}^{-1}$ which is equivalent to a range from 0.0006 to $0.2 \text{ kg N}_2\text{O-N ha}^{-1}\text{year}^{-1}$. In our study, fluxes of $^{15}\text{N}_2\text{O}$ from groundwater to the atmosphere were found to be in a range from 0.0002 to $0.0018 \text{ kg N}_2\text{O-N ha}^{-1} \text{ year}^{-1}$, what is similar to the range of the data of Deurer et al. (2008). However, it remains to be determined to what extent potential N_2O consumption in the unsaturated zone and in the topsoil allows a comparison between the different approaches. More research is needed to quantify consumption of N_2O 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 $7.8 \text{ kg N}_2\text{O-N ha}^{-1} \text{ year}^{-1}$. 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 higher than the N_2O fluxes reported in this study basing on 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; von der Heide et al. 2009). In the light of these studies and of our results, indirect N_2O emissions via the diffusive pathway seem to be hardly significant.

3.5 Interim conclusions

We measured N₂O 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 N₂O to the soil surface that was produced in groundwater by denitrification using a ¹⁵N tracer in-situ approach.

Stable ¹⁵N 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 ¹⁵N₂O to surface emissions was very low within the measuring period and not detectable with the conventional closed chamber method. Using the ¹⁵N tracer technique, we observed highest N₂O fluxes from groundwater in temporal connection with a rapid decrease of the groundwater table which suggests that diffusive indirect N₂O emissions from groundwater can be favoured by such dynamics. Generally, our data support previous assumptions that indirect N₂O emissions from groundwater occurring by upward diffusion to the atmosphere are hardly an important part of total N₂O 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.

3.6 Summary of the chapter

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.

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

4.1 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 on 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 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 und 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 & 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 N_2O concentration in groundwater does not necessarily reflect actual indirect N_2O emission.

N_2O represents an obligate intermediate of the denitrification process. 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 (Heaton, 1983; 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).

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 the 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.

4.2 Materials and Methods

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 4.1.

Table 4.1: 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.

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 4.1). 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 (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 hours. 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 using 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, U.K.). 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 He as well as the solubilities of these gases (Weiss 1970; Weiss 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 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 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 .

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 (Böhlke, 2002). 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 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 (Holocher et al. 2002).

Excess N_2 ($X_{\text{excess } N_2}$) can thus be calculated using the following equation:

$$X_{\text{excess } N_2} = X_{N_2 T} - X_{N_2 EA} - X_{N_2 EQ} \quad (4.1)$$

where X denotes molar concentration of the parameters. $X_{N_2 T}$ represents the molar concentration of the total dissolved N_2 in the groundwater sample. $X_{N_2 EQ}$ 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). $X_{N_2 EQ}$ 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 atmospheric air (Heaton et al., 1983; Aeschbach-Hertig et al., 2002). For this case, $X_{N_2 EA}$ can be calculated from the concentration of only one noble gas, e.g. Argon (Heaton and Vogel, 1981):

$$X_{N_2 EA} = (X_{ArT} - X_{ArEQ}) * \frac{X_{N_2 atm}}{X_{Ar atm}} \quad (4.2)$$

where $X_{N_2 \text{ atm}}$ and $X_{Ar \text{ atm}}$ denote atmospheric mole fractions of N_2 and Ar, respectively. $X_{Ar \text{ T}}$ represents the molar concentration of the total dissolved Ar in the groundwater sample. $X_{Ar \text{ EQ}}$ 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 lowest 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 lowest value is approximated when the dissolution of entrapped air approaches zero. The lowest estimate of $X_{N_2 \text{ EA}}$ is thus given by

$$X_{N_2 \text{ EA}} = (X_{Ar \text{ T}} - X_{Ar \text{ EQ}}) * \frac{X_{N_2 \text{ EQ}}}{X_{Ar \text{ EQ}}} \quad (4.3)$$

where $X_{N_2 \text{ EQ}}$ and $X_{Ar \text{ EQ}}$ 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 $N_2 \text{ EA}$ calculated with Eqs. 2 and 3, and is thus given by

$$U_{N_2 \text{ EA}} = (X_{Ar \text{ T}} - X_{Ar \text{ EQ}}) * (X_{N_2 \text{ atm}} / X_{Ar \text{ atm}} - X_{N_2 \text{ EQ}} / X_{Ar \text{ EQ}}) \quad (4.4)$$

It can be seen that $U_{N_2 \text{ EA}}$ directly depends on excess Ar, i.e., $X_{Ar \text{ T}} - X_{Ar \text{ EQ}}$. We used equations 4.1 to 4.3 to calculate lowest and upper estimates of excess air and excess N_2 and to assess the remaining uncertainty of our excess N_2 estimates connected with excess air fractionation. Finally, we calculated means from the lowest and upper estimates which we considered as best estimates of excess N_2 .

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 $0.000069 \text{ L L}^{-1}$ for Ar and $0.006449 \text{ L L}^{-1}$ for N_2 , respectively. Repeatability (R) was derived from $R = 2\sqrt{2} \sigma$, giving $0.000196 \text{ L L}^{-1}$ for cAr (R_{Ar}) and $0.018241 \text{ L L}^{-1}$ for c N_2 (R_{N_2}). Errors resulting from R_{N_2} and R_{Ar} were obtained using equations 4.1 - 4.3, giving 1.59 and 2.05 mg N L^{-1} , respectively. Finally, total error for excess N_2 was determined by Gaussian error propagation (Mölders et al., 2005) giving 2.58 mg N L^{-1} for excess N_2 .

Initial NO₃⁻ concentration, reaction progress and emission factors

Initial NO₃⁻ concentration (cNO₃⁻_{t0}) 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 cNO₃⁻_{t0} can be calculated from the sum of residual substrate and accumulated products (Böhlke, 2002). Thus, cNO₃-N_{t0} is given by the following equation:

$$cNO_3-N_{t0} = \text{excess } N_2 + cNO_3^- - N + cN_2O - N \quad (4.5)$$

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:

$$RP = \frac{\text{excess } N_2 + cN_2O - N}{cNO_3 - N_{t0}} \quad (4.6)$$

Emission factors (EF) for indirect N₂O emission from the aquifer resulting from N-leaching were calculated as described earlier (Well et al., 2005c). Because cNO₃⁻_{t0} 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):

$$EF(1) = \frac{cN_2O - N}{cNO_3 - N_{t0}} \quad (4.7)$$

Furthermore, we will compare EF(1) with the ratio of cN₂O-N to cNO₃⁻-N (EF(2)), which was used by the IPCC methodology (1997) to derive EF5-g:

$$EF(2) = \frac{cN_2O - N}{cNO_3 - N} \quad (4.8)$$

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 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).

4.3 Results

Basic groundwater properties

Basic groundwater properties of the investigated aquifers are shown in Table 4.1. Groundwater temperatures at these sites 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.

Excess N_2 , measured and initial NO_3^- concentrations

We used the means of lowest and upper estimates for excess N_2 as a possible best estimate which were calculated assuming complete dissolution or maximum fractionation of entrapped gases, respectively (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 Figure 4.1, where *excess N_2 min* and *excess N_2 max* denote lowest and upper estimates for excess N_2 , respectively.

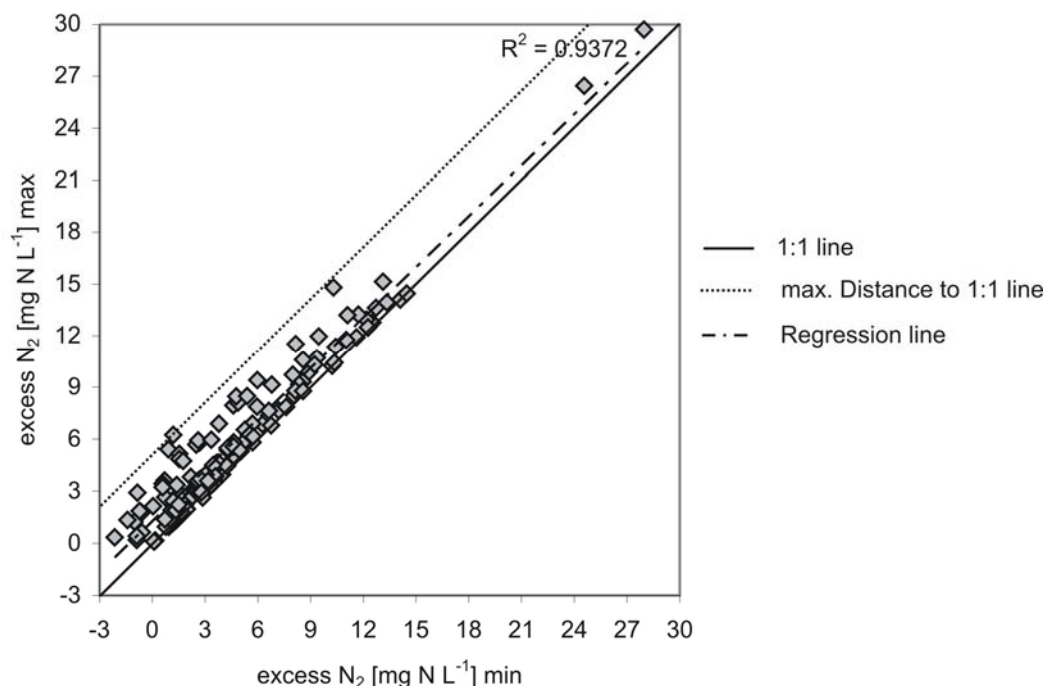


Figure 4.1: Lowest (*excess N₂ min*) and upper (*excess N₂ max*) estimates of excess N₂ for the whole data set as calculated using eqs. (1) and (2) or (1) and (3), respectively. The maximum distance to the 1:1 line denotes the maximum difference between the lowest and upper estimates. The regression line refers to the mean of the lowest and upper estimates for the whole data set.

Derived from the whole data set shown in Figure 4.1, 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 (eq. 4). According to equation (4.5), these error values connected with the uncertainty of excess N₂ are also valid for NO₃⁻_{t0}. Using the uncertainty of excess N₂ and NO₃⁻_{t0} 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⁻_{t0}, giving 4.8 % for the median NO₃⁻_{t0} of 13.15 mg N L⁻¹.

Ranges and site medians of excess N₂ and reaction progress are given in Table 4.2.

Table 4.2: Excess N_2 , N_2O , NO_3^- , and $NO_3^-_{t0}$ concentrations and reaction progress of denitrification (RP) of the investigated aquifers. $NO_3^-_{t0}$ concentrations were calculated using equation 4.5, RP was calculated using equation 4.6.

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	0.17	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

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 (Figure 4.2). At a 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 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 NO_3^- concentrations were highest in the aquifers of Fuhrberg and Sulingen (Figure 4.2) with median values of 8.51 and 9.26 mg N L⁻¹, respectively (Table 4.2). In Thülsfelde and Göttingen measured NO_3^- concentrations were significantly lower (Table 4.2, Figure 4.2). We observed the clear tendency that measured NO_3^- concentrations decreased with increasing sampling depth (Figure 4.2 C).

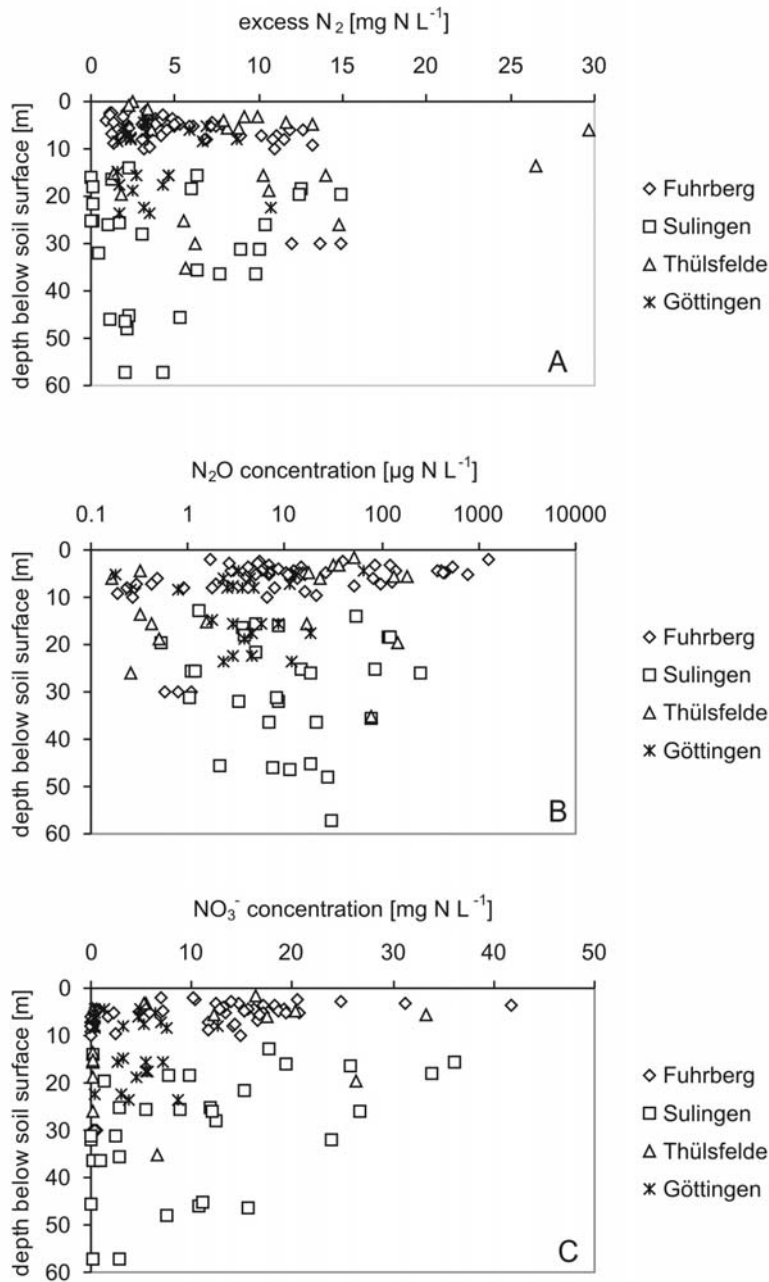


Figure 4.2: Vertical distribution of (A) excess N₂, (B) N₂O concentrations (log scaled) and (C) actual NO₃⁻ concentrations in the investigated aquifers.

Calculated initial NO₃⁻ concentrations (NO₃⁻_{t0}, eq. 5) were substantially higher than measured NO₃⁻ concentrations (Table 4.2), especially in the aquifer of Thülsfelde. The difference between measured NO₃⁻ concentrations and NO₃⁻_{t0} demonstrates that NO₃⁻ consumption by denitrification was an important process in all investigated aquifers.

N₂O concentrations and emission factors

Wide ranges of N₂O concentrations were observed in all aquifers (Figure 4.2 B, Table 4.2). 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 (Figure 4.3).

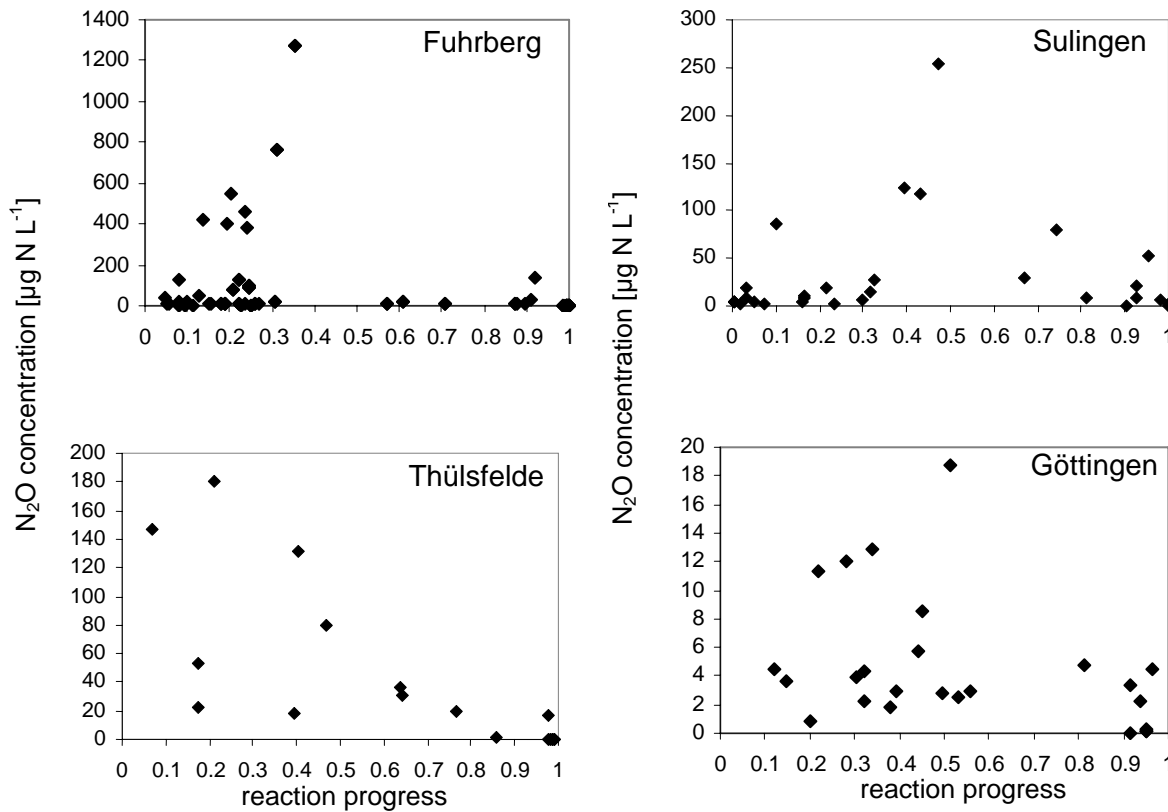


Figure 4.3: N₂O in groundwater samples from 4 different aquifers in relation to reaction progress. Reaction progress is the ratio between denitrification products (excess N₂ + N₂O) and initial NO₃⁻.

Emission factors EF(1) and EF(2) were highly variable within each site (Table 4.3). 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 Figure 4.4. 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 4.3). For both emission factors, we determined highest values for the Fuhrberg aquifer and lowest for the aquifer of Göttingen (Table 4.3). 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.

Table 4.3: Emission factors EF(1) and EF(2) of the investigated aquifers. EF(1) was determined as the ratio of N_2O / NO_3^- concentrations with $\text{NO}_3^- t_0$ as initial NO_3^- concentration. EF(2) was determined as the ratio of N_2O / NO_3^- concentrations with NO_3^- as measured 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.

N_2O 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, N_2O concentrations were still slightly above the ambient level, despite NO_3^- was completely consumed. It can be concluded that EF(1) and EF(2) would approach zero if N_2O is completely reduced to N_2 . In contrast to the lowest values for N_2O concentrations and EF(1) at RP close to 0 and close to 1, N_2O concentrations and EF(1) were relatively high at a RP between 0.2 and 0.6 (Figure 4.3; Figure 4.4). However, at each RP we observed a relatively wide range of N_2O concentrations and EF(1).

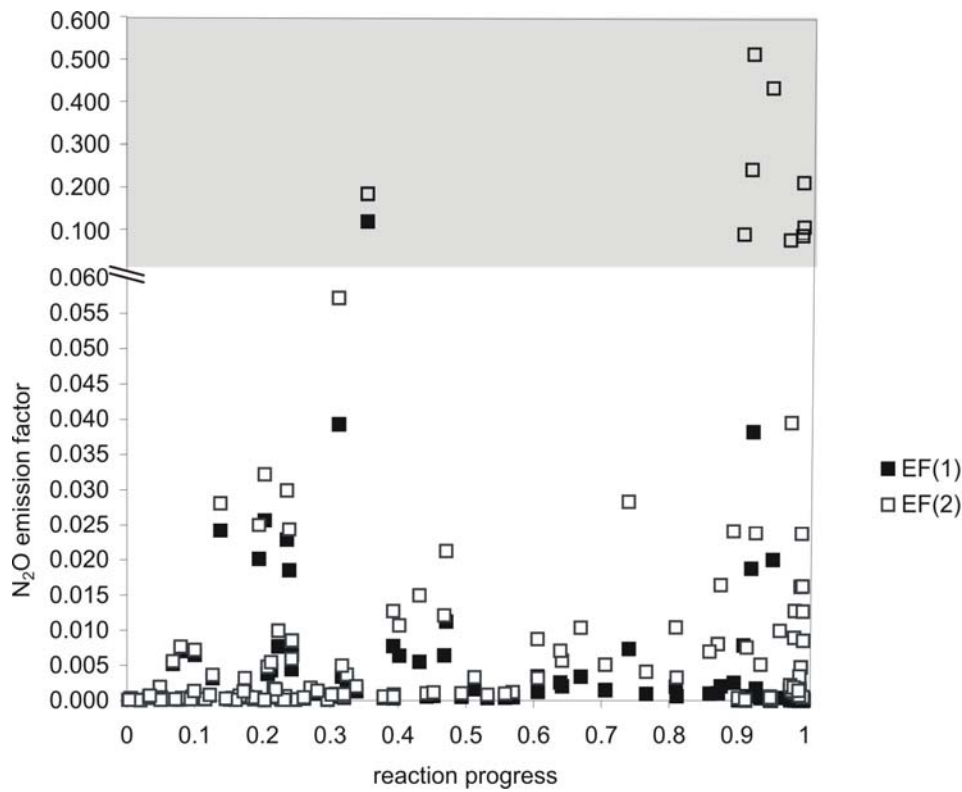


Figure 4.4: N_2O emission factors EF(1) and EF(2) of the investigated aquifers in relation to reaction progress (ratio between denitrification products and initial NO_3^-) and compared to IPCC default EF5-g. EF(1) was determined as the ratio of $\text{N}_2\text{O-N} / \text{NO}_3^- \cdot \text{N}_{t0}$ with $\text{NO}_3^- \cdot \text{N}_{t0}$ as initial NO_3^- concentration. EF(2) was determined as the ratio of $\text{N}_2\text{O-N} / \text{NO}_3^- \cdot \text{N}$ with $\text{NO}_3^- \cdot \text{N}$ as actual NO_3^- concentration.

4.4 Discussion

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 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 (see 4.2). 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 N_2 and of the related parameters was specified in sections 4.2 and 4.3, respectively.

The uncertainty of RP is small and does not affect our conclusion that maximum N_2O concentrations occurred at RP between 0.2 and 0.6. Thus, this uncertainty hardly affects

the relationship between RP and EF(1) shown in Figure 4.4. In view of the large range of EF(1) (Table 4.3), the relative error of EF(1) connected with the uncertainty of NO_3^- is relatively small. Therefore, it can be concluded that the consequences of uncertainties connected with excess N_2 and NO_3^- 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 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 N_2 in the shallow groundwater measured in this study was low. This shows that hydrostatic 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).

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 4.4). 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 N_2 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 NO_3^- and excess N_2 in the whole data-set ($R_s = -0.37$, Table 4.4) demonstrates that denitrification was an important factor for NO_3^- variability within all aquifers.

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 found in this study (Table 4.4). 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 4.1, spearman correlation coefficient (R_s) = -0.33).

Table 4.4: 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	-0.02ns								
NO ₃ ⁻	-0.29***	0.43***							
excess N ₂	0.13ns	-0.19*	-0.37***						
NO ₃ ⁻ _{t0}	-0.22**	0.25**	0.76***	0.18ns					
RP	0.25***	-0.39***	-0.86***	0.74***	-0.43***				
EF(1)	-0.03ns	0.93***	0.19**	-0.28***	-0.08ns	-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***	-0.14ns	0.25**	
O ₂	0.16*	-0.05ns	0.21**	-0.34***	0.03ns	-0.34***	-0.07ns	-0.42***	0.01ns

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.

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 & Bøckman, 1994; Blicher-Mathiesen and Hoffmann, 1999).

The influence of pH on the N₂O-to-N₂ ratio is intensified by high NO₃⁻ concentrations (Blackmer & 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.

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 N_2O 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 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 were 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. However, the occurrence of individual samples with comparatively high N_2O concentrations at RP close to 0 (Figure 4.3, Thülsfelde) indicates that the RP range that covers the highest N_2O 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 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 where 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 4.3) 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, Figure 4.4 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 NO_3^- 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 N_2O budgets further. Consequently, potential N_2O emissions from aquifers should be estimated using EF(1) rather than EF(2).

4.5 Interim conclusions

In the investigated aquifers, NO_3^- consumption by denitrification was 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 . Ranges of N_2O concentrations in groundwater were large in all aquifers, covering an interval between 0 and $1271 \mu\text{g N L}^{-1}$. The pH was found to be a significant controlling factor for N_2O accumulation. Because 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). EF(1) in the investigated denitrifying aquifers was much lower than the values resulting from the earlier concept of groundwater emission factors consisting of N_2O -to- NO_3^- mass 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 and 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.

4.6 Summary of the chapter

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) was investigated to quantify their potential N_2O emission and to evaluate existing concepts of N_2O emission factors. Excess N_2 – i.e. N_2 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 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 $\mu\text{g N L}^{-1}$ and from 3 to 10 mg N L^{-1} , respectively. Reaction progress (RP) of denitrification was determined as the ratio between products ($\text{N}_2\text{O-N} + \text{excess N}_2$) 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 $\text{N}_2\text{O-N}$ and initial NO_3^- -N concentrations (EF1). In addition, we determined a groundwater emission factor (EF2) using a previous concept consisting of the ratio between $\text{N}_2\text{O-N}$ and actual NO_3^- -N concentrations. Depending on RP, EF(1) resulted in smaller values compared to EF(2), demonstrating (i) the relevance of NO_3^- consumption and consequently (ii) the need to take initial NO_3^- -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, this study supports the substantial downward revision of the IPCC default EF5-g from 0.015 (1997) to 0.0025 (2006).

5 Synthesis and general conclusions

5.1 Specific characteristics of denitrification and N_2O accumulation in the Fuhrberger Feld aquifer

Denitrification in the FFA has been already described within the scope of previous studies: Kölle et al. (1985) and Böttcher et al. (1992) demonstrated the autotrophic process. Further, Kölle et al. (1983) assumed that heterotrophic denitrification also occurs within the aquifer. But whereas the existence of autotrophic denitrification was proven by robust in-situ investigations, the heterotrophic process has been revealed in context of a single laboratory study and its relevance was thus under debate (Korom 1991, Böttcher et al. 1991). Böttcher et al. (1991) assumed that heterotrophic denitrification may take place after exhaustion of the reduced sulfur compounds serving as the electron donor for autotrophic denitrification. This assumption was confirmed by von der Heide et al. (2008) basing on the analysis of “denitrification-related factors” in the surface groundwater. Therefore, the process model of denitrification in the FFA was demonstrated as follows: two separated zones of denitrification exist within the aquifer, i.e. the heterotrophic process is dominating in the surface groundwater and autotrophic denitrification is the major process in the deeper aquifer.

The results of this thesis enable a further advancement of this process model with respect to N_2O accumulation and to the vertical distribution of the process zones. Taking the findings of chapter 2 (Figure 2.1) into account, the patterns of the N_2O -, NO_3^- - and SO_4^{2-} concentration profiles revealed that the heterotrophic denitrification zone reaches to a depth of about 3 m below the averaged water table (Figure 5.1). This assumption is supported by the laboratory incubations (chapter 2), because typical low amounts of sulfur in the aquifer material and the typical reaction kinetics of heterotrophic denitrification were found down to 4 m below the soil surface (2.5-to-3.0 m below the water table). Highest N_2O concentrations were measured in the uppermost groundwater in 0.1-to-0.5 m below the water table, what is consistent with the exchange zone that was defined by Deurer et al. (2008). Furthermore, it can be strongly assumed that the autotrophic zone is limited to depths between 3 m and 5 m below the averaged water table as (1) the rapid NO_3^- elimination, (2) the characteristic “autotrophic” N_2O concentration peak and (3) the increase of SO_4^{2-} concentrations at the well I1 reveal (Figure 5.1). Below this depths interval, N_2O and NO_3^- concentrations were found to be negligible, indicating that denitrification progress was complete and heterotrophic desulfurization replaced autotrophic denitrification as the dominating microbial reaction (Korom 1991, Böttcher et al. 1991). It is even possible that the thickness of the autotrophic zone averages only a few decimeters due to the high nitrate removal efficiency of autotrophic denitrification (chapter 2). However, this theory has to be confirmed by refined well measurements within the crucial depth interval in order to improve the knowledge of the dynamics of autotrophic denitrification and of transient, but considerable N_2O accumulation within the autotrophic zone.

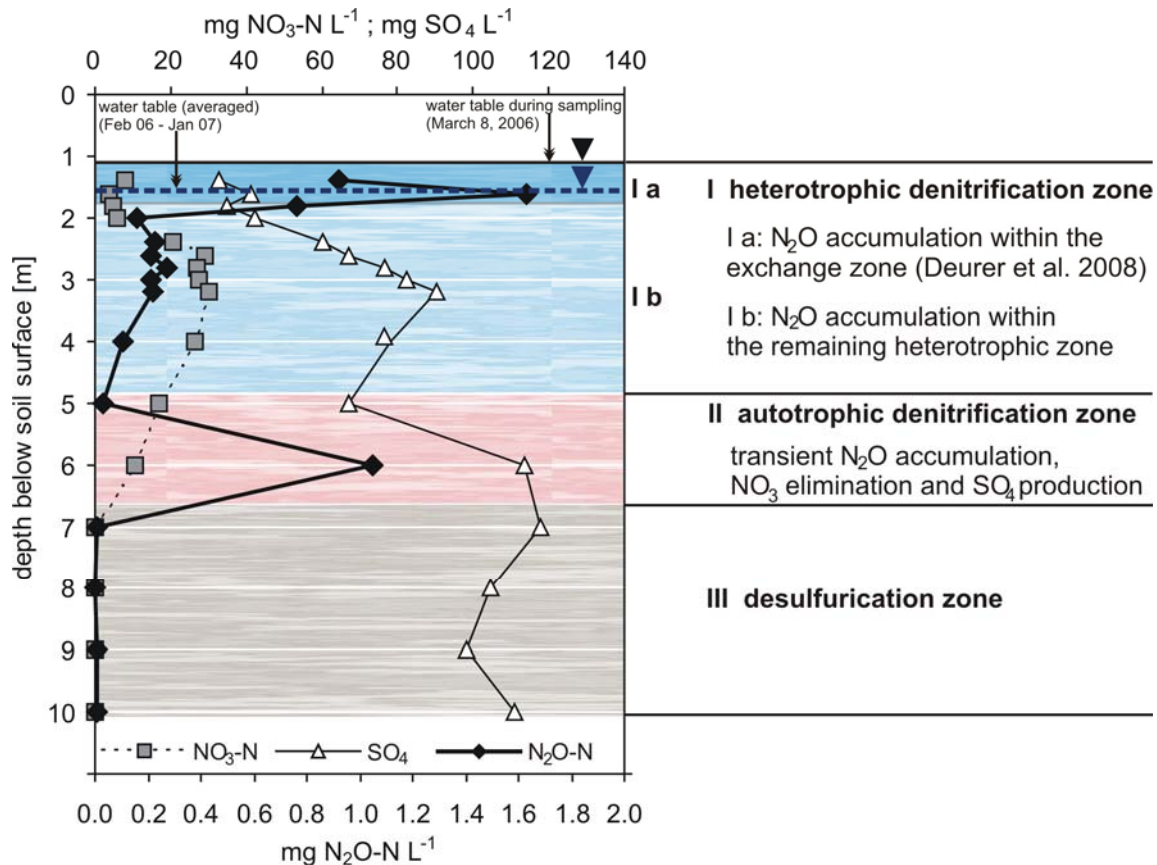


Figure 5.1: Concentration gradients of N_2O , NO_3^- and SO_4^{2-} reveal the zones of denitrification and N_2O accumulation in the Fuhrberger Feld aquifer.

Another important finding was to prove the different reaction kinetics of heterotrophic and autotrophic denitrification, respectively. Böttcher et al. (1991) assumed that heterotrophic denitrification is kinetically by far slower than autotrophic denitrification and attributed this difference to the poor bioavailability of organic matter. Both assumptions were confirmed in course of the laboratory incubations (chapter 2), showing the significantly lower nitrate removal efficiency in the heterotrophic zone and the carbon-limitation of the heterotrophic process. Further, the results found within chapter 4 also confirmed these observations. Excess N_2 of denitrification increased rapidly to 10-to-15 mg N L⁻¹ in the autotrophic zone and was usually one order of magnitude higher than in the (“heterotrophic”) surface groundwater. However, only an in-situ “push-and-pull” ¹⁵N-tracer experiment will be able to verify the laboratory incubations appropriately with focus on denitrification rates. Thus, this approach will be subject of future research activities in the FFA.

Summarizing the obtained results it can be concluded that the low nitrate removal efficiency of heterotrophic denitrification by itself can not be expected to reduce the considerable NO_3^- input originating from agriculture (Böttcher et al. 1991). The water quality related to NO_3^- concentration at the water supply wells thus strongly depends on the occurrence of autotrophic denitrification and will be substantially impaired if this reaction comes to a standstill due to exhaustion of the reduced sulfur compounds.

5.2 Occurrence of N₂O in groundwater

N₂O was produced and accumulated in all of the investigated denitrifying aquifers (Table 4.2). Highest N₂O concentrations were measured in the FFA (Figure 2.1, Figure 4.2) what was attributed to the regulating factors pH and NO₃⁻ (chapter 4) and to the poor bioavailability of organic carbon (chapter 2), respectively. The ranges of N₂O concentrations were large and covered up to four orders of magnitude. This high variability was also described within the course of an independent study in the FFA (von der Heide et al. 2008).

An important finding of chapter 4 was to identify patterns of N₂O accumulation during reaction progress of denitrification (Figure 4.3). Highest N₂O concentrations were usually measured at reaction progress between 0.2 and 0.6 in all aquifers. In contrast, N₂O concentrations were substantially lower at reaction progress close to zero and at reaction progress > 0.6, respectively. The reaction progress may thus help to detect areas of N₂O accumulation within aquifers. Moreover, reaction progress can be considered as an appropriate tool (i) to predict zones where indirect N₂O emissions are likely to occur from and (ii) to investigate where the risk of these emissions is comparatively low. This can provide the basis for further, more detailed investigations of indirect N₂O emissions from groundwater.

5.3 Significance of indirect N₂O emissions

Following the concept introduced by von der Heide et al. (2009a), groundwater-derived N₂O can be indirectly emitted (i) via the vertical pathway after diffusion through the unsaturated zone and (ii) via the lateral pathway when it discharges to wells, springs or ditches where it is directly exposed to the atmosphere.

The vertical emission pathway was discussed in detail in chapter 3. Very low fluxes of groundwater-derived N₂O were found to be in a range between 0.0002 and 0.0018 kg N₂O-N ha⁻¹ year⁻¹. The ¹⁵N tracer study showed that N₂O produced in the surface groundwater of the FFA hardly contributed to total N₂O emissions which were predominantly governed by topsoil parameters. *However, the approach enabled for the first time tracing groundwater-derived N₂O throughout the system groundwater / unsaturated zone / soil surface by direct measurements using stable isotope analysis.* The results were in good agreement with those recently found by Deurer et al. (2008) and von der Heide et al. (2009). Both studies were likewise conducted in the FFA and reported N₂O fluxes from groundwater that were derived from N₂O concentration gradients. Deurer et al. (2008) estimated fluxes into the unsaturated zone that were between 0.0006 and 0.2 kg N₂O-N ha⁻¹ year⁻¹. These fluxes were derived from N₂O concentrations at six wells, i.e. the larger range (compared to that found in the course of chapter 3) can be explained by the spatial variability of N₂O. Interestingly, the upper value of 0.2 kg N₂O-N ha⁻¹ year⁻¹, that was two orders of magnitude higher than that of 0.0018 kg N₂O-N ha⁻¹ year⁻¹ reported in chapter 3, is based on N₂O concentrations in groundwater that were also two orders of magnitude higher than those measured during the ¹⁵N tracer study (Deurer et al. 2008, Figure 3.4 in

this thesis). This fact indicates an excellent agreement of both approaches. However, Deurer et al. (2008) did not analyse N₂O dynamics within the unsaturated zone and at the soil surface. Hence, an uncertainty remains if the fluxes of groundwater-derived N₂O from both studies are compared. The study of von der Heide et al. (2009) aimed to take the system groundwater / unsaturated zone / soil surface into account, i.e. measurements were conducted throughout the profile like it was done during the ¹⁵N tracer study. The authors stressed that groundwater-derived N₂O fluxes to the atmosphere were negligible and masked by N₂O turnover in the unsaturated zone and in the topsoil. Moreover, it was found that fluxes of N₂O from groundwater into the unsaturated zone only occurred in connection with considerable dynamics of the groundwater table. These key findings are definitely in line with the results of the ¹⁵N tracer study related to the magnitude of N₂O emissions from groundwater into the unsaturated zone / atmosphere as well as to the effect of water table fluctuations, especially of a rapid drawdown which enhanced diffusive N₂O fluxes temporarily (chapter 3). But what is the procedure for that? There are indications that the major release of gases is linked to a bubble-mediated mass transfer (Grant and Pattey 2003, Geistlinger et al. 2009). Gas bubbles can arise if the partial pressures of the dissolved gases exceed the hydrostatic pressure (Blicher-Mathiesen et al. 1998). This case is unlikely in the shallow groundwater of the FFA (see chapter 4). Furthermore, bubbles can be formed if soil air is entrapped near the water table during a phreatic rise of the water table or according to the influence of seepage water (Williams and Oostrom 2000). If those bubbles are not completely dissolved under the influence of the hydrostatic pressure, they will equilibrate with N₂O dissolved in the groundwater. Therefore, considerable amounts of N₂O can be entrapped in the bubbles depending on concentration of dissolved N₂O in groundwater. During a drawdown, “bubble-N₂O” may “volatilize with the return to aerobic conditions, creating brief, rapid emission events driven by rapid gaseous diffusion during initial soil drying” (Grant and Pattey 2003).

In conclusion, we can emphasize for the FFA that emission of groundwater-derived N₂O via the vertical pathway is generally very low, but it is also strongly depending on the dynamics of the water table, i.e. rapid drawdowns. It seems that emission is enforced by this physical mechanism or - with other words - emission will be hardly occur without it. However, the question arises whether these findings are site-specific phenomena or transferable to other aquifers. In general, we have to be very cautious to transfer results related to N₂O turnover and -emissions from one ecosystem to another, because of the complexity of the relevant processes and governing factors (section 1.2 and 1.3). Nevertheless, Hiscock et al. (1993) and McMahon et al. (2000) reported in agreement diffusive N₂O fluxes of 0.0005 kg N₂O-N ha⁻¹ year⁻¹ for regional aquifers in the UK and for the Central High Plains aquifer in the USA, respectively. These fluxes strongly confirm the emission data obtained from the FFA. Hence, it seems to be possible to generalize the single results of the studies to a certain extent, at least for temperate regions with similar hydrological conditions, e.g. the dynamics of the groundwater table.

5.4 Assessment of the groundwater N₂O emission factor

In chapter 4, a new concept for calculating the groundwater N₂O emission factor was introduced. *N₂O concentrations were for the first time linked to reconstructed “initial” NO₃⁻ concentrations in order to take the real N-influx to the groundwater table into account (EF(1), Equation 4.7).* Otherwise, the IPCC default emission factor (EF5-g) is principally based on the ratio between N₂O concentrations and measured NO₃⁻ concentrations (EF(2), Equation 4.8). Because measured NO₃⁻ concentrations are often substantially lower than initial ones in denitrifying aquifers (Table 4.2), site medians of EF(2) yielded higher values than site medians of EF(1) and thus overestimated the actual emission (Table 4.3). *Therefore, the concept of EF(1) is an improvement of the methodology to calculate the groundwater emission factor and demonstrates the importance to account for denitrified N in reducing aquifers.*

However, EF(1) has still to be considered a *potential* emission factor quantifying the amount of N₂O that could be emitted if the groundwater is immediately discharged to springs, wells or streams. For example, the site median of EF(1) for the FFA was calculated as 0.0044, i.e. it is assumed that 4.4 g N₂O per kilogram N applied will be emitted into the atmosphere. As both the ¹⁵N tracer study (chapter 3) and the study of von der Heide et al. (2009a) showed, the vertical emission pathway can be neglected. Thus, N₂O should be indirectly emitted via the lateral pathway. But this is obviously not the case: N₂O is almost completely reduced to N₂ during convective transport through the autotrophic zone, i.e. there is no risk of indirect emission during groundwater extraction at the deep wells of the waterworks (von der Heide et al. 2009a) where the very low amounts of N₂O reflect the typical pattern of N₂O concentrations at reaction progress close to 1 (Chapter 4). The anaerobic incubations also confirmed that the autotrophic zone finally functions as an N₂O sink (Figure 2.3). Therefore, N₂O can only be indirectly emitted if N₂O-supersaturated groundwater discharges to drainage ditches or streams, particularly at reaction progress between 0.2 and 0.6 (section 5.2, Figure 4.3). Because drainage ditches and streams cover only 0.2 % of the FFA, these elements probably do not enhance indirect N₂O emissions significantly (von der Heide et al. 2009a).

Summarizing these considerations, it can be concluded that indirect N₂O emissions from groundwater of the FFA via the vertical and the lateral pathway are negligible and the related emission factor EF(1) obviously overestimates these emissions. This can be put down to the fact that processing of N₂O, i.e. the kinetics of N₂O production and reduction, is not taken into account by the concept of EF(1). Geistlinger et al. (2009) stated, that the described emission factors can only be a rough estimate of effective indirect N₂O emission. The authors underlined the need for validated models of reactive N₂O transport to quantify these emissions. A first step to achieve this challenging aim was to characterise the kinetics of N₂O production and reduction during long-term anaerobic incubations and to evaluate the related kinetic rate constants, providing a basis for modeling the reactive N₂O transport and thus to reduce the uncertainties surrounding the N₂O groundwater emission factor.

5.5 Future research and perspectives

As already suggested in the previous chapters, some results obtained in the course of this thesis remained subjects of uncertainty. Investigations also revealed new aspects that could be integrated in future research activities in order to further improve the knowledge of the fate of N_2O from its production in groundwater to the possible ultimate emission into the atmosphere. In the following, some perspectives and recommendations for future research are given.

In-situ tracer test on the reaction kinetics of N_2O production and reduction

The reaction kinetics of N_2O production and reduction was studied during laboratory incubation and linked to concentration gradients measured in the field (chapter 2). Differences between the approaches were observed related to the N_2O accumulation in the heterotrophic denitrification zone. Furthermore, the applied model yielded a limited goodness of fit to the experimental data, especially to the initial NO_3^- concentrations. Therefore, reaction kinetics of N_2O production and reduction should be additionally studied directly under field conditions of the FFA in order to verify the results obtained in the course of this thesis. As an appropriate approach, a ^{15}N push-pull tracer experiment should be conducted (chapter 3.1, Kim 2005, Konrad 2007).

Bioavailability of organic carbon

Heterotrophic denitrification with organic carbon serving as an electron donor yielded considerable N_2O accumulation in the FFA (chapter 2). However, it has not been clarified to which extent dissolved or particulate organic carbon are suppliers of energy for denitrification. This question needs to be solved, e.g. in order to define an adequate reaction equation system for modeling. To achieve this, it will be necessary to link stronger the research on organic carbon at the one hand and on nitrogen at the other.

As a further aspect for future research, it is advisable to investigate the bioavailability of the lignitic pebbles in the FFA. Although Böttcher et al. (1991) assumed a poor bioavailability of these patchy microsites, the correlation analysis in chapter 2 yielded a significant relationship between organic carbon and the denitrification rates in the autotrophic denitrification zone (Table 2.3). The pebbles were obviously not present in the “heterotrophic” aquifer material, i.e. they were probably oxidized. Thus, it can be assumed that the investigated reaction kinetics of heterotrophic denitrification (chapter 2) does not indicate possible heterotrophic denitrification capacity and kinetics in the deeper groundwater. Parkin (1987) and Jacinthe et al. (1998) introduced laboratory approaches to examine patches of organic matter and their influence on denitrification. Furthermore, a laboratory incubation study on the sulfate reduction capacity could provide knowledge of the potential significance of particulate organic matter and its possible function as an electron donor in the deeper groundwater of the FFA.

The fate of groundwater-derived N₂O within the system groundwater / unsaturated zone / soil surface

The ¹⁵N tracer study introduced in chapter 3 aimed to recover groundwater-derived N₂O at the soil surface and to quantify its ultimate emission into the atmosphere. However, this was done without taking processes into account that alter N₂O within the profile. To evaluate the fate of the ¹⁵N-N₂O, a mass balance approach could provide information about the production and consumption rates of N₂O. Therefore, the data on ¹⁵N-N₂O concentration along the soil profile to the atmosphere should be used in combination with a diffusive transport model of N₂O.

Determination of effective emission factors

As noted in chapter 4, the improved concept yielding EF(1) provided still potential emission factors without taking processing of N₂O into account. The determination of an effective emission factor to quantify real N₂O flux from the investigated aquifers will require validated models of reactive N₂O transport (Geistlinger et al. 2009). To provide a solid basis for modeling, the evaluated reaction rate constants (chapter 2) should be complemented by information about reaction kinetics obtained from the planned push-pull ¹⁵N tracer experiment.

6 References

- Addy K, Kellog DQ, Gold AJ, Groffman PM, Ferendo G, Sawyer C (2002) In situ push - pull method to determine ground water denitrification in riparian zones. *J Environ Qual* 31:1017-1024.
- Aeschbach-Hertig W, Beyerle U, Holocher J, Peeters F, Kipfer R (2002) Excess air in groundwater as a potential indicator of past environmental changes. In: Study of environmental change using isotope techniques, Proceedings of the IAEA conference, Vienna, 23-27 April 2001, C&S Papers Series 13/P, pp 174-183.
- Almeida JS, Reis MAM, Carrondo MJT (1997) A unifying kinetic model of denitrification. *J Theor Biol* 186:241-249.
- Ambus P, Lowrance R (1991) Comparison of denitrification in two riparian soils. *Soil Sci Soc Am J* 55: 994-997.
- Blackmer AM, Bremner JM (1978) Inhibitory effect of nitrate on reduction of nitrous oxide to molecular nitrogen by soil microorganisms. *Soil Biol Biochem* 10:187-191.
- Blicher-Mathiesen G, Hoffmann CC (1999) Denitrification as a sink for dissolved nitrous oxide in a freshwater riparian fen. *J Environm Qual* 28:257-262.
- Blicher-Mathiesen G, McCarty GW, Nielsen CP (1998) Denitrification and degassing in groundwater estimated from dissolved nitrogen and argon. *J Hydr*: 208:16-24.
- Böhlke JK, Denver JM (1995) Combined use of groundwater dating, chemical and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. *Water Resour Res* 31: 2319-2339.
- Böhlke JK (2002) Groundwater recharge and agricultural contamination. *Hydrogeol J* 10: 153-179.
- Böttcher J, Strebel O, Duijnisveld WHM (1985) Vertikale Stoffkonzentrationsprofile im Grundwasser eines Lockergesteins - Aquifers und deren Interpretation (Beispiel Fuhrberger Feld). *Zeitschr dt Geol Ges* 136:543-552
- Böttcher J, Strebel O, Duijnisveld WHM (1989) Kinetik und Modellierung gekoppelter Stoffumsetzungen im Grundwasser eines Lockergesteins-Aquifers. *Geol Jahrb Reihe C* 51:3-40.
- Böttcher J, Strebel O, Duijnisveld WHM, Frind O (1991) Reply (to a comment of Scott F. Korom). *Water Resour Res* 27:3275-3278.
- Böttcher J, Strebel O, Kölle W (1992) Redox conditions and microbial sulfur reactions in the Fuhrberger Feld sandy aquifer. In: Matthess G, Frimmel FH, Hirsch P, Schulz

- HD, Usdowski E (eds) Progress in hydrogeochemistry. Springer, Berlin Heidelberg, pp 219-226.
- Böttcher J, Strebel O, Vörkelius S, Schmidt H (1990) Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *J Hydrol* 114:413-424.
- Brady NC, Weil RR (1999) The Nature and Properties of Soils. 12nd ed, Prentice Hall, Upper Sadle River, NJ.
- Butterbach-Bahl K, Breuer L, Gasche, R (2002) Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the northeastern German lowlands: 1. Fluxes of N₂O, NO/NO₂ and CH₄ at forest sites with different N-deposition. *For Ecol Man* 167:123-134.
- Casciotti KL, Sigman DM, Hastings MG, Böhlke JK, Hilkert, A (2002) Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal Chem* 74:4905-4912.
- Chapuis-Lardy L, Wrage N, Metay A, Chotte JL, Bernoux M (2007) Soils, a sink for N₂O? A review. *Glob Ch Biol* 13:1-17. DOI 10.1111/j.1365-2486.2006.01280.x
- Cho CM, Mills JG (1979) Kinetic formulation of the denitrification process in soil. *Can J Soil Sci* 59:249-257.
- Clough TJ, Addy K, Kellog DQ, Nowicki BL, Gold AJ, Groffman PM (2007) Dynamics of nitrous oxide in groundwater at the aquatic-terrestrial interface. *Glob Ch Biol* 13:1528-1537.
- Clough TJ, Jarvis SC, Dixon ER, Stevens RJ, Laughlin RJ, Hatch DJ (1999) Carbon induced subsoil denitrification of ¹⁵N labelled nitrate in 1 m deep soil columns. *Soil Biol Biochem* 31: 31-41.
- Clough TJ, Kelliher FM, Wang YP, Sherlock RR (2006) Diffusion of ¹⁵N-labelled N₂O into soil columns: a promising method to examine the fate of N₂O in subsoils. *Soil Biol Biochem* 38: 1462-1468.
- Clough TJ, Sherlock RR, Rolston DE (2005) A review of the movement and fate of N₂O in the subsoil. *Nutr Cycl Agroecosys* 72:3-11.
- Crutzen PJ (1981) Atmospheric chemical processes of the oxides of nitrogen, including nitrous oxide. In: Delwiche C (ed.): Denitrification, nitrification and nitrous oxide. Wiley, New York
- Davidson EA (1991) Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In Rogers JE, Whitman WB (eds) Microbial production and consumption of

- greenhouse gases: Methane, nitrogen oxides and halomethanes. American Society for Microbiology, Washington DC, pp 219-235.
- Deurer M, von der Heide C, Böttcher J, Duijnisveld WHM, Weymann D, Well R (2008) The dynamics of N₂O in the surface groundwater and its transfer into the unsaturated zone: A case study from a sandy aquifer in Germany. *Catena* 72:362-373.
- Dobbie KE, McTaggart IP, Smith KA (1999) Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. *J Geophys Res* 104:26891-26899.
- Dobbie KE, Smith KA (2003) Nitrous oxide emission factors for agricultural soils in Great Britain: the impact of soil water-filled pore space and other controlling variables. *Glob Ch Biol* 9:204-218.
- Duijnisveld WHM, Strebel O, Böttcher J, Kinzelbach W (1989) Longterm prognosis of the groundwater quality as influenced by landuse and landuse changes in the Fuhrberger Feld using numerical solute transport models. In: Kobus HE, Kinzelbach W (eds.) *Contaminant transport in groundwater*. A.A. Balkema, Rotterdam Brookfield, pp 89-96.
- Dunkle SA, Plummer LN, Busenberg E, Phillips PJ, Denver JM, Hamilton PA, Michel RL, Coplen TB (1993) Chlorofluorocarbons (CCl₃F and CCl₂F₂) as dating tools and hydrologic tracers in shallow ground water of the Delmava Peninsula, Atlantic Coastal Plain, United States. *Water Resour Res* 29:3837-3860.
- Duxbury JM, Mosier AR (1993) Status and issues concerning agricultural emissions of greenhouse gases. In Kaiser HM, Drennen TE (eds) *Agricultural dimensions of global climate change*. pp 229-258, St. Lucie Press, USA.
- Dykaar B, Kitanides P (1996) Macrotransport of biologically reacting solute through porous media. *Wat Resour Res* 32(2):302-320.
- Firestone (1982) Biological denitrification. In Stevenson FJ (ed) *Nitrogen in agriculture soils*. American Soc Agr, Madison, pp. 289-326.
- Firestone MK, Firestone RB, Tiedje JM (1980) Nitrous oxide from soil denitrification: factors controlling its biological production. *Science* 208:749-751.
- Frind E, Duijnisveld WHM, Strebel O, Böttcher J (1990) Modeling of multicomponent transport with microbial transformation in groundwater: The Fuhrberg case. *Water Resour Res* 26:1707-1719.
- Geistlinger H, Jia R, Eisermann D, Stange CF (2009) Spatial and temporal variability of dissolved nitrous oxide in near-surface groundwater and its correlation to dissolved oxygen and groundwater fluctuations. Submitted to *J Pl Nutr Soil Sci*

- George WO, Hastings WW (1951) Nitrate in the groundwater of Texas. *Eos Trans. AGU* 32(3):450-456.
- Ginn TR, Wood BD, Nelson KE, Scheibe TD, Murphy EM, Clement TP (2002) Processes in microbial transport in the natural subsurface. *Adv Wat Res* 25:1017–1042.
- Gold AJ, Jacinthe PA, Groffman PM, Wright WR, Puffer RH (1998) Patchiness in groundwater nitrate removal in a riparian forest. *J Environ Qual* 27:146-155.
- Goldberg SD, Gebauer G (2009) Drought turns a Central European Norway spruce forest soil from an N₂O source to a transient N₂O sink. *Glob Ch Biol* 15:850–860.
- Granli T, Bøckman OC (1994) Nitrous oxide from agriculture. *Norw J Agr Sci* 12:1-128.
- Grant RF, Pattey E (2003) Modelling variability in N₂O emissions from fertilized agricultural fields. *Soil Biol Biochem* 35:225-243.
- Green TC, Puckett LJ, Böhlke JK, Bekins BA, Phillips SP, Kauffman LJ, Denver JM, Johnson HM (2008) Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. *J Environ Qual* 37:994-1009, doi:10.2134/jeq2006.0419.
- Groffman PM, Altabet MA, Böhlke JK, Butterbach-Bahl K, David MB, Firestone MK, Giblin AE, Kana TM, Nielsen LP, Voytek, MA (2006) Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecol appl* 16(6): 2091-2122.
- Groffman PM, Gold AJ, Jacinthe PA (1998) Nitrous oxide production in riparian zones and groundwater. *Nutr Cycl Agroecosys* 52:179-186.
- Groffman PM, Gold AJ, Kellog DQ, Addy K (2002) Mechanisms, rates and assessment of N₂O in groundwater, riparian zones and rivers. In: Van Ham J, Baede APM, Guicherit R, and Williams-Jacobse JGFM (eds) *Non-CO₂ greenhouse gases: Scientific understanding, control options and policy aspects*. Millpress, Rotterdam, pp 159-166.
- Groffman PM, Howard P, Gold AJ, Nelson WM (1996) Microbial nitrate processing in shallow groundwater in a riparian forest. *J Environ Qual* 25:1309-1316.
- Hack J, Kaupenjohann M (2002) N₂O discharge with drain water from agricultural soils of the upper Neckar region in Southern Germany. In: Van Ham J, Baede APM, Guicherit R, and Williams-Jacobse JGFM (eds) *Non-CO₂ greenhouse gases: Scientific understanding, control options and policy aspects*. Millpress, Rotterdam, pp 185-190.
- Heaton THE, Vogel JC (1981) Excess air in groundwater. *J Hydr* 50:201-216.

- Heaton THE, Talma AS, Vogel JC (1983) Origin and history of nitrate in confined groundwater in the Western Kalahari. *J Hydr* 62:243-262.
- Hefting MM, Bobbink R, Janssens MP (2006) Spatial variation in denitrification and N₂O emission in relation to nitrate removal efficiency in a N-stressed riparian buffer zone. *Ecosys* 9:550-563, DOI: 10.1007/s10021-006-0160-8
- Hefting MM, Bobbink R, de Caluwe H (2003) Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *J Environ Qual* 32(4):1194-1203.
- Heincke M, Kaupenjohann M, (1999) Effects of soil solution on the dynamics of N₂O emissions: a review. *Nutr Cycl Agroecosys* 55:133-157.
- Hénault C, Chéneby D, Heurlier K, Garrido F, Perez S, Germon JC (2001) Laboratory kinetics of soil denitrification are useful to discriminate soils with potentially high levels of N₂O emission on the field scale. *Agronomie* 21:713-723
- Hiscock KM, Bateman AS, Fukada T, Dennis P. (2002) The concentration and distribution of groundwater N₂O in the chalk aquifer of eastern England. In: Van Ham J, Baede APM, Guicherit R, and Williams-Jacobse JGFM (eds) *Non-CO₂ greenhouse gases: Scientific understanding, control options and policy aspects*. Millpress, Rotterdam, pp 185-190.
- Hiscock KM, Bateman AS, Mühlherr IH, Fukada, T, Dennis PF (2003) Indirect emissions of nitrous oxide from regional aquifers in the United Kingdom. *Environ Sci Techn* 37:3507-3512.
- Hoehener P, Duwig C, Pasteris G, Kaufmann K, Dakhel N Hauke H (2003) Biodegradation of petroleum hydrocarbon vapors: laboratory studies on rates and kinetics in unsaturated alluvial sand. *J Cont Hydr* 66:93-115.
- Höll BS, Jungkunst HF, Fiedler S, Stahr K (2005) Indirect nitrous oxide emission from a nitrogen saturated spruce forest and general accuracy of the IPCC methodology. *Atm Environ* 39:5959-5970.
- Holocher J, Peeters F, Aeschbach-Hertig W, Hofer M, Brennwald M, Kinzelbach W, Kipfer R (2002) Experimental investigations on the formation of excess air in quasi-saturated porous media. *Geoch Cosm. Acta* 66:4103-4117.
- Holtan-Hartwig L, Dörsch P, Bakken LR (2000) Comparison of denitrifying communities in organic soils: kinetics of NO₃⁻ and N₂O reduction. *Soil Biol Biochem* 32: 833-843.
- Intergovernmental Panel on Climate Change (IPCC) (2006) 2006 IPCC guidelines for national greenhouse gas inventories. Prepared by the National Greenhouse Gas Inventories Programme, Egglestone HS, Buendia L, Miwa K, Ngara T., Tanabe K (eds.), IGES, Japan

- Intergovernmental Panel on Climate Change (IPCC) (2007) Climate Change 2007: AR4 Synthesis Report. IPCC Plenary XXVII, Valencia, Spain, pp 212-217 November 2007
- Intergovernmental Panel on Climate Change (1997) Revised 1996 IPCC guidelines for national greenhouse gas inventories. Reference manual, Vol 3, Organisation for Economic Cooperation and Development, Paris.
- Jacinthe PA, Groffman PM, Gold AJ, Mosier A (1998) Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. *J Environm Qual* 27:156-164.
- Kellman L, Kavanaugh K (2009) Nitrous oxide dynamics in managed northern forest soil profiles: is production offset by consumption? *Biogeochem* 90:115-128.
- Kelly WR, Hornberger GM, Herman JS, Mills AL (1996) Kinetics of BTEX biodegradation and mineralization in batch and column systems. *J Cont Hydr* 23:113-132.
- Kim Y, Kim JH, Son BH, Oa SW (2005) A single well push - pull test method for in situ determination of denitrification rates in a nitrate - contaminated groundwater aquifer. *Wat Sci Techn* 52(8):77-86.
- Kölle W, Strebel O, Böttcher J (1985) Formation of sulfate by microbial denitrification in a reducing aquifer. *Water Supply* 3:35-40.
- Kölle W, Werner P, Strebel O, Böttcher J (1983) Denitrifikation in einem reduzierenden Grundwasserleiter. *Vom Wasser* 61:125-147.
- Konrad C (2007) Methoden zur Bestimmung des Umsatzes von Stickstoff, dargestellt für drei pleistozäne Grundwasserleiter Norddeutschlands, PhD thesis, Dresden Univ of Techn, Germany, 157 pp.
- Korom SF (1991) Comment on "Modeling of multicomponent transport with microbial transformation in groundwater: The Fuhrberg case" by EO Frind et al., *Water Resour Res* 27(12):3271-3274.
- Korom SF (1992) Natural denitrification in the saturated zone: a review. *Wat Resour Res* 28: 1657-1668.
- McIlvin MR, Altabet MA (2005) Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Anal Chem* 77:5589-5595.
- McMahon PB, Bruce BW, Dennehy KF (2000) Occurrence of nitrous oxide in the Central High Plains aquifer. *Environ Sci Technol* 34: 4873-4878.

- McQuarrie KTB, Sudicky EA (2001) Multicomponent simulation of wastewater-derived nitrogen and carbon in shallow unconfined aquifers I. Model formulation and performance. *J Cont Hydr* 47:53–84.
- Mölders N, Jankov M, Kramm G (2005) Application of Gaussian error propagation principles for theoretical assessment of model uncertainty in simulated soil processes caused by thermal and hydraulic parameters. *J Hydromet* 6:1045-1062.
- Mookherji S, McCarty GW, Angier JT (2003) Dissolved gas analysis for assessing the fate of nitrate in wetlands. *J American Wat Res Ass* 39(2):381-387.
- Mosier AR (1989) Chamber and isotope techniques. In: Andreae MO, Schimel DS (eds) *Change of trace gases between terrestrial ecosystems and the atmosphere*. Wiley, Chichester, pp 175-187.
- Mosier AR (1998) Soil processes and global change. *Biol Fertil Soils* 27:221-229.
- Mosier AR, Kroeze C, Nevison C, Oenema O, Seitzinger SP, van Cleemput O (1998) Closing the global N₂O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutr Cycl Agroecosys* 52:225-248.
- Nevison C (2000) Review of the IPCC methodology for estimating nitrous oxide emissions associated with agricultural leaching and runoff. *Chemosphere - Glob Ch Sci* 2:493-500.
- Nömmik, H (1956) Investigations on denitrification in soil. *Acta Agric Scand* 6:195–228.
- Obenhuber DC, Lowrance R (1991) Reduction of nitrate in aquifer microcosms by carbon additions. *J Environ Qual* 20:255-258.
- Paramasivam S, Alva AK, Prakash O, Cui SL (1999) Denitrification in the vadose zone and in surficial groundwater of a sandy entisol with citrus production. *Pl Soil* 208: 307-319.
- Parkin TB (1987) Soil microsites as a source of denitrification variability. *Soil Sci Soc Am J* 51:1194-1199.
- Pätsch M (2006) Analyse des Nitratsumsatzes und dessen Heterogenität im quartären Grundwasserleiter des Wasserwerkes Thülsfelde - Berücksichtigung bei der Modellierung des Transportes. PhD thesis, Dresden Univ of Techn., Germany, 223 pp.
- Reay DS, Smith KA, Edwards AC (2003) Nitrous oxide emission from agricultural drainage waters. *Glob Ch Biol* 9(2):195-203.
- Reay DS, Smith KA, Edwards AC, Hiscock KM, Dong LF, Nedwell D (2005) Indirect nitrous oxide emissions: revised emission factors. *Environ Sci* 2:153-158.

- Rice CW, Rogers KL (1993) Denitrification in subsurface environments: Potential source for atmospheric nitrous oxide. In: Harper et al. (eds) *Agricultural ecosystems effects on trace gases and global climate change*. ASA special publications. American Society of Agronomy, Crop Science Society of America and Soil Science Society of America, Madison, pp 121-132.
- Rodhe H (1990) A comparison of the contribution of various gases to the greenhouse effect. *Science* 248:1217-1219.
- Ronen D, Magaritz M, Almon E (1988) Contaminated aquifers are a forgotten component of the global N₂O budget. *Nature* 335:57-59.
- Ross SM (1995) Overview of the hydrochemistry and solute processes in British wetlands. In: Hughes JMR, Heathwaite AL (eds) *Hydrology and hydrochemistry of British wetlands*. Wiley, New York, pp 133-182.
- Sawamoto T, Nakajima Y, Kasuya M, Tsuruta H, Yagi K (2005) Evaluation of emission factors for indirect N₂O emission due to nitrogen leaching in agro-ecosystems. *Geophys Res Let* 32(3) DOI 10.1029/2004GL021625
- Schack-Kirchner H, Hildebrandt EE, von Wilpert K (1993) Ein konvektionsfreies Sammelssystem für Bodenluft. *J Pl Nutr Soil Sci* 156:307-310.
- Schirmer M, Molson JW, Frind EO, Barker JF (2000) Biodegradation modelling of a dissolved gasoline plume applying independent laboratory and field parameters. *J Cont Hydr* 46:339–374.
- Schlichting E, Blume HP, Stahr K (1995) *Bodenkundliches Praktikum*. Blackwell Wissenschaft, Berlin, 295 p (in German).
- Schlie P (1989) *Hydrogeologie des Grundwasserwerkes Stegemühle in Göttingen*. PhD thesis, University of Göttingen, Germany, pp.137.
- Siemens J, Haas M, Kaupenjohann M (2003) Dissolved organic matter induced denitrification in subsoils and aquifers? *Geoderma* 113:253-271.
- Šimek M, Cooper JE (2002) The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Europ J Soil Sci* 53:345-354.
- Smith RL, Duff JH (1988) Denitrification in a sand and gravel aquifer. *Appl Environ Microbiol* 54(5):1071-1078.
- Smith RL, Garabedian SP, Brooks MH (1996) Comparison of denitrification activity measurements in groundwater using cores and natural-gradient tracer tests. *Environ Sci Technol* 30:3448-3456.

- Spalding RF, Gormly JR, Nash KG (1978) Carbon contents and sources in ground waters of the central Platte region in Nebraska. *J Environ Qual* 7:428-434.
- Spalding RF, Parrott JD (1994) Shallow groundwater denitrification. *Sci Total Environ* 141: 17-25.
- Stevens RJ, Laughlin RJ, Malone JP (1998) Soil pH affects the processes reducing nitrate to nitrous oxide and di-nitrogen. *Soil Biol Biochem* 30:1119-1126.
- Strebel O, Böttcher J, Duijnisveld WHM (1993) Ermittlung von Stoffeinträgen und deren Verbleib im Grundwasserleiter eines norddeutschen Wassergewinnungsgebietes. Texte 46/93, Umweltbundesamt, Berlin.
- Tiedje JM (1994) Denitrifiers. In: Weaver RW, Angle JS, Bottomley PJ (Eds) *Methods of Soil Analysis. Part 2. Microbiological and Biochemical Properties*, SSSA, Madison, WI.
- Tobias CR, Macko SA, Anderson IC, Canuel EA, Harvey JW (2001) Tracking the fate of high concentration groundwater nitrate plume through a fringing marsh: a combined groundwater tracer and in situ isotope study. *Limnol Oceanogr* 46(8):1977-1989.
- van Cleemput O (1998) Subsoils: chemo- and biological denitrification, N₂O and N₂ emissions. *Nutr Cycl Agroecosyst* 52:187-194.
- Van Groenigen JW, Georgius PJ, van Kessel C, Hummelink EWJ, Velthof GL, Zwart KB (2005) Subsoil ¹⁵N-N₂O concentrations in a sandy soil profile after application of ¹⁵N-fertilizer. *Nutr Cycl Agroecosyst* 72:13-25.
- Vieten B, T Blunier, A Neftel, C Alewell F Conen (2007) Fractionation factors for stable isotopes of N and O during N₂O reduction in soil depend on reaction rate constant. *Rap Comm Mass Spectrom* 21:846-850.
- Vogel JC, Talma AS, Heaton THE (1981) Gaseous nitrogen as evidence for denitrification in groundwater. *J. Hydr* 50:191-200.
- von der Heide C, Böttcher J, Deurer M, Duijnisveld WHM, Weymann D, Well R (2009a) Estimation of indirect N₂O emissions from a shallow aquifer: a case study in Northern Germany. *J Environ Qual* (accepted)
- von der Heide C, Böttcher J, Deurer M, Duijnisveld WHM, Weymann D, Well R (2009b) Spatial and temporal variability of N₂O in the surface groundwater: a detailed analysis from a sandy aquifer in northern Germany. submitted to *Nutr Cycl Agroecosys*

- von der Heide C, Böttcher J, Deurer M, Weymann D, Well R, Duijnisveld WHM (2008) Spatial variability of N₂O concentrations and of denitrification-related factors in the surficial groundwater of a catchment in Northern Germany. *J Hydrol* 360:230-241.
- Wagner-Riddle C, Hu QC, van Bochove E, Jayasundara S (2008) Linking nitrous oxide flux during spring thaw to nitrate denitrification in the soil profile. *Soil Sci Soc Am J.* 72:908-916.
- Walther W, Pätsch M, Weller D, Reinstorf F, Harms E, Kersebaum C (2002) Nutrient loads on a Northern German sandy aquifer, reduction processes, their distribution and management tools. In: *New approaches to characterising Groundwater Flow, XXXI. IAH Congress, Munich, Germany, 10-14 September 2001.*
- Walther W (1999) *Diffuser Stoffeintrag in Böden und Gewässer.* Teubner BG, Stuttgart, Germany.
- Weiss RF (1970) The solubility of nitrogen, oxygen and argon in water and sea water. *Deep Sea Res* 17:721-735.
- Weiss RF, Price BA (1980) Nitrous oxide solubility in water and sea water. *Mar Chem* 8: 347-359.
- Weiss RF (1971) The solubility of helium and neon in water and sea water. *J Chem Eng Data* 16:235-241.
- Well R, Flessa H, Jaradat F, Toyoda S, Yoshida N (2005a) Measurement of isotopomer signatures of N₂O in groundwater. *J Geophys Res - Biogeosci* 110:G02006, doi:10.1029/2005JG000044
- Well R, Höper H, Mehranfar O, Meyer K (2005b) Denitrification in the saturated zone of hydromorphic soils – laboratory measurement, regulating factors and stochastic modeling. *Soil Biol Biochem* 37:1822-1836.
- Well R (2002) Methodical approaches for investigating the role of subsurface environments in the global N₂O budget. In: Van Ham J, Baede APM, Guicherit R, and Williams-Jacobse JGFM (eds) *Non-CO₂ greenhouse gases: Scientific understanding, control options and policy aspects.* Millpress, Rotterdam, pp 167-178.
- Well R, Myrold DD (1999) Laboratory evaluation of a new method for in situ measurement of denitrification in water-saturated soils. *Soil Biol Biochem* 31:1109-1119.
- Well R, Augustin J, Meyer K, Myrold DD (2003) Comparison of field and laboratory measurement of denitrification and N₂O production in the saturated zone of hydromorphic soils. *Soil Biol Biochem* 35:783-799.

- Well R, Becker KW, Langel R, Meyer B, Reineking A (1998) Continuous flow equilibration for mass spectrometric analysis of dinitrogen emissions. *Soil Sci Soc Am J* 62:906-910.
- Well R, Weymann D, Flessa H (2005c) Recent research progress on the significance of aquatic systems for indirect agricultural N₂O emissions. *Environ Sci* 2:143-151.
- Weymann D, Well R, Flessa H, von der Heide C, Deurer M, Meyer K, Konrad C, Walther W (2008) Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N₂O accumulation. *Biogeosci* 5:1215–1226.
- Weymann D, Well R, von der Heide C, Flessa H, Böttcher J, Duijnisveld WHM (2009) Recovery of groundwater N₂O at the soil surface and its contribution to total N₂O emissions. *Nutr Cycl Agroecosys* DOI 10.1007/s10705-009-9269-4 (in press).
- Williams MD, Oostrom M (2000) Oxygenation of anoxic water in a fluctuating water table system: an experimental and numerical study. *J Hydrol* 230:70-85.
- World Meteorological Organization (2006) WMO statement on the status of the global climate in 2005. World Meteorological Organization, Geneva, Switzerland, 12 pp.

Curriculum vitae

1976	born on January 7 th in Erfurt
1990-1994	Königin-Luise-Gymnasium in Erfurt
1995-1996	Military service 13 th Military Orchestra in Erfurt
1996-1998	Study of Orchestral Music and Music Education at the Hochschule für Musik und Darstellende Kunst in Stuttgart
1998-2003	Study of Geoecology at the University of Potsdam, specialization in Soil Science and River Ecology
2001-2002	Internship at the Leibniz-Centre for Agricultural Landscape Research (ZALF) in Müncheberg within the project “Characterisation of the sodium pyrophosphate extractable soil organic matter with FT-IR”
2002	Internship at the engineering company “YGGDRASIL” - office for Geology, Landscape- and Environmental Planning in Berlin
2003	Diploma in Geoecology, University of Potsdam and Leibniz-Centre for Agricultural Landscape Research (ZALF) in Müncheberg; Thesis: “Untersuchung verschiedener Aushagerungsverfahren auf eutrophierten Trockenrasen im Nationalpark Unteres Odertal hinsichtlich ihrer Wirkungen auf Nährstoffgehalte und organische Bodensubstanz“
2003-2005	Staffer at the engineering company “YGGDRASIL” in Berlin
2005-2008	Scientist / PhD-Student at the Department of Soil Science of Temperate and Boreal Ecosystems, Georg-August-University of Göttingen
since 2009	PostDoc at the Department of Soil Science of Temperate and Boreal Ecosystems, Georg-August-University of Göttingen and since 2010 guest scientist at the Institute of Agricultural Climate Research, Johann Heinrich von Thünen-Institute in Braunschweig