

# TECHNISCHE UNIVERSITÄT MÜNCHEN

Lehrstuhl für Renaturierungsökologie

In Kooperation mit

Fachgebiet für Vegetationsökologie

Hochschule Weihenstephan-Triesdorf

**Assessment and modeling of greenhouse gas emissions (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) from different land-use types and management practices on drained fen peatlands and associated organic soils – case study  
Freisinger Moos**

Tim Eickenscheidt

Vollständiger Abdruck der von der Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt der Technischen Universität München zur Erlangung des akademischen Grades eines

## **Doktors der Naturwissenschaften**

genehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. J. Schnyder

Prüfer der Dissertation:

1. Univ.-Prof. Dr. J. Kollmann
2. Prof. Dr. M. Drösler (Hochschule Weihenstephan-Triesdorf)
3. Hon.-Prof. Dr. J. Augustin (Martin-Luther-Universität Halle-Wittenberg)

Die Dissertation wurde am 15.04.2015 bei der Technischen Universität München eingereicht und durch die Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt am 17.07.2015 angenommen.



## Summary

In the last century, drainage and intensification of agriculture turned German peatlands into hot-spots for greenhouse gas (GHG) emissions. Particularly peatlands converted into croplands and intensive grasslands have been regarded as the main producers of carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). Despite high research efforts in the last decade, there is still a high uncertainty in defining reliable emission factors (EF) for the climate reporting according to the Intergovernmental Panel on Climate Change (IPCC) guidelines. This is due to the fact that the few observed GHG fluxes on these soils show a large temporal and spatial variability, and the identification of histosols is challenging since several national and international classification systems exist for organic soils. Most studies have focused on typical drained peatlands, which are very rich in organic carbon (C<sub>org</sub>), whereas former peatlands and associated organic soils containing <12% C<sub>org</sub> were neglected, although it is unknown whether they emit less GHG's compared to typical drained peatlands. This issue was examined in the first of three studies (**PUBLICATION I.**). This study addressed the questions as to what extent the soil organic carbon (SOC) content affects the GHG release from different land-use types and management practices on drained organic soils. For this purpose, two soil types with contrasting SOC content were chosen, i.e. a mollic Gleysol (9.4–10.9% C<sub>org</sub> in 0–10 cm soil depth) and a sapric Histosol (16.1–17.2% C<sub>org</sub> in 0–10 cm soil depth). On both soils, four treatments were established once, two croplands (maize or oat) and two intensive grasslands (fertilized with cattle slurry or biogas digestate). GHG fluxes (CO<sub>2</sub>, N<sub>2</sub>O and methane (CH<sub>4</sub>)) were measured and modeled over a period of two years. No differences were found in the estimated net CO<sub>2</sub> balances or global warming potentials (GWP) between the two soil types. Thus, like typical drained peatlands also drained mollic Gleysols can be considered as hot-spot for GHG emissions, provided that they are intensively managed as cropland or grassland. Estimated GWPs in this study, calculated for a time horizon of 100 years, revealed a very high release of GHG's from all treatments investigated ranging from 1837 to 7095 g CO<sub>2</sub> eq. m<sup>-2</sup> yr<sup>-1</sup>. These findings clearly revealed that primarily the management and not the SOC content nor the land-use type itself is responsible for the magnitude of GHG emissions from intensive cropping on drained organic soils.

In addition to the estimation of total GHG emissions examined in **PUBLICATION I.**, the second study (**PUBLICATION II.**) focused in more detail on the short-term effects of biogas digestate and cattle slurry application on the previously mentioned intensive grassland sites, regarding gaseous emissions, mineral nitrogen use efficiency ( $\text{NUE}_{\text{min}}$ ) and grass yields. It is well known that organic fertilization can enhance  $\text{N}_2\text{O}$  production particularly on organic soils. Nevertheless, despite the strong increase in the number of biogas plants in Germany, caused by the change in German energy policy, only a few studies have investigated the effect of biogas digestate application on the formation of gaseous nitrogen and in fact no studies exist which consider organic soils. The objective of **PUBLICATION II.** were to answer the questions i) how does biogas digestate and cattle slurry application affect  $\text{N}_2\text{O}$  and  $\text{CH}_4$  fluxes as well as the  $\text{NUE}_{\text{min}}$  and grass yield, and ii) to what extent different soil organic matter (SOM) and nitrogen (N) contents influence on production of  $\text{N}_2\text{O}$ . Furthermore, ammonia ( $\text{NH}_3$ ) volatilization was determined in the course of one fertilizer application event to obtain first clues with respect to the effects of soil and fertilizer types. The results of the second study (**PUBLICATION II.**) showed that, compared with cattle slurry, the application of biogas digestate significantly enhanced  $\text{N}_2\text{O}$  and  $\text{NH}_3$  emissions and additionally increased the plant N-uptake and  $\text{NUE}_{\text{min}}$ , leading to significantly higher grass yields. This could partly be attributed to the higher ammonium ( $\text{NH}_4^+$ ) content of the digestate and presumably also to a priming effect caused by increased SOM mineralization triggered by digestate application. Furthermore, the results clearly revealed that  $\text{N}_2\text{O}$  fluxes significantly increase with increasing SOM content, probably due to the more favourable soil conditions for denitrification.  $\text{CH}_4$  emissions were found to be negligible at the grassland sites, irrespective of fertilization treatment due to aerobic conditions in the upper soil layer as result of drainage. In conclusion, both studies (**PUBLICATION I.** and **PUBLICATION II.**) revealed a very high release of GHG's, demonstrating the environmentally harmful agricultural use of drained organic soils and the urgent need for the rapid implementation of GHG-mitigation strategies and restoration measures.

Beside croplands and intensive grasslands, also black alder (*Alnus glutinosa* (L.) Gaertn.) forests on drained peat soils have been reported to be hot-spots for high  $\text{N}_2\text{O}$  losses, which has been attributed to alternating water tables of peatlands as well as to the incorporation of high amounts of easily decomposable organic nitrogen into the ecosystem by symbiotic dinitrogen ( $\text{N}_2$ )-fixation of alder trees. However, black alder forests represent the natural vegetation on moist and wet soils, often with high SOC

contents and afforestation in combination with water level management is considered to be one mitigation strategy for the reduction of GHG emissions. In this context, the third study (**PUBLICATION III.**) addressed the questions i) as to what extent drainage enhances the emissions of N<sub>2</sub>O from black alder forests and ii) how N turnover processes and physical factors influence the production of N<sub>2</sub>O and total denitrification rate. This study was conducted in a drained black alder forest with variable groundwater tables at a southern German fen peatland. Additionally, a laboratory incubation experiment was carried out to investigate GHG and N<sub>2</sub> fluxes under different soil temperature and moisture conditions. The study demonstrated that drainage considerably increased net N mineralization and N turnover processes and shifted the dominant process from net ammonification to net nitrification, resulting in nitrate leaching. Observed N<sub>2</sub>O emissions in the field remained low at the drained sites, but the incubation experiment revealed the potential for high N<sub>2</sub>O emissions under changing soil physical conditions at the drained alder sites. Temporally water-saturated conditions were found to enhance N<sub>2</sub> emissions, whereas N<sub>2</sub>O emissions remained unchanged. In contrast, the permanently high groundwater level at the undrained site prevented net nitrification and resulted in negligible gaseous N losses. In conclusion, N mineralization and N turnover processes in black alder forests are very sensitive to alternating groundwater tables and have a high potential for high N<sub>2</sub>O emissions if the soil is not permanently water saturated. The rough estimation of GWPs made in this study highlights the needs for further investigations, particularly regarding the net CO<sub>2</sub> exchange, to verify to what extent water-saturated black alder forests can serve as mitigation strategy for the reduction of GHG emissions.

## Zusammenfassung

Entwässerung und Intensivierung der Landwirtschaft haben im letzten Jahrhundert dazu geführt, dass sich deutsche Moore zu „hot-spots“ von Treibhausgas-Emissionen (THG) entwickelten. Vor allem Moore, die in Ackerland und intensiv genutztes Grünland umgewandelt wurden, zählen zu den Hauptverursachern von Kohlenstoffdioxid- ( $\text{CO}_2$ ) und Distickstoffmonoxid-Emissionen ( $\text{N}_2\text{O}$ ). Trotz enormer Forschungsanstrengungen im letzten Jahrzehnt, besteht nach wie vor hohe Unsicherheit in der Definition zuverlässiger Emissionsfaktoren (EF) für die Klimaberichterstattung, entsprechend den Vorgaben des Intergovernmental Panel on Climate Change (IPCC). Dies ist einerseits auf die Tatsache zurückzuführen, dass die geringe Anzahl, der auf diesen Böden erhobenen THG-Flüsse eine sehr hohe zeitliche und räumliche Variabilität aufweist und andererseits eine Abgrenzung von Histosolen aufgrund der verschiedenen nationalen und internationalen Klassifikationssysteme für organische Böden schwierig ist. Die meisten Untersuchungen konzentrierten sich bisher auf typische entwässerte Moore, die einen hohen Gehalt an organischem Kohlenstoff ( $\text{C}_{\text{org}}$ ) aufweisen, wohingegen rezente Moore und mit Mooren vergesellschaftete organische Böden mit  $\text{C}_{\text{org}}$ -gehalten von weniger als 12%  $\text{C}_{\text{org}}$  vernachlässigt wurden, obwohl nicht geklärt ist, ob diese Böden im Vergleich zu typischen entwässerten Moore geringere THG-Emissionen verursachen. Diese Fragestellung wurde in der ersten von drei Studien aufgegriffen (**Publikation I.**). In dieser Studie wurde untersucht, wie sich der Gehalt an organischem Bodenkohlenstoff (SOC) auf die Freisetzung von THGs aus entwässerten organischen Böden mit unterschiedlichen Landnutzungen und Bewirtschaftungsformen auswirkt. Hierfür wurden zwei, sich in ihrem SOC-Gehalt unterscheidende Böden ausgewählt, zum einen ein mollic Gleysol (9.4–10.9%  $\text{C}_{\text{org}}$  in 0–10 cm Bodentiefe) sowie ein sapric Histosol (16.1–17.2%  $\text{C}_{\text{org}}$  in 0–10 cm Bodentiefe). Auf beiden Böden wurden jeweils vier Untersuchungsvarianten, bestehend aus zwei Acker- (mit Mais oder Hafer) und zwei intensiven Grünlandnutzungen (Düngung mit Rindergülle oder Biogasgärrest) eingerichtet. Über einen Zeitraum von zwei Jahren wurden THG-Flüsse ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$  und Methan ( $\text{CH}_4$ )) gemessen und modelliert. Es konnten keine Unterschiede zwischen den zwei Bodentypen bezüglich der Netto- $\text{CO}_2$ -Bilanzen oder des Globalen Erwärmungspotentials (GWP) nachgewiesen werden. Demzufolge können auch entwässerte und intensiv als Acker oder Grünland genutzte Anmoore, ebenso wie

typische entwässerte Moore als „hot-spots“ für THG-Emissionen angesehen werden. Die abgeschätzten GWPs, die für einen Zeitraum von 100 Jahren berechnet wurden, ergaben eine sehr hohe Freisetzung von THGs für alle Untersuchungsvarianten im Bereich von 1837 bis 7095 g CO<sub>2</sub> eq. m<sup>-2</sup> a<sup>-1</sup>. Die Ergebnisse deuten darauf hin, dass hauptsächlich die Bewirtschaftung und nicht der SOC-Gehalt oder der Landnutzungstyp an sich für die Höhe der THG-Emissionen aus landwirtschaftlich intensiv genutzten und entwässerten organischen Böden verantwortlich ist.

Neben der Abschätzung der THG-Bilanzen (**Publikation I.**), konzentriert sich die zweite Studie im Detail auf die kurzfristigen Auswirkungen der Ausbringung von Biogasgärresten und Rindergülle in Bezug auf gasförmige Emissionen, mineralische Stickstoffausnutzungs-Effizienz (NUE<sub>min</sub>) und Graserträge, auf den zuvor erwähnten intensiv bewirtschafteten Grünlandflächen. Es ist hinlänglich bekannt, dass organische Düngung vor allem auf organischen Böden zu verstärkter Bildung von N<sub>2</sub>O führen kann. Trotz des starken Anstiegs der Anzahl von Biogasanlagen im Zuge der energiepolitischen Veränderungen in Deutschland, existieren bisher nur wenige Studien über die Auswirkungen von Biogasgärrest-Applikationen auf die Bildung von gasförmigem Stickstoff, wobei organische Böden nicht berücksichtigt wurden.

Ziel der zweiten Publikation war die Beantwortung der Fragen i) in wieweit die Ausbringung von Biogasgärrest und Rindergülle die N<sub>2</sub>O- und CH<sub>4</sub>-Flüsse, sowie die NUE<sub>min</sub> und den Grasertrag beeinflussen, und ii) welchen Einfluss unterschiedliche Bodenhumus- (SOM) und Bodenstickstoffgehalte (N) auf die Entstehung von N<sub>2</sub>O haben. Zudem wurde im Zuge eines Düngeereignisses die Ammoniakverflüchtigung (NH<sub>3</sub>) bestimmt, um die Auswirkung der unterschiedlichen Bodentypen und der Düngerarten abschätzen zu können. In der **zweiten Studie (Publikation II.)** wurde gezeigt, dass die Ausbringung von Biogasgärrest im Vergleich zur Düngung mit Rindergülle zu einer signifikanten Erhöhung der N<sub>2</sub>O- und NH<sub>3</sub>-Emissionen sowie der Stickstoffaufnahme und NUE<sub>min</sub> der Pflanzen führte, was wiederum eine signifikante Steigerung der Graserträge zur Folge hatte. Dies könnte zum Teil auf den höheren Ammoniumgehalt (NH<sub>4</sub><sup>+</sup>) im Biogasgärrest zurückzuführen sein sowie möglicherweise auf einen „Priming-Effekt“, ausgelöst durch eine verstärkte SOM-Mineralisation als Folge der Gärrest-Düngung. Darüber hinaus zeigen die Ergebnisse deutlich, dass die N<sub>2</sub>O-Flüsse mit zunehmendem SOM-Gehalt signifikant ansteigen, was wahrscheinlich auf günstigere Bedingungen für Denitrifikation im Boden zurückzuführen ist. Zudem hat sich gezeigt, dass die CH<sub>4</sub>-Emissionen der Grünlandflächen, unabhängig von der

Düngevariante, aufgrund der aeroben Bodenverhältnisse infolge der Entwässerung zu vernachlässigen sind. Zusammenfassend lässt sich sagen, dass in beiden Studien (**Publikation I.** und **II.**) eine sehr hohe Freisetzung von THGs nachgewiesen wurde, was die geringe Nachhaltigkeit der Bewirtschaftung entwässerter organischer Böden veranschaulicht und die dringende Notwendigkeit für die Umsetzung von THG-Minderungsstrategien und Renaturierungsmaßnahmen verdeutlicht.

Neben Ackerland und intensivem Grünland werden auch Schwarzerlenwälder (*Alnus glutinosa* (L.) Gaertn.) auf entwässerten Moorböden, als „hot-spots“ für hohe N<sub>2</sub>O-Verluste angesehen, was auf die stark schwankenden Grundwasserflurabstände von Mooren sowie den Eintrag großer Mengen leicht verfügbaren organischen Stickstoffs durch die symbiotische Distickstoff(N<sub>2</sub>)-Fixierung von Schwarzerlen zurückgeführt wird. Schwarzerlenwälder repräsentieren jedoch die natürliche Vegetation auf feuchten und nassen Böden, häufig mit hohem SOM-Gehalt und die Aufforstung in Kombination mit einem Grundwassermanagement gilt als eine Strategie zur Reduzierung der THG-Emissionen. In diesem Zusammenhang setzt sich die dritte Studie (**Publikation III.**) mit den Fragen auseinander, i) inwieweit die Entwässerung von Schwarzerlenwäldern zu einem Anstieg der N<sub>2</sub>O-Emissionen führt und ii) wie Stickstoffumsetzungsprozesse und physikalische Einflussfaktoren die Bildung von N<sub>2</sub>O und die Gesamt-Denitrifikationsraten beeinflussen. Diese Studie wurde in einem drainierten Schwarzerlenbestand in einem süddeutschen Niedermoor mit unterschiedlichen Grundwasserflurabständen durchgeführt. Zudem wurde im Rahmen eines Laborinkubationsexperiments der Einfluss von Bodentemperatur und -feuchte auf die THG- und N<sub>2</sub>-Flüsse untersucht. Die Studie zeigte, dass die Netto-N-Mineralisierung und die N-Umsetzungsprozesse durch Entwässerung deutlich anstiegen und die vorherrschende Netto-Ammonifikation zugunsten der Netto-Nitrifikation verschoben wurde, was eine erhöhte Auswaschung von Nitrat zur Folge hatte. Obwohl im Feld auf den entwässerten Standorten nur niedrige N<sub>2</sub>O-Austauschraten beobachtet wurden, konnte im Rahmen des Inkubationsexperiments nachgewiesen werden, dass veränderte bodenphysikalische Bedingungen im entwässerten Erlenwald zu hohen N<sub>2</sub>O Emissionen führen können. Temporär wassergesättigte Bedingungen verursachten einen Anstieg der N<sub>2</sub>-Emissionen, wohingegen kein Einfluss auf die N<sub>2</sub>O-Emissionen beobachtet wurde. Im Gegensatz dazu verhinderte der konstant hohe Grundwasserstand des nicht drainierten Untersuchungsstandorts die Netto-Nitrifikation was in vernachlässigbaren gasförmigen N-Verlusten resultierte. Zusammenfassend

kann festgestellt werden, dass die N-Mineralisierung und die N-Umsetzungsprozesse in Schwarzerlenwälder sehr sensitiv auf sich ändernde Grundwasserflurabstände reagieren und bei nicht dauerhaft gewährleisteter Wassersättigung des Bodens ein hohes N<sub>2</sub>O-Bildungspotenzial bergen. Die in dieser Studie vorgenommene grobe Abschätzung des GWPs macht deutlich, dass weitere Untersuchungen vor allem bezüglich des Nett-CO<sub>2</sub>-Austauschs erforderlich sind, um zu überprüfen inwieweit Erlenwälder eine Option zur Verminderung von THG-Emissionen darstellen.

## Table of Contents

1	General Introduction .....	1
1.1	Background .....	1
1.2	Peatlands – Definition, Genesis and their global Distribution .....	2
1.3	Carbon cycle in peatlands and its human alteration .....	5
1.3.1	Net primary production and C input into peatlands .....	6
1.3.2	Carbon decomposition, accumulation and losses in peatlands.....	7
1.4	Nitrogen cycle in peatlands and its human alteration.....	11
1.4.1	Input pathways of N in peatland ecosystems .....	12
1.4.2	Nitrogen mineralization and immobilization .....	14
1.4.3	Nitrogen absorption and leaching.....	16
1.4.4	Gaseous N production processes .....	16
1.5	Peatlands and the Climate change.....	19
1.5.1	Greenhouse effect and climate change.....	19
1.5.2	Contribution of peatlands to climate change – Past, Present and Future perspectives .....	22
1.6	Objectives.....	25
2	Methods for observation and quantification of trace gas emissions.....	29
3	General Discussion and Outlook .....	33
3.1	Impact of SOC and management .....	33
3.2	GHG policy .....	37
4	Conclusion.....	42
5	References .....	44
6	Acknowledgment .....	59
7	Appendix.....	61
7.1	Publication I. ....	61
7.2	Publication II. ....	118
7.3	Publication III. ....	140
7.4	Calculation approach to estimate net GHG fluxes of the alder forest .....	157
8	Eidesstattliche Erklärung .....	159
9	Curriculum vitae.....	160

## List of Figures

- Figure 1** Global peatland distribution (green areas). Dots showing peatland study sites with basal peat age (colors showing the ages of peatland initiation: black <8 ka (ka =1000 yr), red 8-12 ka, and blue >12 ka) (Source: Yu et al., 2010).....3
- Figure 2** Simplified carbon cycle of a pristine and drained fen peatland. ....6
- Figure 3** Simplified nitrogen cycle of a pristine and drained fen peatland. ....12
- Figure 4** Simplified scheme of plant induced interactions of aerobic and anaerobic zones around a macrophyte root (modified after Cleemput van et al., 2007).....15
- Figure 5** Atmospheric concentrations of the three important greenhouse gases CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O over the last 10,000 years. Increases since about 1750 (inset panels) are attributed to human activities in the industrial era (source: IPCC, 2007). ....21
- Figure 6** Maps of CMIP5 multi-model mean results for the scenarios RCP2.6 and RCP8.5 in 2081–2100 of (a) annual mean surface temperature change, (b) average percent change in annual mean precipitation, For the Fifth Assessment Report of IPCC, the scientific community has defined a set of four new scenarios, denoted Representative Concentration Pathways (RCPs, see Glossary). They are identified by their approximate total radiative forcing in year 2100 relative to 1750: 2.6 W m<sup>-2</sup> for RCP2.6, 4.5 W m<sup>-2</sup> for RCP4.5, 6.0 W m<sup>-2</sup> for RCP6.0, and 8.5 W m<sup>-2</sup> for RCP8.5. (source: IPCC, 2013) .....21
- Figure 7** Estimated CO<sub>2</sub> emissions in Mt (10<sup>6</sup> t) from degrading peat for the year 2008. Bar chart shows European countries; pie chart shows total global emissions in Mt (Joosten, 2010).....23
- Figure 8** Different Measurement systems and analyzing units for the determination of soil gas fluxes which were used in the present study. a) Closed dynamic manual chamber system for the determination of NEE (transparent chamber) or R<sub>ECO</sub> (opaque chamber, not shown) coupled to an b) infrared gas analyzer (IRGA, LI-820); c) Closed static manual chamber system for the determination of N<sub>2</sub>O and CH<sub>4</sub> fluxes. Gas samples were analyzed via a GC d) equipped with an FID and an ECD; e) Open dynamic chamber method (“Dräger-Tube Method” for the determination of NH<sub>3</sub> volatilization, NH<sub>3</sub> concentrations were analyzed via ammonia indicator tubes f); g) Helium-oxygen flow-through the chamber incubation system at the laboratory of the Institute of Landscape Matter Dynamics, Leibniz Centre for Agricultural Landscape Research (ZALF; Müncheberg, Germany) for the simultaneously determination of N<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> fluxes in an controlled environment, h) concentration of N<sub>2</sub> were analyzed by a micro-GC equipped with a TCD. Concentrations of trace gases were analyzed by a GC equipped with an FID and an ECD. ....29

## List of Tables

<b>Table 1</b> Peatland relevant GHGs and their lifetimes, radiative efficiencies and direct GWPs relative to CO <sub>2</sub> (according to Forster et al., 2007). .....	20
<b>Table 2</b> Advantages and disadvantages of different approaches for measuring trace gas fluxes between landscapes and the atmosphere. The extent to which a system is suitable or not can range between ++ to --, in which ++ stands for very suitable or low and -- stands for unsuitable or high (extended from Drösler, 2008b). .....	32

## List of Abbreviations and Acronyms

AFOLU	Agriculture, Forestry and Other Land Uses
AIC	Akaike Information Criterion
Ar	Argon
C	Carbon
CaCl <sub>2</sub>	Calcium dichloride
CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon dioxide
C <sub>org</sub>	Organic carbon
C <sub>tot</sub>	Total soil carbon
DM	Dry matter
DTM	Dräger-Tube Method
E <sub>0</sub>	Activation energy
ECD	Electron capture detector
EF	Emission factor
FID	Flame ionization detector
GC	Gas chromatograph
GHG	Greenhouse gases
GPP	Gross primary production
GPP <sub>2000</sub>	Gross primary production at PAR 2000
GW	Groundwater
GWP	Global Warming Potential
He	Helium
IPCC	Intergovernmental Panel on Climate Change
LULUCF	Land Use, Land-Use Change and Forestry
MIT	Microbial mineralization-immobilization turnover
N	Nitrogen
N <sub>2</sub>	Dinitrogen
N <sub>2</sub> O	Nitrous oxide
NECB	Net Ecosystem Carbon Balance
NEE	Net ecosystem exchange of CO <sub>2</sub>
N <sub>dep</sub>	Nitrogen deposition
Nr	Reactive nitrogen (Nr includes inorganic reduced forms of N (e.g., NH <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> ), inorganic oxidized forms (e.g., NO <sub>x</sub> , HNO <sub>3</sub> , N <sub>2</sub> O, NO <sub>3</sub> <sup>-</sup> ), and organic compounds (e.g., urea, amines, proteins, nucleic acids)).
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium
NH <sub>2</sub> OH	Hydroxylamine
N <sub>org</sub> /R-NH <sub>2</sub>	Monomeric organically bound N forms
N <sub>min</sub>	Mineral soil nitrogen
NNM	Net nitrogen mineralization
NO	Nitric oxide
NO <sub>2</sub> <sup>-</sup>	Nitrite
NO <sub>2</sub>	Nitrogen dioxide
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>x</sub>	Nitric oxide + nitrogen dioxide
NPP	Net primary production
NSE	Nash-Sutcliffe efficiency

$N_{\text{tot}}$	Total soil nitrogen
NUE	Nitrogen use efficiency
$NUE_{\text{min}}$	Mineral nitrogen use efficiency
$O_2$	Molecular oxygen
$O_3$	Ozone
PAR	Photon flux density of the photosynthetic active radiation
PBIAS	Percent bias
$Q_{10}$	Temperature quotient
$r$	Pearson's correlation coefficient
$R_a$	Autotrophic respiration
$R_{\text{ECO}}$	Ecosystem respiration
RF	Radiative Forcing
$R_h$	Heterotrophic respiration
$R_{\text{ref}}$	Respiration at $T_{\text{ref}}$
RSR	Ratio of the root mean square error to the standard deviation of measured data
SD	Standard Deviation
SE	Standard Error
SOC	Soil organic carbon
SOM	Soil organic matter
$ST_{2/5/10}$	Soil temperature in 2, 5 or 10 cm soil depths
$T_0$	Temperature constant for the start of biological processes: 227.13 [K]
$T_{\text{air}}$	Air temperature in 20 cm above soil surface
TCD	Thermal conductivity detector
$T_{\text{ref}}$	Reference temperature: 283.15 [K]
UNFCCC	United Nation Framework Convention on Climate Change
VDS	Volatile dry solid
WFPS	Water filled pore space
$\alpha$	Light use efficiency

## List of Publications and Contributions

### Research papers as first author

- I. Eickenscheidt, T., Heinichen, J., and Drösler, M.: The greenhouse gas balance of a drained fen peatland is mainly controlled by land-use rather than soil organic carbon content, *Biogeosciences Discuss* (submitted for publication in *Biogeosciences*).
- II. Eickenscheidt, T., Freibauer, A.; Heinichen, J., Augustin, J., and Drösler, M.: Short-term effects of biogas digestate and cattle slurry application on greenhouse gas emissions affected by N availability from grasslands on drained fen peatlands and associated organic soils, *Biogeosciences*, 11, 6187–6207, doi:10.5194/bg-11-6187-2014, 2014
- III. Eickenscheidt, T., Heinichen, J., Augustin, J., Freibauer, A., and Drösler, M.: Nitrogen mineralization and gaseous nitrogen losses from waterlogged and drained organic soils in a black alder (*Alnus glutinosa* (L.) Gaertn.) forest, *Biogeosciences*, 11, 2961–2976, doi:10.5194/bg-11-2961-2014, 2014.

The dissertation is based on the above named publications.

### Research papers as co-author

- IV. Metzger, C., Jansson, P.-E., Lohila, A., Aurela, M., Eickenscheidt, T., Belelli-Marchesini, L., Dinsmore, K. J., Drewer, J., van Huissteden, J., and Drösler, M.: CO<sub>2</sub> fluxes and ecosystem dynamics at five European treeless peatlands – merging data and process oriented modeling, *Biogeosciences*, 12, 125–146, doi:10.5194/bg-12-125-2015, 2015.
- V. Metzger, C., Heinichen, J., Eickenscheidt, T., and Drösler, M.: Impact of land use intensity on the relationships between vegetation indices (NDVI, LAI), photosynthesis and biomass on temperate grassland fens, *Grass and Forage Science* (submitted).

## **The contributions to the publications were as follows**

### **General contribution to publication I.–III.**

General contribution was the construction and further development of measurement equipment, installation and maintenance of measurement sites and climate stations, implementation and management of all GHG (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) measurements, and the soil sampling and sample preparation for the determination of soil properties (carbon and nitrogen content, bulk density) and mineral nitrogen ( $N_{\min} = \text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$ ). All steps were carried out in close agreement with M. Drösler.

### **Specific contribution to publication I.–III.**

**I.** Specific contribution comprised the topic development in close agreement with M. Drösler, data preparation and calculations, modeling of CO<sub>2</sub>, statistical analyses, and the preparation of the manuscript.

**II.** Here, the contribution mainly included the topic development in agreement with M. Drösler and the advice of J. Augustin and A. Freibauer, additional measurements of NH<sub>3</sub>, data preparation and calculations, statistical analyses, and the main preparation of the manuscript.

**III.** Contribution involved topic development in agreement with M. Drösler and J. Augustin, soil sampling and sample preparation for the incubation procedure and for the determination of net nitrogen mineralization, assistance in N<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> measurements in the laboratory of the Institute of Landscape Matter Dynamics, Leibniz Centre for Agricultural Landscape Research (ZALF) as well as data preparation and calculations, statistical analyses, and the main preparation of the manuscript.

### **Contribution as co-author**

**IV.** The contributions covered the supply of data sets from the Freisinger Moos (sites FsA and FsB) for the time period 03/2009–01/2012, the installation and maintenance of measurement sites and climate stations, the implementation and management of all CO<sub>2</sub> measurements, soil sampling and sample preparation, data preparation and calculations as well as the modeling of CO<sub>2</sub>.

**V.** Here, contributions comprised supply of the GPP data sets from the sites E3a, E3b, I1 and I2, the installation and maintenance of measurement sites and climate stations, the implementation and management of all CO<sub>2</sub> measurements, data preparation and calculations as well as the modeling of GPP.

# 1 GENERAL INTRODUCTION

## 1.1 BACKGROUND

In the last century, drainage and intensification of agriculture turned European peatlands to hot-spots for greenhouse gas (GHG) emissions (Drösler et al., 2008a). According to estimates, peatlands in Germany account for approximately 98% of soil derived net CO<sub>2</sub> emissions, which corresponds to approximately 5.1% of the national GHG emissions, although peatlands cover only 5.1% of the land surface area (Drösler et al., 2011). Thus drained peatlands represent the largest source of GHG emissions in the Agriculture, Forestry and Other Land Uses (AFOLU) sector and in addition the largest single source for GHG emissions outside the energy sector in Germany (Drösler et al., 2011). Hence, according to the Intergovernmental Panel on Climate Change (IPCC) guidelines, drained peatlands are identified as key category which leads to the fact that Germany is obligated to calculate the annual GHG emission inventory on the basis of national specific emission factors (EF). However, the national climate reporting in the Land Use, Land-Use Change and Forestry (LULUCF) sector as well as in the AFOLU sector is a challenging task for organic soils. This is partly because reliable measurements of GHGs from temperate drained peatlands are rare and also because observed GHG fluxes show a large temporal and spatial variability. Furthermore, the definition of histosols is complex and several national and international classification systems exist for organic soils. According to the United Nations Framework Conventions on Climate Change (UNFCCC) and the Kyoto protocol, the reporting of GHG emissions from a key category demands an increased requirement on the data base (Tier 2 or Tier 3 methods). Since such an extensive dataset was not available for the German climate reporting, a large research project was started in the year 2008 by the Thünen Institute, Federal Research Institute for Rural Areas, Forestry and Fisheries to fill the gaps of knowledge. The present PhD thesis was part of this joint research project, called “Organic soils”; Acquisition and development of methods, activity data and emission factors for the climate reporting under LULUCF/AFOLU.

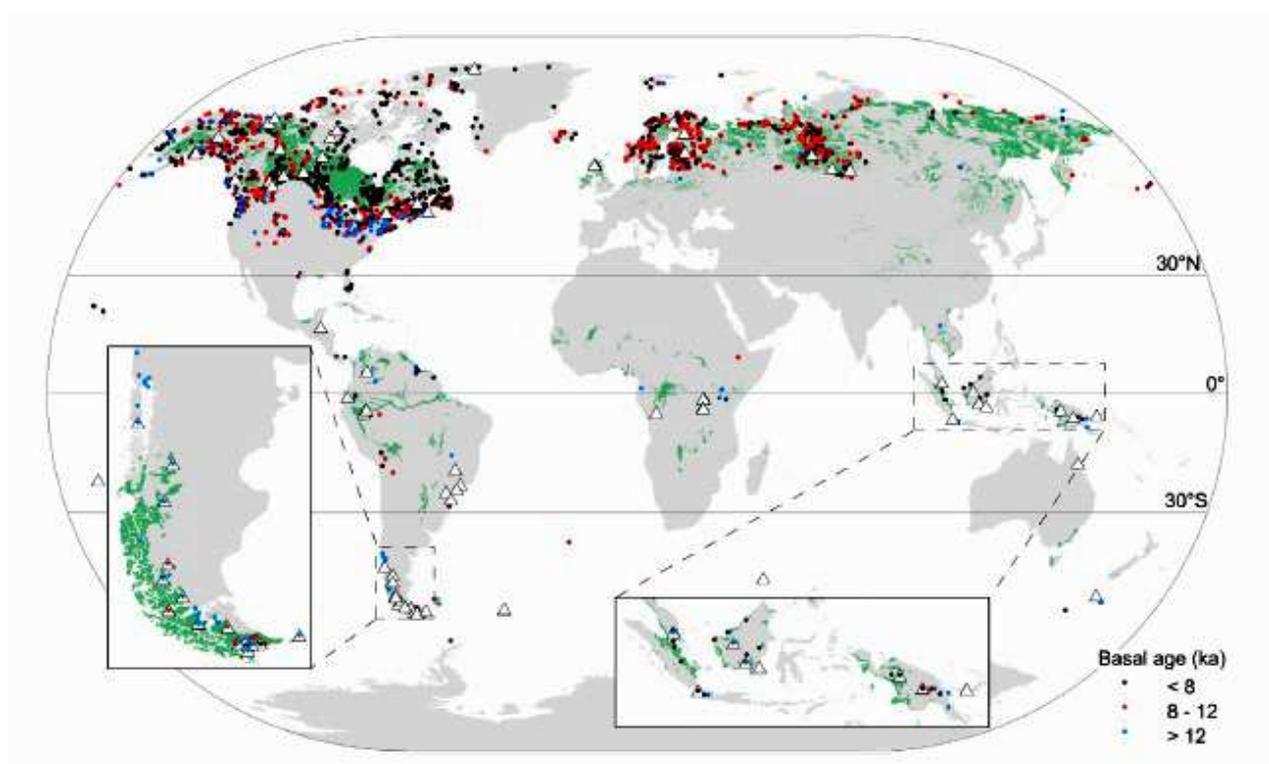
## 1.2 PEATLANDS – DEFINITION, GENESIS AND THEIR GLOBAL DISTRIBUTION

Peatlands comprise very special kinds of transitional ecosystems with habitats between uplands and water, covered with a tree and/or moss layer (Rydin and Jeglum, 2006; Limpens et al., 2008). Peatland ecosystems are characterized by a waterlogged, anoxic soil layer (catotelm), in which organic matter from adapted plants accumulates and finally leads to the formation of peat, owing to incomplete decomposition (Limpens et al., 2008). However, depending on hydrological and geomorphological building conditions the upper peat layer can temporarily be water unsaturated (acrotelm), leading to a shift in the depth of the anoxic-oxic boundary layer during the year.

Peatland ecosystems can be found all over the world except for arid and permanently ice-covered areas (Rydin and Jeglum, 2006). They develop mostly in regions or altitudes where precipitation exceeds evapotranspiration (Göttlich, 1990), but groundwater-driven peatlands can develop as well in generally drier surroundings, as long as the water saturation of the soil is sufficient for peat formation. Globally, peatland cover about 4 million km<sup>2</sup> which corresponds to approximately 3% of the earth's land surface (Rydin and Jeglum, 2006). Approximately 75–85% of worldwide peatlands are situated in the boreal and subarctic regions of the northern hemisphere, particularly in Russia, Canada and the USA (Fig. 1). The remaining peatlands are found in the subtropical and tropical regions (10–15%), particularly in Indonesia, Malaysia and Papua New Guinea and approximately 10% in the temperate regions (Joosten, 2004; Limpens et al., 2008; Yu et al., 2010; Frohling et al., 2011).

Based on their water origin and trophic status, peatlands are mostly classified in fens, bogs and transition peatlands (Rydin and Jeglum, 2006). Fens are minerotrophic peatlands, which can further be divided in topogenous (basin) or soligenous (sloping) fens (Rydin and Jeglum, 2006). The term minerotrophic indicates that the water is originated from groundwater or from surface inflow from surrounding mineral soils, leading to a higher nutrient availability as compared to bogs and approximately neutral pH. Bogs are ombrotrophic peatlands, isolated from groundwater or other mineral-rich soil water, receiving their water and nutrients solely from precipitation and airborne dust (Rydin and Jeglum, 2006). Thus, bogs are typically nutrient poor and strongly acid, usually having pH values lower than four. The shape of bogs varies from convex (raised bogs), to flat with potential sloping. Bogs and fens are often not sharply separated and

several transition forms of peatlands can occur. The different nutrient supply and acid status of fens and bogs significantly affect the peat-forming vegetation, leading to characteristic plant communities. Fens are mostly dominated by sedges (e.g. *Carex elata*, *C. rostrata*, *C. lasiocarpa*, *C. elongata*) but depending on development stage, water table height and nutrient supply also brown mosses (e.g. *Drepanocladus revolvens*), grasses (e.g. *Molina caerulea*), trees (*Alnus*, *Salix*) and several other groups with a grass-like morphology such as cotton grasses (e.g. *Eriophorum angustifolium*), rushes (e.g. *Schoenus ferrugineus*) and reed (e.g. *Phragmites australis*, *Thypha latifolia*) can be found (Göttlich, 1990; Rydin and Jeglum, 2006). Bogs however, are mainly dominated by peat mosses of the genus *Sphagnum*. In dependence of the water table height, important species are *S. magellanicum* and *S. rubellum* (in dryer areas), *S. cuspidatum* and *S. dusenii* (typically in flooded hollows) and several others like *S. fuscum*, *S. palustre*, *S. majus*, *S. subsecundum*. (Göttlich, 1990; Rydin and Jeglum, 2006). Additionally, some few other species like *Eriophorum vaginatum*, *Trichophorum caespitosum*, *Oxycoccus palustris*, *Andromeda polifolia*, *Drosera rotundifolia*, *Erica tetralix* are also characteristically for bogs (Göttlich, 1990).



**Figure 1** Global peatland distribution (green areas). Dots showing peatland study sites with basal peat age (colors showing the ages of peatland initiation: black <8 ka (ka =1000 yr), red 8-12 ka, and blue >12 ka) (Source: Yu et al., 2010).

Peatlands or peats also appear in several national soil classification systems e.g. as Moore (Germany), Organosols (Australia), Organossolos (Brazil), Organic order (Canada), and Histosols (United States of America), of which the US classification system has formed the basis for the effective international standard (Couwenberg, 2011). However, the definition of organic soils/histosols is complex and not entirely consistent (Couwenberg, 2011). Most definitions refers to the thicknesses of soil layers, their organic matter content, their water origin, underlying material, clay content as well as the mean duration of the annual period of water saturation (Couwenberg, 2011). For the climate reporting under LULUCF/AFOLU, the 2006 IPCC Guidelines (Annex 3A.5, Chapter 3 in Volume 4) and the Wetlands Supplement (2014a) largely follow the definition of organic soils (Histosols) by the Food and Agriculture Organization (FAO). Therefore, a soil is defined as an organic soil when fulfilling criteria 1 and 2, or 1 and 3 of those listed below:

- “1. Thickness of organic horizon greater than or equal to 10 cm. A horizon of less than 20 cm must have 12 percent or more organic carbon when mixed to a depth of 20 cm.*
- 2. Soils that are never saturated with water for more than a few days must contain more than 20 percent organic carbon by weight (i.e., about 35 percent organic matter).*
- 3. Soils are subject to water saturation episodes and have either*
  - a. at least 12 percent organic carbon by weight (i.e., about 20 percent organic matter) if the soil has no clay; or*
  - b. at least 18 percent organic carbon by weight (i.e., about 30 percent organic matter) if the soil has 60% or more clay; or*
  - c. an intermediate proportional amount of organic carbon for intermediate amounts of clay.”*

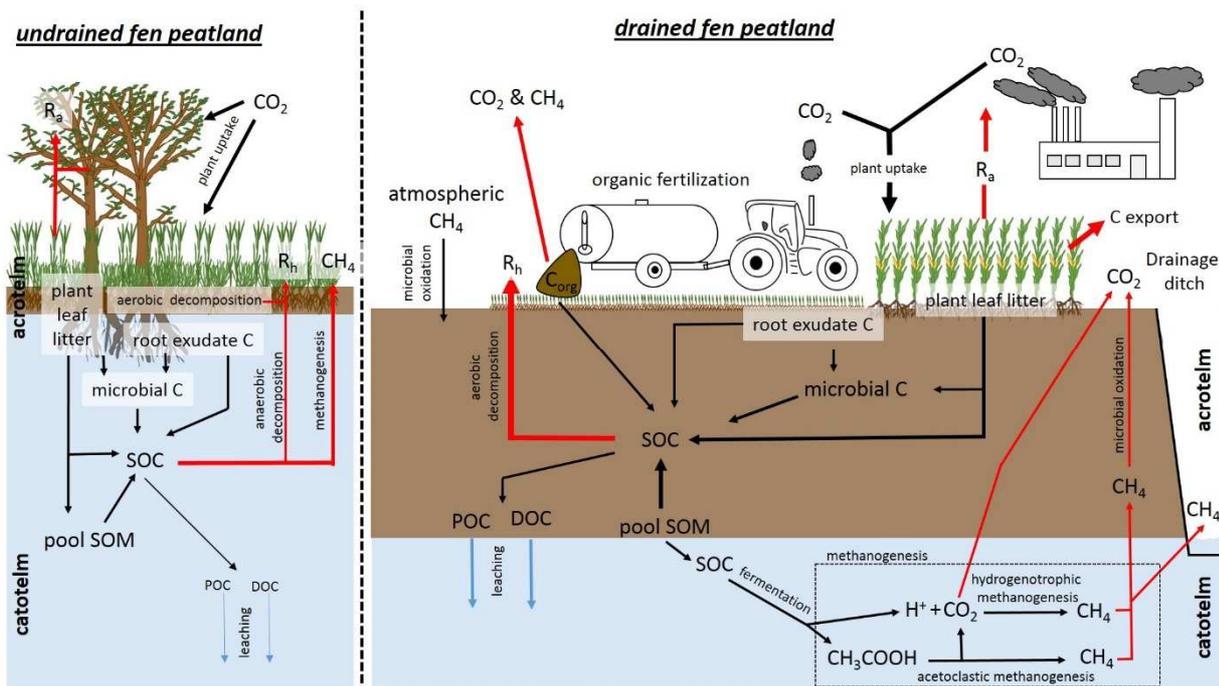
In contrast to the FAO definition of Histosols, the IPCC definition (2006) does not include the criterion of >40 cm thickness of the organic horizon to allow for deviating, often historically derived, country-specific definitions of organic soils (IPCC, 2014a). Thus the IPCC definition of organic soils is broader than the definition of histosols in the FAO (1998) or in the World Reference Base for soil resources (WRB, 2006). However, the interpretation of the IPCC (2006) deviates also from most European definitions of peat (Couwenberg, 2011), providing a challenge for the climate reporting under the UNFCCC.

For example the German classification system (KA5; Ad-hoc-AG Boden, 2005) usually requires a thickness of more than 30 cm. Furthermore, a distinction is made between soil horizons with  $\geq 30\%$  SOM content (called organic horizon) and those containing 15–30% SOM (called anmoor horizon). Particularly at the boundary between mineral and organic soils, the conversion from SOM to  $C_{org}$  contents leads to uncertainties due to the difference in conversion factors for mineral soils (1.72) and peat soils (2.00) according to the KA5 (Tiemeyer et al., 2013). Depending on the used conversion factor the upper limit of IPCC requirement is between 21 and 24% SOM by weight (Tiemeyer et al., 2013). Thus the IPCC guidelines consider only a fraction of the entire area, defined as anmoor, whereas other parts are not taken into account for the climate reporting of drained organic soils.

### 1.3 CARBON CYCLE IN PEATLANDS AND ITS HUMAN ALTERATION

Incomplete decomposition due to anoxic and sometimes acid conditions, coupled with low litter quality, has led to significant C accumulation in peatlands, particularly since the last ice age about 10,000 years ago (Rydin and Jeglum, 2006). Estimated carbon stocks for peatlands differ widely, mainly due to uncertainties for peat depth, bulk density and mean C content (Turunen et al., 2002). However, it is assumed that peatlands globally store about 400–612 Gt C, of which 270–547 Gt have accumulated in the northern hemisphere, 42–52 Gt have been stored in tropical latitudes and approximately 15 Gt have accumulated in the southern hemisphere, particularly in Patagonia (Lappalainen, 1996; Turunen et al., 2002; Hooijer et al., 2006 & 2010; Tarnocai et al., 2009; Page et al., 2011; Yu et al., 2010 & 2011). Thus, the global peatland C pool size equals the amount of organic C contained in the global living biomass (~560 Gt) and corresponds to 50–80% of the  $CO_2$ -C held in the atmosphere (Lal, 2004). Moreover, peatlands store approximately 26–39% or 16–25% of the global soil C pool estimated to a depth of one or two meters, respectively (Gorham, 1991; Batjes, 1992; Eswaran et al., 1995). Generally, the SOC provides the energy essential to biological processes and its associated nutrients (e.g. N, P, S) can contribute to the resilience of plant/soil systems to disturbances (Baldock, 2007). Moreover, the quality and quantity of SOC influence several physical and chemical properties, including peat structure, water retention, thermal properties and the cation exchange and buffer capacities of peatlands (Scheffer and Schachtschabel, 2002). The substantial accumulation of organic C and the long-term storage function of peatlands have markedly altered the global C cycle and also

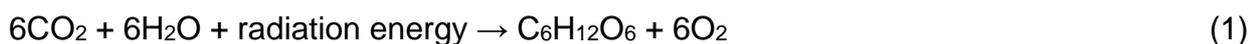
significantly contributed to global cooling during the Holocene (see chapter 1.5) (Frolking and Roulet, 2007; Limpens et al., 2008). However, in the last century human-induced activities (e.g. drainage, land-use change) and associated consequences (e.g. increased nitrogen deposition) have massively altered peatland C cycle on a global scale. Many ecosystem components and processes are involved in peatlands C cycle. The most important flows of the C cycles in a natural and a drained and cultivated fen peatland are depicted in Figure 2.



**Figure 2** Simplified carbon cycle of a pristine and drained fen peatland.

### 1.3.1 Net primary production and C input into peatlands

Carbon input in pristine peatlands is mainly controlled by the net primary productivity (NPP), originating from photosynthesis of autotrophic plants (Nilsson and Öquist, 2009). During photosynthesis, radiation energy is absorbed and transformed into chemically bounded energy, as basically shown in Equation 1 (Larcher, 2001).



The total amount of  $\text{CO}_2$  fixed in the process of photosynthesis is called gross primary production (GPP). GPP is principally a function of incident photosynthetically active radiation (PAR), which includes the wavelength range of 380–710 nm (Frolking et al., 1998). While GPP results in the formation of energy containing compounds (e.g. sugars, starch), several metabolic processes in the plant consume them, resulting in the continuous release of  $\text{CO}_2$ , which is referred as autotrophic respiration ( $R_a$ ; reverse

function of Eq.1). The amount of C converted to CO<sub>2</sub> by R<sub>a</sub> is estimated to be half of the C fixed by GPP (Larcher, 2001). The sum of GPP (positive flow) and R<sub>a</sub> (negative flow) refers to as net primary production (NPP). Several studies indicate that pristine peatlands had both significantly lower productivity at high PAR levels (gross primary production at PAR infinite (GP<sub>max</sub>) range from 5.2 to 12.4 μmol m<sup>-2</sup> s<sup>-1</sup>) and a lower apparent quantum yield at low light (α values range from 0.017 to 0.027 μmol CO<sub>2</sub> μmol<sup>-1</sup> PAR) compared to croplands and forest ecosystems on mineral soils (GP<sub>max</sub> up to 82.9 μmol m<sup>-2</sup> s<sup>-1</sup> and α up to 0.056 μmol CO<sub>2</sub> μmol<sup>-1</sup> PAR; Frohking et al., 1998). According to Blodau (2002), the NPP of peatlands range between 5 g DM m<sup>-2</sup> yr<sup>-1</sup> in northern regions and more than 1000 g DM m<sup>-2</sup> yr<sup>-1</sup> in the tropics with most common values between 100 and 400 g DM m<sup>-2</sup> yr<sup>-1</sup>. This is in accordance with Gorham (1995) and Schulze et al. (2010), who reported NPP values of about 230 g C m<sup>-2</sup> yr<sup>-1</sup> and 295 g C m<sup>-2</sup> yr<sup>-1</sup>, respectively, for naturally peatlands. Although NPP is relatively low in pristine peatlands, at least in Nordic regions (Frohking et al., 1998), the imbalance between NPP and decomposition is strong enough to cause a significant SOM accumulation (Bragazza et al., 2009). However, when peatlands are drained and intensively cultivated, NPP significantly increases as a result of cultivated field-crops, especially those developed to produce high biomass yields in a short time. According to Schulze et al. (2010), NPP of European grassland and cropland averaged 750 g C m<sup>-2</sup> yr<sup>-1</sup> and 550 g C m<sup>-2</sup> yr<sup>-1</sup>, respectively. However, depending on crop, dry matter yields of up to 1650 g DM m<sup>-2</sup> yr<sup>-1</sup> for winter wheat and up to 2500 g DM m<sup>-2</sup> yr<sup>-1</sup> for silo maize were reported for Germany (Aigner et al., 2012).

In contrast to natural peatlands, cultivated peatlands often additionally receive C through the application of organic fertilizers. However, the effects of this input on the C balance of the ecosystem is difficult to estimate, since organic fertilizers vary widely in their physical and chemical composition. Also, annual application rates differ in their quantities and frequencies between different land-use types, land-use intensities and regions. In order to obtain a balanced humus balance, C application rates of about 40–60 g C m<sup>-2</sup> yr<sup>-1</sup> are required for mineral soils according to the European cross-compliance regulations (Gutser et al., 2010), thus reflecting approximately the average C input on agricultural land in Europe.

### 1.3.2 Carbon decomposition, accumulation and losses in peatlands

SOM decomposition is controlled by several abiotic and biotic factors. Generally, decomposition refers to the breakdown of organic matter, ending with the conversion

into inorganic substances (mineralization), and is primarily driven by bacteria, invertebrate and fungi (Rydin and Jeglum, 2006). The total CO<sub>2</sub> release from soil during decomposition is called heterotrophic respiration ( $R_h$ ). The sum of  $R_a$  and  $R_h$  is referred to as ecosystem respiration ( $R_{ECO}$ ). According to Cicerone and Oremland (1988),  $R_{ECO}$  is responsible for returning a substantial part of up to 90% of C entering the plant/soil system by GPP to the atmosphere.

In peatlands, the high water level and the resulting anoxic soil conditions, at least in the catotelm, is considered as the key factor for the low decomposition rates of organic matter. Litter-bag studies under aerobic and anaerobic conditions revealed that the percentage of mass losses from vascular plant litter and *Sphagnum* litter was on average 2.3 times higher under aerobic conditions (Bragazza et al., 2009). Also in laboratory studies it was shown that the ratio of aerobic/anaerobic CO<sub>2</sub> production averaged 2.5 to 2.8 in peatlands (Moore and Dalva, 1993; Updegraff et al., 1995). Generally, the slowness of anaerobic decay is caused by the fact that anaerobic transformation processes provide less energy than aerobic processes (Succow and Josten, 2012). Beside anoxic soil conditions, decomposition rate is mainly constrained by plant litter recalcitrance, low temperatures and acid soil conditions (Bragazza et al., 2009). At an ecosystem scale, water level and pH mostly control the vegetation composition. In turn the vegetation composition determines the C balance through its effects on NPP and litter quality (Limpens et al., 2008). For example, the residues from many peatland adapted plants (e.g. sedges, *Sphagnum* species, alder, etc.) are often of low quality with high contents of lignin or lignin-like polymeric phenolic substances (Bragazza et al., 2009). Apart from the macromolecular organic composition of the peat forming vegetation, the SOM quality of peat strongly depends on hydrological and geomorphological building conditions during peat formation (Heller and Zeitz, 2012).

In most peatlands, the degradation of organic matter is totally dominated by fungi and bacteria (Nilsson and Öquist, 2009), whereas fungi numerically dominate in the acrotelm (Artz, 2009). Since microbes are unable to take up particulate organic matter (POM), the first step of mineralization involves the breakdown of solid, insoluble biopolymers into soluble components (hydrolyzation; Nilsson and Öquist, 2009). In the oxic zone, the dominant decomposition pathway is via aerobic, exo-enzym-driven decomposition (Artz, 2009). Oxygen has two main functions, it serves as terminal e<sup>-</sup> acceptor during respiration and it acts as a direct oxidant of organic molecules (Nilsson and Öquist, 2009). However, when biomass residues (e.g. litter, roots, root exudates, faunal fecal

input) are deposited on or in the aerobic peat layer, a rapid mineralization starts, accompanied by the release of CO<sub>2</sub>. First of all, simple organic compounds (e.g. sugar, starches, amino acids) and monomeric molecules are quickly metabolized and serve as energy source, followed by the turnover of carbohydrate polymers, amorphous cellulose and hemicellulose. Substances like lignin, cutins and tannins are quite resistant and thus the decomposition occurs much more slowly leading to a selective accumulation.

With increasing anoxic conditions the proportion of aerobic respiration decreases whereas fermentative processes and methanogenesis gain in importance (Artz, 2009). Under states of anoxia, only easily degradable substrates undergo a slow, incomplete decomposition with lactic acid, ethanol and acetate as intermediate products, accompanied by the release of CO<sub>2</sub> (called anaerobic respiration). In contrast, the breakdown of complex substances like lignin is almost impossible and only low molecular weight lignin components and lignin precursors are attacked by the organisms or their exo-enzymes. As a result, lignin and other aromatic compounds accumulate in the catotelm, are humified and gradually form peat (Artz, 2009; Scheffer and Schachtschabel, 2002). In natural peatlands or in the catotelm of drained peatlands, CH<sub>4</sub> is produced either through the reduction of acetate (acetoclastic methanogenesis), with the simultaneous release of CO<sub>2</sub>, or through the reduction of CO<sub>2</sub> with H<sub>2</sub> (hydrogenotrophic methanogenesis; Artz, 2009). Acetoclastic methanogenesis is considered as the terminal step of anaerobic decomposition in peatlands and it is assumed that around two thirds of global CH<sub>4</sub> production originate from this process (Artz, 2009). Once CH<sub>4</sub> is produced, it can be released to the atmosphere via three main pathways, diffusion in the soil towards the surface, ebullition (release of bubbles) and plant-mediated transport (Wahlen, 2005). Once CH<sub>4</sub> passes through an oxic layer at the soil surface, aerobic methanotrophs, particularly alpha- and gamma-proteobacteria take it up and oxidize it to CO<sub>2</sub>. Thus the amount of CH<sub>4</sub> that reaches the atmosphere depends mainly on the thickness of the acrotelm. Nevertheless, aerenchymatic vascular transport of CH<sub>4</sub> from an anaerobic layer to the atmosphere, bypassing the oxic zone at the soil surface, can account for up to 90% of total CH<sub>4</sub> emissions (Grosse et al., 1992; Svensson and Sundh, 1992; Wahlen, 2005). In turn, also O<sub>2</sub> can be transported within the plant into an anoxic zone, leading to the oxidation of CH<sub>4</sub> in close vicinity of the root (Wahlen, 2005). Recently, there has been growing evidence that beside aerobic CH<sub>4</sub> oxidation also anaerobic CH<sub>4</sub> oxidation (AMO) can play a major role in the C-cycle of natural peatlands (e.g. Gupta et al., 2013). Up to date the mechanisms of AMO are not

well understood (Valentine and Reeburgh, 2000), but evidence suggests that AMO is coupled to  $\text{NO}_3^-$ ,  $\text{SO}_4^{3-}$  or  $\text{Fe}^{3+}$  reduction as well as to “reverse methanogenesis” carried out by methanogens (Segers, 1998; Gupta et al., 2013). In the last decade, several investigations have been carried out to determine  $\text{CH}_4$  fluxes from peatlands all over the world. Observed  $\text{CH}_4$  fluxes range from  $-1.3$  to  $644 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  for northern peatlands and from  $21$  to  $912 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  for temperate and subtropical peatlands (Whalen, 2005), demonstrating the high temporal and spatial variability. However, annual  $\text{CH}_4$  emission for drier bogs commonly averaged  $<1 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Christinsen et al., 2004; Roulet et al., 2007), while wetter bogs averaged  $5\text{--}8 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Laine et al., 2007), whereas wetter fens covered by sedges can have annual  $\text{CH}_4$  emissions exceeding  $15 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Limpens et al., 2008).

With increasing peat depth the organic matter gets more and more recalcitrant and thus the anaerobic decomposition rates decrease (Rydin and Jeglum, 2006). Although anaerobic decay rates reach only a hundredth or even a thousandth of aerobic decay rates in the acrotelm, the C lost due to anaerobic decay integrated over the whole peat profile can be substantial and could finally balance the amount of NPP (Rydin and Jeglum, 2006). When this happens, the peatland no longer exhibits net accumulation of organic substrates as it has reached an equilibrium of litter input and decomposition, setting a limit to peat growth (Rydin and Jeglum, 2006). However, in natural peatlands, observed net ecosystem exchange ( $\text{NEE} = \text{GPP} - \text{R}_{\text{ECO}}$ ) rates of  $\text{CO}_2$  ranged from small losses of  $3 \text{ g C m}^{-2} \text{ yr}^{-1}$  to large uptakes of  $-90 \text{ g C m}^{-2} \text{ yr}^{-1}$ , with multiple-year averages between  $-20$  and  $-60 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Alm et al., 1997; Bryne et al., 2004; Limpens et al., 2008).

When peatlands are drained, aerobic decomposition processes speed up as a result of higher  $\text{O}_2$  availability in the upper soil profile. Simultaneously, anaerobic decomposition distinctly decreases and peatlands turn from a significant  $\text{CH}_4$  source to a small sink of atmospheric  $\text{CH}_4$  (Crill et al., 1994; Flessa et al., 1998). Water table manipulation experiments show that heterotrophic  $\text{CO}_2$  emission rates are 4 to 6 times larger when the water table is lowered to a depth of  $-40$  to  $-50 \text{ cm}$  below the soil surface compared to water table heights close to the peat surface (Moore and Knowles, 1989; Moore and Dalva, 1993). However, the release of C varies strongly, especially as a result of differences in the type and intensity of land-use (Fell et al., 2014). In particular management activities such as tillage and fertilization are known to enhance the microbial SOM decomposition directly and by increasing the amount of easily

decomposable organic substances they possibly cause a priming effect, i.e. the further acceleration of SOM decomposition (Kandel et al., 2013). Thus, highest CO<sub>2</sub> emissions from drained organic soils in boreal and temperate zones were observed from croplands and grasslands. According to the IPCC (2014a), observed NEE rates ranged from 650 to 940 g C m<sup>-2</sup> yr<sup>-1</sup> for boreal and temperate croplands and from 500 to 730 g C m<sup>-2</sup> yr<sup>-1</sup> for temperate nutrient-rich grasslands.

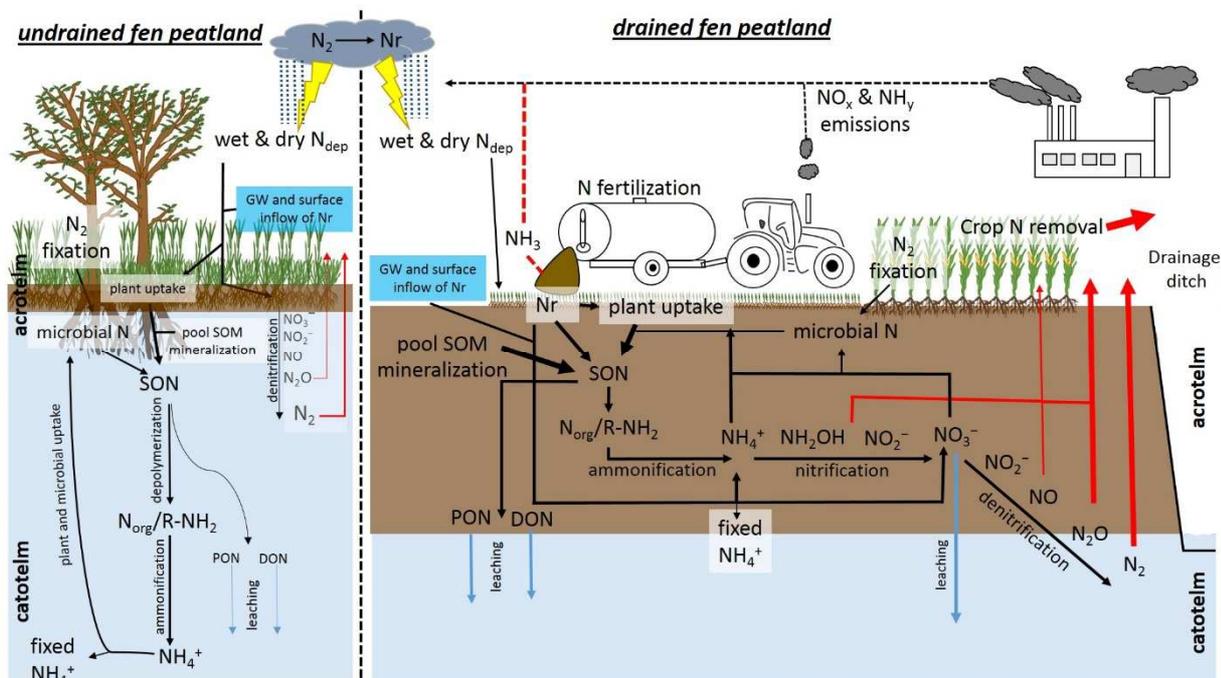
Beside CO<sub>2</sub>-C losses of particulate organic carbon (POC) and dissolved organic carbon (DOC) significantly increase after drainage and cultivation of organic soils (Nilsson and Öquist, 2009). Generally, DOC is formed via hydrolyzation of POM (Nilsson and Öquist, 2009) and commonly is the largest component of total waterborne C losses from peatlands (IPCC, 2014a). Even in natural peatlands, measured DOC fluxes range from 4 to 63 g C m<sup>-2</sup> yr<sup>-1</sup> in boreal and tropical regions, which clearly shows that this flux is of the same magnitude as the rate of long-term C accumulation and thus can control whether these ecosystems are carbon sinks or sources (IPCC, 2014a). Moreover, after drainage DOC fluxes of up to 118% compared to natural sites were reported (IPCC, 2014a). Nevertheless, when peatlands are drained and cultivated the crop export via harvesting is quantitatively the second most important pathway of C losses after CO<sub>2</sub> emissions and corresponds to nearly the amount of NPP.

## 1.4 NITROGEN CYCLE IN PEATLANDS AND ITS HUMAN ALTERATION

Since the last deglaciation, huge amounts of organic matter have accumulated in peatlands, leading to considerable organic N stocks (McNeill and Unkovich, 2007). The accumulation of N in peatlands is caused by several abiotic and biotic factors, most of all the low rate of soil organic matter mineralization and the low gaseous and hydrologic N losses (Limpens et al., 2006). According to estimates, 9–16% of the world's soil nitrogen is stored in peatlands (Limpens et al., 2006), particularly in the northern latitudes. The N availability controls many aspects of ecosystem productivity (Vile et al., 2014), since N is an essential macronutrient for all organisms, being a key component of plant amino acids, nucleic acids and chlorophyll and it is also usually quantitatively the most required element for plants from the soil (McNeill and Unkovich, 2007). As in plant dry matter, N is also one of the most abundant non-C elements in peat (Rydin and Jeglum, 2006).

In the last century, human activities have massively accelerated the N cycle on a global scale (Vitousek et al., 1997; Galloway et al., 2008). One key factor was the

invention of the Haber-Bosch process (industrial reduction of  $N_2$  to  $\rightarrow NH_3$ ), which made possible the industrial production of mineral N fertilizers on a large scale (Gruber and Galloway, 2008). Simultaneously, fossil fuel combustion increased the emission of N oxides into the atmosphere and agricultural productivity enhanced the biological N fixation by cropping increasing areas with legume crops (Vitousek et al., 1997; Jenkinson, 2001). According to Galloway (1995), every year approximately 160 million metric tonnes N are incorporated in terrestrial ecosystems, of which 61% are derived from industrial  $N_2$  fixation, mainly as fertilizers, and 14% from combustion of fossils fuels. As a consequence, peatland ecosystems have been exposed to increased N deposition ( $N_{dep}$ ) for several decades, particularly in Central Europe. Generally, natural peatlands, particularly bogs, are considered as N-limited ecosystems, in which the rates of N input and output are very small compared with the total storage of N (Ambus and Zechmeister-Boltenstern, 2007). However, drainage and the increased use of N-fertilizers to maintain soil/peat productivity as well as the widespread increase in anthropogenic  $N_{dep}$  have drastically changed the N-cycle of peatlands in the last century. Figure 2 presents a simplified scheme of the N cycling in a pristine and human-disturbed fen peatland, showing inputs, internal fluxes, storages and outputs.



**Figure 3** Simplified nitrogen cycle of a pristine and drained fen peatland.

### 1.4.1 Input pathways of N in peatland ecosystems

Natural bogs solely receive their N by the biological fixation of atmospheric  $N_2$  and through wet and dry deposition of reactive N ( $N_r$ ), whereas pristine fen peatlands

additionally receive Nr through groundwater and surface inflow. In the present manuscript, Nr includes all forms of N that are principally available for biological assimilation or transformation except of the relative inert dinitrogen (N<sub>2</sub>), which makes up approximately 78% of the atmosphere (Galloway, 1998). Only a few genera of specialized microorganisms (diazotrophs) are able to incorporate atmospheric N<sub>2</sub> into organic molecules through the reduction of N<sub>2</sub> to 2NH<sub>3</sub>, using the enzyme complex *nitrogenase* (McNeill and Unkovich, 2007). The reduction of N<sub>2</sub> is a very energy demanding process (consuming 16 ATP), which requires between 8 and >100 g C per gram N (Vitousek et al., 2002). In peatlands, N-fixing microorganisms exist as free-living forms or in complex symbioses with plants, e.g. autotrophic Cyanobacteria as well as proteobacterial methanotrophs in association with *Sphagnum* (Vile et al., 2014) or Actinomycete (*Frankia*) within root-nodules of *Alder* trees (Rydin and Jeglum, 2006; McNeill and Unkovich, 2007). Beside the biological N fixation, the conversion of atmospheric N<sub>2</sub> to Nr additionally occurs naturally through lightning (N<sub>2</sub> → NO), leading to wet and dry deposition of Nr. Natural N deposition rates are in the range of < 6 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Pitcairn and Fowler, 1995; Koopmans et al., 1998) depending on latitude. In contrast, the annual N supply through biological N<sub>2</sub>-fixation ranges between 0.3–62 kg N ha<sup>-1</sup> for bogs and 1.6–115 kg N ha<sup>-1</sup> for fen peatlands (Dittert, 1992; Succow and Joosten, 2012; Vile et al., 2014). Thus, it is assumed that the biological N<sub>2</sub>-fixation represented the dominant input of new N into most pristine ecosystems in pre-industrial times (Vitousek et al., 2002; Vile et al., 2014). However, in the last decades anthropogenic N<sub>dep</sub> has drastically increased by a factor of >10 (Galloway et al., 2004). In Germany, prevailing total N<sub>dep</sub> rates in open land are estimated to be on average 26 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Wochele and Kiese, 2010). In contrast, critical N loads have been estimated to constitute 5–10 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Bobbink and Roelofs, 1995; UNECE, 2004; Bobbink et al., 2010). It is well known that particularly NH<sub>3</sub> deposition causes soil acidification and eutrophication of ecosystems (e.g., Fangmeier et al., 1994; Galloway, 1995, 2001; Smith et al., 1999). Mainly N limited ecosystems like ombrotrophic bogs are highly sensitive to enhanced N inputs, since their characteristic plants and microbes are adapted to conditions of restricted N availability (Bobbink et al., 1998; Sheppard et al., 2013). Field studies of increased N-deposition on peatlands have shown changes in species composition, particularly the loss of *Sphagnum* mosses (Heijmans et al. 2001; Tomassen et al. 2004; Bubier et al. 2007). Such crucial changes in species composition

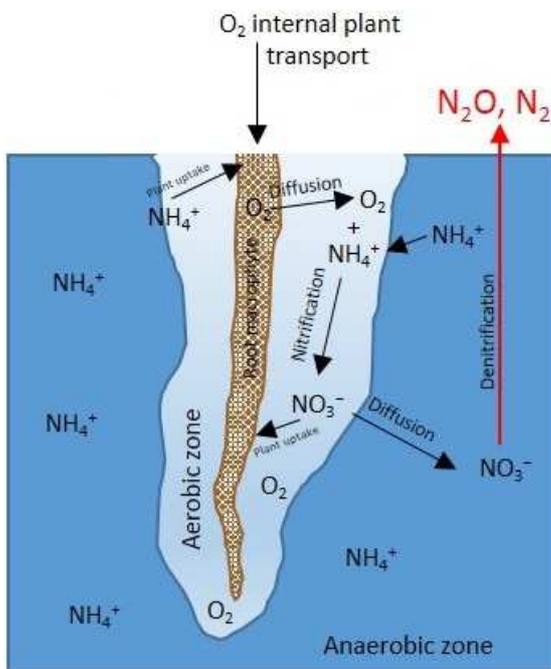
can have important implications for key processes within the peatland and peatland services (Sheppard et al., 2013).

Beside biological  $N_2$  fixation,  $N_{dep}$  and inflow of  $N_r$  with groundwater (GW) and surface, fertilization represent quantitatively the dominant input of N in drained and cultivated peatlands. However, amount and form of N applied to cultivated peatlands to maintain productivity widely differ among geographical regions, land-use types and management practices.

#### 1.4.2 Nitrogen mineralization and immobilization

Generally, the SOM represents the largest N pool in the soil, but the organically bound N forms are mostly unavailable to plants, since they acquire nitrogen in inorganic forms (e.g. as  $NH_4^+$ ,  $NO_2^-$  or  $NO_3^-$ ). Some plants, mainly found in SOM-rich environments in arctic, boreal and alpine regions are able to take up simple organic N forms, like amino acids and proteins (Chapin, 1995; Lipson and Monson, 1998). During SOM decomposition, mostly heterotrophic bacteria (both aerobic and anaerobic) and fungi breakdown polymeric organic N compounds firstly into simpler monomeric N compounds (collectively abbreviated as  $N_{org-NH_2}$ ) and finally to ammonia ( $NH_3$ ) or ammonium ( $NH_4^+$ ); a process called ammonification (Rydin and Jeglum, 2006; McNeill and Unkovich, 2007). In natural peatlands, anoxic conditions predominate in the soil profile since the diffusion of oxygen in water is about  $10^4$  times slower than that in air, and thus the microbial and chemical demand for oxygen distinctly exceeds its supply (Cleemput van et al., 2007). Generally, anaerobicity slows down decomposition processes and thus also ammonification rates (Vepraskas and Faulkner, 2001). However, SOM decomposition is a complex process and its rates depend on several abiotic and biotic factors, of which the subsequent supply of newly added plant and microbial residues is a key element since this alters the stage of decay and the degree of recalcitrance of the SOM (McNeill and Unkovich, 2007). Under aerobic conditions, once  $NH_4^+$  is released into the soil it will be quickly oxidized by chemolithoautotrophic and very likely by heterotrophic bacteria; a process called nitrification (Ferguson et al., 2007). In this process, the chemolithoautotrophic *Nitrosomonas* firstly convert  $NH_4^+$  (or  $NH_3$ ) into hydroxylamine ( $NH_2OH$ ) using the enzyme ammonia mono-oxygenase and then, in a second step,  $NH_2OH$  is oxidized to nitrite ( $NO_2^-$ ) (Ferguson et al., 2007). The further oxidation of  $NO_2^-$  to nitrate ( $NO_3^-$ ) takes place in species of the chemolithoautotrophic *Nitrobacter*. However, due to the very low cell numbers in the soil and the difficulty to cultivate sufficient quantities of cells in the lab to investigate e.g. vesicular membranes

and purified proteins, the biochemistry and molecular biology of chemolithoautotrophic and heterotrophic nitrification is still poorly understood (Ferguson et al., 2007). In natural peatlands, nitrification is usually hampered mainly by anoxic conditions and in bogs additionally by low pH (McNeill and Unkovich, 2007). Nevertheless,  $O_2$  can be transported with the surface- or groundwater inflow in fen peatlands, or by diffusion in the uppermost centimeters of the peat layer, partly creating an aerobic zone and appropriate conditions for nitrification (Cleemput van et al., 2007). Also, peatland-adapted plants with aerenchymatic tissue (e.g. *Carex*, *Phragmites*, *Typha*) can promote an oxic zone in close vicinity to their roots, resulting in the formation of  $NO_3^-$  via nitrification as schematically shown in Fig. 4 (Rydin and Jeglum, 2006; Cleemput van et al., 2007). However, these transformation processes only play a minor role for the N cycle of pristine peatlands and were therefore not included in Fig. 3.



**Figure 4** Simplified scheme of plant induced interactions of aerobic and anaerobic zones around a macrophyte root (modified after Cleemput van et al., 2007).

After drainage and cultivation of peatlands, N-mineralization and -transformation processes speed up and the concentrations of inorganic N forms, particularly  $NO_3^-$ , distinctly increase (Rydin and Jeglum, 2006). Moreover, the application of mineral or organic fertilizers enhances the soil N pool and further stimulates SOM mineralization, leading to additional inorganic N (Gutser et al., 2005; Jones et al., 2007). The annual N supply provided by aerobic peat mineralization can vary between 70 and 570 kg N ha<sup>-1</sup> yr<sup>-1</sup> for intensively used crop- or grasslands, whereas under anaerobic conditions, net N mineralization rates are relatively low with approximately 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Schothorst, 1977; Göttlich, 1990; Flessa et al., 1998; Sonneveld and Lantinga, 2011; Leppelt et al., 2014).

Plant uptake of N depends on the concentration of  $NH_4^+$ ,  $NO_2^-$  and  $NO_3^-$  in the soil solution, the physiological plant stage, root distribution and soil water content (Mc Neil and Unkovich, 2007). Since in acid, anoxic peat  $NH_4^+$  is the main form of plant-available

Plant uptake of N depends on the concentration of  $NH_4^+$ ,  $NO_2^-$  and  $NO_3^-$  in the soil solution, the physiological plant stage, root distribution and soil water content (Mc Neil and Unkovich, 2007). Since in acid, anoxic peat  $NH_4^+$  is the main form of plant-available

N, many peatland-adapted plants prefer  $\text{NH}_4^+$  as N source (Succow and Joosten, 2012). Also, some plants are not able to utilize  $\text{NO}_3^-$  because they lack the enzyme *nitroreductase*, which is necessary for the reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (nitrate assimilation) (Succow and Joosten, 2012), and are thus restricted to  $\text{NH}_4^+$ . To avoid  $\text{NH}_4^+$  toxicity, absorbed or reduced  $\text{NH}_4^+$  is rapidly assimilated (ammonium assimilation) into glutamine ( $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$ ), which is readily transported, stored or converted into other amino acids within the plant (Burgiere et al., 1997; McNeill and Unkovich, 2007). Generally, plants and microbes compete for inorganic N and once N is immobilized in microbial biomass it can only become plant available by microbe death. The continuous transfer of mineral N into organic material via the incorporation of N into microbial biomass and the release of N during microbial decomposition of SOM or by microbial death is called the microbial mineralization-immobilization turnover (MIT) (Jansson and Persson, 1982; McNeill and Unkovich, 2007). The ratio of immobilization to mineralisation upon decomposition mainly depends on the C/N ratio of the organic substrate; C/N ratios  $>25$  require additional N from the inorganic pool for decomposition of the organic material while C/N ratio  $<10$  lead to a release of N (Göttlich, 1990).

#### 1.4.3 Nitrogen absorption and leaching

When  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  or  $\text{NO}_3^-$  is transferred into the soil solution, a portion of the N is taken up by plants and microbes, whereas some N can partially be fixed at the humus surface, is lost in gaseous forms to the atmosphere or is leached to the groundwater (McNeill and Unkovich, 2007). Since organic particle surfaces in peatlands are mostly negatively charged,  $\text{NH}_4^+$  is readily absorbed while the anion  $\text{NO}_3^-$  can relatively easily be leached into the groundwater (McNeill and Unkovich, 2007). Furthermore drainage was found to significantly increase leaching of particulate organic N (PON) and dissolved organic N (DON) into the ground- and surface water (total leaching losses of up to  $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ), whereas leaching losses of PON and DON were found to be of minor importance in natural peatlands ( $3\text{--}6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) (Göttlich, 1990).

#### 1.4.4 Gaseous N production processes

In peatland soils several abiotic and biotic processes produce gaseous N compounds ( $\text{NH}_3$ ,  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ),  $\text{N}_2\text{O}$  or  $\text{N}_2$ ) which can rapidly be lost to the atmosphere. Commonly, microbial denitrification and nitrification are cited as the main sources of gaseous N forms, but this is just a simplification, because microbial metabolic pathways provide a wealth of processes that form gaseous N (Butterbach-Bahl et al., 2013). The reduction

of ionic oxidized nitrogen forms ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) to the gaseous oxides  $\text{NO}_x$  and  $\text{N}_2\text{O}$ , which may themselves be further reduced to the inert atmospheric  $\text{N}_2$ , is called biological denitrification (Knowles, 1982). Denitrification presupposes restricted  $\text{O}_2$  availability and the presence of easily degradable C-sources (Ambus and Zechmeister-Boltenstern, 2007). The stepwise reduction is catalyzed by several enzymes, mostly in heterotrophic bacteria and fungi which are able to use N oxides as terminal electron acceptors and the organic C as electron donors (McNeil and Unkovich, 2007). Which gas ( $\text{NO}_x$ ,  $\text{N}_2\text{O}$  or  $\text{N}_2$ ) will finally be released to the atmosphere depends inter alia on the degree of anaerobicity, but as well on the organism group carrying out denitrification. For example the fungal denitrification chain is often ending with the formation of  $\text{N}_2\text{O}$  (Philipoot et al., 2011). It was found that with increasing anoxic conditions, the percentage of  $\text{N}_2$  increases until it becomes the major gas evolved (Rolston et al., 1978; Davidson, 1991). Moreover, high contents of available  $\text{NO}_3^-$  inhibit  $\text{N}_2\text{O}$  reductase activity, the enzyme responsible for the conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$  (Blackmer and Bremner, 1978; Firestone et al., 1979; Weier et al., 1993; Regina et al., 1996). Apart from biological denitrification, in acidic soils ( $\text{pH} < 5$ ) with high concentrations of  $\text{NO}_2^-$ , various purely abiotic reactions can lead to the formation of  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$ , generally summarized as chemodenitrification (Nelson, 1982; van Cleemput, 1998). However, the importance of chemodenitrification to total gaseous N losses has rarely been studied and further investigations, particularly for drained bog ecosystems, are necessary.

Heterotrophic and autotrophic bacteria and archaea are known to produce  $\text{NO}$  and  $\text{N}_2\text{O}$  in the course of nitrification. According to Butterbach-Bahl et al. (2013), there are two direct pathways in which N gases can be produced. Firstly, the chemical decomposition of  $\text{NH}_2\text{OH}$  can lead to  $\text{N}_2\text{O}$  and perhaps  $\text{N}_2$ , with  $\text{NO}$  as precursor (Wrage et al., 2005; Frame and Casciotti, 2010), and secondly,  $\text{N}_2\text{O}$  can be produced during nitrifier-denitrification (Poth and Focht, 1985; Butterbach-Bahl et al.; 2013). Nitrifier-denitrification describes the oxidation of  $\text{NH}_4^+$  (or  $\text{NH}_3$ ) to  $\text{NO}_2^-$  and its subsequent stepwise reduction to  $\text{NO}$ ,  $\text{N}_2\text{O}$  and perhaps  $\text{N}_2$  by the same autotrophic ammonia oxidizers. This process requires conditions of high N availability but low organic C and  $\text{O}_2$  availability (Poth and Focht, 1985; Colliver and Stephenson, 2000; Braker and Conrad, 2011). In environments where aerobic and anaerobic microsites exist in close proximity (e.g. drained peatlands or other hydromorphic soils) nitrification and denitrification can occur in a concerted action, called “coupled nitrification-denitrification” (Wrage et al., 2001; Butterbach-Bahl et al.; 2013). Several further processes (e.g. Co-

denitrification with  $\text{NO}$  or  $\text{N}_2\text{O}$ , dissimilatory nitrate reduction to ammonium (DNRA), anaerobic ammonia oxidation (ANAMMOX)) can lead to the production of nitrogenous gases (Butterbach-Bahl et al.; 2013). However, the source of N gas production in peatlands is often uncertain because within the peat profile different physical and chemical conditions exist and thus several processes producing N gases can run simultaneously and within close proximity (Davidson et al., 1986; Butterbach-Bahl et al., 2013). Generally, gaseous N losses from pristine peatlands were found to be close to zero (Kasimir-Klemendtsson et al., 1997; Flessa et al., 1998; Couwenberg et al., 2011) since all processes leading to N emissions presuppose at least product parts of nitrification. Nevertheless, beside N deposition, small amounts of oxidized N can enter the anaerobic peat layer through GW or surface water inflow in natural fen peatlands, resulting mainly in  $\text{N}_2$  or partially  $\text{N}_2\text{O}$  emissions due to denitrification. In contrast, drainage and fertilization have turned peatlands into a significant source of gaseous N emissions. Several studies reported  $\text{N}_2\text{O}$  emissions from drained organic soils ranging from 0 to 61 kg  $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$  for arable lands (Kasimir-Klemendtsson et al., 1997; Augustin et al., 1998a; Flessa et al., 1998; Petersen et al., 2012; Drösler et al., 2013) and ranging from 1.15 to 41 kg  $\text{N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$  for grasslands (Velthof et al., 1996; Augustin et al., 1998a; Flessa et al., 1997 and 1998; van Beek et al., 2010 and 2011; Petersen et al., 2012; Beetz et al., 2013; Drösler et al., 2013). Additionally, organic fertilization is known to produce high  $\text{NH}_3$  emissions particularly after splash plate application on grassland (Rubæk et al., 1996; Wulf et al., 2002). Depending on climatic factors and manure composition, up to 90% of applied  $\text{NH}_4^+\text{-N}$  can be lost as  $\text{NH}_3$  in a few hours (Vandre et al., 1997). Since  $\text{NH}_3$  is a highly reactive, alkaline gas it is often deposited within a radius of 1–2 km from the source (Sheppard et al., 2013). However, in dependence of the water table depth, it is assumed that highest gaseous N losses occur in the form of  $\text{N}_2$  in drained peatlands. Mainly due to analytical difficulties in the determination of microbial produced  $\text{N}_2$ , to date the total denitrification potential from peatlands has rarely been estimated. First results revealed annual  $\text{N}_2$  emissions ranging between 15 and 650 kg  $\text{N}_2\text{-N ha}^{-1} \text{ yr}^{-1}$  (Teiter and Mander, 2005; Wray and Bayley, 2007; Mander et al., 2008; Roobroeck et al., 2010; Soosaar et al., 2011), confirming the importance of gaseous N losses through denitrification in the case of peatland disturbance. Beside gaseous losses and leaching of N, highest N losses originate from harvesting crops at intensively used drained peatlands (Göttlich, 1990).

## 1.5 PEATLANDS AND THE CLIMATE CHANGE

### 1.5.1 Greenhouse effect and climate change

The earth-atmosphere system is heated by a net absorption of solar short-wave radiation (Bowman, 1990). In an equilibrium state this is balanced by a net emission of long-wave radiation from the earth-atmosphere to space (Bowman, 1990; Jain, 1993). Certain atmospheric gases (called greenhouse gases; GHG) are relatively transparent to the incoming short-wave radiation, but are absorbing the outgoing long-wave (infrared) radiation and re-radiate it back to the earth's surface and space, leading to a net warming of the earth-atmosphere, which is called "natural greenhouse effect" (Bowman, 1990; Jain, 1993). Several natural and anthropogenic drivers (e.g. GHGs such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, halocarbons; aerosols such as mineral dust, black carbon, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>; change in albedo and solar irradiance) affect the earth's energy budget (IPCC, 2013). The natural greenhouse effect ensures that life is possible on earth since it leads to an increase of global mean surface temperature of about 33°C (IPCC, 1994). The strength of a driver to change the energy flux is quantified as radiative forcing (RF) in units of watts per square meter (W m<sup>-2</sup>), and is a measure of how the energy balance of the earth-atmosphere system (incoming and outgoing energy) is altered by this driver (IPCC, 2013). The RF of the climate system is dominated by the long-lived greenhouse gases (GHGs) (IPCC, 2007). Greenhouse gases differ in their ability to absorb infrared radiation and also have different turnover-times and pathways of chemical breakdown in the atmosphere. Therefore, GHGs contribute to different extents to the warming of the global climate system (IPCC, 2007). To take this into account, the warming influence of a long-lived GHG may be expressed as Global Warming Potential (GWP), which is based on the time-integrated RF of CO<sub>2</sub> (GWP = 1; IPCC, 2007). Table 1 shows relevant GHGs from peatlands and their GWPs for different time horizons.

**Table 1** Peatland relevant GHGs and their lifetimes, radiative efficiencies and direct GWPs relative to CO<sub>2</sub> (according to Forster et al., 2007).

Industrial Designation or Common Name	Chemical Formula	Lifetime [years]	Radiative Efficiency [W m <sup>-2</sup> ppb <sup>-1</sup> ]	Global Warming Potential for Given Time Horizon		
				20-yr	100-yr	500-yr
Carbon dioxide	CO <sub>2</sub>	a	1.4x10 <sup>-5</sup>	1	1	1
Methane	CH <sub>4</sub>	12 <sup>b</sup>	3.7x10 <sup>-4</sup>	72	25	7.6
Nitrous oxide	N <sub>2</sub> O	114	3.03x10 <sup>-3</sup>	289	298	153

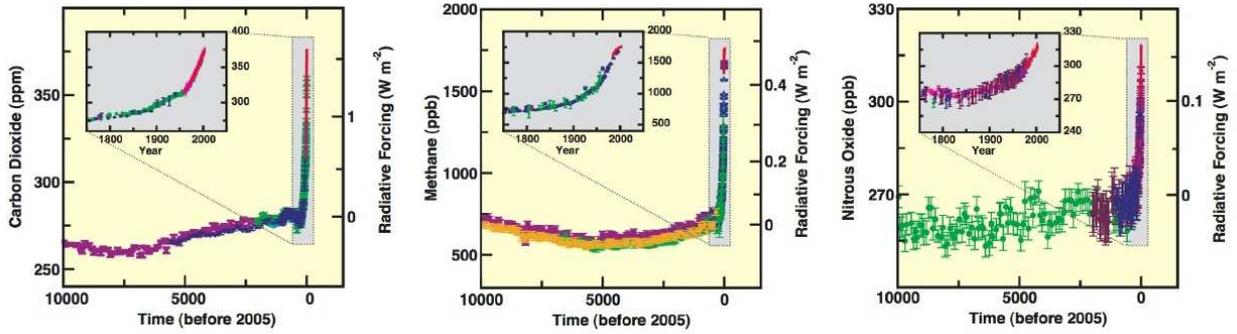
a The CO<sub>2</sub> response function is based on the revised version of the Bern Carbon cycle model using a background CO<sub>2</sub> concentration value of 378 ppm. The decay of a pulse of CO<sub>2</sub> with time  $t$  is given by

$$a_0 + \sum_{i=1}^3 a_i \cdot e^{-t/\tau_i}$$

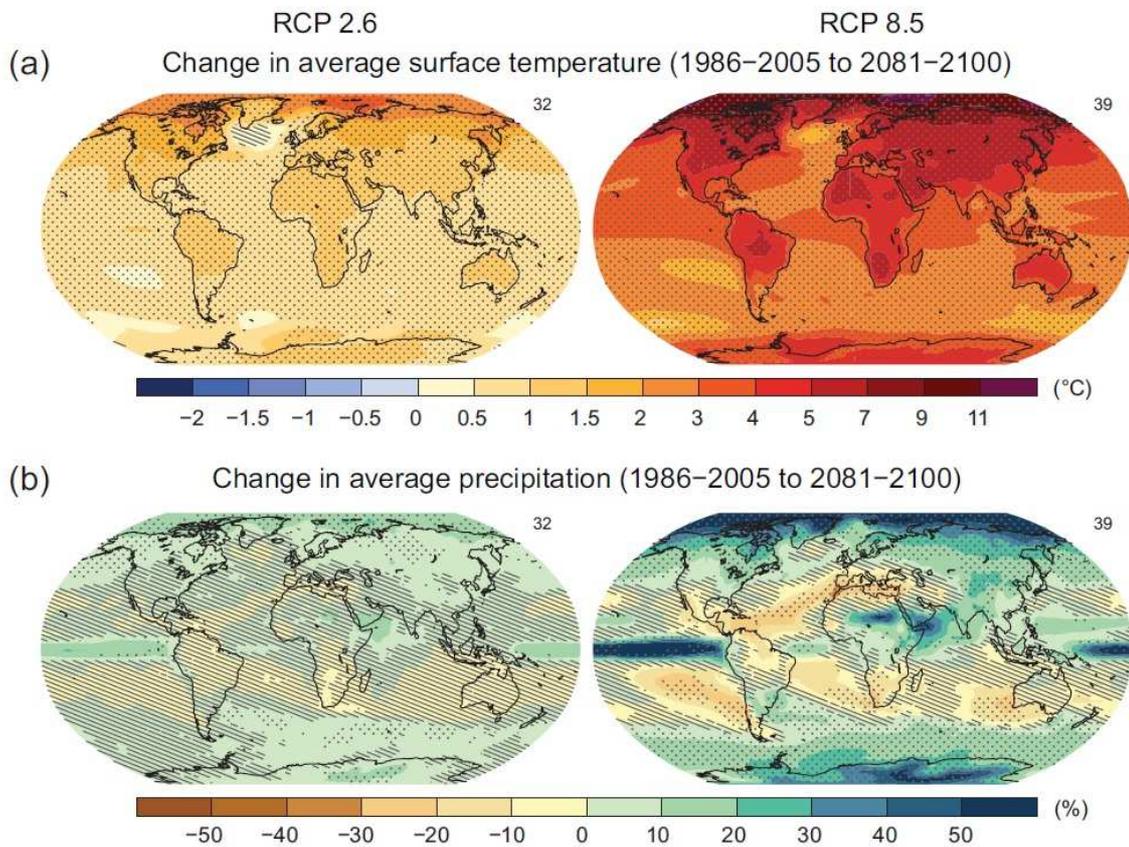
Where  $a_0 = 0.217$ ,  $a_1 = 0.259$ ,  $a_2 = 0.338$ ,  $a_3 = 0.186$ ,  $\tau_1 = 172.9$  years,  $\tau_2 = 18.51$  years, and  $\tau_3 = 1.186$  years.

b The perturbation lifetime for CH<sub>4</sub> is 12 years. The GWP for CH<sub>4</sub> includes indirect effects from enhancements of ozone and stratospheric water vapor.

Global atmospheric concentrations of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O have increased markedly since 1750, mainly due to human activities (Figure 5; IPCC, 2007). In April 2014, for the first time monthly concentrations of CO<sub>2</sub> in the atmosphere topped 400 parts per million (ppm) throughout the northern hemisphere (WMO, 2014). Also atmospheric CH<sub>4</sub> and N<sub>2</sub>O concentrations reached new records of about 1819 parts per billion (ppb) and 325.1 ppb in 2012 (WMO, 2014), and thus exceeded the pre-industrial levels by about 150%, and 20%, respectively (IPCC, 2013). The entire human-induced emissions of GHG had led to a total anthropogenic RF of 2.29 W m<sup>-2</sup> for 2011 relative to 1750 (IPCC, 2013). Because of that the global climate system has changed. For example, the averaged combined land and ocean surface temperature has increased by 0.85 °C between the years 1880 and 2012 (IPCC, 2013). Additionally, a shift in precipitation as well as extreme weather and climate events (e.g. increase in heat waves and heavy precipitation events) and a decrease in the Greenland and Antarctic ice sheets, with the consequence of a rising sea level have been observed (IPCC, 2013). The future global and regional climate changes are unknown. However, despite their uncertainty all climate models predict a further reinforcement of the changes observed in the last decades. In dependence of the chosen model scenarios of anthropogenic forcing, the simulations predict an increase of global mean surface temperatures for 2081–2100 relative to 1986–2005 of 0.3–1.7°C or 2.6–4.8°C in the case of the RCP2.6 or RCP8.5 scenario, respectively (see Fig. 6; ICPP, 2013).



**Figure 5** Atmospheric concentrations of the three important greenhouse gases CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O over the last 10,000 years. Increases since about 1750 (inset panels) are attributed to human activities in the industrial era (source: IPCC, 2007).



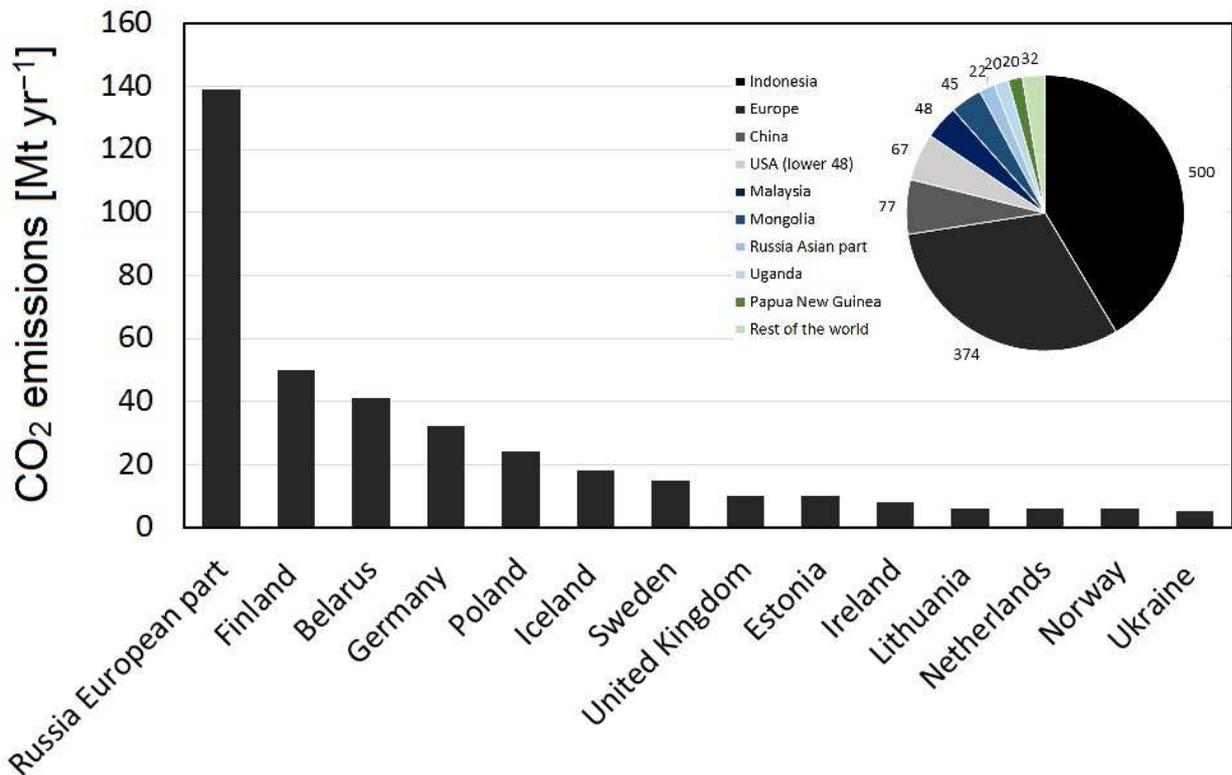
**Figure 6** Maps of CMIP5 multi-model mean results for the scenarios RCP2.6 and RCP8.5 in 2081–2100 of (a) annual mean surface temperature change, (b) average percent change in annual mean precipitation, For the Fifth Assessment Report of IPCC, the scientific community has defined a set of four new scenarios, denoted Representative Concentration Pathways (RCPs, see Glossary). They are identified by their approximate total radiative forcing in year 2100 relative to 1750: 2.6 W m<sup>-2</sup> for RCP2.6, 4.5 W m<sup>-2</sup> for RCP4.5, 6.0 W m<sup>-2</sup> for RCP6.0, and 8.5 W m<sup>-2</sup> for RCP8.5. (source: IPCC, 2013)

### 1.5.2 Contribution of peatlands to climate change – Past, Present and Future perspectives

Globally, peatlands store approximately 30% and 16% of the world's soil C and N, although they cover less than 3% of the earth's land surface (Yu et al., 2010 & 2011; Limpens et al., 2006). Based on a simple conversion from change in carbon pool to atmospheric CO<sub>2</sub> (1 ppmv = 2.123 Gt C), by taking into account the compensation effect of ocean outgassing, Charman et al. (2013) estimated that the uptake of CO<sub>2</sub> by peatlands reduced atmospheric CO<sub>2</sub> concentration by 7–12 ppm over a 1000 yr period. Thus the capability of pristine peatlands to act as a long-term sink for C and N, have significantly contributed to global cooling since the last ice age (~10,000 years) (Frolking and Roulet, 2007; Limpens et al., 2008). As extensively discussed in section 1.3 and 1.4, today peatlands are undergoing major transformations due to human alteration (e.g. drainage, cultivation, peat extraction and burning) and thereby the radiative forcing (RF) caused by peatland-atmosphere exchange has shifted from a net cooling to a net warming.

In 2010, total anthropogenic GHG emissions reached  $49 \pm 4.5$  Gt CO<sub>2</sub> eq. yr<sup>-1</sup> and were the highest between 2000 and 2010 (IPCC, 2014b). Carbon dioxide is the most important GHG accounting for 76% of total anthropogenic GHG emissions in 2010 (IPCC, 2014b). Its concentrations have increased primarily due to emissions from fossil fuel combustion (38.2 Gt CO<sub>2</sub> eq. yr<sup>-1</sup>) and secondarily due to emissions from land-use change (deforestation, agricultural soil and nutrient management, livestock farming), which accounts for approximately 10–12 Gt CO<sub>2</sub> eq. yr<sup>-1</sup> (IPCC, 2014b). From 1750 to 2011, CO<sub>2</sub> emissions from deforestation and other land use change are estimated to have released 180 Gt C (Hooijer et al., 2010). According to the Food and Agriculture Organization of the United Nations (FAO), globally 250,000 km<sup>2</sup> of peatland area are estimated to be drained, leading to approximately total annual GHG emissions of 0.9 Gt CO<sub>2</sub> eq. yr<sup>-1</sup> in 2010 (FAOSTAT, 2013). Furthermore, Joosten (2010) estimated worldwide 500,000 km<sup>2</sup> of degraded peatland, leading to annual CO<sub>2</sub> emissions of approximately 1.30 Gt CO<sub>2</sub> yr<sup>-1</sup> (excl. extracted peat and fires) in 2008, of which 0.5 Gt are emitted from Indonesia, 0.174 Gt from the EU (27 countries) and 0.161 Gt from Russia (see Fig. 7). Including peat fire and peat extraction, Joosten (2010) assumed that degraded peatlands (0.3% of earth's land surface) may exceed 2 Gt CO<sub>2</sub> yr<sup>-1</sup> globally, which corresponds to 5.4% of global anthropogenic CO<sub>2</sub> emissions. Nevertheless, under

the present climate, northern peatlands still act as small C sinks of up to  $60 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Lafleur et al., 2003; Roulet et al., 2007; Nilsson et al., 2008; Sagerfors et al., 2008).



**Figure 7** Estimated CO<sub>2</sub> emissions in Mt ( $10^6$  t) from degrading peat for the year 2008. Bar chart shows European countries; pie chart shows total global emissions in Mt (Joosten, 2010).

Beside the uptake capacity of CO<sub>2</sub> since the last glaciation, peatland development has likewise significantly increased atmospheric CH<sub>4</sub> concentrations as is documented in atmospheric records from ice cores (Blodau, 2002; Yu, 2010). Methane is the second most important anthropogenic GHG (16% or  $7.8 \pm 1.6 \text{ Gt CO}_2 \text{ eq. yr}^{-1}$ ) and its increase has primarily been caused by human activities related to agriculture, natural gas distribution and landfills (IPCC, 2014b). However, CH<sub>4</sub> is also released from natural ecosystems, of which pristine peatlands and other wetlands are the largest sources with estimated emissions of  $55\text{--}150 \text{ Tg CH}_4 \text{ yr}^{-1}$  (Watson et al., 2000). According to Rydin and Jeglum (2006), northern peatlands are responsible for 6–9% of the global CH<sub>4</sub> emissions. However, as previously pointed out, CH<sub>4</sub> emissions from drained organic soils (e.g., drained peat soils and soils developed in wet conditions) are assumed to be negligible and, depending on drainage status, they may even become small atmospheric CH<sub>4</sub> sink (IPCC, 2014a).

N<sub>2</sub>O is the third most important GHG accounting for 6.2% of total anthropogenic GHG, which corresponds to  $3.1 \pm 1.9 \text{ Gt CO}_2 \text{ eq. yr}^{-1}$ . It is emitted into the atmosphere from

both natural (approx. 60%) and anthropogenic sources (approx. 40%), including oceans, soils, biomass burning, fertilizer use, and various industrial processes (IPCC, 2007; IPCC, 2014b). In particular, cultivated organic soils are considered as hotspots of N<sub>2</sub>O emissions (Kasimir-Klemmedtsson et al., 1997; Freibauer et al., 2004; Leppelt et al., 2014). According to Leppelt et al. (2014), direct N<sub>2</sub>O emissions from organic soils in Europe amount up to 149.5 Gg N<sub>2</sub>O-N yr<sup>-1</sup>, which represents 13% of total European N<sub>2</sub>O emissions reported in the European Union (EU) greenhouse gas inventory of 2011. Additionally, peatland cultivation can lead to NH<sub>3</sub> as well as NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions. Besides acidification and eutrophication, NH<sub>3</sub> deposition promotes the formation of N<sub>2</sub>O at the immission sites and therefore NH<sub>3</sub> is considered as indirect GHG (Moiser, 2001). However, the contribution of peatland cultivation to NH<sub>3</sub> emissions is still unclear, but overall agriculture is responsible for 95.3% of anthropogenic NH<sub>3</sub> emissions in Germany (Haenel et al., 2010). Due to high reactivity, NO and NO<sub>2</sub> are considered as Near-Term Climate Forcers (NTCFs) since they are involved in a sequence of photochemical reactions, which may lead to the formation of the GHG ozone (O<sub>3</sub>) and hydroxyl radicals (OH·) in the troposphere (IPCC, 2007). Additionally, NO<sub>x</sub> also causes RF through NO<sub>3</sub><sup>-</sup> formation, and via reaction with CH<sub>4</sub> it increases stratospheric water vapour (IPCC, 2013).

As previously mentioned, current climate scenarios partly predict a drastic increase in global warming and further aspects of the climate. This actually triggered questions as to what extent this will affect peatlands globally. Principally, higher temperatures are assumed to increase peat decay, causing a positive feedback on climate warming (Charman et al., 2013). As depicted in Fig. 6a, boreal and arctic regions are predicted to warm faster and more strongly than temperate latitudes (Treat et al., 2013). Also precipitation is predicted to significantly increase in this region (Fig. 6b; IPCC, 2014b). Worldwide, 75–85% of all peatlands are situated in the northern hemisphere, storing 270–547 Gt C (Turunen et al., 2002; Frolking et al., 2011; Charman et al., 2013). It is expected that increased temperatures cause permafrost melting as well as increased thawing of the perennially-frozen peat in the arctic and northern boreal region, leading to water-saturated conditions. This, together with higher temperatures, will probably result in anaerobic decomposition, leading to the production of CH<sub>4</sub> (Tarnocai, 2006; Arneth et al., 2010; Charman et al., 2013). In the RCP8.5 climate scenario, thawing of frozen peat and permafrost is assessed to release 50 to 250 Gt C as CO<sub>2</sub> and CH<sub>4</sub> to the atmosphere, causing a positive feedback on climate change (IPCC, 2013). In other

latitudes (e.g. south boreal wetland belt, temperate and tropical regions), higher temperatures will cause higher evapo-transpiration leading to drought conditions. Under such conditions, peatlands can become a net source of CO<sub>2</sub> and also N<sub>2</sub>O due to enhanced decomposition (Tarnocai, 2006; Hooijer et al., 2010; Sulman et al., 2010). Moreover, dryer conditions enhance the risk of wild- and peat fires, particularly in the tropic regions, further promoting CO<sub>2</sub> emissions (Turetsky et al., 2004; Limpens et al., 2008). In contrast, several authors (e.g. Tarnocai, 2006; Arneth et al., 2010; Charman et al., 2013) suggested that in the mid and high arctic latitudes, higher temperatures, longer growing seasons, and higher atmospheric CO<sub>2</sub> could stimulate photosynthesis leading to increasing biomass production and thus promote peat accumulation, and may provide a negative climate feedback in a warmer future (Yu et al., 2011). However, climate change as well as feedbacks in vegetation type shifts and land-use changes (e.g. drainage of peatlands) are difficult to predict with highly uncertain projections, limiting our ability to draw conclusions. Nevertheless, the impact of climate change will be considerable and trigger feedback mechanisms that might further accelerate climate change (Houghton and Woodwell, 1989; Davidson and Janssens, 2006).

## 1.6 OBJECTIVES

The present PhD thesis was part of the joint research project “Organic soils”; Acquisition and development of methods, activity data and emission factors for the climate reporting under LULUCF/AFOLU. In the course of this joint research project, several open questions were to be answered to fulfil the requirements for the German climate reporting according to the extended methodology of the Tier 2 and Tier 3 approach of the IPCC guidelines. According to Drösler et al. (2008b) the main goals of the joint research project were:

- 1) Geo-referenced assessment of organic soils according to the IPCC guidelines to draw up a dynamic land register of organic soils in Germany.
- 2) Assessment of national EF for different soil-types (including soils containing 15–30% SOM), climate regions, land-use types (including forests) and management practices to reduce the uncertainty derived from the high spatial and temporal variability in GHG fluxes.
- 3) Development, adjustment, parametrization and validation of models for the calculation of GHGs, derived from drained organic soils.

- 4) Assessment and development of methods and parameters for the nationwide regionalization of investigated data sets.
- 5) Quantification of uncertainties in determined activity data sets and emission calculation methods, as well as the estimation of the overall uncertainties from the national climate reporting for drained organic soils.

The objectives of the present thesis focused on **three key issues**, which fall within the scope of point 2 of the above mentioned goals of the joint research project.

The **first key issue (study I)** addressed the question as to what extent the soil organic carbon (SOC) content affects the GHG release of drained organic soils under arable land and intensively used grassland in South Germany. Both land-use types have been regarded as the main producers of CO<sub>2</sub> and N<sub>2</sub>O, due to tillage and fertilization which additionally enhance microbial SOM decomposition and N turnover at drained organic soils (Kandel et al., 2013). Beside management practices, several other physical and chemical factors control the intensity of mineralization processes of which the SOC content and quality counts as one key element that may control the release of GHG emissions. It can be assumed that at a similar aeration status and temperature, mineralization processes are more intensive at peatlands containing higher amounts of SOC. However, most studies have focused on typical drained peatlands, rich in organic carbon (C<sub>org</sub>), whereas former peatlands and associated organic soils containing <12% C<sub>org</sub> were neglected by scientific research, although it is unknown whether they emit less GHG's compared to typical drained peatlands.

Following hypotheses were examined:

- (i) Greenhouse gas emissions significantly increase with increasing SOC content in drained organic soils.
- (ii) Greenhouse gas emissions from arable soils exceed GHG emissions from intensive managed grassland soils.

The first key issue provides the basis for **Publication I**.

The **second key issue (study II)** focuses on the effects of different organic fertilizers (cattle slurry vs. biogas digestate), on N<sub>2</sub>O and CH<sub>4</sub> fluxes for two types of organic soils with contrasting SOC and N contents. Furthermore, the question was targeted as to what extent biogas digestate and cattle slurry application affect N availability and grass yield.

The background of this was that Germany has become the largest biogas producing country in the world (Weiland, 2010). The strong increase in the number of biogas plants has caused a land-use change towards agro-biomass production and additionally raised land-use intensity to satisfy the huge demand for fermentative substrates (Don et al., 2011). Today, also drained peatlands are increasingly used to satisfy the huge demand for fermentative substrates (e.g., energy crops, grass silage) and the remaining nutrient-rich residues are returned to the peatlands to maintain nutrient supply and grass yield. Generally, drained organic soils are considered as hot spots for N<sub>2</sub>O emissions and organic fertilization is known to increase N<sub>2</sub>O emissions from managed grasslands. Digested products are considered to be more recalcitrant than fresh slurry and some authors (e.g. Clemens and Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009) assume that microbial degradation is slower, resulting in fewer anoxic microsites and reduced N<sub>2</sub>O emissions compared with fresh slurry. However, the effect of biogas digestate application on drained organic soils has not been studied before.

Following hypotheses were examined:

- (i) More N<sub>2</sub>O is emitted after biogas digestate than after slurry application because of higher NH<sub>4</sub><sup>+</sup>-N concentrations in the substrate and, thus, higher NH<sub>4</sub><sup>+</sup>-N amounts when using equal volumetric application rates. The more recalcitrant nature of the carbon in the biogas digestate does not matter for GHG formation in high organic carbon soils.
- (ii) N<sub>2</sub>O emissions increase with increasing soil C<sub>org</sub> and N content due to more favorable conditions for denitrification after organic fertilizer application.
- (iii) Biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to cattle slurry due to the higher N availability of the digestate.

In addition, NH<sub>3</sub> volatilization was determined in the course of one fertilization event to obtain first clues with respect to the effects of soil and fertilizer types on this gas. The second key issue provides the basis for **Publication II**.

The **third key issue (study III)** addressed the questions as to what extent drainage enhances the emissions of N<sub>2</sub>O from black alder (*Alnus glutinosa* (L.) Gaertn.) forests and as to how N turnover processes and physical factors influence the production of N<sub>2</sub>O and total denitrification rates. Unlike most other wetlands, black alder forests on peatland represent non N-limited ecosystems. To date, there are only a few studies on

N turnover and N transformation processes in black alder forests on peatlands, but first results indicate that these ecosystems show high N-transfer rates between the atmosphere, the alder trees and the soil (Augustin, 2003). High N<sub>2</sub>O emissions from alder forests on drained organic soils are attributed to alternating water tables and to the incorporation of high amounts of easily decomposable N into the ecosystem by symbiotic N<sub>2</sub>-fixation of the alder trees. The high magnitude of observed N<sub>2</sub>O emissions from black alder forests, which exceed by far the IPCC default emission factor, requires in-depth process understanding of N<sub>2</sub>O formation, not least because of the attempt to reduce the climate impact of drained fen peatland by rewetting and afforestation with black alder trees (Schäfer and Joosten, 2005; Wichtmann and Joosten, 2007).

Following hypotheses were examined:

- (i) In drained black alder forests high N<sub>2</sub>O emissions occur due to accelerated N turnover and N mineralization.
- (ii) N<sub>2</sub>O losses are replaced by N<sub>2</sub> losses during periods of temporarily high water levels. In contrast, in permanently waterlogged peat soils NO<sub>3</sub><sup>-</sup> limitation results in negligible N<sub>2</sub>O and N<sub>2</sub> losses.

The third key issue provides the basis for **Publication III**.

## 2 METHODS FOR OBSERVATION AND QUANTIFICATION OF TRACE GAS EMISSIONS

In the last two decades, a range of different measurement techniques, highly precise sensors and analyzing units as well as various mathematical models have been developed to determine and quantify trace gas exchange between landscapes and the atmosphere. Figure 8 summarizes the used measurement techniques of the present work. All applied methods are extensively explained in the three papers attached to this thesis, but various other measurement approaches are available and thus should be briefly compared and discussed. From the outset, it should be emphasized that each technique has its advantages and disadvantages. There is no system that is superior in all situations; instead each has its own “niche”. Table 2 gives an overview of different approaches for measuring trace gas exchange between landscapes and the atmosphere, presenting their advantages and disadvantages.



**Figure 8** Different Measurement systems and analyzing units for the determination of soil gas fluxes which were used in the present study. a) Closed dynamic manual chamber system for the determination of NEE (transparent chamber) or  $R_{eco}$  (opaque chamber, not shown) coupled to an b) infrared gas analyzer (IRGA, LI-820); c) Closed static manual chamber system for the determination of  $N_2O$  and  $CH_4$  fluxes. Gas samples were analyzed via a GC d) equipped with an FID and an ECD; e) Open dynamic chamber method (“Dräger-Tube Method” for the determination of  $NH_3$  volatilization,  $NH_3$  concentrations were analyzed via ammonia indicator tubes f); g) Helium-oxygen flow-through the chamber incubation system at the laboratory of the Institute of Landscape Matter Dynamics, Leibniz Centre for Agricultural Landscape Research (ZALF; Müncheberg, Germany) for the simultaneously determination of  $N_2$ ,  $N_2O$ ,  $CO_2$  and  $CH_4$  fluxes in an controlled environment, h) concentration of  $N_2$  were analyzed by a micro-GC equipped with a TCD. Concentrations of trace gases were analyzed by a GC equipped with an FID and an ECD.

To date, chambers are the most common tool for measuring trace gases (Denmead, 2008). Their operating principle is simple, mostly inexpensive, normally requires no

electricity supply in the field and allows process studies and experiments with numerous treatments and very small gas fluxes (up to 100 times smaller compared to micrometeorological applications; Denmead, 2008). However, the chamber technique also has disadvantages owing to the effects of the measurement itself on environmental variables (e.g. temperature, soil evaporation rate, relative humidity, plant damage, disturbance of diffusion gradient, inhibition of the flux through a buildup in head space concentration), to the limited coverage of the soil surface, requiring lots of replications, and perhaps, most important, to the temporal resolution of gas flux measurements (Butterbach-Bahl, 2013). The latter can be greatly improved by the use of automatic chamber systems, with the consequence of higher demands for infrastructure and higher costs. Where practicable, flow-through chambers are to be preferred because these enable controlling the increase in gas concentration by adjustment of the volume flow rate (Denmead, 2008). However, this technique requires highly precise analyzing units to detect even slight flux rates reliably and it is also more complicated in its technical implementation. In the last few years, high effort has been made to construct fast (less than 1 Hz), highly precise and sensitive operating analyzers, mostly based on laser technology (e.g. tunable diode laser (TDL) or quantum cascade laser (QCL)) for the micrometeorological detection of trace gases (Denmead, 2008; Butterbach-Bahl, 2013). In combination with chamber techniques (fast-Box method), they allow a significant reduction in the closure time of chambers, reducing unwanted impacts on environmental parameters to a minimum, and they further enable the investigation of spatial variability by quickly changing chamber positions (Butterbach-Bahl, 2013). Additionally, an instant verification of the measurement quality is given through the on-line concentration detection. However, the big disadvantage of these techniques is the enormous cost.

Micrometeorological applications are mostly related to eddy covariance, eddy accumulation and flux-gradient methods. They are very suitable for the continuous detection of integrated trace gas fluxes from large landscapes with homogeneous surfaces, without any restrictions on gas exchange (Denmead, 2008). Usually, gas concentration and wind speed in the air are measured with fast response instruments (>10 Hz) and average values are calculated over sampling periods of 15 min to 1 h (Denmead, 2008). Thus, temporal and spatial variability are considered but the spatial variability is unquantifiable, since typically no replications exist for micrometeorological approaches. From the above-mentioned three methods, the eddy covariance approach is the micrometeorologist's preferred approach because it gives the vertical flux at the

point of measurement. The disadvantages of micrometeorological approaches are diverse and include dealing with the effects of simultaneous fluxes of heat and water vapour, problems occurring from pre-conditioning air samples before measuring their gas concentration, problems with lags between measuring vertical wind speeds and gas concentrations, correct mounting heights in relation to sensor path lengths, flow distortion from neighboring instruments and support structures, and others. However, the main issue results from the fact that the measuring principle relies on theories of turbulent transport in the atmosphere, so that this method can only be applied when weather conditions are favorable. This applies equally to the backward Lagrangian stochastic dispersion technique (bLs). Moreover, micrometeorological techniques are very cost-intensive and often require high demands for the infrastructure.

Mass balance techniques are very suitable for small and well-defined areas, irrespective of homogeneous or heterogeneous source distributions and thus fill the gap between chamber and micrometeorological approaches (Denmead, 2008). Mass balance methods use a vertical gas concentration profile in combination with the vertical windspeed gradient (Hensen, 2011). They have a simple theoretical basis and require no special form of the wind profile or corrections for atmospheric stability like micrometeorological approaches (Denmead, 2008). Moreover, there is no need for very fast sensors as is the case for eddy covariance measurements, which lowers the cost. However, mass balance methods require a small background concentration and therefore are only suitable for determining emissions of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  in fertilizer applications studies or  $\text{CH}_4$  emissions from small-scale grazing systems (Denmead, 2008; Hensen, 2011). However, some uncertainty remains about the magnitude of the diffusive flux which necessitates mathematical corrections or the implementation of fast response instrumentation (Denmead, 2008).

The backward Lagrangian stochastic dispersion techniques (bLs) represents a suitable tool for measuring gas emissions from small, well-defined source areas of any shape (Denmead, 2008). The bLs method neither alters the gas exchange nor ambient surface conditions (e.g. surface temperature, wind speed; Gao et al., 2009). As the mass balance method, the bLs is particularly appropriate for determining gas fluxes with high temporal resolution from treated fields and intensive animal production systems with small background concentrations. Its main advantage is that gas fluxes can be determined from just one concentration measurement, providing that the background concentration is known. This keeps the installation costs lower compared to mass

balance methods (Denmead, 2008). However, gas measurements based on laser or FTIR systems will often cause the corresponding costs. The main disadvantage of the bLs technique derives from the complex parameterization of turbulent transport, so that these methods can only be applied when weather conditions are favorable as mentioned above.

**Table 2** Advantages and disadvantages of different approaches for measuring trace gas fluxes between landscapes and the atmosphere. The extent to which a system is suitable or not can range between ++ to --, in which ++ stands for very suitable or low and -- stands for unsuitable or high (extended from Drösler, 2008b).

	Chamber techniques <sup>1</sup>		Micrometeorological techniques	Mass balance methods <sup>3</sup>	Backward Lagrangian stochastic dispersion technique
	manual systems	automatic systems	Eddy covariance <sup>2</sup>		
Undisturbed gas exchange	+/--	+/--	++	++	++
Detecting the spatial variability in gas exchange	+/-	-	-	-	-
Detecting the temporal variability in gas exchange	-	++	++	++	++
homogeneous, large-scale	--	--	++	+/-	+/-
Suitable for Heterogeneous, small scale process studies and experiments	+	+	-	++	++
Sensitivity of gas fluxes	++/-	++/-	+/-	-	-
Detectable gases	All trace gases*	All trace gases*	CO <sub>2</sub> , NH <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>	CH <sub>4</sub> , N <sub>2</sub> O, NH <sub>3</sub>	CH <sub>4</sub> , N <sub>2</sub> O, NH <sub>3</sub>
Workload	--	++	++	++	++
Straightforward application	++	+	-	+	-
Demands on infrastructure including power supply	++/-	-	--	-	-
Costs	++/-**	-/--**	-/--**	+/--**	+/-**

<sup>1</sup> including open and closed systems; closed systems contain static and dynamic gas detection.

<sup>2</sup> including eddy accumulation, relaxed eddy accumulation and flux-gradient methods.

<sup>3</sup> including open and closed systems with adaption of open systems to circular source areas.

\* e.g. CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, NH<sub>3</sub>, and several more; dissection in subcomponents and production processes possible.

\*\* In dependence of used analyzing unit and detection precision.

## 3 GENERAL DISCUSSION AND OUTLOOK

### 3.1 IMPACT OF SOC AND MANAGEMENT

In the present thesis, it is hypothesized that drainage of peatlands, rich in SOC, leads to significantly higher GHG emissions compared to organic soils containing lower SOC contents. With exception of N<sub>2</sub>O fluxes, this assumption could not be confirmed by the present study. Instead, the **first study** gave evidence that the GHG balance of a drained and intensively cropped organic soil is mainly affected by management (e.g. fertilization, tillage, crop target) rather than SOC content or land-use type.

Despite significantly higher annual sums of GPP, calculated sums of NEE were significantly higher at the grassland treatments compared to treatments of the arable land, which was caused by distinctly increased R<sub>ECO</sub> at these plots (Table 3, **Publication I.**). With the exception of the maize plot at the C<sub>medium</sub> site in the year 2011, all treatments showed positive NEE balances in both years investigated, as expected for drained organic soils and as commonly reported in the literature. (e.g. Maljanen et al. 2001; Grønlund et al., 2006 and 2008; Maljanen et al., 2010; Elsgaard et al., 2012; Beetz et al., 2013; Drösler et al., 2013). NEE rates observed in **study I** ranged between  $-6 \pm 546$  and  $1707 \pm 619$  g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup> at the arable land and between  $1354 \pm 740$  and  $1823 \pm 851$  g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup> at the grassland. Generally, the annual CO<sub>2</sub> emissions observed were in the upper range or partly higher compared to literature values (e.g. Maljanen et al., 2001, 2007, 2010; Grønlund et al., 2008; Höper et al., 2008; Leifeld et al., 2011; Elsgaard et al., 2012; Beetz et al., 2013; Drösler et al., 2013; Leifeld et al., 2014; Renou-Wilson et al., 2014) and also partly exceed the IPCC default emission factors up to threefold. However, in respect to the SOC content, the comparison of the determined CO<sub>2</sub> or CH<sub>4</sub> fluxes is difficult because no further studies exist concerning intensively used organic soils with SOC contents comparable to the C<sub>medium</sub> sites. Nevertheless, our findings were corroborated in the framework of the joint research project “organic soils” (e.g. Tiemeyer et al., 2014; M. Drösler, personal communication 2014) and are in line with investigations from Leiber-Sauheitl et al. (2014), who reported that CO<sub>2</sub> fluxes from extensive grasslands on organic soils were not related to different SOM contents. It can be assumed that not only the SOC content itself acts as a key factor controlling the CO<sub>2</sub> release, but the quality of SOC and particularly the proportion of SOC which is exposed to aerobic mineralization. However, in accordance to investigations made by Leiber-

Sauheitl et al. (2014) and Tiemeyer et al. (2014), no relation was found between the effective C stock and the C flux components (Publication I, Figure 10), demonstrating the complexity of SOM decomposition. Nevertheless, the separation of the dataset according to land-use types revealed comparable effective C stocks at the grassland sites, probably explaining the equal CO<sub>2</sub> loss rates despite different SOC contents. Recent studies have shown that in particular the SOM quality and its labile and more recalcitrant fractions act as key variables affecting the decomposability of the SOM and thus control CO<sub>2</sub> fluxes from peatlands (Byrne and Farrell, 2005; Heller and Zeitz, 2012; Leifeld et al., 2012). In the present study, the SOM quality was not examined, but all sites showed equal narrow C/N ratios, indicating high organic matter quality at all sites investigated, perhaps explaining the comparable CO<sub>2</sub> emission patterns.

Despite different SOC and groundwater levels, no differences in CH<sub>4</sub> fluxes were found between the two soil types investigated (**Publication I.** and **II.**). In contrast to literature (e.g. Maljanen et al., 2010) CH<sub>4</sub> emissions of the arable land significantly exceeded those of the grassland (**Publication I.**), whereas neither fertilization with cattle slurry nor with biogas digestate led to significantly different CH<sub>4</sub> emission patterns, despite of distinctly different fertilizer composition. Generally, the position of the groundwater table is considered as the key factor, regulating methanogenic and methanotrophic processes in peatlands (Whalen, 2005). Thus, it can be assumed that the intensive drainage effectively inhibited microbial methanogenesis at both soil types investigated. However, annual CH<sub>4</sub> exchange rates were low in the present study, ranging between  $-0.10$  and  $0.51$  g C m<sup>-2</sup> yr<sup>-1</sup> at the arable plots and between  $-0.11$  and  $-0.02$  g C m<sup>-2</sup> yr<sup>-1</sup> at the grassland plots. However, in accordance with several other authors (e.g. Maljanen et al., 2010; Petersen et al., 2012; Schäfer et al., 2012; Drösler et al., 2013; Renou-Wilson et al., 2014), **study I** and **II** demonstrate that CH<sub>4</sub> exchange was only of minor importance, considering total GHG emissions.

In line with our hypotheses examined in **study I** and **study II** significantly higher N<sub>2</sub>O emissions were found at the C<sub>high</sub> sites compared to the C<sub>medium</sub> sites, regardless of land-use type and management practices. Likewise, significantly higher NO<sub>3</sub><sup>-</sup> contents and higher GW levels were observed at these sites. From the calculated net C losses in the **first study** it can be concluded, that high amounts of N must be released in the course of SOM degradation. As revealed by the **second study**, an equal amount of available N resulted in a higher proportion of N<sub>2</sub>O losses at the sapric histosol compared to the mollic gleysol (**Publication II.**, Figure 5b), which was attributed to the probably more

favorable soil conditions for denitrification. Nevertheless, the source of N<sub>2</sub>O production in soils is often uncertain since aerobic and anaerobic microsites occur within close proximity and thus different biotic and abiotic N<sub>2</sub>O production processes can run simultaneously (Davidson et al., 1986; Butterbach-Bahl et al., 2013).

In the framework of the **second study**, fertilization was found to significantly increase N<sub>2</sub>O emissions from the grasslands investigated. However, the **second study** demonstrated that NH<sub>3</sub> volatilization is quantitatively the most important N loss from surface application (Flessa and Beese, 2000), particularly when slurries contain high concentrations of NH<sub>4</sub><sup>+</sup> and had high pH values. In line with our expectations, the **second study** revealed that the application of biogas digestate significantly enhances annual N<sub>2</sub>O emissions as well as biomass production and NUE compared to the application of cattle slurry. Calculated harvest-related N<sub>2</sub>O emissions averaged 0.20 kg N<sub>2</sub>O-N t<sup>-1</sup> DM<sup>-1</sup> at the biogas treatments compared to 0.17 kg N<sub>2</sub>O-N t<sup>-1</sup> DM<sup>-1</sup> at the cattle slurry treatments, demonstrating that the higher grass yield could not compensate for the significantly higher N<sub>2</sub>O emissions at these treatments. However, contrary to our hypothesis, the significantly higher N<sub>2</sub>O emissions as well as biomass production from the digestate treatments cannot solely be explained by the higher content of available N in the biogas digestate, since the amount of applied NH<sub>4</sub><sup>+</sup>-N in the substrate was not markedly different. Nevertheless, the much higher N-uptake at the biogas treatments (**Publication II.**, Fig. 5a) indicated that the application of this fertilizer resulted in a markedly higher N availability probably promoting N<sub>2</sub>O and biomass production. Beside a assumed slightly enhanced SOM mineralization, caused by differences in fertilizer composition (e.g. C/N ratio, pH), it is conceivable, that the significantly increased biomass production at the biogas treatments itself is related to the increased N<sub>2</sub>O emissions, due to the stimulating effect of plant roots (i.e. root exudates) on denitrification activity (Klemedtsson et al., 1987; Bakken, 1988). In addition, **study I** revealed significantly higher R<sub>ECO</sub> rates at the grassland site compared to the arable sites, corroborating the assumption that, firstly fertilization probably increase SOM mineralization (Gutser et al. 2005; Jones et al., 2007), and secondly, a higher GPP may increase the transport of photosynthates to the plant rhizosphere, favoring bacterial metabolism through increased root exudates (Mounier et al., 2004; Henry et al., 2008; Sey et al., 2010). However, in line with Velthof et al. (2003) the **second study** confirms our assumption that the more recalcitrant nature of the carbon in the biogas digestate is not predominantly responsible for GHG formation in high organic carbon soils, since

sufficient metabolizable C is generally widely available in those soils. Nevertheless, N<sub>2</sub>O fluxes from the unfertilized arable treatments significantly exceeded those of the grassland sites, which was also reported by Maljanen et al. (2007 and 2010) and Petersen et al. (2012) and was additionally confirmed by Leppelt et al. (2014) for European organic soils. (**Publication I.**, Table 3). Determined N<sub>min</sub> contents in the soil at the arable sites were significantly lower compared to the grassland sites, but Silvan et al. (2005) assumed that the temporary absent of plants resulted in a higher N availability for microbial denitrification and thus in higher N<sub>2</sub>O fluxes at croplands. Moreover, GW levels were found to be significantly higher at the arable sites compared to the grassland sites, further favoring denitrificative N losses.

Estimated net climate effects (GWPs) ranged between 1837 and 4562 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup> at the arable land and between 5884 and 7095 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup> at the grassland (**Publication I.**, Table 6), revealing a very high release of greenhouse gases from all treatments. According to the IPCC (2014a), the emission factor for total GWP from temperate drained cropland averaged 3508 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup> with a 95% confidence interval of 2769 to 4292 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup>, whereas the GWP of deep drained nutrient-rich grassland averaged 2662 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup> with a 95% confidence interval of 2070 to 3266 g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup>. Thus, for the grassland investigated, estimated GWPs are markedly higher compared to the default emission factor of the Tier 1 approach and, in addition, are located far outside of the 95% confidence interval. In contrast, estimated GWPs of the arable land cover the entire span of the 95% confidence interval, with slightly higher values at the upper confidence limit and distinctly lower values at the lower confidence limit. However, Kasimir-Klemendsson et al. (1997) reported distinctly higher net CO<sub>2</sub> exchange rates ranging from 800 to 11500 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> for farmed organic soils, demonstrating the high bandwidth of measured CO<sub>2</sub>-balances. Nevertheless, the question arises, to what extent model as well as measurement uncertainties triggered the magnitude of estimated GWPs. As mentioned above, N<sub>2</sub>O and CH<sub>4</sub> contributed only negligible to total GWP but we cannot rule out that we may have missed at least high N<sub>2</sub>O emission events, due to our regular measurement intervals. It is well known that peak emissions significantly alter total GHG balances, as was also confirmed in the present study. However, the main uncertainty in **study I** derived from R<sub>Eco</sub> as well as GPP model accuracy constrained by partly insufficient parameterisation. Particularly, management activities like ploughing at the arable sites as well as harvesting and fertilization at the grassland sites were partly not sufficiently accurate covered by

additional measurements. In addition, despite high model accuracy, the calculated PBIAS revealed a slightly model overestimation bias for  $R_{ECO}$  and NEE for both years ( $R_{ECO}$  only in 2010). Thus, modeled  $R_{ECO}$  and calculated NEE rates should be considered as a conservative estimation. Nevertheless, the comparison of GWPs relative to each other, regarding the effect of SOC contents or within land-use types, is unaffected of potential bias in the absolute magnitude of GWP.

With the exception of Denmark, organic soil containing <12%  $C_{org}$  were so far neglected in national GHG emission inventories. Since GHG emissions are not expected to be zero from organic soils containing 6–12%  $C_{org}$ , Denmark introduced a fixed emission factor, half as much as for drained peatlands (Nielsen et al., 2012). However, despite being subject to uncertainties, **study I** clearly reveal that the GHG emission potential of soils intermediate between mineral and organic soils can be as high or partly higher as for drained peatlands under intensive agricultural use. Therefore, we suggest establishing a further category in the wetland supplement (IPCC, 2014a) which provides emission factors for different land-use types on former drained peatlands or associated organic soils, containing <12%  $C_{org}$ , in order to avoid a significant underestimation of GHG emissions in the LULUCF/AFOLU sector.

### 3.2 GHG POLICY

To mitigate GHG emissions, the European Commission set out a long-term strategy to increase the proportion of renewable energy (e.g. biomass, wind power, photovoltaic) from 9% in 2010 to 21% of total energy consumption in 2020 (EU, 2009; Schleupner and Schneider, 2010; Don et al., 2011). As one measure, heat and power from biogas plants can substitute for fossil fuels and thus is considered to mitigate GHG emissions (Weiland, 2010; Don et al., 2011). However, bioenergy is not necessarily C neutral, since GHG release during crop production may reduce or completely counterbalance  $CO_2$  savings of the substituted fossil fuels (Don et al., 2011). For illustration, assuming an average  $CH_4$  yield of  $310 \text{ m}^3 \text{ CH}_4 \text{ t VDS}^{-1}$  (VDS = Volatile dry solids, VDS is equivalent to 90% DM content; Gerin, 2008; Steffen, 1998 cited in Smyth et al., 2009) and an average  $CH_4$  content of 55% in the biogas (Smyth et al., 2009), the gross energy production of the grasslands investigated (**study I** and **II**) is calculated as  $70\text{--}77 \text{ GJ ha}^{-1}$ , which correspond to 19–21 MWh primary energy per hectare for the year 2011. This estimated value is in good agreement with Rösch et al., (2009) who reported that approximately 19 MWh primary energy per hectare could be substituted through wet

fermentation of grass silage. Thus considering an emission factor of  $0.315 \text{ kg CO}_2 \text{ kWh}^{-1}$  for a fossil fuel mix of natural gas, hard coal and brown coal (Icha, 2013), approximately  $6.1\text{--}6.7 \text{ t CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$  of fossil fuels can be substituted through the production of biogas from the grasslands investigated. In contrast, approximately  $70 \text{ t CO}_2 \text{ eq. ha}^{-1} \text{ yr}^{-1}$  are released during grass silage production at these sites, clearly demonstrating the partially contradictory development in the implementation of GHG mitigation strategies.

Beside of grassland used for biogas production, **study I** revealed that all land-use and management forms investigated, show a very high release of GHGs, demonstrating the unsustainable agricultural use of drained organic soils and the current need for the implementation of GHG mitigation strategies and peatland restoration measures. Nevertheless, the enhanced bioenergy demand increases the value of land and thus, the marginal costs for peatland restoration measures (Schleupner and Schneider, 2010). As an alternative to abandoned rewetted peatlands, new management strategies, collectively referred to as paludiculture, are currently being tested to verify whether they can satisfy climate, ecologically as well as economic benefits.

In order to achieve a reduction in peat mineralization and to mitigate greenhouse gases, the enhancement of the water table height in combination with reduced land-use intensity are generally considered as the key components in peatland restoration measures (Höper et al., 2008). In line with this, the **third study** demonstrated the effect of anaerobicity on decomposition and turnover processes. At the undrained site NNM rates observed were significantly lower ( $84 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) compared to the drained sites ( $519\text{--}653 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ). However, despite of distinctly different C and N contents, significantly different NNM rates between the two drained sites were not found, corroborating the findings from **study I** and **II**.

Generally,  $\text{NO}_3^-$  availability is considered as the main driver of  $\text{N}_2\text{O}$  emissions from drained histosols (Klemetsson et al., 2005), but despite of significant differences in NNM rates and  $\text{NO}_3^-$  contents in the soil of the three sites, no differences were found regarding field  $\text{N}_2\text{O}$  fluxes. Generally, annual  $\text{N}_2\text{O}$  emissions observed in the **third study** were very low and ranged from  $0.51 \pm 0.07 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at the undrained site to  $0.97 \pm 0.13 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at the drained sites. Different studies reported considerably higher values for  $\text{N}_2\text{O}$  emissions from drained black alder stands, varying from 5 to  $75 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Mogge et al., 1998; Augustin, 1998b; Brumme et al., 1999; Merbach et al., 2001; Hefting et al., 2003; von Arnold et al., 2005). This contrasts our hypothesis that in drained black alder forests high  $\text{N}_2\text{O}$  emissions occur due to accelerated N turnover and

transformation processes. However, in contrast to the field observations significant differences in the  $\text{N}_2\text{O}$  fluxes between the two investigated sites were found in the incubation experiment at both soil moisture contents. Thus, the question arises which key factors are responsible for  $\text{N}_2\text{O}$  production in the alder forest investigated. As expected, at the undrained site anoxic conditions prevent net nitrification for most of the time in the year, as was confirmed by the finding that ammonification entirely controls NNM and observed  $\text{N}_{\text{min}}$  contents were solely dominated by  $\text{NH}_4^+$  at this site. In line with this observation,  $\text{N}_2\text{O}$  and  $\text{N}_2$  flux pattern observed in the incubation experiment demonstrated that denitrification was limited by  $\text{NO}_3^-$  availability, confirming our hypothesis that  $\text{NO}_3^-$  limitation in permanently waterlogged peat soils results in negligible  $\text{N}_2\text{O}$  and  $\text{N}_2$  losses.

In contrast, the very high NNM rates at the drained sites revealed that  $\text{NH}_4^+$  produced becomes immediately oxidized to  $\text{NO}_3^-$ . Nevertheless, no relationship was found between field  $\text{N}_2\text{O}$  fluxes and  $\text{NO}_3^-$  availability, and less than 0.2% of nitrified N was emitted as  $\text{N}_2\text{O}$ -N at these sites. However, the **third study** gave evidence that field  $\text{N}_2\text{O}$  fluxes obviously are triggered by temperature and the GW level. This relationship becomes even more apparent regarding the results from the incubation experiment. At both soil moisture contents, increasing temperature resulted in significantly enhanced  $\text{N}_2\text{O}$  fluxes. Observed exchange rates at 100% WFPS increase from  $37.3 \pm 4.5 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  at  $0^\circ\text{C}$  to  $115.2 \pm 22.6 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  at  $15^\circ\text{C}$ , followed by a decline to  $80.0 \pm 29.4 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  at  $25^\circ\text{C}$ , whereas at 70% WFPS,  $\text{N}_2\text{O}$  fluxes increase from  $19.1 \pm 3.1 \mu\text{g N m}^{-2} \text{ h}^{-1}$  at  $0^\circ\text{C}$  to  $132.4 \pm 31.7 \mu\text{g N m}^{-2} \text{ h}^{-1}$  at  $25^\circ\text{C}$ . Furthermore, considering soil core samples from the drained site separately, it was found that  $\text{N}_2\text{O}$  fluxes at the first three temperature levels at 70% WFPS were lower compared to samples at 100% WFPS, but differences were not significant. However, overall  $\text{N}_2\text{O}$  fluxes were comparable between 100% and 70/83% WFPS, but total denitrification significantly increased, which is in line with studies by Scholefield et al. (1997). The low proportion of  $\text{N}_2\text{O}$  emissions of total N release from denitrification indicated that in the present alder stand losses of  $\text{N}_2\text{O}$  are only of minor importance compared to  $\text{N}_2$  losses at water saturated conditions. Moreover, the observed decline of  $\text{N}_2\text{O}$  fluxes at water-saturated conditions and  $25^\circ\text{C}$  with simultaneously exponentially increasing or at least constant  $\text{N}_2$  fluxes supports our hypothesis that  $\text{N}_2\text{O}$  release is displaced by  $\text{N}_2$  losses during periods of temporarily high water levels. However, the field observations never reached the point in which the decreasing  $\text{N}_2\text{O}:\text{N}_2$  ratio overcompensated the increasing denitrification

rate. The up to four times higher N<sub>2</sub>O emissions measured in the incubation experiment at 70% WFPS compared to the field fluxes revealed the potential of high N<sub>2</sub>O emissions under changing soil physical conditions. This assumption was confirmed by continued N<sub>2</sub>O gas flux measurements for the time period 2012–2013 at these sites (unpublished data), where annual N<sub>2</sub>O emission of up to  $2.65 \pm 0.23 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  and  $2.62 \pm 0.85 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  were observed at the undrained and drained sites, respectively. The equal N<sub>2</sub>O emissions, despite of distinctly different C and N contents, observed at the drained alder sites contrasts the findings of **study I** and **II**. Enhanced N<sub>2</sub>O emissions at the C<sub>org</sub> high sites in study **I** and **II** are related to more favorable conditions for denitrification. However, high net nitrification rates in combination with low N<sub>2</sub>O and N<sub>2</sub> fluxes indicate that, for most of the year, aerobic or only slightly anaerobic soil conditions are predominant, preventing denitrification. Determined bulk densities and higher porosity additionally supports the assumption of a better aeration and thus a faster O<sub>2</sub> diffusion into deeper soil layers of the alder forest compared to the intensively used grassland and cropland.

Besides N<sub>2</sub>O, particularly CO<sub>2</sub> emissions dominate the GHG balances from drained organic soils as shown in **study I** and additionally confirmed by several other studies (e.g. Grønlund et al., 2006; Maljanen et al., 2010; Leiber-Sauheitl et al., 2014). In contrast, in pristine or restored peatlands with high groundwater tables, mainly CH<sub>4</sub> emissions are responsible for the climate impact. Unpublished data of determined CH<sub>4</sub> fluxes from the alder forest investigated, revealed annual CH<sub>4</sub> exchange rates of  $8.93 \pm 1.58 \text{ (U)}$ ,  $-0.27 \pm 0.01 \text{ (D-1)}$  and  $-0.20 \pm 0.01 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1} \text{ (D-2)}$ , for the year 2011. So far there is no report in the literature of an entirely measured greenhouse gas budget from an alder forest on a fen peatland. Particularly the estimation of net CO<sub>2</sub> fluxes displays a high uncertainty due to a lack of data. All published gas fluxes from previous studies based on the dark chamber measurement technique, which does not allow a conclusion about the net CO<sub>2</sub> exchange of a forest ecosystem. Some studies estimate the GWP using a combination of compiled biomass-data, measured flux data and assumptions based on literature values (Augustin, 2003; von Arnold et al., 2005; Mander et al., 2008). The reported net GHG fluxes range between  $-736.3$  and  $1113 \text{ g CO}_2\text{-C}_{\text{equ.}} \text{ m}^{-2} \text{ yr}^{-1}$  for drained alder stands and between  $-469.6$  and  $487 \text{ g CO}_2\text{-C}_{\text{equ.}} \text{ m}^{-2} \text{ yr}^{-1}$  for undrained alder forests (Augustin, 2003; von Arnold et al., 2005; Mander et al., 2008). In order to assess the climate impact of the alder forest investigated, a rough estimation of net GHG fluxes was carried out and described in detail in Appendix 7.4. Calculated

GWP<sub>100</sub> values indicated that both sites slightly contributed to global warming with GWP<sub>100</sub> values of about 72–76 g CO<sub>2</sub>-C<sub>equ.</sub> m<sup>-2</sup> yr<sup>-1</sup> for the undrained site and about 98–127 g CO<sub>2</sub>-C<sub>equ.</sub> m<sup>-2</sup> yr<sup>-1</sup> for the drained sites. The estimated GWP<sub>100</sub> values are in the order of magnitude reported for semi-natural or restored fen peatlands in Germany (Drösler et al., 2012). These findings support the assumption that black alder forests can serve as one mitigation strategy to reduce GHG's from drained fen peatlands, providing groundwater level enhancement and perhaps a partial forest-use restriction. However, further investigations particularly for NEE are required to improve the accuracy of greenhouse gas budgets from alder forests on fen peatlands.

## 4 CONCLUSION

The present PhD thesis shed new lights on GHG emissions from drained organic soils not fulfilling the definition of organic soils according to the IPCC guidelines for the national climate reporting in the LULUCF/AFOLU sector. Two years of GHG measurements clearly revealed that drained mollic Gleysols can also be considered as hotspots for GHG emissions likewise SOC-rich sapric Histosols, provided that they are intensively managed as arable land or grassland. The results gave evidence that the GHG balance, of a drained and intensively cropped organic soil is mainly affected by management rather than SOC content or land-use type. The study indicated that N<sub>2</sub>O emissions increase with increasing C<sub>org</sub> content, whereas CH<sub>4</sub> exchanges were of only minor importance at the intensively drained and cropped organic soils. However, CO<sub>2</sub> emissions dominated total GHG balances of all treatments to nearly 100%. Estimated GWPs partly more than doubled the emission factor of the Tier 1 approach of the IPCC regardless of the SOC content in the topsoil. Thus, to avoid a significant underestimation of GHG emissions in the LULUCF/AFOLU sector, there is a corresponding need to extend the IPCC guidelines for drained inland organic soils in respect to former peatlands and associated organic soils containing <12% C<sub>org</sub>. However, further investigations are needed to define the lower boundary for C<sub>org</sub> limits.

Furthermore, the effects of biogas digestate application on short-term N<sub>2</sub>O and CH<sub>4</sub> emissions as well as on biomass production and NUE from grasslands on drained organic soils were discussed for the first time. It was found that N<sub>2</sub>O fluxes were significantly higher after digestate than after cattle slurry fertilization, which probably could be attributed to a higher N availability in the soil caused by increased SOM mineralization or other sources of labile carbon triggered by digestate application. Moreover, the study demonstrated that the higher grass yield could not compensate for the significantly higher N<sub>2</sub>O emissions at the biogas digestate treatments. Generally, the apparent NUE<sub>min</sub> indicated that a frequent but low dosage application of fertilizer and quick N uptake by plants avoid conditions favorable for high N<sub>2</sub>O emissions. However, the observed linear increase in cumulative N<sub>2</sub>O emissions with increasing NH<sub>4</sub><sup>+</sup> fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C<sub>org</sub> rich grasslands.

In contrast to the intensively cropped drained organic soils, different SOC and N contents did not affect N<sub>2</sub>O emissions in a drained black alder forest. Regardless of waterlogging or drained conditions, it could be shown that despite considerably increased NNM and different N turnover processes N<sub>2</sub>O production remained low at least in the year 2011. In general, a permanently high groundwater level was found to prevent net nitrification resulting in negligible gaseous N losses. In contrast, drainage shifted N transformation processes from net ammonification to net nitrification. The conducted helium-incubation experiment showed that temporarily water-saturated conditions mainly increased N<sub>2</sub> fluxes. Nevertheless, the laboratory study gave evidence that changing soil physical conditions can result in enhanced N<sub>2</sub>O emissions at the drained alder sites. Continuous N<sub>2</sub>O measurements in two subsequent years confirmed the findings from the incubation experiment, but it has to be pointed out that N<sub>2</sub>O emissions also markedly increased at the waterlogged site. A rough estimated GHG balance revealed that black alder forests, which represent the natural vegetation of fen peatlands, can serve as one mitigation strategy to reduce GHGs from drained fen peatlands, providing groundwater level enhancement and perhaps a partial forest-use restriction.

In conclusion, the observed very high release of GHGs demonstrated the unsustainable agricultural use of drained organic soils and the current need for rapid implementation of mitigation strategies and restoration measures.

## 5 REFERENCES

- Ad-Hoc AG Boden: Bodenkundliche Kartieranleitung, 5. Aufl., Schweizerbart'sche Verlagsbuchhandlung, Hannover, 438 pp., 2005.
- Aigner, A., Biertümpel, A., Conrad, M., Deiglmayr, K., Diepolder, M., Eder, B., Eder, J., Formowitz, B., Fritz, M., Gehring, K., Hartmann, A., Hartmann, S., Heiermann, M., Herrmann, C., Hofmann, D., Idler, C., Kawasch, M., Kornatz, P., Lichti, F., Nehring, A., Salzeder, G., Schaffner, S., Sticksei, E., Stockmann, F., Vetter, A., Vollrath, B., von Buttlar, C., Wendland, M., Willms, M., Wolf, G., Zeise, K.: Energiepflanzen für Biogasanlagen, Fachagentur Nachwachsende Rohstoffe e.V. (FNR), Bestell-Nr. 558, 1. Auflage, 116 pp., 2012.
- Alm, J., Talanov, A., Saarnio, S., Silvola, J., Ikkonen, E., Aaltonen, H., Nykanen, H., and Martikainen, P.J.: Reconstruction of the carbon balance for microsites in a boreal oligotrophic pine fen, Finland, *Oecologia*, 110, 423–431, 1997.
- Ambus, P., and Zechmeister-Boltenstern, S.: Denitrification and N-Cycling in Forest Ecosystems, In: *Biology of the Nitrogen Cycle*, Bothe, H., Ferguson, S.J., and Newton, W.E., (eds.), Elsevier B.V., 2007.
- Arnth, A., Harrison, S.P., Zaehle, S., Tsigaridis, K., Menon, S., Bartlein, P.J., Feichter, J., Korhola, A., Kulmala, M., O'Donnell, D., Schurgers, G., Sorvari, S., and Vesala, T.: Terrestrial biogeochemical feedbacks in the climate system, *Nature Geoscience*, 3, 525–532, 2010.
- Arnold von, K., Nilsson, M., Hånell, B., Weslien, P., and Klemetsson, L.: Fluxes of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O from drained organic soils in deciduous forests, *Soil Biology and Biochemistry*, 37, 1059–1071, 2005.
- Artz, R.R.E.: Microbial community structure and carbon substrate use in northern peatlands, In: *Carbon Cycling in Northern Peatlands*, Baird, A.,J., Belyea, L.R., Comas, X., Reeve, A.S., and Slater, L.D. (eds.), Geophysical Monograph, 184, American Geophysical Union, Washington, DC, 2009.
- Augustin, J., Merbach, W., Steffens, L., and Snelinski, B.: Nitrous Oxide Fluxes of Disturbed Minerotrophic Peatlands, *Agribiol. Res.*, 51 (1), 47–57, 1998a.
- Augustin, J., Merbach, W., and Rogasik, J.: Factors influencing nitrous oxide and methane emissions from minerotrophic fens in northeast Germany, *Biol. Fertil. Soils*, 28, 1–4, 1998b.
- Augustin, J.: Erlenstandorte als Quelle und Senke klimarelevanter Spurengase. (Alder forests as a source and sink of Greenhouse gases), In: *Die Schwarz-Erle (Alnus glutinosa [L.] GAERTN.) im nordostdeutschen Tiefland*, Eberswalder Forstliche Schriftenreihe, 17, 46–59, 2003.
- Baird, A.J., Comas, X., Slater, L.D., Belyea, L.R., and Reeve, A.S.: Understanding Carbon Cycling in Northern Peatlands: Recent Developments and Future Prospects, In: *Carbon Cycling in Northern Peatlands*, Baird, A.,J., Belyea, L.R., Comas, X., Reeve, A.S., and Slater, L.D. (eds.), Geophysical Monograph, 184, American Geophysical Union, Washington, DC, 2009.
- Bakken, L.R.: Denitrification under different cultivated plants: effects of soil moisture tension, nitrate concentration, and photosynthetic activity, *Biol. Fertil. Soils*, 6, 271–278, 1988.
- Baldock, J.A.: Composition and Cycling of Organic Carbon in Soil, in *Nutrient Cycling in Terrestrial Ecosystems*, Eds. Marschner, R., Rengel, Z., *Soil Biology*, Volume 10, 397 pp., 2007.

- Batjes, N.H.: Total carbon and nitrogen in the soils of the world, *European Journal of Soil Sciences*, 47, 151–163, 1996.
- Beetz, S., Liebersbach, H., Glatzel, S., Jurasinski, G., Buczko, U., and Höper, H.: Effects of land-use intensity on the full greenhouse gas balance in an Atlantic peat bog, *Biogeosciences*, 10, 1067–1082, doi:10.5194/bg-10-1067-2013, 2013.
- Berndes, G. Hoogwilk, M., and van den Broek, R.: The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass Bioenergy* 25, 1–28, 2003.
- Blackmer, A. M. and Bremner, J. M.: Inhibitory effect of nitrate on reduction of N<sub>2</sub>O to N<sub>2</sub> by soil microorganisms, *Soil Biol. Biochem.*, 10, 187–191, 1978.
- Blodau, C.: Carbon cycling in peatlands – A review of processes and controls, *Environ. Rev.*, 10, 111–134, 2002.
- Bobbink, R., and Roelofs, J.G.M.: Nitrogen critical loads for natural and seminatural ecosystems: the empirical approach. *Water Air Soil Pollut.* 85, 2413–2418, 1995.
- Bobbink, R., Hornung, M., and Roelofs, J.G.: The effects of airborne nitrogen pollutants on species diversity in natural and semi-natural European vegetation, *J. Ecol.*, 86, 717–738, 1998.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B.A., Erisman, J.W., Fenn, M., Gilliam, F.S., Nordin, A., Pardo, L., and de Vries, W.: Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol. Appl.*, 20, 30–59, 2010.
- Bowman, J.: The greenhouse effect, *Land Use Policy*, 7 (2), 101–108, 1990.
- Braker, G., and Conrad, R.: Diversity, structure, and size of N<sub>2</sub>O-producing microbial communities in soils - what matters for their functioning?, *Adv. Appl. Microbiol.*, 75, 33–70, 2011.
- Bragazza, L., Buttler, A., Siegenthaler, A., and Mitchell, E.A.D.: Plant litter decomposition and nutrient release in peatlands, In: *Carbon Cycling in Northern Peatlands*, Baird, A.,J., Belyea, L.R., Comas, X., Reeve, A.S., and Slater, L.D. (eds.), *Geophysical Monograph*, 184, American Geophysical Union, Washington, DC, 2009.
- Brumme, R., Borken, W., and Finke, S.: Hierarchical control on nitrous oxide emission in forest ecosystems, *Global Biogeochem. Cy.*, 13 (4), 1137–1148, 1999.
- Bubier, J., Moore, T., and Bledzki, L.: Effects of nutrient addition on vegetation and carbon cycling in an ombrotrophic bog, *Glob. Change Biol.*, 13 (6), 1168–1186, 2007.
- Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R., Zechmeister-Boltenstern, S.: Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, *Phil trans R Soc B*, 368:20130122, 2013.
- Brugiere, N., Suzuki, A., and Hirel, B.: Ammonium assimilation, In: *Nitrogen assimilation by plants; physiological, biochemical and molecular aspects*, Morot-Gaudry J-F (ed.), Science Publishers, Enfield, NH, 71–94, 1997.
- Byrne, K. A., Chojnicki, B., Christensen, T. R., Drösler, M., Freibauer, A., Friborg, T., Froking, S., Lindroth, A., Mailhammer, J., Malmer, N., Selin, P., Turunen, J., Valentini, R., and Zetterberg, L.: EU peatlands: Current carbon stocks and trace gas fluxes, *Carbo-Europe-GHG Concerted Action-Synthesis of the European Greenhouse Gas Budget*, Report, 4, 2004.
- Byrne, K.A., and Farrell, E.P.: The effect of afforestation on soil carbon dioxide emissions in blanket peatland in Ireland, *Forestry*, 78, 217–227, doi:10.1093/forestry/cpi020, 2005.
- Chapin, F.S.: New cog in the nitrogen cycle, *Nature*, 377, 199–200, 1995.

- Charman, D. J., Beilman, D. W., Blaauw, M., Booth, R. K., Brewer, S., Chambers, F. M., Christen, J. A., Gallego-Sala, A., Harrison, S. P., Hughes, P. D. M., Jackson, S. T., Korhola, A., Mauquoy, D., Mitchell, F. J. G., Prentice, I. C., van der Linden, M., De Vleeschouwer, F., Yu, Z. C., Alm, J., Bauer, I. E., Corish, Y. M. C., Garneau, M., Hohl, V., Huang, Y., Karofeld, E., Le Roux, G., Loisel, J., Moschen, R., Nichols, J. E., Nieminen, T. M., MacDonald, G. M., Phadtare, N. R., Rausch, N., Sillasoo, Ü., Swindles, G. T., Tuittila, E.-S., Ukonmaanaho, L., Väiliranta, M., van Bellen, S., van Geel, B., Vitt, D. H., and Zhao, Y.: Climate-related changes in peatland carbon accumulation during the last millennium, *Biogeosciences*, 10, 929-944, doi:10.5194/bg-10-929-2013, 2013.
- Christensen, T.R., Johansson, T.R., Akerman, H.J., Mastepanov, M., Malmer, N., Friborg, T., Crill, P., and Svensson, B.H.: Thawing sub-arctic permafrost: Effects on vegetation and methane emissions, *Geophys. Res. Lett.*, 31, L04501, doi:10.1029/2003GL018680, 2004.
- Cicerone, R.J. and Oremland, R.S.: Biogeochemical aspects of atmospheric methane, *Global Biogeochemical Cycles*, 2, 288–327, 1988.
- Cleemput van, O., Boeckx, P., Lindgren, P.-E., and Tonderski, K.: Denitrification in Wetlands, In: *Biology of the Nitrogen Cycle*, Bothe, H., Ferguson, S.J., and Newton, W.E., (eds.), Elsevier B.V., 2007.
- Clemens, J. and Huschka, A.: The effect of biological oxygen demand of cattle slurry and soil moisture on nitrous oxide emissions, *Nutr. Cycling Agroecosyst.* 59, 193–198, 2001.
- Colliver, B.B. and Stephenson, T.: Production of nitrogen oxide and dinitrogen oxide by autotrophic nitrifiers, *Biotechnology Advances*, 18, 219–232, 2000.
- Couwenberg, J.: Greenhouse gas emissions from managed peat soils: is the IPCC reporting guidance realistic, *Mires and Peat*, 8, 1–10, 2011.
- Crill, P.M., Martikainen, P.J., Nykänen, H., and Silvola, J.: Temperature and fertilization effects on methane oxidation in a drained peatland soil, *Soil Biol. Biochem.*, 26(10), 1331–1339, 1994.
- Davidson, E.A., Swank, W.T., and Perry, T.O.: Distinguishing between nitrification and denitrification as sources of gaseous nitrogen production in soil, *Applied and Environmental Microbiology*, 52 (6), 1280–1286, 1986.
- Davidson, E. A.: Fluxes of nitrous and nitric oxide from terrestrial ecosystems. In: *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*, edited by: Rogers, J. E. and Whitman, W. P., American Society for Microbiology, Washington, D.C., 219–235, 1991.
- Davidson, E.A., and Janssens, I.A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, *Nature*, 440, 165–173, 2006.
- Denmead, O.T.: Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere, *Plant Soil*, 309, 5–24, 2008.
- Dittert, K.: Die stickstofffixierende Schwarzlerle- Frankia-Symbiose in einem Erlenbruch der Bornhöveder Seenkette, *EcoSys. Suppl.*, 5, 1–98, 1992.
- Don, A., Osborne, B., Hastings, A., Skiba, U., Carter, M.S., Drewer, J., Flessa, H., Freibauer, A., Hyvönen, N., Jones, M.B., Lanigan, G.J., Mander, Ü., Monti, A., Djomo, S.N., Valentine, J., Walter, K., Zegada-Lizarazu, W., and Zenone, T.: Land-use change to bioenergy production in Europe: implications for the greenhouse gas balance and soil carbon, *GCB Bioenergy*, doi: 10.1111/j.1757-1707.2011.01116.x, 2011.
- Drösler, M., Freibauer, A., Christensen, T. and Friborg, T.: Observation and status of peatland greenhouse gas emission in Europe, In: Dolman, H., Valentini, R. &

- Freibauer, A. (eds) The Continental-Scale Greenhouse Gas Balance of Europe. *Ecological Studies*, 203, 237–255, 2008a.
- Drösler, M., Fiedler, S., Zeitz, J., Höper, H., Glatzel, S., Sommer, M., Augustin, J., Pretzsch, H., Rötzer, T., and Edom, F.: Verbundvorhaben: Klimaberichterstattung „organische Böden“ – Ermittlung und Bereitstellung von Methoden, Aktivitätsdaten und Emissionsfaktoren für die Klimaberichterstattung LU-LUCS/AFOLU. Projektskizze zur Begleitforschung, 2008b.
- Drösler, M., Freibauer, A., Adelman, W., Augustin, J., Bergman, L., Beyer, C., Chojnicki, B., Förster, C., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H., Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P., Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz in der Praxis, Arbeitsbericht aus dem vTI-Institut für Agrarrelevante Klimaforschung, p. 21, available at <http://www.vti.bund.de/de/startseite/institute/ak/publikationen.html>, 2011.
- Drösler, M., Augustin, J., Bergmann, L., Förster, C., Fuchs, D., Hermann, J.M., Kantelhardt, J., Kapfer, A., Krüger, G., Schaller, L., Sommer, M., Schweiger, M., Steffenhagen, P., Tiemeyer, B., and Wehrhan, M.: Beitrag ausgewählter Schutzgebiete zum Klimaschutz und dessen monetäre Bewertung. Abschlussbericht des gleichnamigen F+E-Vorhabens (FKZ 3509850500), BfN-Skripten, 328, 152 pp., 2012.
- Drösler, M., Adelman, W., Augustin, J., Bergmann, L., Beyer, C., Chojnicki, B., Förster, C., Freibauer, A., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H., Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P., Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz. Schlussbericht des Vorhabens „Klimaschutz – Moorschutzstrategien“, 2006–2010, 2013.
- Elsgaard, L., Gorres, C.-M., Hoffmann, C. C., Blicher-Mathiesen, G., Schelde, K., and Petersen, S. O.: Net ecosystem exchange of CO<sub>2</sub> and carbon balance for eight temperate organic soils under agricultural management, *Agr. Ecosyst. Environ.*, 162, 52–67, 2012.
- Eswaran, H., van den Berg, E., Reich, P., and Kimbel, J.: Global soil carbon resources. In: *Soils and Global Change*, Lewis Publishers, Boca Raton, FL (1995), 27–43, 1995.
- EU: Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, O. J. o. t. E. Union (ed Union OjotE), EU, Brussels, 2009.
- Fangmeier, A., Hadwiger-Fangmeier, A., van der Eerden, L., and Jäger, H.J.: Effects of atmospheric ammonia on vegetation – a review, *Environmental pollution*, 86, 43–82, 1994.
- FAO, Food and Agriculture Organization of the United Nations: World Reference Base for Soil Resources, *World Soil Resources Reports*, 84, 88 pp., 1998.
- FAOSTAT, 2013. Statistics Division of the Food and Agriculture Organization of the United Nations. Rome, Italy: FAOSTAT. <http://faostat.fao.org>. Viewed Feb 2015.
- Fell, H., Roßkopf, N., and Zeitz, J.: Impact of the spatial resolution of soils data on climate reporting for organic soils using the example of Germany, *Mires and Peat*, 14, 1–9, 2014.
- Ferguson, S.J., Richardson, D.J., and Spanning, R.J.M.: Biochemistry and Molecular Biology of Nitrification, In: *Biology of the Nitrogen Cycle*, Bothe, H., Ferguson, S.J., and Newton, W.E., (eds.), Elsevier B.V., 2007.

- Firestone, M. K., Smith, M. S., Firestone, R. B., and Tiedje, J. M.: The influence of nitrate, nitrite, and oxygen on the composition of the gaseous products of denitrification in soil, *Soil Sci. Soc. Am. J.*, 43, 1140–1144, 1979.
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: C- und N-Stoffflüsse auf Torfstichsimulationsflächen im Donaumoos, *Z. f. Kulturtechnik und Landentwicklung*, 38, 11–17, 1997.
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: Nitrous oxide and methane fluxes from organic soils under agriculture, *European Journal of Soil Science*, 49, 327–335, 1998.
- Flessa, H., and Beese, F.: Laboratory Estimates of Trace Gas Emissions following Surface Application and Injection of Cattle Slurry, *J. Environ. Qual.*, 29, 262–268, 2000.
- Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland, 2007: Changes in Atmospheric Constituents and in Radiative Forcing. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.
- Frame, C.H., and Casciotti, K.L.: Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium, *Biogeosciences*, 7, 2695–2709, 2010.
- Freibauer, A., Rounsevell, M.D.A., Smith, P., and Verhagen, J.: Carbon sequestration in the agricultural soils of Europe, *Geoderma*, 122, 1–23, 2004.
- Frolking S., Bubier, J.L., Moore, T.R., Ball, T., Bellisario, L.M., Bharwaj, A., Carroll, P., Crill, P.M., Lafleur, P.M., McCaughey, J.H., Roulet, N.T., Suyker, A.E., Verma, S.B., Waddington, J.M., and Whiting, G.M.: Relationship between ecosystem productivity and photosynthetically active radiation for northern peatlands, *Global Biogeochemical Cycles*, 12 (1), 115–126, 1998.
- Frolking, S. and Roulet, N. T.: Holocene radiative forcing impact of northern peatland carbon accumulation and methane emissions, *Glob. Change Biol.*, 13, 1079–1088, 2007.
- Frolking, S., Talbot, J., Jones, M.C., Treat, C.C., Kauffman, B., Tuittila, E.S., and Roulet, N.: Peatlands in the Earth's 21<sup>st</sup> century climate system, *Environ. Rev.*, 19, 371–396, 2011.
- Galloway, J.N.: Acid deposition: Perspectives in time and space, *Water, air and Soil Pollution*, 85, 15–24, 1995.
- Galloway, J.N.: The global nitrogen cycle: changes and consequences, *Environmental Pollution*, 102, 15–24, 1998.
- Galloway, J.N.: Acidification of the world: natural and anthropogenic, *Journal of Water, Air, and Soil Pollution*, 130, 17–24, 2001.
- Galloway, J.N., Cowling, E.B., Seitzinger, S.P., and Socolow, R.H.: Reactive Nitrogen: Too Much of a Good Thing?, *Ambio*, 31 (2), 60–63, 2002.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., and Vorosmarty, C.J.: Nitrogen cycles: past, present, and future, *Biogeochemistry*, 70, 153–226, 2004.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z.C., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., and Sutton, M.A.: Transformation of the nitrogen

- cycle: Recent trends, questions, and potential solutions, *Science*, 320(5878), 889–892, 2008.
- Gao, Z., Desjardins, R.L., and Flesch, T.K.: Comparison of a simplified micrometeorological mass difference technique and an inverse dispersion technique for estimating methane emissions from small area sources, *Agricultural and forest Meteorology*, 149, 891–898, 2009.
- Gerin PA, Vliegen F, and Jossart J-M.: Energy and CO<sub>2</sub> balance of maize and grass as energy crops for anaerobic digestion, *Bioresource Technology*, 99 (7), 2620–2627, 2008.
- Gorham, E.: Northern peatlands: Role in the carbon cycle and probable responses to climatic warming, *Ecological Applications*, 1, 182–195, 1991.
- Gorham, E.: The biogeochemistry of northern peatlands and its possible responses to global warming, in: *Biotic Feedbacks in The Global Climate System: Will the Warming Feed the Warming?*, Woodwell, G.M., and Mackenzie, F.T. (ed.), Oxford Univ. Press, New York, 169–187, 1995.
- Göttlich, K.: *Moor- und Torfkunde*, E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller) Stuttgart, 3. Auflage, 520 pp., 1990.
- Grønlund, A., Sveistrup, T.E., Søvik, A.K., Rasse, D.P., and Kløve, B.: Degradation of cultivated peat soils in northern Norway based on field scale CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission measurements, *Arch Agron. Soil Sci.*, 52, 149–159, 2006.
- Grønlund, A., Hauge, A., Hovde, A., and Rasse, D.A.: Carbon loss estimates from cultivated peat soils in Norway: a comparison of three methods, *Nutr. Cycl. Agroecosyst.*, 81, 157–167, 2008.
- Grosse, W., Frye, J., and Lattermann, S.: Root aeration in wetland trees by pressurized gas transport, *Tree Physiology*, 10, 285–295, 1992.
- Grote, R., and Pretzsch, H.: A Model for Individual Tree Development Based on Physiological Processes, *Plant Biology*, 4 (2), 167–180, 2002.
- Gruber, N., and Galloway, J.N.: An Earth-system perspective of the global nitrogen cycle, *Nature*, 451 (7176), 293–296, 2008.
- Gupta, V., Smemo, K.A., Yavitt, J.B., Fowle, D., Branfireun, B., and Basiliko, N.: Stable isotopes reveal widespread anaerobic methane oxidation across latitude and peatland type, *Environ. Sci. technol.*, 47, 8273–8279, 2013.
- Gutser, R., Ebertseder, Th., Weber, A., Schraml, M., and Schmidhalter, U.: Short-term and residual availability of nitrogen after long-term application of organic fertilizers on arable land, *J. Plant Nutr. Soil Sci.*, 168, 439–446, 2005.
- Gutser, R., Ebertseder, T., Schraml, M., von Tucher, S., and Schmidhalter, U.: Stickstoffeffiziente und umweltschonende organische Düngung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, 384 pp., 2010.
- Haenel, H.D., Freibauer, A., Rösemann, C., Poddey, E., Gensior, A., Menden, B.M., and Döhler, H.: Emissionen landwirtschaftlich genutzter Böden im Rahmen der deutschen Klimaberichterstattung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, 384 pp., 2010.
- Hefting, M.M., Bobbink, R., and Caluwe, H.: Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones, *J. Environ. Qual.*, 32, 1194–1203, 2003.
- Heijmans, M.P.D., Berendse, F., Arp, W.J., Masselink, A.B.K., Klees, H., de Visser, W., and van Breemen, N.: Effects of elevated carbon dioxide and increased nitrogen deposition on bog vegetation in the Netherlands, *J. Ecol.*, 89(2), 268–279, 2001.
- Heller, C., and Zeitz, J.: Stability of soil organic matter in two northeastern German fen soils: the influence of site and soil development, *J. Soils Sediments*, 12, 1231–1240, DOI 10.1007/s11368-012-0500-6, 2012.

- Henry, S., Texier, S., Hallet, S., Bru, D., Dambreville, C., Chèneby, D., Bizouard, F., Germon, J.C., and Philippot, L.: Disentangling the rhizosphere effect on nitrate reducers and denitrifiers: insight into the role of root exudates, *Environ. Microbiol.*, 10, 3082–3092, 2008.
- Hensen, A.: Methods for observation and quantification of trace gas emissions from diffuse sources, PhD thesis, VU Amsterdam, 144 pp., 2011.
- Hooijer, A., Silvius, M., Woesten, H., and Page, S.: Peat-CO<sub>2</sub>: Assessment of CO<sub>2</sub> emissions from drained peatlands in SE Asia, Delft Hydraulics report Q3943, 41 pp., 2006.
- Hooijer, A., Page, S., Canadell, J.G., Silvius, M., Kwadijk, J., Wösten, H., and Jauhiainen, J.: Current and future CO<sub>2</sub> emissions from drained peatlands in Southeast Asia, *Biogeosciences*, 7, 1505–1514, 2010.
- Höper, H., Augustin, J., Cagampan, J. P., Drösler, M., Lundin, L., Moors, E. J., Vasander, H., Waddington, J. M., and Wilson, D.: Restoration of peatlands and greenhouse gas balances, in: *Peatlands and Climate Change*. edited by: Strack, D. M., International Peat Society, Jyväskylä, 182–210, 2008.
- Houghton, J.T., and Woodwell, G.M.: Global climate change, *Sci. Am.*, 260, 36–44, 1989.
- Icha, P.: Entwicklung der spezifischen Kohlendioxid-Emissionen des deutschen Strommix in den Jahren 1990 bis 2012, Umweltbundesamt, Climate Change 07/2013, <http://www.uba.de/uba-info-medien/4488.html>, p. 18, 2013.
- IPCC: Climate Change 1994: Radiative Forcing of Climate Change and An Evaluation of the IPCC IS92, Emission Scenarios, J.T. Houghton, L.G. Meira Filho, J. Bruce, Hoesung Lee, B.A. Callander, E. Haites, N. Harris and K. Maskell (Eds.), Cambridge University Press, UK, 339 pp., 1994.
- IPCC: 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published: IGES, Japan, 2006.
- IPCC: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007, Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA., 2007.
- IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., 2013.
- IPCC: 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands, Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M. and Troxler, T.G. (eds). Published: IPCC, Switzerland, 2014a.
- IPCC: Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Edenhofer, O., R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C. Minx (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2014b.

- Jain, P.C.: Greenhouse effect and climate change: Scientific basis and overview, *Renewable Energy*, 3 (4/5), 403–420, 1993.
- Jansson, S., and Persson, J.: Mineralization and immobilization of soil nitrogen, In: *Nitrogen in agricultural soils*, Stevenson, F.J. (ed.), ASA/CSSA/SSSA, Madison, 229–252, 1982.
- Jenkinson, D.S., Adams, D.E., and Wild, A.: Model estimates of CO<sub>2</sub> emissions from soil in response to global warming, *Nature*, 351, 304–306, 1991.
- Jenkinson, D.S.: The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture, *Plant Soil*, 228, 3–15, 2001.
- Jones, S.K., Rees, R.M., Skiba, U.M., and Ball, B.C.: Influence of organic and mineral N fertiliser on N<sub>2</sub>O fluxes from temperate grassland, *Agriculture, Ecosystems and Environment*, 121, 74–83, 2007.
- Joosten, H.: The IMCG Global Peatland Database. [www.imcg.net/gpd/gpd.htm](http://www.imcg.net/gpd/gpd.htm), 2004.
- Joosten, H.: The global peatland CO<sub>2</sub> picture. Peatland status and drainage related emissions in all countries of the world, report, *Wetlands Int.*, Ede, Netherlands, 36 pp., 2010.
- Kandel, T.P., Elsgaard, L., Karki, S., and Lærke, P.E.: Biomass yield and greenhouse gas emissions from a drained fen peatland cultivated with reed canary grass under different harvest and fertilizer regimes, *Bioenerg. Res.*, 6, 883–895, DOI 10.1007/s12155-013-9316-5, 2013.
- Kasimir-Klemedtsson, Å., Klemedtsson, L., Berglund, K., Martikainen, P., Silvola, J., and Oenema, O.: Greenhouse gas emissions from farmed organic soils: a review, *Soil Use and Management*, 13, 245–250, 1997.
- Klemedtsson, L., Svensson, B.O.H., and Rosswall, T.: Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants, *Plant and Soil*, 99, 303–319, 1987.
- Klemedtsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, *Global Change Biology*, 11, 1142–1147, 2005.
- Kiehl, J.T., and Trenberth, K.E.: Earth's annual global mean energy budget, *Bulletin of the American Meteorological Society*, 78 (2), 197–208, 1997.
- Knowles, R.: Denitrification, *Microbiol. Rev.*, 46, 43–70, 1982.
- Koopmans, C.J., Tietema, A., and Verstraten, J.M.: Effects of reduced N deposition on litter decomposition and N cycling in two N saturated forests in the Netherlands, *Soil Biol. Biochem.*, 30 (2), 141–151, 1998.
- Lafleur, P.M., Roulet, N. T., Bubier, J.L., Frohling, S., and Moore, T.R.: Interannual variability in the peatland-atmosphere carbon dioxide exchange at an ombrotrophic bog, *Global Biogeochemical Cycles*, 17 (2), doi:10.1029/2002GB001983, 2003.
- Lal, R.: Soil carbon sequestration to mitigate climate change, *Geoderma*, 123 (1–2), 1–22, 2004.
- Laine, A., Wilson, D., Kiely, G., and Byrne, K.A.: Methane flux dynamics in an Irish lowland blanket bog, *Plant Soil*, 299, 181–193, 2007.
- Lappalainen, E.: General review on world peatland and peat resources. In Lappalainen, E., editor, *Global peat resources*, Helsinki: International Peat Society and Geological Survey of Finland, 53–56, 1996.
- Larcher, W.: *Ökophysiologie der Pflanzen: Leben, Leistung und Stressbewältigung der Pflanzen in ihrer Umwelt*, Verlag Eugen Ulmer GmbH & Co., 6. Neubearb. Aufl., 408 pp., 2001.

- Leiber-Sauheitl, K., Fuß, R., Voigt, C., and Freibauer, A.: High CO<sub>2</sub> fluxes from grassland on histic Gleysol along soil carbon and drainage gradients, *Biogeosciences*, 11, 749–761, doi:10.5194/bg-11-749-2014, 2014.
- Leifeld, J., Müller, M., and Fuhrer, J.: Peatland subsidence and carbon loss from drained temperate fens, *Soil Use Manage.*, 27, 170–176, 2011.
- Leifeld, J., Steffens, M., and Galego-Sala, A.: Sensitivity of peatland carbon loss to organic matter quality, *Geophys. Res. Lett.*, 39, L14704, doi:10.1029/2012GL051856, 2012.
- Leifeld, J., Bader, C., Borraz, E., Hoffmann, M., Giebels, M., Sommer, M., and Augustin, J.: Are C-loss rates from drained peatlands constant over time? The additive value of soil profile based and flux budget approach, *Biogeosciences Discuss.*, 11, 12341–12373, 2014.
- Leppelt, T., Dechow, R., Gebbert, S., Freibauer, A., Lohila, A., Augustin, J., Drösler, M., Fiedler, S., Glatzel, S., Höper, H., Järveoja, J., Lærke, P.E., Maljanen, M., Mander, Ü., Mäkiranta, P., Minkkinen, K., Ojanen, P., Regina, K., and Strömngren, M.: Nitrous oxide emission hotspots from organic soils in Europe, *Biogeosciences Discuss.*, 11, 9135–9182, 2014.
- Lipson, D., and Monson, R.: Plant-microbe competition for amino acids in the alpine tundra: effect of freeze-thaw and dry-wet events, *Oecologia*, 113, 406–414, 1998.
- Limpens, J., Heijmans, M.M.P.D., Berendse, F.: Nitrogen in boreal peatlands, In: *Boreal Peatland Ecosystems*, Wieder, R.K., Vitt, D.H. (eds.), Ecological Studies Series, 188, Springer-Verlag, Berlin, 2006.
- Limpens, J., Berendse, F., Blodau, C., Canadell, J.G., Freeman, C., Holden, J., Roulet, N., Rydin, H., and Schaepman-Strub, G.: Peatlands and the carbon cycle: from local processes to global implications – a synthesis, *Biogeosciences*, 5, 1475–1491, 2008.
- Maljanen, M., Hytönen, J., and Martikainen, P. J.: Fluxes of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> on afforested boreal agricultural soils, *Plant Soil*, 231, 113–121, 2001.
- Maljanen, M., Hytönen, J., Mäkiranta, P., Alm, J., Minkkinen, K., Laine, J. and Martikainen, P.J.: Greenhouse gas emissions from cultivated and abandoned organic arable lands in Finland, *Boreal Environment Research*, 12, 133–144, 2007.
- Maljanen, M., Sigurdsson, B. D., Guðmundsson, J., Óskarsson, H., Huttunen, J. T., and Martikainen, P. J.: Greenhouse gas balances of managed peatlands in the Nordic countries – present knowledge and gaps, *Biogeosciences*, 7, 2711–2738, doi:10.5194/bg-7-2711-2010, 2010.
- Mander, Ü., Lõhmus, K., Teiter, S., Mäuring, T., Nurk, K., and Augustin, J.: Gaseous fluxes in the nitrogen and carbon budgets of subsurface flow constructed wetlands, *Sci. Total Environ.*, 404, 343–353, 2008.
- McNeill, A., and Unkovich, M.: The nitrogen Cycle in Terrestrial Ecosystems, in *Nutrient Cycling in Terrestrial Ecosystems*, Eds. Marschner, R., Rengel, Z., Soil Biology, Volume 10, 397 pp., 2007.
- Merbach, W., Augustin, J., and Gans, W.: Nitrous oxide emissions from fen mires in dependence of anthropogenic activities, *Journal of Applied Botany*, 75, 118–123, 2001.
- Mogge, B., Kaiser, E.A., and Munch, J.C.: Nitrous oxide emissions and denitrification N-losses from forest soils in the Bornhöved lake region (northern Germany), *Soil Biol. Biochem.*, 30 (6), 703–710, 1998.
- Möller, K., and Stinner, W.: Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and gaseous nitrogen losses (ammonia, nitrous oxide), *Europ. J. Agronomy*, 30, 1–16, 2009.

- Moiser, A.R.: Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere. *Plant Soil*, 228, 17–27, 2001.
- Moore, T.R., and Knowles, R.: The influence of water table on methane and carbon dioxide emissions from peatland soils, *Can. J. Soil Sci.*, 69, 33–38, 1989.
- Moore, T.R., and Dalva, M.: The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils, *J. Soil Sciences*, 44, 651–664, 1993.
- Mounier, E., Hallet, S., Chèneby, D., Benizri, E., Gruet, Y., Nguyen, C., Piutti, S., Robin, C., Slezack-Deschaumes, S., Martin-Laurent, F., Germon, J.C., and Philippot, L.: Influence of maize mucilage on the diversity and activity of the denitrifying community, *Environ. Microbiol.*, 6, 301–312, 2004.
- Nelson, D.W.: Gaseous loss of nitrogen other than through denitrification. In: *Nitrogen in agricultural soils*, Stevenson FJ (ed.), ASA-CSSA-SSSA, Madison, 327–363, 1982.
- Nielsen, O.-K., Mikkelsen, M.H., Hoffmann, L., Gyldenkærne, S., Winther, M., Nielsen, M., Fauser, P., Thomsen, M., Plejdrup, M.S., Albrektsen, R., Hjelgaard, K., Bruun, H.G., Johannsen, V.K., Nord-Larsen, T., Bastrup-Birk, A., Vesterdal, L., Møller, I.S., Rasmussen, E., Arfaoui, K., Baunbæk, L. & Hansen, M.G.: Denmark's National Inventory Report 2012. Emission Inventories 1990-2010 - Submitted under the United Nations Framework Convention on Climate Change and the Kyoto Protocol. Aarhus University, DCE – Danish Centre for Environment and Energy, Scientific Report from DCE – Danish Centre for Environment and Energy No. 19 <http://www.dmu.dk/Pub/SR19.pdf>, 1168 pp., 2012.
- Nilsson, M., Sagerfors, J. Buffam, I. Laudon, H. Eriksson, T. Grelle, A. Klemetsson, L. Weslien, P. and Lindroth, A.: Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - A significant sink after accounting for all C-fluxes, *Global Change Biol.*, 14 (10), 2317–2332, 2008.
- Nilsson, M., and Öquist, M.: Partitioning litter mass loss into carbon dioxide and methane in peatland ecosystem, In: *Carbon Cycling in Northern Peatlands*, Baird, A.,J., Belyea, L.R., Comas, X., Reeve, A.S., and Slater, L.D. (eds.), Geophysical Monograph, 184, American Geophysical Union, Washington, DC, 2009.
- NIR 2010: National Emission Inventory Report (NIR) 2010 for 2008 – Calculation of Emissions from German Agriculture, Ed. Haenel, H.D., vTI Agriculture and Forestry Research, Special Issue 334, 428 pp., 2010.
- Oenema, O., Wrage, N., Velthof, G.L., van Groenigen, J.W., Dolfing, J., and Kuikman, P.J.: Trends in global nitrous oxide emissions from animal production systems, *Nutrient Cycling in Agroecosystems*, 72, 51–65, 2005.
- Page, S.E., Rieley, J.O., and Banks, C.J.: Global and regional importance of the tropical peatland carbon pool, *Global Change Biol.*, 17 (2), 798–818, 2011.
- Petersen, S.O., Hoffmann, C.C., Schäfer, C.-M., Bilcher-Mathiesen, G., Elsgaard, L., Kristensen, K., Larsen, S.E., Torp, S.B., and Greve, M.H.: Annual emissions of CH<sub>4</sub> and N<sub>2</sub>O, and ecosystem respiration, from eight organic soils in Western Denmark managed by agriculture, *Biogeosciences*, 9, 403–422, 2012.
- Philippot, L., Andert, J., Jones, C.M., Bru, D. & Hallin, S.: Importance of denitrifiers lacking the genes encoding the nitrous oxide reductase for N<sub>2</sub>O emissions from soil. *Global Change Biol.*, 17, 1497–1504, 2011.
- Pitcairn, C.E. R., and Fowler, D.: Deposition of fixed atmospheric nitrogen and foliar nitrogen content of Bryophytes and *Calluna vulgaris* (L.) Hull, *Environmental Pollution*, 88, 193205, 1995.

- Poth, M., and Focht, D.D.: N-15 kinetic analysis of N<sub>2</sub>O production by *Nitrosomonas europaea* – an examination of nitrifier denitrification, *Appl. Environm. Microbiol.*, 49, 1134–1141, 1985.
- Pretzsch, H., Biber, P., and Dursky, J.: The single tree-based stand simulator SILVA: construction, application and evaluation, *Forest Ecology and Management*, 162, 3–21, 2002.
- Regina, K., Nykänen, H., Silvola, J., and Martikainen, P. J.: Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity, *Biogeochemistry*, 35, 401–418, 1996.
- Renou-Wilson, F., Barry, C., Müller, C., and Wilson, D.: The impacts of drainage, nutrient status and management practice on the full carbon balance of grasslands on organic soils in a maritime temperate zone, *Biogeosciences*, 11, 4361–4379, 2014.
- Rolston, D. E., Hoffman, D. L., and Toy, D.W.: Field measurements of denitrification: 1. Flux of N<sub>2</sub> and N<sub>2</sub>O, *Soil Sci. Soc. Am. J.*, 42, 863–869, 1978.
- Roobroeck, D., Butterbach-Bahl, K., Brüggemann, N., and Boeckx, P.: Dinitrogen and nitrous oxide exchanges from an undrained monolith fen: short-term responses following nitrate addition, *Eur. J. Soil Sci.*, 61, 662–670, 2010.
- Roulet, N.T., Lafleur, P.M., Richard, P.J.H., Moore, T.R., Humphreys, E.R., and Bubier, J.: Contemporary carbon balance and late holocene carbon accumulation in a northern peatland, *Glob. Change Biol.*, 13, 397–411, 2007.
- Rösch, C., Skarka, J., Raab, K., and Stelzer, V.: Energy production from grassland – Assessing the sustainability of different process chains under German conditions, *Biomass and Bioenergy*, 33, 689–700, 2009.
- Rubæk, G.H., Henriksen, K., Petersen, J., Rasmussen, B., and Sommer, S.G.: Effects of application technique and anaerobic digestion on gaseous loss from animal slurry applied to ryegrass (*Lolium perenne*), *J. Agric. Sci. Camb.*, 126, 481–492, 1996.
- Rydin, H., and Jeglum, J.K.: *The Biology of Peatlands*, with contributions from Hooijer, A., Clarkson, B.R., Clarkson, B.D., Mauquoy, D., and Bennett, K.D., *The Biology of Habitats series*, Oxford University Press, 343 pp., 2006.
- Sagerfors, J., Lindroth, A., Grelle, A., Klemmedtsson, L., Weslien, P., and Nilsson, M.: Annual CO<sub>2</sub> exchange between a nutrient-poor, minerotrophic, boreal mire and the atmosphere, *Journal of Geophysical Research*, 113 (G1), <http://dx.doi.org/10.1029/2006JG000306>, 2008.
- Schäfer, A., and Joosten, H., (eds.): *Erlenaufforstung auf wiedervernässten Niedermooren. (Alnus afforestation on restored fen peatlands)*, Greifswald: Institute for Sustainable Development of Landscapes of the Earth, 68 pp., 2005.
- Schäfer, C.M., Elsgaard, L., Hoffmann, C.C., and Petersen, S.O.: Seasonal methane dynamics in three temperate grasslands on peat, *Plant Soil*, 357, 339–353, 2012.
- Scheffer, F., and Schachtschabel, P.: *Lehrbuch der Bodenkunde*. Neu bearbeitet und erweitert von Blume, H. P. & Brümmer, G. W. & Schwertmann, U. & Horn, R. & Kögler-Knabner, I. & Stahr, K. & Auerswald, K. & Beyer, L. & Hartmann, A. & Litz, N. & Scheinost, A. & Stanjek, H. & Welp, G. & Wilke, B. M., Spektrum Akademischer Verlag, Heidelberg, 2002, 15, 593 pp., 2002.
- Schleupner, C., and Schneider, U.A.: Effects of bioenergie policies and targests on European wetland restoration options, *Environmental Science & Policy*, 13, 721–732, 2010.
- Scholefield, D., Hawkins, J.M.B., and Jackson, S.M.: Use of a flowing helium atmosphere incubation technique to measure the effects of denitrification controls

- applied to intact cores of a clay soil, *Soil Biol. Biochem.*, 29 (9–10), 1337–1344, 1997.
- Schothorst, C.J.: Subsidence of low moor peat soils in the Western Netherlands, *Geoderma*, 17, 265–291, 1977.
- Schulze, E.D., Ciais, P., Luyssaert, S., Schrumppf, M., Janssens, I.A., Thiruchittampalam, B., Theloke, J., Saurat, M., Bringezu, S., Lelieveld, J., Lohila, A., Rebmann, C., Jung, M., Bastviken, D., Abril, G., Grassi, G., Leip, A., Freibauer, A., Kutsch, W., Don, A., Nieschulze, J., Boerner, A., Gash, J.H., and Dolman, A.J.: The European carbon balance. Part 4: integration of carbon and other trace-gas fluxes, *Glob. Change Biol.*, 16 (5), 1451–1469, 2010.
- Segers, R.: Methane production and methane consumption: a review of processes underlying wetland methane fluxes, *Biogeochemistry*, 41, 23–51, 1998.
- Sey, B.K., Manceur, A.M., Wahlen, J.K., Gregorich, E.G, and Rochette, P.: Root-derived respiration and nitrous oxide production as affected by crop phenology and nitrogen fertilization, *Plant Soil*, 326, 369–379, 2010.
- Sheppard, L.J., Leith, I.D., Leeson, S.R., van Dijk, N., Field, C., and Levy, P.: Fate of N in a peatland, Whim bog: immobilisation in the vegetation and peat, leakage into pore water and losses as N<sub>2</sub>O depend on the form of N, *Biogeosciences*, 10, 149–160, 2013.
- Silvan, N., Tuittila, E.-S., Kitunen, V., Vasander, H., and Laine, J.: Nitrate uptake by *Eriophorum vaginatum* controls N<sub>2</sub>O production in a restored peatland, *Soil Biol. Biochem.*, 37, 1519–1526, 2005.
- Smith, V.H., Tilman, G.D., and Nekola, J.C.: Eutrophication: impacts of excess nutrient input on freshwater, marine, and terrestrial ecosystems, *Environmental Pollution*, 100, 179–196, 1999.
- Smyth, B.M., Murphy, J.D., and O'Brien, C.M.: What is the energy balance of grass biomethane in Ireland and other temperate northern European climates?, *Renewable and Suitable Energy Reviews*, 13, 2349–2360, 2009.
- Sonneveld, M.P.W., and Lantinga, E.A.: The contribution of mineralization to grassland N uptake on peatland soils with anthropogenic A horizons, *Plant Soil*; 340, 357–368, 2011.
- Soosaar, K., Mander, Ü., Maddison, M., Kanal, A., Kull, A., Lõhmus, K., Truu, J., and Augustin, J.: Dynamics of gaseous nitrogen and carbon fluxes in riparian alder forests, *Ecol. Eng.*, 37, 40–53, 2011.
- Steffen R, Szolar O, and Braun R.: Feedstocks for anaerobic digestion, Vienna: Institute for Agrobiotechnology Tulln, University of Agricultural Sciences; 1998.
- Succow, M., and Joosten, H.: *Landschaftsökologische Moorkunde*, Unveränderter Nachdruck der 2. Auflage, E.Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, 622 pp., 2012.
- Sulman, B.N., Desai, A.R., Saliendra, N.Z., Lafleur, P.M., Flanagan, L.B., Sonnentag, O., Mackay, D.S., Barr, A.G., and Kamp, G.V.D.: CO<sub>2</sub> fluxes at northern fens and bogs have opposite responses to inter-annual fluctuations in water table, *Geophys. Res. Lett.*, 37, L19702, doi:10.1029/2010GL044018, 2010.
- Svensson, B.H., and Sundh, I.: Factors affecting methane production in peat soils. *Suo.*, 43, 183–190, 1992.
- Tarnocai, C.: The effect of climate change on carbon in Canadian peatlands, *Global and Planetary Change*, 53, 222–232, 2006.
- Tarnocai, C., Canadell, J.G., Schuur, E.A.G., Kuhry, P., Mazhitova, G., and Zimov, S.: Soil organic carbon pools in the northern circumpolar permafrost region, *Global Biogeochem. Cycles*, 23, 1–11 2009.

- Teiter, S. and Mander, Ü.: Emission of N<sub>2</sub>O, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> from constructed wetlands for wastewater treatment and from riparian buffer zones, *Ecol. Eng.*, 25, 528–541, 2005.
- Tiemeyer, B., Freibauer, A., Drösler, M., Albiac-Borraz, E., Augustin J., Bechtold, M., Beetz, S., Belting, S., Bernrieder, M., Beyer, C., Eberl, J., Eickenscheidt, T., Fell, H., Fiedler, S., Förster, C., Frahm, E., Frank, S., Giebels, M., Glatzel, S., Grünwald, T., Heinichen, J., Hoffmann, M., Hommeltenberg, J., Höper, H., Laggner, A., Leiber-Sauheitl, K., Leppelt, T., Metzger, C., Peichl-Brak, M., Röhling, S., Roskopf, N., Rötzer, T., Sommer, M., Wehrhan, M., Werle, P., and Zeitz, J.: Klimarelevanz von Mooren und Anmooren in Deutschland: Ergebnisse aus dem Verbundprojekt "Organische Böden in der Emissionsberichterstattung", Thünen Working Paper, No. 15, <http://nbn-resolving.de/urn:nbn:de:gbv:253-201311-dn052806-7>, 2013.
- Tiemeyer, B., Borraz, E.A, Augustin, J., Bechtold, M., Beetz, S., Beyer, C., Eickenscheidt, T., Drösler, M., Förster C., Freibauer, A., Giebels, M., Glatzel, S., Heinichen, J., Hoffmann, M., Höper, H., Leiber-Sauheitl, K., Roskopf, N., and Zeitz, J.: Greenhouse gas budgets for grasslands on peatlands and other organic soils, *Geophysical Research Abstracts*, Vol. 16, EGU2014-14825, 2014, EGU General Assembly, 2014.
- Tomassen, H.B.M., Smolders, A.J.P., Limpens, J., Lamers, L.P.M., and Roelofs, J.G.M.: Expansion of invasive species on ombrotrophic bogs: desiccation or high N deposition?, *J. Appl. Ecol.*, 41 (1), 139–150, 2004.
- Treat, C.C., Wisser, D., Marchenko, S., and Frolking, S.: Modelling the effects of climate change and disturbance on permafrost stability in northern organic soils, *Mires and Peat*, 12 (2), 1–17, 2013.
- Turetsky, M. R., Amiro, B. D., Bosch, E., and Bhatti, J. S.: Historical burn area in western Canadian peatlands and its relationship to fire weather indices, *Glob. Biogeochem. Cycles*, 18 (4), GBD4014, 2004.
- Turunen, J., Tomppo, E., Tolonen, K., and Reinikainen, A.: Estimating carbon accumulation rates of undrained mires in Finland – application to boreal and subarctic regions, *The Holocene*, 12 (1), 69–80, 2002.
- UNECE: Manual on Methodologies and Criteria for Modeling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends, 52/04. Federal Environmental Agency, Germany, 2004.
- Updegraff, K., Pastor, J., Bridgham, S.D., and Johnston, C.A.: Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands, *Ecol. Appl.*, 5, 151–163, 1995.
- Valentine, D.L., and Reeburgh, W.S.: New perspectives on anaerobic methane oxidation, *Environmental Microbiology*, 2 (5), 477–484, 2000.
- Van Beek, C.L., Pleijter, M., Jacobs, C.M.J., Velthof, G.L., van Groenigen, J.W., and Kuikman, P.J.: Emissions of N<sub>2</sub>O from fertilized and grazed grassland on organic soil in relation to groundwater level, *Nutr. Cycl. Agroecosyst.*, 86, 331–340, 2010.
- Van Beek, C.L., Pleijter, M., and Kuikman, P.J.: Nitrous oxide emissions from fertilized and unfertilized grasslands on peat soil, *Nutr. Cycl. Agroecosyst.*, 89, 453–461, 2011.
- Van Cleemput, O.: Subsoils: chemo- and biological denitrification, N<sub>2</sub>O and N<sub>2</sub> emissions, *Nutrient Cycl. Agroecosystems*, 52, 187–194, 1998.
- Van Cleemput, O., Boeckx, P., Lindgren, P.-E., and Tonderski, K.: Denitrification in wetlands. In: *Biology of the Nitrogen Cycle*, Bothe, H., Ferguson, S.J., and Newton, W.E., (eds.), Elsevier B.V., 2007.

- Vandré, R., Clemens, J., Goldbach, H., and Kaupenjohann, M.: NH<sub>3</sub> and N<sub>2</sub>O Emissions after Landspreading of Slurry as Influenced by Application Technique and Dry Matter-Reduction. I. NH<sub>3</sub> Emissions, *Z. Pflanzenernähr. Bodenk.*, 160, 303–307, 1997.
- Velthof, G.L., Brader, A.B., and Oenema, O.: Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands, *Plant and Soil*, 181, 263–274, 1996.
- Velthof, G.L., Kuikman, P.J., and Oenema, O.: Nitrous oxide emission from animal manures applied to soil under controlled conditions, *Biol. Fertil. Soils*, 37, 221–230, 2003.
- Venterea, R.T.: Simplified method for Quantifying theoretical underestimation of chamber-based trace gas fluxes, *J. Environ. Qual.*, 39, 126–135, 2010.
- Vepraskas M.J., and Faulkner, S.P.: Redox Chemistry of Hydric soils, in: *Wetland Soils: Genesis, Hydrology, Landscapes, and Classification* J.L., Richardson and M.J., Vepraskas (eds.), Lewis Publisher, Boca Raton, 84–105, 2001.
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, D.G.: Human alteration of the global nitrogen cycle: sources and consequences, *Ecol. Appl.*, 7 (3), 737–750, 1997.
- Vitousek, P.M., Cassman, K., Cleveland, C., Crews, T., Field, C.B., Grimm, N.B., Howarth, R.W., Marino, R., Martinelli, L., Rastetter, E.B., and Sprent, J.I.: Towards an ecological understanding of biological nitrogen fixation. *Biogeochemistry* 57, 1–45. (doi:10.1023/A:1015798428743), 2002.
- Vile, M.A., Kelman Wieder, R., Živković, T., Scott, K.D., Vitt, D.H., Hartsock, J.A., Iosue, C.L., Quinn, J.C., Petix, M., Fillingim, H.M., Popma, J.M.A., Dynarski, K.A., Jackman, T.R., Albright, C.M., and Wyckoff, D.D.: N<sub>2</sub>-fixation by methanotrophs sustains carbon and nitrogen accumulation in pristine peatlands, *Biogeochemistry*, 121, 317–328, 2014.
- Watson, R.T., Noble, I.R., Bolin, B., Ravindranath, N.H., Verardo, D.J. and Dokken, D.J.: *Special Report of the IPCC on Land Use, Land-Use Change, and Forestry*, Cambridge University Press, UK, 375 pp., 2000.
- Weier, K. L., Doran, J. W., Power, J. F., and Walters, D. T.: Denitrification and dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate, *Soil Sci. Soc. Am. J.*, 57, 66–72, 1993.
- Weiland, P.: Biogas production: current state and perspectives, *Appl. Microbiol. Biotechnol.*, 85, 849–860, 2010.
- Whalen, S.C.: Biogeochemistry of methane exchange between natural wetlands and the atmosphere, *Environmental Engineering Science*, 22 (1), 73–94, 2005.
- Wichtmann, W., and Joosten, H.: Paludiculture: peat formation and renewable resources from rewetted peatlands, In: *IMCG-Newsletter 3/2007*, 24–28, 2007.
- Wochele, S. and Kiese, R.: Modellierung und Kartierung räumlich differenzierter Wirkungen von Stickstoffeinträgen in Ökosysteme im Rahmen der UNECE-Luftreinhaltkonvention - Teilbericht I: Simulationen ökosystemarer Stoffumsetzungen und Stoffausträge aus Waldökosystemen in Deutschland unter Berücksichtigung geänderter Stoffeinträge und Klimabedingungen, Umweltbundesamt, Dessau, 115 pp., 2010.
- World Meteorological Organization (WMO): *Global Atmosphere Watch Programme*: [http://www.wmo.int/pages/mediacentre/press\\_releases/pr\\_980\\_en.html](http://www.wmo.int/pages/mediacentre/press_releases/pr_980_en.html), 11-2014.
- Wrage, N., Velthof, G.L., Van Beusichem, M.L., and Oenema, O.: The role of nitrifier denitrification in the production of nitrous oxide, *Soil Biol. Biochem.*, 33, 1723–1732, 2001.

- Wrage, N., Van Groeningen, J.W., Oenema, O. & Baggs, E.M.: A novel dualisotope labelling method for distinguishing between soil sources of N<sub>2</sub>O, *Rapid Comm. Mass Spectrom.*, 19, 3298–3306, 2005.
- Wray, H. E. and Bayley, S. E.: Denitrification rates in marsh frings and fens in two boreal peatlands in Alberta, Canada, *Wetlands*, 27, 1036–1045, 2007.
- WRB, 2006 – IUSS Working Group: World Reference Base for Soil Resources 2006, 2nd edition, World Soil Resources Reports No. 103. Rome. 2006.
- Wulf, S., Maeting, M., and Clemens, J.: Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: II Greenhouse Gas Emissions, *J. Environ. Qual.*, 31, 1795–1801, 2002.
- Yu, Z., Loisel, J., Brosseau, D.P., Beilman, D.W., and Hunt, S.: Global peatland dynamics since the Last Glacial Maximum, *Geophysical Research Letters*, 37, 1–5, 2010.
- Yu, Z., Beilman, D.W., Froking, S., MacDonald, G.M., Roulet, N.T., Camill, P., and Charman, D.J.: Peatland and Their Role in the Global Carbon Cycle, *EOS*, 92 (12), 97–108.

## 6 ACKNOWLEDGMENT

I would never have been able to finish my dissertation without the help and support of the kind people around me. For only some of whom it is possible to express my gratitude here. To all the others who made this thesis possible and were omitted, I would like to thank them for their individual support and helpfulness.

My special thanks go to my supervisor Prof. Dr. Matthias Drösler for providing me an interesting and challenging research topic, his efforts to guarantee a continuous financial funding during the last six years, for his help in scientific questions and especially for leaving room for independent work and ideas, which he always unreservedly supported. I would wish to express my special gratitude to Prof. Dr. Johannes Kollmann for acting as referee for this thesis.

I wish to express my special thanks to Prof. Dr. Jürgen Augustin for acting as co-referee of this thesis, for the opportunity to conduct the helium-incubation experiment at the laboratory of the ZALF and his support and help especially during the manuscript preparation and review process. His scientific knowledge contribute a lot to the success of this work.

Further I thank Prof. Dr. Hans Schnyder for acting as chairman of the examination committee.

I would like to thank Priv.-Doz. Dr. Harald Albrecht for stepping in to act as supervisor after the retirement of Prof. Dr. Jörg Pfadenhauer.

Most importantly, I want to express my gratitude with all my heart to my sister Dr. Nadine Eickenscheidt for her tireless support and help in all scientific questions, critical review of all manuscripts and belief in me. Without you, I would not have finished my PhD thesis. I am very grateful to Jan Heinichen, despite the high work load regarding his own PhD project, he gave tireless support during all the years of excessive field sampling and laboratory work, as well as during data analysis and manuscript preparations.

Furthermore, I like to emphasize the support of Annette Freibauer, especially her motivating and impressing way for writing scientific papers and her profound scientific knowledge, which distinctly improve the quality of the first two publications.

Special thanks deserve all my colleagues from the chairs of Vegetation ecology and Restoration ecology namely: Jan, Gawan, Jörg, Shom, Michael, Alicia, Martina, Christoph, Christine, Marika, Julia, Wolfram, Ingrid Kapps and Michaela Bücherl for their

great help during field- and laboratory work, the familiar atmosphere, unforgettable football matches and the special sense of humor which made the countless hours of field- and office work so comfortable.

Many thanks to all voluntary helpers, namely: Lukas Aberl, Helen Dizinger, Kevin Hose, Elsa Florentine Kündiger, Claudia Kurzböck, Melissa Mayer, Phillip Metzner, Björn Ridders, Lukas Rosenlöhner, Anna Steinert, Benedikt Springer, Moritz Then, Jonas Weng and Veronika Wolf as well as all student and “IAESTE” helpers for their support during field- and laboratory work.

Furthermore, I would like to thank Niko Roßkopf (Humboldt-Universität zu Berlin) for providing his data of soil parameters and soil description, Steffi Röhling for providing her data of tree growth from the alder forest as well as Enrico Frahm, Bärbel Tiemeyer and Michel Bechtold for providing DOC and DON concentrations and for processing data sets of groundwater time series.

I would further like to thank the landowners Georg Baumgartner, Ludwig Büchler and Josef Pellmeyer for the opportunity to conduct the measurements during the regular management as well for their excellent cooperation and help.

Besides my colleagues at work, there are several other very good friends, who contributed in their individual way to refresh my mind and help to gain new energy to finish this thesis. Special thanks to Florian, Sarah, Vroni, Torsten, Robert and the members of “Senioren gegen die Schwerkraft”.

I also like to thank Leif Nett for the critical review of this manuscript.

Last but not least, I wish to thank my parents Rosi and Hans for their unwavering support, love and for always being available to give me a hand.

## 7 APPENDIX

### 7.1 PUBLICATION I.



**Eickenscheidt, T.,** Heinichen, J., and Drösler, M.: The greenhouse gas balance of a drained fen peatland is mainly controlled by land-use rather than soil organic carbon content, *Biogeosciences Discuss.* (submitted for publication in *Biogeosciences*).

1 **The greenhouse gas balance of a drained fen peatland is**  
2 **mainly controlled by land-use rather than soil organic carbon**  
3 **content.**

4  
5 T. Eickenscheidt<sup>1,2</sup>, J. Heinichen<sup>1,2</sup>, M. Drösler<sup>1</sup>

6 [1] {University of Applied Sciences Weihenstephan-Triesdorf, Chair of Vegetation  
7 Ecology, Weihenstephaner Berg 4, 85354 Freising, Germany}

8 [2] {Technische Universität München, Chair of Restoration Ecology, Emil-Ramann-Str.  
9 6, 85354 Freising, Germany}

10  
11 Correspondence to: T. Eickenscheidt ([tim.eickenscheidt@hswt.de](mailto:tim.eickenscheidt@hswt.de))

12

### 13 Abstract

14 Drained organic soils are considered as hotspots for greenhouse gas (GHG) emissions.  
15 Particularly arable lands and intensively used grasslands have been regarded as the  
16 main producers of carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). However, GHG  
17 balances of former peatlands and associated organic soils not considered as peatland  
18 according to the definition of the Intergovernmental Panel on Climate Change (IPCC)  
19 have not been investigated so far. Therefore, our study addressed the question to what  
20 extent the soil organic carbon (SOC) content affects the GHG release of drained organic  
21 soils under two different land-use types (arable land and intensively used grassland).  
22 Both land-use types were established on a mollic Gleysol (named C<sub>medium</sub>) as well as on  
23 a sapric Histosol (named C<sub>high</sub>). The two soil types significantly differed in their SOC  
24 contents in the topsoil (C<sub>medium</sub>: 9.4–10.9% SOC; C<sub>high</sub>: 16.1–17.2% SOC). We  
25 determined GHG fluxes (CO<sub>2</sub>, N<sub>2</sub>O and methane (CH<sub>4</sub>)) over a period of 2 years. The  
26 daily and annual net ecosystem exchange (NEE) of CO<sub>2</sub> was determined with the closed  
27 dynamic chamber technique and by modeling the ecosystem respiration (R<sub>ECO</sub>) and the  
28 gross primary production (GPP). N<sub>2</sub>O and CH<sub>4</sub> were determined by the close chamber  
29 technique. Estimated NEE of CO<sub>2</sub> significantly differed between the two land-use types  
30 with lower NEE values (–6 to 1707 g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup>) at the arable sites and higher  
31 values (1354 to 1823 g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup>) at the grassland sites. No effect on NEE was  
32 found regarding the SOC content. Significantly higher annual N<sub>2</sub>O exchange rates were  
33 observed at the arable sites (0.23–0.86 g N m<sup>-2</sup> yr<sup>-1</sup>) compared to the grassland sites

34 (0.12–0.31 g N m<sup>-2</sup> yr<sup>-1</sup>). Furthermore, N<sub>2</sub>O fluxes from the C<sub>high</sub> sites significantly  
35 exceeded those of the C<sub>medium</sub> sites. CH<sub>4</sub> fluxes were found to be close to zero at all plots.  
36 Estimated global warming potential, calculated for a time horizon of 100 years (GWP<sub>100</sub>)  
37 revealed a very high release of GHGs from all plots ranging from 1837 to 7095 g CO<sub>2</sub> eq.  
38 m<sup>-2</sup> yr<sup>-1</sup>. Calculated global warming potential (GWP) values did not differ between soil  
39 types and partly exceeded the IPCC default emission factors of the Tier 1 approach by  
40 far. However, despite being subject to high uncertainties, the results clearly highlight the  
41 importance to adjust the IPCC guidelines for organic soils not falling under the definition,  
42 to avoid a significant underestimation of GHG emissions in the corresponding sectors of  
43 the national climate reporting. Furthermore, the present results revealed that mainly the  
44 land-use including the management and not the SOC content is responsible for the  
45 height of GHG exchange from intensive farming on drained organic soils.

46

## 47 **1.Introduction**

48 Natural peatlands act as a sink for atmospheric carbon dioxide (CO<sub>2</sub>) and as a source  
49 for methane (CH<sub>4</sub>) (Blodau, 2002; Whalen, 2005; Drösler et al., 2008). The net climate  
50 effect of natural peatlands regarding the greenhouse gas (GHG) fluxes, however, is  
51 close to zero (Drösler et al. 2008). In the last century, drainage and intensification of  
52 agriculture turned European peatlands to hot spots for GHG emissions (Drösler et al.,  
53 2008). Increased CO<sub>2</sub> and nitrous oxide (N<sub>2</sub>O) emissions have been observed from  
54 drained peatlands as a result of enhanced decomposition of organic matter (Martikainen  
55 et al., 1993, Silvola et al.,1996). The mentioned gases (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) act as  
56 climatic relevant greenhouse gases (IPCC, 2007). Additionally, N<sub>2</sub>O contributes to the  
57 chemical destruction of stratospheric ozone (Crutzen, 1979).

58 Through the ratification of several international agreements on climate protection (e.g.  
59 UNFCCC 1992, Kyoto protocol 1997 – specified by the Bonn Agreements and  
60 Marrakesh Accords, several EU decisions) Germany is obliged to publish annual  
61 national greenhouse gas emissions inventories according to the Intergovernmental  
62 Panel on Climate Change (IPCC) guidelines. However, the national climate reporting in  
63 the Land-use, Land-Use Change and Forestry (LULUCF) sector as well in the  
64 Agriculture, Forestry and Other Land-uses (AFOLU) sector is challenging for organic  
65 soils. This is mainly because reliable measurements of GHGs from temperate drained  
66 peatlands are rare and observed GHG fluxes show a large temporal and spatial  
67 variability ranging from –2 to 31 t CO<sub>2</sub>-C ha<sup>-1</sup> yr<sup>-1</sup> and 2 to 38 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> (IPCC,

2014). Furthermore, the definition of histosols is complex (Couwenberg, 2011) and several national and international classification systems exist for organic soils. For the climate reporting under LULUCF/AFOLU, the IPCC guidelines require at least  $\geq 10$  cm thickness of the soil/peat layer and a  $C_{org}$  content of  $\geq 12\%$  in case of a soil thickness  $\leq 20$  cm for peat soils. Thus, the IPCC definition of peat soils is broader than the definition of histosols in the world reference base for soil resources (WRB, 2008). In the German classification system (KA5) (Ad-hoc-AG Boden, 2005) a distinction is made between soil horizons with  $\geq 30\%$  soil organic matter (SOM) content (called organic horizon) and those containing 15–30% SOM (called anmoor horizon). Particularly at the boundary between mineral and organic soils, the conversion from SOM to  $C_{org}$  leads to uncertainties due to different conversion factors which are commonly used for mineral soils and peat soils according to the KA5 (Tiemeyer et al., 2013). Depending on the conversion factor (1.72 for mineral soils or 2 for peat soils), the maximum limit of IPCC requirement is between 21% and 24% SOM (Tiemeyer et al., 2013). Up to date, soils which are, by definition in the transition between mineral and organic soils were mostly neglected in the national GHG inventory of most countries (Leiber-Sauheitl et al., 2014). In the Danish greenhouse gas inventory, for example, GHG emissions from very thin and shallow organic soils, which do not meet the definition of organic soils according to the IPCC, were additionally considered. Due to a lack of information about the release of GHG emissions of those soils, a fixed emission factor, half as much as for typical organic soils ( $>12\% C_{org}$ ), has been introduced in Denmark for soils containing 6–12% organic carbon (Nielsen et al., 2012).

According to estimates, peatlands in Germany account for approximately 5.1% of the national GHG emissions although they only account for 5.1% of the total area (NIR, 2010; Drösler et al., 2011). Drained peatlands even represent the largest single source for GHG emissions outside the energy sector in Germany (Drösler et al., 2011; NIR, 2010). Hence, according to the IPCC guidelines, drained peatlands are identified as key category which leads to the fact that Germany is obligated to calculate the annual GHG emission inventory on the basis of national specific emission factors (EF; Tier 2 or Tier 3 methods). The main reason for the critical climate balance is caused by the fact that more than two-thirds of the German peatlands are intensively used as grassland or arable land (Drösler et al., 2008). Both land-use types have been regarded as the main producers of  $CO_2$  and  $N_2O$  from farmed organic soils (Kasimir-Klemedtsson et al., 1997; Kroeze et al., 1999; Drösler et al., 2008; International Peat Society, 2008). Highest GHG

102 emissions from drained organic soils were related to management activities such as  
103 tillage and fertilization which enhance microbial SOM decomposition and nitrogen  
104 turnover (Kandel et al., 2013). Beside management practices, several other physical and  
105 chemical factors control the intensity of mineralization processes (Heller and Zeitz, 2012)  
106 in which soil temperature and soil moisture are considered to be the primary regulators  
107 for CO<sub>2</sub> emissions from soils (Silvola et al. 1996; Maljanen et al., 2001; Hardie et al.,  
108 2011). However, recent studies have shown that in particular the SOM quality and its  
109 labile and more recalcitrant fractions act as key variables affecting the decomposability  
110 of SOM and thus control CO<sub>2</sub> fluxes from peatlands (Byrne and Farrell, 2005; Heller and  
111 Zeitz, 2012; Leifeld et al., 2012). Beside the macromolecular organic composition (e.g.  
112 polysaccharides, lignin, aliphatic biopolymers) of the peat forming vegetation, the SOM  
113 quality of peat strongly depends on hydrological and geomorphological building  
114 conditions during peat formation (Heller and Zeitz, 2012). Additionally, peat and SOM  
115 quality is strongly affected by human impact which leads to peat shrinking, secondary  
116 decomposition and mineralization (Heller and Zeitz, 2012). It can be assumed that with  
117 increasing peat humification, aggregation and organo-mineral association gain in  
118 importance in the SOM stabilization and thus decrease the CO<sub>2</sub> emissions from peat  
119 soils which are by definition in the transition between mineral soils and peat compared  
120 to peat soils with higher SOM content. However, those soils were mostly neglected and  
121 to our knowledge no GHG studies exist for such soil types under intensive agricultural  
122 land-use.

123 The objective of this study was to quantify GHG emissions from arable lands and  
124 grasslands on two types of drained organic soils with different C<sub>org</sub> contents in South  
125 Germany. We hypothesize: i) that GHG emissions significantly increase with increasing  
126 SOC content in the soil and ii) that GHG emissions from arable soils exceed GHG  
127 emissions from intensive managed grassland soils.

128

## 129 **2. Material and methods**

### 130 **3. Study area and experimental design**

131 The study was conducted at a drained fen peatland 30 km north-east of Munich  
132 (Freisinger Moos, 48°21'N, 11°41'E; 450 m a.s.l.). Since 1914 the Freisinger Moos (FSM)  
133 was systematically drained for intensive cultivation (Zehlius-Eckert et al., 2003). Today  
134 about 40% of the whole area is used as grassland and 20% as arable land (Schober et  
135 al., 2008).

136 According to the climate station in Weißenstephan, located 10 km northeast of the study  
137 sites, the 30-years mean annual temperature was 7.5 °C and the mean annual  
138 precipitation was 787 mm (1961–1990). Annual atmospheric N deposition amounted to  
139 6.22 and 7.20 kg N ha<sup>-1</sup> yr<sup>-1</sup> in 2010 and 2011. Data of N deposition was collected by  
140 the Bavarian State Institute of Forestry at a German Level II monitoring plot (Forest  
141 Intensive Monitoring Programme of the UNECE), located in 7 km distance to the  
142 investigated sites.

143 In October 2009, we selected two adjacent areas, one used as intensive grassland and  
144 the other as arable land. Both areas are characterized by a distinct gradient in their soil  
145 organic carbon (SOC) content in the top soil (Table 1), which increases from southeast  
146 to northwest. In March 2010 the arable land was split into two equal halves to simulate  
147 two different crop rotations (maize (*Zea mays*) and oat (*Avena sativa*); see Table 2)  
148 along the SOC gradient (named A1 and A2). At the grassland area a similar design was  
149 conducted to investigate the effect of two different organic fertilizers (named G1,  
150 fertilized with cattle slurry and G2, fertilized with biogas digestate). Within these areas  
151 we selected two sites with maximum different SOC contents per land-use (Fig. 1).  
152 According to the WRB (2006), soil types at the sites were classified as mollic Gleysol  
153 (named C<sub>medium</sub>) or as sapric Histosol (named C<sub>high</sub>) (N. Roßkopf personal  
154 communication, 2010). At each site two plots were selected according to the  
155 management type (Fig. 1). A detailed description of the experimental design of the  
156 grassland sites and the chemical and physical composition of the applied fertilizers is  
157 given in Eickenscheidt et al. (2014b). The arable land was managed according to organic  
158 farming criteria but without any fertilization during the investigated period.

159 At each plot, three PVC-collars for GHG measurements (inside dimension 75 x 75 cm)  
160 were permanently inserted 10 cm into the soil with a distance of 1.5–2 m to each other.  
161 In case of management activities, collars were removed for a short period at the arable  
162 land. To prevent oscillations of the peat through movements during the measurements,  
163 boardwalks were installed. In March 2010, climate stations were centrally set up  
164 between two identical land-use and soil types for the continuously recording (every 0.5  
165 hour) of air temperature (T<sub>air</sub>) and humidity at 20 cm above soil surface, soil temperatures  
166 at the depth –2, –5 and –10 cm (ST<sub>2, 5, 10</sub>) and soil moisture content at –5 cm depth. In  
167 addition, two further climate stations, additionally equipped with air temperature in 200  
168 cm above soil surface and photosynthetic active radiation (PAR) sensors were operated  
169 in close proximity to the investigated areas. For measuring the groundwater table, plastic

170 perforated tubes (JK-casings DN 50, 60 mm diameter, 1 m length) were inserted close  
171 to each collar for plot-specific measurements of groundwater (GW) tables during gas  
172 flux measurements at the grassland plots. At the arable land only three tubes were  
173 inserted between the two plots of the same soil type. In April 2010, we equipped one  
174 tube per plot or, in case of the arable land one tube per soil type, with a water level  
175 logger (Type MiniDiver, Schlumberger water services), which recorded the water tables  
176 every 15 minutes. Additionally to the recorded data, plot-specific soil temperatures in  
177 three soil depths (-2, -5 and -10 cm) were determined with penetration thermometers  
178 at the beginning and end of each gas flux measurement.

179

#### 180 **4.Crop yield, soil sampling and laboratory analyses**

181 Crop yield was determined by harvesting the biomass inside the PVC-collars with a  
182 scissor at each harvesting event (same cutting height as the farmers) (Table 2). To  
183 determine the annual crop yield, grass samples were oven dried at 60°C for 48 hours  
184 and phytomasses of each harvesting event per year were summed. To determine the  
185 total carbon ( $C_{\text{tot}}$ ) and total nitrogen ( $N_{\text{tot}}$ ) content, total phytomasses was milled (0.5 mm)  
186 and a pooled and homogenized sample from each PVC-collar and harvesting event was  
187 analysed by the AGROLAB Labor GmbH (Bruckberg, Germany).

188 Mineral N ( $N_{\text{min}} = \text{NH}_4^+-\text{N} + \text{NO}_3^--\text{N}$ ) contents of each plot were determined according  
189 to VDLUFA (1997). Samples were taken during every  $\text{CH}_4/\text{N}_2\text{O}$  gas flux measurement.  
190 For the determination of  $C_{\text{tot}}$  and organic carbon ( $C_{\text{org}}$ ), a mixed soil sample of nine  
191 individual samples was collected close to each collar at two soil depths (0–10, 10–20  
192 cm) using a 3 cm diameter auger. After drying for 72 hours at 40 °C, soil samples were  
193 sieved to 2 mm to remove stones and living roots. Analyses were conducted at the  
194 Division of Soil Science and Site Science (Humboldt Universität zu Berlin, Germany). For  
195 the determination of bulk density and porosity, three undisturbed core cutter samples  
196 ( $100 \text{ cm}^3$ ) were randomly taken at four depths (0–5, 5–10, 10–15, 15–20 cm) for each  
197 plot.

198

#### 199 **5.GHG measurements**

200 We measured fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  every second week from December 2009 to  
201 January 2012 using the static manual chamber method (Livingston and Hutchinson;  
202 1995). In periods when the vegetation grew higher than the chamber height was (0.5 m),  
203 extensions were used between the collar and chamber (white, opaque, volume varied

204 between 309 and 1236 L). A detailed description of chamber dimension and  
205 configuration is given in Drösler (2005). N<sub>2</sub>O and CH<sub>4</sub> gas flux rates were calculated  
206 from the linear change in gas concentration over time (four gas samples; 60 min  
207 enclosure time, 120 min in case of two or more extensions) considering chamber air  
208 temperature and atmospheric pressure. Gas fluxes were accepted when the linear  
209 regression was significant ( $P \leq 0.05$ ). In case of small N<sub>2</sub>O or CH<sub>4</sub> fluxes, fluxes were  
210 also accepted if the coefficient of determination was  $\geq 0.90$  and the regression slope  
211 was between  $-1$  and  $1 \text{ ppb min}^{-1}$ . The cumulative annual mean exchange rate was  
212 calculated by linear interpolation between the measurement dates. To minimize diurnal  
213 variation in the flux pattern, N<sub>2</sub>O and CH<sub>4</sub> sampling was always carried out between 9.00  
214 a.m. and 11.30 a.m. We removed the gas fluxes measured in 2010 from the data set  
215 due to errors in the gas chromatography analysis and due to long vial storage. A detailed  
216 description of gas sampling and gas chromatograph settings is given in Eickenscheidt  
217 et al. (2014a and 2014b).

218 For CO<sub>2</sub> flux measurements we used the closed dynamic manual chamber system which  
219 was described in detail by Drösler (2005) and Elsgaard et al. (2012). CO<sub>2</sub> measurement  
220 campaigns took place in irregular time intervals depending on weather conditions,  
221 management activities and the phenological stage of plants (Table S1–S8 in the  
222 Supplement). Measurement campaigns always started one hour before sunrise and  
223 lasted till late afternoon to cover the full range of the photosynthetic active radiation (PAR)  
224 and air and soil temperature. Opaque and transparent chambers (same dimension as  
225 for N<sub>2</sub>O and CH<sub>4</sub> measurements) were alternately used at each of the three collars per  
226 plot during the time course of a measurement campaign to obtain the ecosystem  
227 respiration ( $R_{\text{ECO}}$ ) and the net ecosystem exchange (NEE). In total up to 55 NEE  
228 measurements and 33  $R_{\text{ECO}}$  measurements were conducted per measurement day and  
229 plot (Table S1–S8 in the Supplement). As for N<sub>2</sub>O and CH<sub>4</sub> measurements, extensions  
230 were installed between the collar and chamber in case of vegetation growing higher than  
231 the chamber height was (transparent or opaque, volume varied between 309 and 1236  
232 L). Chambers were connected to an infrared gas analyser (IRGA, LI-820, LI-COR, USA),  
233 which continuously determined the CO<sub>2</sub> headspace concentration. In the case that  
234 extensions were used, chamber air from each level of an extension (every 0.5 m) was  
235 sucked and merged to guarantee a reliable mixture signal from inside the chamber.  
236 Additionally, three fans (SUNON® Super Silence MAGLev®-Lüfter) continuously  
237 operated during the measurement to ensure a constant mixing of the chamber air.

238 Chamber enclosure time was 120 s for transparent chambers and 240 s for opaque  
 239 chambers, respectively. The CO<sub>2</sub> concentration, air temperature from inside the  
 240 chamber and site specific PAR was recorded every 5 s with a data logger (GP1 Data  
 241 logger, Delta-T Devices, UK). To prevent heating of the air in the transparent chambers,  
 242 freezer packs (1–10 pieces) were positioned in the air stream of the fans at the inner  
 243 surface of the PVC collar (Drösler, 2005; Beetz et al., 2013). Single measurements  
 244 where the PAR changed more than 15% of the starting value or the temperature inside  
 245 the chamber increased more than 1.5 °C compared to the outside air temperature were  
 246 discarded and measurement was repeated (Leiber-Sauheitl et al., 2014). CO<sub>2</sub> gas fluxes  
 247 were calculated by linear regression. Non significant gas fluxes ( $P \geq 0.05$ ) with slopes  
 248 close to zero or zero (equilibrium between GPP and R<sub>ECO</sub>) were not discarded (Alm et  
 249 al., 2007; Leiber-Sauheitl et al., 2014). For NEE flux calculation, a minimum time interval  
 250 of 25 s was used, whereas for R<sub>ECO</sub> fluxes a minimum interval of 60 s was applied.

251

## 252 **6. Modeling of CO<sub>2</sub> net ecosystem exchange**

253 The net ecosystem exchange (NEE) of CO<sub>2</sub> is defined as the product of the gross  
 254 primary production (GPP) and the ecosystem respiration (R<sub>ECO</sub>) (Chapin et al., 2006).

255

$$256 \quad NEE = GPP + R_{ECO} \quad (1)$$

257

258 In the present study we followed the atmospheric sign convention in which a positive  
 259 NEE is defined as a net flux of CO<sub>2</sub> to the atmosphere (Elsgaard et al., 2012).

260

## 261 **7. Modeling of ecosystem respiration**

262 The measured R<sub>ECO</sub> fluxes are the sum of autotrophic (R<sub>a</sub>) and heterotrophic (R<sub>h</sub>)  
 263 respiration. Both compartments are mainly controlled by temperature (Lloyd and Taylor,  
 264 1994; Tjoelker et al., 2001). For each measurement campaign and plot the dependency  
 265 between R<sub>ECO</sub> and temperature was modeled according to Lloyd and Taylor (1994) who  
 266 developed an Arrhenius type relationship to predict soil respiration rates (Eq. 2).

$$267 \quad R_{ECO} = R_{ref} \cdot e^{\frac{E_0}{T_{ref} - T_0} - \frac{1}{T - T_0}} \quad (2)$$

268  $R_{ECO}$  ecosystem respiration [mg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>]

269  $R_{ref}$  respiration at the reference temperature [mg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>]

270  $E_0$  activation energy [K]

271  $T_{ref}$  reference temperature: 283.15 [K]

272	$T_0$	temperature constant for the start of biological processes: 227.13 [K]
273	$T$	air or soil temperature [K]
274		

275 In response to the phenological stage of the plants, management activities or changing  
 276 soil moisture conditions, the applied temperature as explanatory variable could change  
 277 during the year. Therefore, the  $R_{ECO}$  model was fitted to the appropriate temperature  
 278 type (air temperature in 20 cm or soil temperature in -2, -5 or -10 cm) which showed  
 279 the best explanatory power for  $R_{ECO}$ . In case that the temperature span was too small  
 280 for model building (e.g. winter time, snow cover) or a significant relationship between the  
 281 temperature and  $R_{ECO}$  could not be observed (e.g. after ploughing), an average  $CO_2$  flux  
 282 was calculated for the measurement campaign. Annual sums of  $R_{ECO}$  were calculated by  
 283 summing 0.5 hourly  $R_{ECO}$  fluxes recalculated from Eq. (2), based on the linear  
 284 interpolated parameters  $R_{ref}$  and  $E_0$  of two consecutive measurement campaigns and the  
 285 continuous time series of air and soil temperatures (Elsgaard et al., 2012). In case of  
 286 management events (e.g. harvesting, plugging, etc.) or snow cover,  $R_{ref}$  and  $E_0$  were kept  
 287 constant from the previous measurement campaign until the management date. After  
 288 the management, parameters were taken from the subsequent measurement campaign  
 289 (Leiber-Sauheithl et al., 2013). However, in case of harvesting at the grassland plots,  
 290 estimated parameters were linearly interpolated over this period. Estimated parameters  
 291 and used temperatures for  $R_{ECO}$  are shown in Table S1 to S8.

292

### 293 **8. Modeling of gross primary production**

294 We estimated GPP as the product of measured NEE minus modeled  $R_{ECO}$  at the same  
 295 time step, since it is not possible to determine GPP through measurements. The  
 296 relationship between GPP and PAR was modeled by a Michaelis-Menten type  
 297 rectangular hyperbolic function proposed by Falge et al (2001) (Eq. 3).

$$298 \quad GPP = \frac{\alpha \cdot PAR}{\left(1 - \left(\frac{PAR}{2000}\right) + \left(\frac{\alpha \cdot PAR}{GPP_{2000}}\right)\right)} \quad (3)$$

299	$GPP$	gross primary production [ $mg\ CO_2-C\ m^{-2}\ h^{-1}$ ]
300	$\alpha$	initial slope of the curve; light use efficiency [ $mg\ CO_2-C\ m^{-2}\ h^{-1}/\mu mol\ m^{-2}\ s^{-1}$ ]
301	$PAR$	photon flux density of the photosynthetic active radiation [ $\mu mol\ m^{-2}\ s^{-1}$ ]
302	$GPP_{2000}$	gross primary production at PAR 2000 [ $mg\ CO_2-C\ m^{-2}\ h^{-1}$ ]
303		

304 Prior to modeling GPP, we corrected the plot specific PAR values since the acrylic glass  
 305 of the transparent chambers absorbed at least 5% of the incoming radiation (PS-plastic,

306 Eching, Germany) (Leiber-Sauheitl et al., 2014). Annual sums of *GPP* were calculated  
307 based on the linear interpolation of  $\alpha$  and  $GPP_{2000}$  between two consecutive  
308 measurement campaigns and the continuous time series of the PAR (Drösler, 2005;  
309 Elsgaard et al., 2012). In case of management events (e.g. harvesting, plugging, etc.)  $\alpha$   
310 and  $GPP_{2000}$  were kept constant from the preceding measurement until the management  
311 time and were set to zero at the 0.5 hour time step during the working process.  
312 Thereafter, parameters were immediately linearly interpolated from the subsequent  
313 measurement campaign for the grassland plots. For the arable land plots, parameter  
314 interpolation started after the establishment of the seed. Estimated parameters are  
315 shown in Table S1 to S8 in the Supplement.

316

### 317 **9. Model evaluation and uncertainties analysis**

318 For  $R_{ECO}$  and NEE model evaluation, we used Pearson's correlation coefficient ( $r$ ), Nash-  
319 Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970), percent bias (PBIAS) and the ratio  
320 of the root mean square error to the standard deviation of measured data (RSR) (Moriassi  
321 et al., 2007). According to Moriassi et al. (2007) model simulation can be judged as  
322 satisfactory if  $NSE > 0.50$  and  $RSR \leq 0.70$ . For PBIAS, the optimal value is 0.0, with low-  
323 magnitude values indicating accurate model simulation. Additionally, positive PBIAS  
324 values indicate model underestimation bias, and negative values indicate model  
325 overestimation bias (Gupta et al., 1999; Moriassi et al., 2007). To account for the  
326 uncertainties in annual  $R_{ECO}$  and annual GPP modeling, annual sums from the upper  
327 and lower limits of the determined parameters ( $R_{ref}$ ,  $E_0$ ,  $\alpha$ ,  $GPP_{2000}$ ), based on their  
328 standard errors (SE) were estimated (Drösler, 2005; Elsgaard et al., 2012). However,  
329 quantifying total model uncertainties is challenging because of the multiple sources of  
330 errors (Beetz et al., 2013) and due to a lack of independent data for gap-filling verification.  
331 The main uncertainty in the present study may derive from management activities where  
332 no additional measurements were conducted and parameters were kept constant (e.g.  
333  $R_{ref}$  and  $E_0$  at the grassland) or set to zero (e.g.  $\alpha$  and  $GPP_{2000}$  at the grassland).

334

### 335 **10. Estimation of NECB and GWP**

336 A simple net ecosystem carbon balance (NECB) was calculated for each plot based on  
337 the NEE, the carbon export of harvested phytomass, the carbon input through organic  
338 fertilizer application and the cumulative annual  $CH_4$  exchange (Elsgaard et al., 2012;  
339 Beetz et al., 2013).

340 To assess the global warming potential (GWP) from the different plots the net emissions  
341 of carbon equivalents of NECB and N<sub>2</sub>O were summed according to Beetz et al (2013).  
342 For the conversion of CH<sub>4</sub> and N<sub>2</sub>O to CO<sub>2</sub> equivalents, radiative forcing factors of 25  
343 and 298 were used (Forster et al., 2007).

344

## 345 **11. Statistical analyses**

346 Statistical analyses were conducted using R 3.0.1 (R Development Core Team, 2013).  
347 The assumption of normality of residuals was tested using the Lilliefors or Shapiro-Wilk  
348 test and by plotting the Quantile-Quantile plots. Homogeneity of variances of residuals  
349 was checked using the Levene or Breusch-Pagan test and by plotting the residuals  
350 against the fitted values. Where necessary, data were box-cox transformed prior to  
351 analyses. For the comparison of cumulative modeled GPP, R<sub>ECO</sub> and NEE as well as for  
352 annual yields and N<sub>min</sub> values we used a two-factorial ANOVA with land-use and soil  
353 type as fixed effects (including an interaction term in the model), neglecting the individual  
354 plot specific standard error for modeled CO<sub>2</sub> values. Non-significant terms were removed  
355 from the model structure. In case of significant differences among the means, we used  
356 Tukey's honest significant differences (TukeyHSD). For GW level we used the  
357 nonparametric Kruskal-Wallis Rank Sum test and the non-parametric Pairwise Wilcoxon  
358 Rank Sum test with Bonferroni correction for multiple comparisons. For testing two  
359 independent sample means regarding the two investigated years 2010 and 2011, we  
360 use the Welch two sample t-test (C<sub>org</sub> contents, bulk density, yields) or the non  
361 parametric Mann-Whitney U-test (for N<sub>min</sub>). Due to temporal pseudoreplication of time  
362 series data (N<sub>2</sub>O, CH<sub>4</sub> field measurements) we applied linear mixed effects models  
363 (Crawley 2007; Hahn-Schöfl et al., 2011; Eickenscheidt et al., 2014a and 2014b). For  
364 N<sub>2</sub>O fluxes we set up a basic model with land-use type and soil type as fixed effects and  
365 the spatial replication (individual plot) nested in time as random effect. We extended the  
366 basic model by a variance function due to observed heteroscedasticity. Furthermore,  
367 N<sub>2</sub>O fluxes showed significant serial correlation. To take this into account, a first-order  
368 temporal autoregressive function was included in the model. Autocorrelation was tested  
369 using the Durbin-Watson test and by plotting the empirical autocorrelation structure. The  
370 model extension was proved by the Akaike Information Criterion (AIC). For multiple  
371 comparisons we conducted Tukey contrasts using the General Linear Hypotheses  
372 function from the "multcomp" package (Hothorn et al., 2013). CH<sub>4</sub> fluxes did not satisfy  
373 the necessary requirements for the linear mixed effects model therefore CH<sub>4</sub> analysis

374 were restricted to the nonparametric Mann-Whitney U-test. We accepted significant  
375 differences if  $P \leq 0.05$ . Results in the text are given as means  $\pm$  1 standard deviation.

376

## 377 **12.Results**

### 378 **13.Environmental variables**

379 Temperatures between the two investigated land-use types and soil types did not differ  
380 considerably. In 2010 and 2011, air temperature in 20 cm height ranged from  $-17.5$  to  
381  $39.5^{\circ}\text{C}$  with an annual mean of  $8.6^{\circ}\text{C}$  at both grassland sites in 2011. Soil temperature  
382 in  $-2$  cm soil depth averaged  $10.3^{\circ}\text{C}$  at the  $\text{GC}_{\text{medium}}$  site and  $10.5^{\circ}\text{C}$  at the  $\text{GC}_{\text{high}}$  site  
383 in 2011. At the arable land air temperature in 20 cm height ranged from  $-15.0$  to  $39.5^{\circ}\text{C}$   
384 in 2010 and 2011, with an annual mean of  $8.8^{\circ}\text{C}$   $\text{AC}_{\text{medium}}$  and  $8.7^{\circ}\text{C}$   $\text{AC}_{\text{high}}$  in 2011. Soil  
385 temperature in  $-2$  cm soil depth averaged  $10.1^{\circ}\text{C}$  at both arable land sites in 2011.  
386 Longer periods of snow cover occurred in the period 1<sup>st</sup> of January to 12<sup>th</sup> of March 2010,  
387 28<sup>th</sup> of November 2010 to 10<sup>th</sup> of January 2011 and from 24<sup>th</sup> of January to 5<sup>th</sup> of  
388 February 2011 (see also Fig. 4 and Fig. 5). In 2011, the annual sum of PAR was 17%  
389 higher compared to the year 2010. Annual precipitation amounted to 850 mm (2010)  
390 and 841 mm (2011) in the investigated period, which was slightly above the 30-years  
391 mean of the period 1961–1990. Mean annual groundwater levels of the  $\text{C}_{\text{high}}$  sites were  
392 significantly higher (all  $P < 0.001$ ) compared to the  $\text{C}_{\text{medium}}$  sites in 2010 and 2011  
393 (Table 1). Furthermore the GW level at the arable sites were significantly higher (all  $P <$   
394  $0.001$ ) compared to the grassland sites in both investigated years. Longer periods of  
395 flooding and water saturation were only observed at the  $\text{AC}_{\text{high}}$  sites for the period from  
396 1<sup>st</sup> to 17<sup>th</sup> June 2010.

397

### 398 **14.Soil properties and mineral nitrogen contents**

399 Total organic carbon contents and bulk density in the 0–10 cm and 10–20 cm soil layers  
400 significantly (all  $P < 0.01$ ) differed between the two soil types investigated (Table 1). At  
401 the grassland sites pH values in the 0–20 cm soil layer were approximately one decade  
402 lower compared to the arable land (Table 1). Observed C/N ratios at the soil depth 0–20  
403 cm were between 10 and 12 (Table 1), indicating nitrogen-rich conditions at all plots.  
404 Extractable  $\text{N}_{\text{min}}$  contents of the soils ranged from 1 to  $178 \text{ mg N kg}^{-1}$  at the arable sites  
405 and from 2 to  $115 \text{ mg N kg}^{-1}$  at the grassland sites (Fig. 2, Fig 3). In both years, the  $\text{N}_{\text{min}}$   
406 contents at the grassland sites significantly ( $P < 0.001$ ) exceeded those from the arable  
407 site (Fig. 3). Furthermore the  $\text{N}_{\text{min}}$  contents of the  $\text{C}_{\text{high}}$  sites were significantly ( $P < 0.01$ )

408 higher compared to the  $C_{\text{medium}}$  sites (Fig. 3), but this was not valid considering the arable  
409 land separately. Slightly higher  $N_{\text{min}}$  contents were found at the soil depth 10–20 cm  
410 compared to the soil depth 0–10 cm, but differences were only significant for the  
411 grassland sites ( $P < 0.05$ ). In both years,  $N_{\text{min}}$  was mainly dominated by  $\text{NO}_3^-$ , whereas  
412  $\text{NH}_4^+$  was only of minor importance. However, at the  $AC_{\text{high}}$  sites the proportion of  $\text{NO}_3^-$   
413 in the soil depth 0–10 cm was lower (approximately 80%) compared to the  $AC_{\text{medium}}$  sites  
414 (approximately 97%), whereas at the grassland sites no differences were found between  
415 the two soil types investigated (91–95%).

416

### 417 **15. Biomass yield**

418 The mean annual crop yield ranged from  $1.2 \pm 0.5$  to  $10.2 \pm 1.6$  t DM ha<sup>-1</sup> yr<sup>-1</sup> at the  
419 arable land and from  $6.2 \pm 0.7$  to  $13.1 \pm 2.9$  t DM ha<sup>-1</sup> yr<sup>-1</sup> at the grassland in 2010 and  
420 2011 (see also Eickenscheidt et al., 2014b) (Table 3). For both land-use types the crop  
421 yield was significantly ( $P < 0.01$ ) lower in the year 2010 compared to the year 2011 (73%  
422 at the A sites and 52% at the G sites). However, it has to be taken into consideration  
423 that at the grassland sites three instead of two cuts were carried out in 2011. At the  
424 arable land a longer period with partially flooding and high water saturation damaged or  
425 partly killed the maize seedlings as well as the oat plants in June 2010, especially at the  
426  $C_{\text{high}}$  sites. Furthermore, in 2010 the entire plants were harvested and used as silo maize  
427 or oat corn and straw respectively, whereas in 2011 only the grains were harvested  
428 regarding both management practices and the remaining plants were left on the field. In  
429 both years investigated, the yield from the grassland sites significantly exceeded those  
430 from the arable land (all  $P < 0.001$ ), whereas no significant differences were found  
431 between the two soil types observed.

432

### 433 **16. CO<sub>2</sub> fluxes**

434 The modeling showed that the air temperature in 20 cm above soil surface and soil  
435 temperature in –2 cm are the main drivers of  $R_{\text{ECO}}$  in the present study, while soil  
436 temperatures in –5 cm and –10 cm soil depth mostly showed distinctly weaker  
437 correlations (Table S1-S8 in the Supplement). At the arable land, 88% of the calculated  
438 models based on  $T_{\text{air}}$ , and only 12% on  $ST_2$ , whereas at the grassland sites 54% of the  
439 models based on  $T_{\text{air}}$  and 39% on  $ST_2$ . Model evaluation statistics from observed  $R_{\text{ECO}}$   
440 versus modeled  $R_{\text{ECO}}$  generally revealed a good model performance with a slight  
441 tendency of model overestimation bias for the year 2010 (mean PBIAS –2.39).

442 Pearson's correlations coefficients for observed  $R_{ECO}$  versus modeled  $R_{ECO}$  ranged  
443 between 0.89 and 0.98, NSE values ranged from 0.70 to 0.97 and RSR values were  $\leq$   
444 0.55 (Table 4, Fig. S3–S4 in the Supplement). According to the annual temperature trend,  
445  $R_{ECO}$  showed a clear seasonality with maximum flux rates during the summer time. In  
446 2010, highest daily  $R_{ECO}$  fluxes of up to  $41 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  were modeled at the  
447  $A2C_{\text{medium}}$  (oat) and  $G1C_{\text{medium}}$  plot, whereas in 2011, distinctly lower maximum daily  
448  $R_{ECO}$  fluxes of up to  $28 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  and  $32 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  were modeled for the  
449  $A2C_{\text{high}}$  (maize) plot and the  $G2C_{\text{high}}$  plot, respectively (Fig. 4 and 5). At the grassland  
450 sites, annual sums of modeled  $R_{ECO}$  ranged from  $3521 \pm 1041$  to  $4316 \pm 562 \text{ g CO}_2\text{-C}$   
451  $\text{m}^{-2} \text{ yr}^{-1}$ , which was significantly ( $P < 0.001$ ) higher compared to the arable sites where  
452  $R_{ECO}$  ranged from  $2012 \pm 284$  to  $2992 \pm 230 \text{ g CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$  (Table 3, Fig. 6a).  
453 Differences in  $R_{ECO}$  between the two soil types investigated were only small and not  
454 significantly different (Fig.6a).

455 Like  $R_{ECO}$ , GPP showed a clear seasonal trend with increasing  $\text{CO}_2$  uptake capacity with  
456 increasing PAR intensity in summer time. In 2010, highest maximum daily GPP of up to  
457  $-25 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  were modeled for the arable land (maize,  $C_{\text{medium}}$ ) and up to  $-20 \text{ g}$   
458  $\text{CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  for the grassland ( $G2C_{\text{high}}$ ), whereas in 2011, distinctly higher GPP values  
459 up to  $-35 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$  were modeled for both maize plots and up to  $-28 \text{ g CO}_2\text{-C}$   
460  $\text{m}^{-2} \text{ d}^{-1}$  for the  $G2C_{\text{high}}$  plot (Fig. 4 and 5). At the grassland sites annual sums of GPP  
461 ranged between  $-2093 \pm 152$  and  $-2962 \pm 178 \text{ g CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$ , which was significantly  
462 ( $P < 0.01$ ) higher compared to the arable sites where GPP ranged between  $-873 \pm 110$   
463 and  $-2360 \pm 237 \text{ g CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$  (Table 3, Fig 6b). Differences in GPP between the  
464 two soil types were not significant.

465 Calculated NEE were in good agreement with observed NEE (Fig. S1 and S2 in the  
466 Supplement). Nevertheless, the calculated percent bias revealed a tendency of model  
467 overestimation for both years (mean PBIAS  $-7.5$  in 2010 and  $-6.1$  in 2011). Pearson's  
468 correlations coefficients for observed NEE versus calculated NEE ranged from 0.79 to  
469 0.98, NSE values ranged from 0.61 to 0.96 (Table 5). The mean RSR values was 0.36.  
470 Annual NEE significantly ( $P < 0.01$ ) differed between the two land-use types with lower  
471 NEE values at the arable sites, ranging from  $-6 \pm 546$  to  $1707 \pm 619 \text{ g CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$ ,  
472 compared to the grassland sites where NEE ranged from  $1354 \pm 740$  to  $1823 \pm 851 \text{ g}$   
473  $\text{CO}_2\text{-C m}^{-2} \text{ yr}^{-1}$  (Table 3, Fig 6c). Differences between the two soil types were not  
474 significant for NEE.

475

**476 17.N<sub>2</sub>O and CH<sub>4</sub> fluxes**

477 Nitrous oxide emissions were generally low at all plots (Fig 7). N<sub>2</sub>O fluxes rarely  
478 exceeded 50 µg N m<sup>-2</sup> h<sup>-1</sup>. However, single N<sub>2</sub>O peaks with maximum flux rates of up  
479 to 2832 µg N m<sup>-2</sup> h<sup>-1</sup> were detected at the 3<sup>rd</sup> June at both maize plots as well as at the  
480 6<sup>th</sup> of September at both oat plots with maximum flux rates of up to 289 µg N m<sup>-2</sup> h<sup>-1</sup>. At  
481 the grassland sites, highest N<sub>2</sub>O fluxes of up to 992 µg N m<sup>-2</sup> h<sup>-1</sup> were found immediately  
482 after fertilizer application (see Eickenscheidt et al., 2014b). In general, N<sub>2</sub>O fluxes from  
483 the arable sites were significantly ( $P < 0.01$ ) higher compared to the grassland sites (Fig.  
484 8a). Furthermore, N<sub>2</sub>O fluxes from the C<sub>high</sub> sites significantly ( $P < 0.05$ ) exceeded N<sub>2</sub>O  
485 fluxes from the C<sub>medium</sub> sites, but this was not valid considering the arable land separately.  
486 Significant differences within the land-use types, regarding N<sub>2</sub>O flux rates, were only  
487 found between the grassland plots, where the application of biogas digestate  
488 significantly ( $P < 0.01$ ) enhanced the N<sub>2</sub>O fluxes compared to the application of cattle  
489 slurry (see Eickenscheidt et al., 2014b). At the arable land distinctly different N<sub>2</sub>O flux  
490 rates between maize and oat were not found, but the single peak emissions observed  
491 led to significantly ( $P < 0.01$ ) higher annual cumulative N<sub>2</sub>O emissions at the maize plots  
492 (Table 3, Fig 8a). N<sub>2</sub>O peaks accounted for 75% and 87% of the annual N<sub>2</sub>O balances  
493 at the maize plots, whereas at the oat plots peaks account for 63% and 54% of the  
494 annual N<sub>2</sub>O sums (at C<sub>medium</sub> and C<sub>high</sub>, respectively). Annual cumulative N<sub>2</sub>O emissions  
495 ranged from  $0.12 \pm 0.01$  g N m<sup>-2</sup> yr<sup>-1</sup> (G1C<sub>medium</sub>) to  $0.86 \pm 0.21$  g N m<sup>-2</sup> yr<sup>-1</sup> (A2C<sub>high</sub>)  
496 (Table 3).

497 Most of the time, all sites showed a weak uptake of CH<sub>4</sub> or zero fluxes. CH<sub>4</sub> peaks up to  
498 173 µg C m<sup>-2</sup> h<sup>-1</sup> were occasionally found immediately after fertilization at the G1 sites  
499 (see Eickenscheidt et al., 2014b). Moreover, a high CH<sub>4</sub> peak event of up to 2177 µg C  
500 m<sup>-2</sup> h<sup>-1</sup> occurred on the 14<sup>th</sup> of July 2011 at the oat plots. Generally, CH<sub>4</sub> fluxes of the  
501 arable sites significantly ( $P < 0.01$ ) exceeded CH<sub>4</sub> fluxes of the grassland sites, whereas  
502 no differences were found between the two soil types investigated (Fig 7, and 8b).  
503 Significantly different CH<sub>4</sub> fluxes within the land-use types could not be observed  
504 regarding the annual fluxes in 2011. However, considering the annual cumulative  
505 exchange rates, CH<sub>4</sub> emissions of the oat plots significantly ( $P < 0.05$ ) exceeded those  
506 of the maize plots. The observed weak CH<sub>4</sub> emissions or uptakes amounted to  
507 cumulative annual CH<sub>4</sub> exchange rates ranging between  $-0.11 \pm 0.05$  g C m<sup>-2</sup> yr<sup>-1</sup>  
508 (G2C<sub>medium</sub>) and  $0.51 \pm 0.17$  g C m<sup>-2</sup> yr<sup>-1</sup> (A1C<sub>medium</sub>) (Table 3). However, as previously  
509 mentioned for N<sub>2</sub>O, the single CH<sub>4</sub> peak event observed at the arable sites entirely

510 controls the cumulative sum of CH<sub>4</sub> and turns the plots from a sink into a source of CH<sub>4</sub>.

511

## 512 **18.NECB and GWP**

513 Including the C export from harvested phytomass, C import from fertilization and CH<sub>4</sub>  
514 exchange to NEE, calculated NECB ranged from  $451 \pm 617$  to  $1894 \pm 872$  g C m<sup>-2</sup> yr<sup>-1</sup>.

515 Estimated GWP's ranged from  $1837 \pm 2293$  to  $7095 \pm 3243$  g CO<sub>2eq.</sub> m<sup>-2</sup> yr<sup>-1</sup>, revealing  
516 a very high release of greenhouse gases from all plots (Table 6). However, CO<sub>2</sub>  
517 dominated the GWP of all plot to nearly 100% (range between 97–99% and for maize  
518 86–90%), whereas the contribution of N<sub>2</sub>O and CH<sub>4</sub> were almost negligible, with  
519 exception of the maize plots.

520

## 521 **19.Discussion**

### 522 **20.Magnitude of GHG fluxes**

523 The observed annual CO<sub>2</sub> emissions were in the upper range or partly higher than CO<sub>2</sub>  
524 exchange rates reported in the literature from temperate drained arable lands (e.g.  
525 Maljanen et al., 2001 and 2007; Grønlund et al., 2008; Höper et al., 2008; Maljanen et  
526 al., 2010; Leifeld et al., 2011; Elsgaard et al., 2012; Drösler et al., 2013) and grasslands  
527 (e.g. Maljanen et al., 2001; Grønlund et al., 2006 and 2008; Maljanen et al., 2010;  
528 Elsgaard et al., 2012; Beetz et al., 2013; Drösler et al., 2013; Leifeld et al., 2014; Renou-  
529 Wilson et al., 2014). No differences in the CO<sub>2</sub> release of the C<sub>medium</sub> and C<sub>high</sub> sites were  
530 found in the current study, and no information about CO<sub>2</sub> fluxes of comparable soils to  
531 those of the C<sub>medium</sub> sites were available in the literature. Observed CO<sub>2</sub> emissions from  
532 the arable land were in the range or partly doubled ( $4.51$ – $12.04$  t CO<sub>2</sub>-C ha yr<sup>-1</sup>) the  
533 IPCC default emission factor from the Tier 1 approach for drained boreal and temperate  
534 arable lands ( $7.9$  t CO<sub>2</sub>-C ha yr<sup>-1</sup>; IPCC, 2014) whereas more than three times higher  
535 CO<sub>2</sub> emissions were observed at the grassland sites ( $15.81$ – $18.94$  t CO<sub>2</sub>-C ha yr<sup>-1</sup>)  
536 compared to the IPCC default emission factor for deep-drained temperate grasslands  
537 ( $6.1$  t CO<sub>2</sub>-C ha yr<sup>-1</sup>; IPCC, 2014). However, comparison of CO<sub>2</sub> exchange rates is  
538 difficult since annual variability is very high. For example Leifeld et al. (2014) reported  
539 that the NECB of a temperate grassland in Germany ranged from  $0.98$  to  $19.46$  t C ha<sup>-1</sup>  
540 yr<sup>-1</sup>, with a five year mean of  $9.06 \pm 6.64$  t C ha<sup>-1</sup> yr<sup>-1</sup>. In this study the highest value  
541 was observed for the period 2010 to 2011 which was in good agreement with the values  
542 estimated by us during this period. The finding is also in line with Kasimir-Klemendtsson  
543 et al. (1997), who reported net CO<sub>2</sub> exchange rates ranging from  $2.2$  to  $31.3$  t C ha<sup>-1</sup> yr<sup>-1</sup>

544 for farmed organic soils, demonstrating the high bandwidth of measured CO<sub>2</sub>-balances.  
545 Observed cumulative annual N<sub>2</sub>O emissions were distinctly lower than the default  
546 emission factor from the Tier 1 approach for boreal and temperate, drained arable land  
547 (13 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>; IPCC. 2014) and for temperate deep drained, nutrient rich  
548 grassland (8.2 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>; IPCC. 2014). In line with this, several other authors  
549 reported much higher N<sub>2</sub>O emissions from organic soils ranging from 0 to 61 kg N<sub>2</sub>O-N  
550 ha<sup>-1</sup> yr<sup>-1</sup> for arable lands (Kasimir-Klemendtsson et al., 1997; Augustin et al., 1998;  
551 Flessa et al., 1998; Petersen et al., 2012; Drösler et al., 2013) and ranging from 1.15 to  
552 41 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> for grasslands (Velthof et al., 1996; Augustin et al., 1998; Flessa  
553 et al., 1997 and 1998; van Beek et al., 2010 and 2011; Kroon et al., 2010; Petersen et  
554 al., 2012; Beetz et al., 2013; Drösler et al., 2013).

555 As expected, observed CH<sub>4</sub> fluxes from all plots were low, which is in line with generally  
556 low groundwater levels and the absence of aerenchymous plant species which can  
557 transport CH<sub>4</sub> from an anaerobic layer to the atmosphere, bypassing the oxic zone at  
558 the soil surface (Grosse et al., 1992; Svensson & Sundh, 1992; Wahlen, 2005).  
559 Cumulative annual CH<sub>4</sub> emissions or uptakes were in the range reported for other deep  
560 drained arable lands and grasslands (Maljanen et al., 2010; Petersen et al., 2012; Beetz  
561 et al., 2013; Drösler et al., 2013; Renou-Wilson et al., 2014) and fit also well with the  
562 IPCC default emission factor for boreal and temperate drained arable land (0 kg CH<sub>4</sub>  
563 ha<sup>-1</sup> yr<sup>-1</sup>; IPCC, 2014). A distinctly higher emission factor however is given by the IPCC  
564 for a temperate deep-drained, nutrient-rich grassland (16 kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup>; IPCC, 2014)  
565 compared to our estimations.

566

## 567 **21.Uncertainties in GHG fluxes and modeling**

568 Several factors probably influenced the accuracy of estimated CO<sub>2</sub> exchange rates.  
569 Firstly, the R<sub>Eco</sub> model based only on temperature changes disregarding the effect of  
570 soil moisture or GW level. Thus changing soil moisture contents or GW levels between  
571 two consecutive measurements campaigns were neglected since we assume a linear  
572 change in derived model parameters (see also Beetz et al., 2013 and Leiber-Sauheitl et  
573 al., 2014). Secondly, management activities like ploughing at the arable sites probably  
574 produced peak CO<sub>2</sub> emissions, which we may have missed. Additionally, it can be  
575 assumed that after harvesting at the grassland sites, R<sub>Eco</sub> decreased due to the reduced  
576 phytomass. However, additional measurement campaigns to capture this effect did not  
577 take place in the current study and no corresponding data were found in the literature.

578 Furthermore, it is well known that the application of organic fertilizers produced short-  
579 term CO<sub>2</sub> emission peaks, which were also not sufficiently detected. However, both  
580 sources of errors may even have an opposite effect. Thirdly for GPP, linearly  
581 interpolation of parameters produced some uncertainties since it can be assumed that  
582 plant growth after cutting did not increase linearly (Horrocks and Valentine, 1999; Beetz  
583 et al., 2013). However with the available data set, it was not possible to quantify the error  
584 by the used interpolation approach of parameters since the dataset was too small for  
585 cross validation and no additional measurements for an independent model validation  
586 were conducted. In addition, despite high model accuracy, the calculated PBIAS  
587 revealed a slightly model overestimation bias for R<sub>ECO</sub> and NEE for both years (R<sub>ECO</sub>  
588 only in 2010). Thus, modeled R<sub>ECO</sub> and calculated NEE rates should be considered as  
589 a conservative estimation. However, modeled values fit well with values reported in the  
590 literature (see Figure 9).

591 Several studies indicated that dissolved organic C can significantly contribute to  
592 terrestrial C balances (e.g. Worrall et al., 2009; Dinsmore et al., 2010 Renou-Wilson et  
593 al., 2014). Thus, for the calculation of NECB from drained organic soils, fluvial C losses  
594 should additionally be considered in future investigations.

595 Observed N<sub>2</sub>O fluxes showed a high temporal variability with long periods of low  
596 background emissions and a few high peaks, mainly after management activities.  
597 Measurement frequency was increased after fertilization at the grassland plots for at  
598 least two weeks (see Eickenscheidt et al., 2014b) but due to our regular measurement  
599 intervals in the remaining year we cannot rule out that we may have missed high N<sub>2</sub>O  
600 events driven by changing climate conditions (e.g. drying–rain or freeze–thaw events)  
601 and/or management activities, particularly at the arable sites. N<sub>2</sub>O peaks are known to  
602 last a couple of days up to several weeks (Stolk et al., 2011). Due to our measurement  
603 intervals and interpolation approach, observed N<sub>2</sub>O and CH<sub>4</sub> peaks distinctly altered the  
604 cumulative annual budgets, increasing the overall uncertainties in estimated GHG  
605 emissions. However, for future investigations in GHG emissions we strongly advocate  
606 the combined use of automatic and manual chamber systems to maintain a higher  
607 accuracy of data.

608

609

## 610 **22. Soil organic carbon effects**

611 With exception of N<sub>2</sub>O, significantly different GHG emissions between the two soil types

612 investigated were not found in the present study, although significantly different SOC  
613 contents in the upper soil horizon were detected. The observation is in strong contrast  
614 to our hypothesis that GHG emissions significantly increase with increasing SOM  
615 content (hypothesis i).

616 Regarding CO<sub>2</sub> fluxes, the current findings are however in line with investigations from  
617 Leiber-Sauheitl et al. (2014), who reported that CO<sub>2</sub> emissions were not related to  
618 different SOM contents in the upper horizon of an extensive grassland in North Germany.  
619 Contrary, Veenendaal et al. (2007) and Renou-Wilson et al. (2014) assumed that their  
620 different estimated respiration rates for grassland sites were driven by different  
621 SOC/SOM contents. However, it can be assumed that not only the SOM content itself  
622 acts as a key factor controlling the CO<sub>2</sub> release, but the proportion of SOM which is  
623 exposed to mineralization, which in turn is driven by drainage depth. Therefore we  
624 calculated the effective C stock as the fraction of aerated carbon in the soil profile  
625 according to Leiber-Sauheitl et al. (2014) (Fig. 10). No relationship was found between  
626 the effective C stock and the C flux components (expressed as NECB), which was also  
627 reported by Leiber-Sauheitl et al. (2014) and Tiemeyer et al. (2014). However, Fig. 10  
628 shows that at the grassland sites, C stocks available for mineralization processes are  
629 comparable (40–45 kg C m<sup>-2</sup>), probably explaining the equal CO<sub>2</sub> loss rates from this  
630 land-use type. Temperature and soil moisture are considered to be the primary  
631 regulators for CO<sub>2</sub> emissions from soils (Silvola et al. 1996; Maljanen et al., 2001; Hardie  
632 et al., 2011), since they directly affect microbial activity and the rate of enzymatic  
633 processes (Michaelis and Menten, 1913; Tietema et al., 1992). In the present study,  
634 temperatures are found to be equal at all sites due to their close proximity, whereas the  
635 soil moisture contents significantly differed between the C<sub>high</sub> and C<sub>medium</sub> sites mainly  
636 according to the GW oscillation. It is well known that the water level height has a strong  
637 influence on CO<sub>2</sub> emissions from peatlands as it directly affects the oxygen availability  
638 for microbial activity as was reported in several studies (e.g. Silvola et al., 1996; Berglund  
639 and Berglund, 2011; Renou-Wilson et al., 2014; Leiber-Sauheitl et al., 2014). Beside  
640 abiotic factors substrate chemistry, in particular the SOM quality and its labile and more  
641 recalcitrant fractions, are considered to act as key variables affecting the  
642 decomposability of SOM and thus controlling CO<sub>2</sub> fluxes from peatlands (Byrne and  
643 Farrell, 2005; Heller and Zeitz, 2012; Leifeld et al., 2012). For example, Leifeld et al.  
644 (2012) showed that the soil respiration rate of a disturbed temperate peatland was  
645 strongly controlled by its polysaccharides content, particularly the O-alkyl-C content was

646 found to be a useful proxy for respiration rates. SOM quality was not examined in our  
647 study, but both soil types at all plots investigated exhibited highly decomposed organic  
648 material (H10, according to Von Post's humification scale; N. Roßkopf personal  
649 communication, 2013). This is typical for organic soils which have been drained and  
650 intensively managed for a long time, and is in line with Leifeld et al. (2012), who found  
651 that organic matter quality declines with ongoing decomposition, resulting in low  
652 polysaccharides contents and a lower sensitivity for heterotrophic metabolism.  
653 Nevertheless, observed NECB revealed very high C loss rates from the SOC pool.  
654 Leifeld et al. (2014) suggested that intensive management, drainage and changed  
655 climate drivers accelerate peat decomposition today, and therefore outweighed  
656 declining peat quality. Additionally, Reiche et al. (2010) reported that the degree of  
657 humification is not suitable for the prediction of CO<sub>2</sub> and CH<sub>4</sub> fluxes from anaerobic  
658 decomposition, which stands in contrast to assumptions made by Glatzel et al. (2004).  
659 However, observed equal narrow C/N ratios (10–12) in the upper soil reveal firstly a high  
660 organic matter quality, easily to mineralize, and secondly comparable SOM qualities at  
661 all plots, probably explaining why no significantly different C loss rates between the two  
662 different soil types were found in the present study.

663 In line with CO<sub>2</sub>, CH<sub>4</sub> fluxes were also not different between the two soil types  
664 investigated, but this can mainly be attributed to the intensive drainage and thus soil  
665 aeration, which effectively inhibited microbial methanogenesis at the C<sub>medium</sub> and C<sub>high</sub>  
666 sites. It is known that the availability and quality of organic substrates influences the  
667 amount of produced CH<sub>4</sub>. Nevertheless, several studies indicate that high CH<sub>4</sub> fluxes in  
668 bogs are mainly controlled by labile organic substrates such as root exudates or plant  
669 litter and not by bulk peat (Minchin & McNaughton, 1984; Chanton et al., 1995; Bridgman  
670 et al., 1998; Wahlen, 2005; Hahn-Schöfl et al., 2011).

671 In contrast to CO<sub>2</sub> and CH<sub>4</sub> fluxes, N<sub>2</sub>O fluxes from the C<sub>high</sub> sites significantly exceeded  
672 N<sub>2</sub>O fluxes from the C<sub>medium</sub> sites. This can probably be attributed to the more favorable  
673 soil conditions for denitrification, supported by higher N<sub>min</sub> contents and higher  
674 groundwater levels at these sites (Eickenscheidt et al., 2014b). In both years N<sub>min</sub> was  
675 mainly dominated by NO<sub>3</sub><sup>-</sup>, demonstrating that net nitrification entirely controls net  
676 nitrogen mineralization at all plots. Thus, nitrification provided the substrate for  
677 denitrification and additionally, may itself have contributed to N<sub>2</sub>O production. In general,  
678 N<sub>2</sub>O production processes are various and can occur simultaneously within close  
679 proximity (Davidson et al., 1986; Butterbach-Bahl et al., 2013). Both nitrification as well

680 as denitrification depending on the availability of labile organic compounds as C and/or  
681 energy source (Butterbach-Bahl et al., 2013). However, for denitrification the actual  
682 regulation by C is currently not yet understood (Baggs and Philippot, 2011), but it can  
683 be assumed that sufficient metabolizable C was widely available at all plots investigated.

684

### 685 **23.Land-use and management effects**

686 At peatlands GW level and land-use type are closely linked. From a meta-analysis of 53  
687 German peatlands Tiemeyer et al. (2013) found that the mean annual GW level was  
688 lower for arable land than for intensive grassland with median GW levels of  
689 approximately –70 and –37 cm above soil surface. The GW levels observed in our study  
690 were on average lower at the arable land and higher at the grassland compared with the  
691 average of the meta-analysis. In general, intensive farming at peatlands presupposes  
692 low GW levels, since most of the arable crops are not adapted to low oxygen contents  
693 in the rhizosphere as could be seen in the present study, were the temporarily high GW  
694 level caused plant damage and yield losses at the arable sites in 2010. The effect of  
695 reduced biomass productivity due to high GW levels which inhibited photosynthesis by  
696 slowing the rate of gas diffusion through the vegetation (Lohila, 2008) was also reported  
697 by Renou-Wilson et al. (2014). Both annual sums of GPP as well as yields were in good  
698 agreement with those reported from other peatlands as can be seen in Figure 9.  
699 Statistical analysis revealed significantly higher yields at the grassland sites compared  
700 to the arable sites, but it has to be taken into account that at the arable sites only the  
701 grains were harvested in 2011 and up to 3.84 t DM ha<sup>-1</sup> and 9.05 t DM ha<sup>-1</sup> remained  
702 on the field regarding the oat and maize plots, respectively. Due to the continuous plant  
703 cover over the whole year at the grassland plots annual sums of GPP were significantly  
704 higher at these plots compared to the arable plots in 2010 as well as in 2011.

705 As GPP, modeled annual sums of R<sub>ECO</sub> significantly differed between the two land-use  
706 types with distinctly higher R<sub>ECO</sub> values at the grassland sites. As mentioned above, R<sub>ECO</sub>  
707 is strongly controlled by temperature since it stimulates both R<sub>a</sub> and R<sub>h</sub>, as can be seen  
708 in the pronounced seasonality of R<sub>ECO</sub>. From the model fits it can be concluded that the  
709 more frequent model adaptation with T<sub>air</sub> (88%) reveals a higher share of R<sub>a</sub> at the arable  
710 site compared to the grassland sites. At the later, approximately 40% of the R<sub>ECO</sub> models  
711 based on ST<sub>2</sub>, perhaps demonstrating a more balanced ratio of R<sub>a</sub> and R<sub>h</sub>. Nevertheless,  
712 the proportion of the different respiration compartments of R<sub>ECO</sub> is unknown, but Silvola  
713 et al. (1996) reported that root-derived respiration from grasslands established on

714 peatland accounted for 35–45% of total soil respiration. Furthermore, Maljanen et al.  
715 (2001) found that root-associated respiration on grasslands was distinctly higher  
716 compared to arable lands. However, the significantly higher  $R_{ECO}$  at the grassland sites  
717 can firstly perhaps be related to the higher biomass production at these sites, because  
718 a higher GPP also results in higher above- and below-ground autotrophic respiration  
719 (Leiber-Sauheitl et al., 2014; Renou-Wilson et al., 2014). Moreover, the increased  
720 transport of photosynthates to the plant rhizosphere due to the higher GPP may favor  
721 bacterial metabolism through increased root exudates (Mounier et al., 2004; Henry et  
722 al., 2008; Sey et al., 2010), additionally enhancing  $R_h$ . Secondly, the organic fertilizer  
723 application at the grassland plots stimulates microbial growth and thus SOM  
724 mineralization (Gutser et al., 2005; Jones et al., 2007). Additionally, a large part of the  
725 C from the organic fertilizer will quickly be metabolized to  $CO_2$  (Vuichard et al., 2007).  
726 Several authors (see e.g. Dao, 1998; Maljanen et al., 2010) reported that regularly  
727 ploughed and fertilized arable lands are larger sources of  $CO_2$  than non-tilled arable land  
728 soils or grasslands, due to aerating and mixing of crop residues into the soil. However,  
729 in the current study the effect of management is difficult to capture.

730 Despite of higher modeled GPP values, the distinctly higher modeled  $R_{ECO}$  values led to  
731 significantly higher calculated NEE values at the grassland sites compared to the arable  
732 sites. With the exception of the maize plot at the  $C_{medium}$  site in the year 2011, all plots  
733 show positive NEE balances in both years investigated, as expected for drained organic  
734 soils and as commonly reported in the literature (e.g. Maljanen et al., 2001; Grønlund et  
735 al., 2006 and 2008; Maljanen et al., 2010; Elsgaard et al., 2012; Beetz et al., 2013;  
736 Drösler et al., 2013). However, the huge  $CO_2$  uptake capacity during the short growth  
737 period of the maize plants, compensates for the soil  $CO_2$  release due to microbial  
738 decomposition of organic matter at least in the year 2010. Nevertheless, as seen in the  
739 NECB, the C export also reversed the maize cultivation on the  $C_{medium}$  site to a C source.

740 Previous studies of annual NEE from maize on organic soils are rare in literature, but  
741 our results are in line with Drösler et al. (2013) who reported NEE values ranging from  
742  $-216.2$  to  $443.8$  g C  $m^{-2}$   $yr^{-1}$ . As mentioned above, it has to be take into account that in  
743 the year 2011 only the grains were harvested at all arable plots. Assuming that silage  
744 maize would have been produced instead of maize grains or the straw was additionally  
745 harvested at the oat plots, NECB would partly be doubled and more comparable to  
746 calculated grassland values.

747 According to Maljanen et al. (2010) the better aeration of regularly ploughed arable land

748 leads to a larger sink of atmospheric CH<sub>4</sub> compared to permanent grasslands. This  
749 contrasted our results, where the CH<sub>4</sub> fluxes from the arable plots significantly exceeded  
750 CH<sub>4</sub> fluxes from the grassland plots. However, all measured CH<sub>4</sub> fluxes were very low  
751 and CH<sub>4</sub> emissions and uptakes were almost negligible in the NECB of the plots, as was  
752 also reported by several other authors for drained organic soils (e.g. Maljanen et al.,  
753 2010; Petersen et al., 2012; Schäfer et al., 2012; Drösler et al., 2013; Renou-Wilson et  
754 al., 2014). Moreover, the C import through fertilization contributed only marginally (3–  
755 14%) to the NECB of the grassland plots.

756 In the course of the present study, fertilization was found to enhance N<sub>2</sub>O fluxes at the  
757 grassland sites, where the application of biogas digestate led to significantly higher N<sub>2</sub>O  
758 emissions compared to cattle slurry application (for further discussion see Eickenscheidt  
759 et al., 2014b). From a meta-study of European organic soils Leppelt et al. (2014) found  
760 that the amount of N fertilizer was directly linked to N<sub>2</sub>O fluxes from grasslands, whereas  
761 no significant relationship between N fertilization and N<sub>2</sub>O fluxes from arable lands were  
762 found. Nevertheless, N<sub>2</sub>O fluxes from the arable plots significantly exceeded those of  
763 the grassland sites, as was also reported by Maljanen et al. (2007 and 2010) and  
764 Petersen et al. (2012) and additionally confirmed by Leppelt et al. (2014) for European  
765 organic soils. Observed N<sub>2</sub>O peaks at the arable sites can be related to harvesting and/or  
766 several consecutive tillage steps (e.g. ploughing, milling, mattocking) in the previous  
767 weeks. This is in line with Silvan et al. (2005) who supposed that higher N<sub>2</sub>O fluxes from  
768 arable lands are related to the higher N availability for microbial denitrification in the  
769 absence of plants. No fertilizer was applied at the arable plots, which is also reflected in  
770 the significantly lower N<sub>min</sub> contents and perhaps higher pH values compared to the  
771 grassland plots. However, it is well known that drainage and intensive management  
772 enhanced the degradation of SOM and thus stimulates net nitrogen mineralization and  
773 nitrogen transformation processes (Kasimir Klemetsson et al., 1997; Freibauer et al.,  
774 2004; Goldberg et al., 2010). Several authors reported an annual N supply through peat  
775 mineralization of approximately 70–425 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Schothorst, 1977; Flessa et al.,  
776 1998; Sonneveld and Lantinga, 2011; Leppelt et al., 2014). Taking into account the  
777 calculated soil carbon losses and plot specific C/N ratios of the upper soil/peat layer,  
778 estimated SOM mineralization leads to an annual N supply of approximately 451–1720  
779 kg N ha<sup>-1</sup> yr<sup>-1</sup>. This estimation seems very high but regardless of the high uncertainties  
780 it clearly indicates that sufficient N must be available for nitrification and denitrification,  
781 independent of fertilizer application as previously assumed by Leppelt et al. (2014).

782 Furthermore, the admixture of *Vicia sativa* or *Vicia faba minor*, both N<sub>2</sub> fixing  
783 leguminoses further increase the soil N<sub>min</sub> pool of the arable sites through the release of  
784 N-rich root exudates (Rochette et al. 2004; Sey et al., 2010) as well as their incorporation  
785 into the soil, albeit to an unknown extent.

786 In conclusion, taking together estimated GHG emissions, calculated GWPs clearly differ  
787 between the two land-use types investigated with distinctly higher GWP's observed at  
788 the grassland plots compared to the arable land. However, all plots show a very high  
789 release of GHGs, demonstrating the unsustainable agricultural use of drained organic  
790 soils and the current need for the implementation of mitigation strategies and restoration  
791 measures. We hypothesized that GHG emissions from arable soils exceed GHG  
792 emissions from intensively managed grassland soils. The contrary was found in the  
793 present study; therefore we have to reject hypothesis ii. However, from the present  
794 results it can be concluded that mainly the management and not the land-use type itself  
795 or the SOC content is responsible for the amount of released GHGs from intensive  
796 farming on drained organic soils.

797

#### 798 **24. Implications for the climate reporting under LULUCF/AFOLU**

799 For the climate reporting under LULUCF/AFOLU, the IPCC guidelines consider GHG  
800 emissions from peat soils having at least ≥10 cm thickness of the soil/peat layer and a  
801 C<sub>org</sub> content of ≥12% in case of a soil thickness ≤20 cm. However, the intensive  
802 cultivation of organic soils leads to a continuous decrease in the amount of SOM and  
803 thus the area of soils which fulfil the requirements of the IPCC guidelines for organic  
804 soils rapidly declined in the last decades. For example Nielsen et al. (2012) reported an  
805 average annual decrease of organic soils of approximately 1400 ha in Denmark since  
806 1975. The remaining soils often contain >6% C<sub>org</sub> and not the required >12% (Nielsen et  
807 al., 2012). Contrary to mineral soils or natural peatlands in equilibrium, Nielsen et al.  
808 (2012) assume that drained and managed soils having >6% C<sub>org</sub> will evidently lose  
809 carbon until a new equilibrium is reached. Since no data was available in literature for  
810 those soils, Nielsen et al. (2012) decided to allocate an fixed emission factor half of the  
811 amount of what was measured for soils having >12% C<sub>org</sub> to account for these losses in  
812 the Danish greenhouse gas inventory. However, despite being subject to high  
813 uncertainties, our results reveal that the GHG emission potential of soils intermediate  
814 between mineral and organic soils can be as high or partly higher as for typical drained  
815 organic soils under intensive agricultural use. This is in line with observations from

816 Leiber-Sauheitl et al. (2013) for extensive grasslands. To avoid a significant  
817 underestimation of GHG emissions in the LULUCF/AFOLU sector, there is a  
818 corresponding need to adjust the IPCC guidelines for drained inland organic soils  
819 accordingly. The new 2013 Supplement to the IPCC guidelines for national GHG  
820 inventories on wetlands distinguishes several emission factors for different land-use  
821 types, climate regions, nutrient status and drainage intensities (IPCC, 2014). We  
822 suggest establishing a further category which provides emission factors for different  
823 land-use types on former drained peatlands or associated organic soils, which do not  
824 fulfil the necessary requirements of typical organic soils but also contain high amounts  
825 of C<sub>org</sub>. To define reliable emissions factors for those soils further investigations  
826 regarding their potential to release GHGs are needed. Furthermore, it has to be clarified  
827 to what extent the composition of the SOM is responsible for the magnitude of GHG  
828 release from drained organic soils.

829

## 830 **25.Conclusion**

831 This study presents estimations of GHG fluxes from arable lands and intensive  
832 grasslands on sapric Histosol and mollic Gleysol, which significantly differed in their SOC  
833 content in the top soil. The present results clearly revealed that like typical drained  
834 peatlands also drained mollic Gleysols can be considered as hotspots for GHG  
835 emissions, provided that they are intensively managed as arable land or grassland.  
836 However, observed GHG fluxes revealed a very high sensitivity against changing key  
837 factors like climate variables (e.g. temperature, precipitation) and management.  
838 Estimated GHG emission factors partly more than doubled the emission factor of the  
839 Tier 1 approach of the IPCC independent of the SOC content in the topsoil. Thus former  
840 peatlands and associated organic soils, containing <12% C<sub>org</sub> should be integrated in  
841 the national GHG emission inventories to avoid a significant underestimation in the  
842 climate reporting. Moreover there is a current need to adjust the IPCC guidelines for  
843 drained inland organic soils accordingly. Besides climate reporting, the observed very  
844 high release of GHGs demonstrates the unsustainable agricultural use of drained  
845 organic soils and the current need for rapid implementation of mitigation strategies and  
846 restoration measures.

847

## 848 **26.Acknowledgements**

849 We thank the landowners Georg Baumgartner, Ludwig Büchler and Josef Pellmeyer for

850 the opportunity to conduct the measurements during the regular management as well  
851 for their excellent cooperation and help. Furthermore we would thank Niko Roßkopf  
852 (Humboldt-Universität zu Berlin) for soil description as well as Stephan Raspe from the  
853 Bavarian State Institute of Forestry for providing the N deposition data. Further the  
854 authors thank Nadine Eickenscheidt (Thünen Institute) for helpful discussion and critical  
855 review as well as all voluntary and student helpers, namely: Lukas Aberl, Kevin Hose,  
856 Elsa Florentine Kündiger, Claudia Kurzböck, Melissa Mayer, Phillip Metzner, Björn  
857 Ridders, Anna Steinert, Benedikt Springer, Moritz Then and Jonas Weng for their help  
858 during field work. The publication was supported by the German Research Foundation  
859 (DFG) and the Technische Universität München (TUM) within the funding programme  
860 Open Access Publishing. This study was part of the joint research project ‘Organic soils’;  
861 Acquisition and development of methods, activity data and emission factors for the  
862 climate reporting under LULUCF/AFOLU, founded by the Thünen Institute.

863

## 864 **27. References**

- 865 Ad-Hoc AG Boden: Bodenkundliche Kartieranleitung, 5. Aufl., Schweizerbart'sche  
866 Verlagsbuchhandlung, Hannover, 438 pp., 2005.
- 867  
868 Alm, J., Shurpali, N. J., Tuittila, E.-S., Laurila, T., Maljanen, M., Saarnio, S., and  
869 Minkinen, K.: Methods for determining emission factors for the use of peat and  
870 peatlands – flux measurements and modeling, *Boreal Environ. Res.*, 12, 85–100, 2007.
- 871  
872 Augustin, J., Merbach, W., Steffens, L., and Snelinski, B.: Nitrous Oxide Fluxes of  
873 Disturbed Minerotrophic Peatlands, *Agribiol. Res.*, 51 (1), 47–57, 1998.
- 874  
875 Baggs, E.M., and Philippot, L.: Nitrous oxide production in the terrestrial environment,  
876 *Nitrogen Cycl. In Bacteria: Molecular Analysis*, 211–232, Caister Academic Press,  
877 England, 2011.
- 878  
879 Beek van, C.L., Pleijter, M., Jacobs, C.M.J., Velthof, G.L., van Groenigen, J.W., and  
880 Kuikman, P.J.: Emissions of N<sub>2</sub>O from fertilized and grazed grassland on organic soil in  
881 relation to groundwater level, *Nutr. Cycl. Agroecosyst.*, 86, 331–340, 2010.
- 882  
883 Beek van, C.L., Pleijter, M., and Kuikman, P.J.: Nitrous oxide emissions from fertilized  
884 and unfertilized grasslands on peat soil, *Nutr. Cycl. Agroecosyst.*, 89, 453–461, 2011.
- 885  
886 Beetz, S., Liebersbach, H., Glatzel, S., Jurasinski, G., Buczko, U., and Höper, H.: Effects  
887 of land-use intensity on the full greenhouse gas balance in an Atlantic peat bog,  
888 *Biogeosciences*, 10, 1067–1082, doi:10.5194/bg-10-1067-2013, 2013.
- 889  
890 Berglund, Ö., and Berglund, K.: Influence of water table level and soil properties on  
891 emissions of greenhouse gases from cultivated peat soil, *Soil Biology and Biochemistry*,  
892 43(5), 923–931, 2011.
- 893

- 894 Blodau, C.: Carbon cycling in peatlands – A review of processes and controls, *Environ.*  
895 *Rev.*, 10, 111–134, 2002.
- 896
- 897 Bridgman, S.D., Updegraff, K., and Pastor, J.: Carbon, nitrogen, and phosphorus  
898 mineralization in northern wetlands, *Ecology*, 79(5), 1545–1561, 1998,  
899
- 900 Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R., Zechmeister-Boltenstern,  
901 S.: Nitrous oxide emissions from soils: how well do we understand the processes and  
902 their controls?, *Phil trans R Soc B*, 368:20130122, 2013.
- 903
- 904 Byrne, K.A., and Farrell, E.P.: The effect of afforestation on soil carbon dioxide  
905 emissions in blanket peatland in Ireland, *Forestry*, 78, 217–227,  
906 doi:10.1093/forestry/cpi020, 2005.
- 907
- 908 Byrne, K. A., Chojnicki, B., Christensen, T. R., Drösler, M., Freibauer, A., Friborg, T.,  
909 Frolking, S., Lindroth, A., Mailhammer, J., Malmer, N., Selin, P., Turunen, J., Valentini,  
910 R., and Zetterberg, L.: EU peatlands: Current carbon stocks and trace gas fluxes, *Carbo-*  
911 *Europe-GHG Concerted Action-Synthesis of the European Greenhouse Gas Budget,*  
912 *Report, 4, 2004.*
- 913
- 914 Chanton, J.P., Bauer, J.E., Glaser, P.A., Siegel, D.I., Kelley, C.A., Tyler, S.C.,  
915 Romanowicz, E.H., and Lazrus, A.: Radiocarbon evidence for the substrates supporting  
916 methane formation within northern Minnesota peatlands, *Geochimica et Cosmochimica*  
917 *Acta*, 59(17), 3663–3668, 1995.
- 918
- 919 Chapin, F. S., Woodwell, G. M., Randerson, J. T., Rastetter, E. B., Lovett, G. M.,  
920 Baldocchi, D. D., Clark, D. A., Harmon, M. E., Schimel, D. S., Valentini, R., Wirth, C.,  
921 Aber, J. D., Cole, J. J., Goulden, M. L., Harden, J. W., Heimann, M., Howarth, R. W.,  
922 Matson, P. A., McGuire, A. D., Melillo, J. M., Mooney, H. A., Neff, J. C., Houghton, R. A.,  
923 Pace, M. L., Ryan, M. G., Running, S. W., Sala, O. E., Schlesinger, W. H., and Schulze,  
924 E.-D.: Reconciling Carbon-cycle Concepts, Terminology, and Methods, *Ecosystems*, 9,  
925 1041–1050, 2006.
- 926
- 927 Couwenberg, J.: Greenhouse gas emissions from managed peat soils: is the IPCC  
928 reporting guidance realistic, *Mires and Peat*, 8, 1–10, 2011.
- 929
- 930 Crutzen, P.J.: the role of NO and NO<sub>2</sub> in the chemistry of the troposphere and  
931 stratosphere, *Annu. Rev. Earth Planet. Sci.*, 7 (1), 443–472, 1979.
- 932
- 933 Crawley, M. J.: *The R Book*, John Wiley and Sons Ltd, Chichester, p. 942, 2007.
- 934
- 935 Dao, T.H.: Tillage and crop residue effects on carbon dioxide evolution and carbon  
936 storage in a paleustoll, *Soil Science Society of America Journal*, 62, 250–256, 1998.
- 937
- 938 Davidson, E.A., Swank, W.T., and Perry, T.O.: Distinguishing between nitrification and  
939 denitrification as sources of gaseous nitrogen production in soil, *Applied and*  
940 *Environmental Microbiology*, 52 (6), 1280–1286, 1986.
- 941
- 942 Dinsmore, K. J., Billet, M. F., Skiba, U. M., Rees, R. M., Drewer, J., and Helfter, C.: Role  
943 of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland  
944 catchment, *Glob. Change Biol.*, 16, 2750–2762, 2010.

- 945  
946 Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems, Southern  
947 Germany, PhD thesis, Chair of Vegetation Ecology, Department of Ecology, Technical  
948 University Munich, p. 179, 2005.
- 949  
950 Drösler, M., Freibauer, A., Christensen, T. and Friborg, T.: Observation and status of  
951 peatland greenhouse gas emission in Europe, In: Dolman, H., Valentini, R. & Freibauer,  
952 A. (eds) The Continental-Scale Greenhouse Gas Balance of Europe. Ecological Studies,  
953 203, 237–255, 2008.
- 954  
955 Drösler, M., Freibauer, A., Adelman, W., Augustin, J., Bergman, L., Beyer, C., Chojnicki,  
956 B., Förster, C., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H.,  
957 Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P.,  
958 Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz in der Praxis,  
959 Arbeitsbericht aus dem vTI-Institut für Agrarrelevante Klimaforschung, p. 21, available  
960 at <http://www.vti.bund.de/de/startseite/institute/ak/publikationen.html>, 2011.
- 961  
962 Drösler, M., Adelman, W., Augustin, J., Bergmann, L., Beyer, C., Chojnicki, B., Förster,  
963 C., Freibauer, A., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H.,  
964 Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P.,  
965 Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz.  
966 Schlussbericht des Vorhabens “Klimaschutz – Moorschutzstrategien”, 2006–2010, 2013.
- 967  
968 Eickenscheidt, T., Heinichen, J., Augustin, J., Freibauer, A., and Drösler, M.: Nitrogen  
969 mineralization and gaseous nitrogen losses from waterlogged and drained organic soils  
970 in a black alder (*Alnus glutinosa* (L.) Gaertn.) forest, Biogeosciences, 11, 2961–2976,  
971 2014a.
- 972  
973 Eickenscheidt, T., Freibauer, A., Heinichen, J., Augustin, J., and Drösler, M.: Short-term  
974 effects of biogas digestate and cattle slurry application on greenhouse gas emissions  
975 affected by N availability from grasslands on drained fen peatlands and associated  
976 organic soils, Biogeosciences, 11, 6187–6207, 2014b.
- 977  
978 Elsgaard, L., Gorres, C.-M., Hoffmann, C. C., Blicher-Mathiesen, G., Schelde, K., and  
979 Petersen, S. O.: Net ecosystem exchange of CO<sub>2</sub> and carbon balance for eight  
980 temperate organic soils under agricultural management, Agr. Ecosyst. Environ., 162,  
981 52–67, 2012.
- 982  
983 Falge, E., Baldocchi, D., Olson, R., Anthoni, P., Aubinet, M., Bernhofer, C., Burba, G.,  
984 Ceulemans, R., Clement, R., Dolman, H., Granier, A., Gross, P., Grunwald, T., Hollinger,  
985 D., Jensen, N. O., Katul, G., Keronen, P., Kowalski, A., Lai, C. T., Law, B. E., Meyers,  
986 T., Moncrieff, H., Moors, E., Munger, J. W., Pilegaard, K., Rannik, U., Rebmann, C.,  
987 Suyker, A., Tenhunen, J., Tu, K., Verma, S., Vesala, T., Wilson, K., and Wofsy, S.: Gap  
988 filling strategies for defensible annual sums of net ecosystem exchange, Agr. Forest  
989 Meteorol., 107, 43–69, 2001.
- 990  
991 Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: C- und N-Stoffflüsse auf  
992 Torfstichsimulationsflächen im Donaumoos, Z. f. Kulturtechnik und Landentwicklung, 38,  
993 11–17, 1997.
- 994  
995 Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: Nitrous oxide and methane

- 996 fluxes from organic soils under agriculture, *European Journal of Soil Science*, 49, 327–  
997 335. 1998.
- 998
- 999 Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D. W., Haywood,  
1000 J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and  
1001 Van Dorland, R.: Changes in Atmospheric Constituents and in Radiative Forcing, in:  
1002 *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to*  
1003 *the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*,  
1004 edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor,  
1005 M., and Miller, H. L., Cambridge University Press, Cambridge, United Kingdom and New  
1006 York, NY, USA, 2007.
- 1007
- 1008 Freibauer, A., Rounsevell, M.D.A., Smith, P., and Verhagen, J.: Carbon sequestration in  
1009 the agricultural soils of Europe, *Geoderma*, 122, 1–23, 2004.
- 1010
- 1011 Glatzel, S., Basiliko, N., and Moore, T.: Carbon dioxide and methane production  
1012 potential of peats from natural, harvested and restored sites, Eastern Québec, Canada,  
1013 *Wetlands*, 24(2), 261–267, 2004.
- 1014
- 1015 Goldberg, S.D., Knorr, K.H., Blodau, C., Lischeid, G., and Gebauer, G.: Impact of  
1016 altering the water table height of an acidic fen on N<sub>2</sub>O and NO fluxes and soil  
1017 concentrations, *Global Change Biol.*, 16, 220–233, 2010.
- 1018
- 1019 Grønlund, A., Sveistrup, T.E., Søvik, A.K., Rasse, D.P., and Kløve, B.: Degradation of  
1020 cultivated peat soils in northern Norway based on field scale CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission  
1021 measurements, *Arch Agron. Soil Sci.*, 52, 149–159, 2006.
- 1022
- 1023 Grønlund, A., Hauge, A., Hovde, A., and Rasse, D.A.: Carbon loss estimates from  
1024 cultivated peat soils in Norway: a comparison of three methods, *Nutr. Cycl. Agroecosyst.*,  
1025 81, 157–167, 2008.
- 1026
- 1027 Grosse, W., Frye, J., and Lattermann, S.: Root aeration in wetland trees by pressurized  
1028 gas transport, *Tree Physiology*, 10 285–295, 1992.
- 1029
- 1030 Gupta, H.V., Sorooshian, S., and Yapo, P.O.: Status of automatic calibration for  
1031 hydrologic models: Comparison with multilevel expert calibration, *J. Hydrologic Eng.*,  
1032 4(2), 135–143, 1999.
- 1033
- 1034 Gutser, R., Ebertseder, Th., Weber, A., Schraml, M., and Schmidhalter, U.: Short-term  
1035 and residual availability of nitrogen after long-term application of organic fertilizers on  
1036 arable land, *J. Plant Nutr. Soil Sci.*, 168, 439–446, 2005.
- 1037
- 1038 Hahn-Schöfl, M., Zak, D., Minke, M., Gelbrecht, J., Augustin, J., and Freibauer, A.:  
1039 Organic sediment formed during inundation of a degraded fen grassland emits large  
1040 fluxes of CH<sub>4</sub> and CO<sub>2</sub>, *Biogosciences*, 8, 1539–1550, 2011.
- 1041
- 1042 Hardie, S.M.L., Garnett, M.H., Fallick, A.E., Rowland, A.P., Ostle, N.J., and Flowers,  
1043 T.H.: Abiotic drivers and their interactive effect on the flux and carbon isotope (<sup>14</sup>C and  
1044 <sup>δ</sup><sup>13</sup>C) composition of peat-respired CO<sub>2</sub>, *Soil Biol. Biochem.*, 43, 2432–2440,  
1045 doi:10.1016/j.soilbio.2011.08.010, 2011.
- 1046

- 1047 Heller, C., and Zeitz, J.: Stability of soil organic matter in two northeastern German fen  
1048 soils: the influence of site and soil development, *J. Soils Sediments*, 12, 1231–1240,  
1049 DOI 10.1007/s11368-012-0500-6, 2012.  
1050
- 1051 Henry, S., Texier, S., Hallet, S., Bru, D., Dambreville, C., Chèneby, D., Bizouard, F.,  
1052 Germon, J.C., and Philippot, L.: Disentangling the rhizosphere effect on nitrate reducers  
1053 and denitrifiers: insight into the role of root exudates, *Environ. Microbiol.*, 10, 3082–3092,  
1054 2008.  
1055
- 1056 Hothorn, T., Bretz, F., Westfall, P., Heiberger, R.M., and Schuetzenmeister, A.:  
1057 Simultaneous Inference in General Parametric Models: R package version 1.2-17, 2013.  
1058
- 1059 Höper, H., Augustin, J., Cagampan, J. P., Drösler, M., Lundin, L., Moors, E. J., Vasander,  
1060 H., Waddington, J. M., and Wilson, D.: Restoration of peatlands and greenhouse gas  
1061 balances, in: *Peatlands and Climate Change*. edited by: Strack, D. M., International Peat  
1062 Society, Jyvaskyla, 182–210, 2008.  
1063
- 1064 Horrocks, R.D., and Valentine, J.F.: *Harvested forages*, Academic Press, 1999.  
1065
- 1066 International Peat Society: *Peatlands and climate change*, Ed. Strack, M., Publish by the  
1067 International Peat Society, p. 227, 2008.  
1068
- 1069 IPCC: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change*  
1070 *2007: The physical science basis. Contribution of Working Group I to the Fourth*  
1071 *Assessment Report of the Intergovernmental Panel on Climate Change*, edited by:  
1072 Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and  
1073 Miller, H. L., Cambridge University Press, Cambridge, UK and New York, USA, 2007.  
1074
- 1075 IPCC, 2014: 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse  
1076 Gas Inventories: Wetlands, editd by: Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N.,  
1077 Baasansuren, J., Fukuda, M., and Troxler, T. G., IPCC, Switzerland, 2014.  
1078
- 1079 Jones, S.K., Rees, R.M., Skiba, U.M., and Ball, B.C.: Influence of organic and mineral N  
1080 fertiliser on N<sub>2</sub>O fluxes from temperate grassland, *Agriculture, Ecosystems and*  
1081 *Environment*, 121, 74–83, 2007.  
1082
- 1083 Kandel, T.P., Elsgaard, L., Karki, S., and Lærke, P.E.: Biomass yield and greenhouse  
1084 gas emissions from a drained fen peatland cultivated with reed canary grass under  
1085 different harvest and fertilizer regimes, *Bioenerg. Res.*, 6, 883–895, DOI  
1086 10.1007/s12155-013-9316-5, 2013.  
1087
- 1088 Kasimir-Klemedtsson, Å., Klemedtsson, L., Berglund, K., Martikainen, P., Silvola, J., and  
1089 Oenema, O.: Greenhouse gas emissions from farmed organic soils: a review, *Soil Use*  
1090 *and Management*, 13, 245–250, 1997.  
1091
- 1092 Kroeze, C., Mosier, A., and Bouwman, L.:1999. Closing the global N<sub>2</sub>O budget: A  
1093 retrospective analysis 1500 – 1994, *Global Biogeochemical Cycles*, 13 (1), 1–8, 1999.  
1094
- 1095 Krull, E.S., Baldock, J.A., and Skjemstad, J.O: Importance of mechanisms and  
1096 processes of the stabilisation of soil organic matter for modeling carbon turnover,  
1097 *Functional Plant biology*, 30, 207–222, 2003.

- 1098  
1099 Leiber-Sauheitl, K., Fuß, R., Voigt, C., and Freibauer, A.: High CO<sub>2</sub> fluxes from grassland  
1100 on histic Gleysol along soil carbon and drainage gradients, *Biogeosciences*, 11, 749–  
1101 761, doi:10.5194/bg-11-749-2014, 2014.
- 1102  
1103 Leifeld, J., Müller, M., and Fuhrer, J.: Peatland subsidence and carbon loss from drained  
1104 temperate fens, *Soil Use Manage.*, 27, 170–176, 2011.
- 1105  
1106 Leifeld, J., Steffens, M., and Galego-Sala, A.: Sensitivity of peatland carbon loss to  
1107 organic matter quality, *Geophys. Res. Lett.*, 39, L14704, doi:10.1029/2012GL051856,  
1108 2012.
- 1109  
1110 Leifeld, J., Bader, C., Borraz, E., Hoffmann, M., Giebels, M., Sommer, M., and Augustin,  
1111 J.: Are C-loss rates from drained peatlands constant over time? The additive value of  
1112 soil profile based and flux budget approach, *Biogeosciences Discuss.*, 11, 12341–12373,  
1113 2014.
- 1114  
1115 Leppelt, T. Dechow, R., Gebbert, S., Freibauer, A., Lohila, A., Augustin, J., Drösler, M.,  
1116 Fiedler, S., Glatzel, S., Höper, H., Järveoja, J., Lærke, P.E., Maljanen, M., Mander, Ü.,  
1117 Mäkiranta, P., Minkkinen, K., Ojanen, P., Regina, K., and Strömngren, M.: Nitrous oxide  
1118 emission hotspots from organic soils in Europe, *Biogeosciences Discuss.*, 11, 9135–  
1119 9182, 2014.
- 1120  
1121 Livingston, G.P., and Hutchinson, G.L.: Enclosure-based measurement of trace gas  
1122 exchange: application and sources of error, In: Matson, PA, Harriss, RC, (eds.), *Biogenic*  
1123 *Trace Gases: Measuring Emissions from Soil and Water*. Blackwell Science, Cambridge,  
1124 14–50, 1995.
- 1125  
1126 Lloyd, J. and Taylor, J. A.: On the temperature dependence of soil respiration, *Funct.*  
1127 *Ecol.*, 8, 315–323, 1994.
- 1128  
1129 Lohila, A.: Carbon dioxide exchange on cultivated and afforested boreal peatlands,  
1130 *Finnish Meteorological Institute Contributions*, 73, 1–47, 2008.
- 1131  
1132 Lützow, v.M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G.,  
1133 Marschner, B., and Flessa, H.: Stabilization of organic matter in temperate soils:  
1134 mechanisms and their relevance under different soil conditions – a review, *European*  
1135 *Journal of Soil Science*, 57, 426–445, doi: 10.1111/j.1365-2389.2006.00809.x, 2006.
- 1136  
1137 Maljanen, M., Hytönen, J., and Martikainen, P. J.: Fluxes of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> on  
1138 afforested boreal agricultural soils, *Plant Soil*, 231, 113–121, 2001.
- 1139  
1140 Maljanen, M., Hytönen, J., Mäkiranta, P., Alm, J., Minkkinen, K., Laine, J. and  
1141 Martikainen, P.J.: Greenhouse gas emissions from cultivated and abandoned organic  
1142 arable lands in Finland, *Boreal Environment Research*, 12, 133–144, 2007.
- 1143  
1144 Maljanen, M., Sigurdsson, B. D., Guðmundsson, J., Óskarsson, H., Huttunen, J. T., and  
1145 Martikainen, P. J.: Greenhouse gas balances of managed peatlands in the Nordic  
1146 countries – present knowledge and gaps, *Biogeosciences*, 7, 2711–2738,  
1147 doi:10.5194/bg-7-2711-2010, 2010.
- 1148

- 1149 Martikainen, P.J., Nykänen, H., Crill, P., and Silvola, J.: Effect of a lowered water table  
1150 on nitrous oxide fluxes from northern peatlands, *Nature*, 366, 51–53, 1993.  
1151
- 1152 Michaelis, L. and Menten, M. L.: Die Kinetik der Invertinwirkung, *Biochem. Z.*, 49, 333–  
1153 369, 1913.  
1154
- 1155 Minchin, P.E.H., and McNaughton, G.S.: Exudation of recently fixed carbon by non-  
1156 sterile roots, *Journal of Experimental Botany*, 35(150), 74–82, 1984.  
1157
- 1158 Moriasi, D.N, Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., and Veith, T.L.:  
1159 Model evaluation guidelines for systematic quantification of accuracy in watershed  
1160 simulations, *American Society of Agricultural and Biological Engineers*, 50(3), 885–900,  
1161 2007.  
1162
- 1163 Mounier, E., Hallet, S., Chèneby, D., Benizri, E., Gruet, Y., Nguyen, C., Piutti, S., Robin,  
1164 C., Slezack-Deschaumes, S., Martin-Laurent, F., Germon, J.C., and Philippot, L.:  
1165 Influence of maize mucilage on the diversity and activity of the denitrifying community,  
1166 *Environ. Microbiol.*, 6, 301–312, 2004.  
1167
- 1168 Nash, J.E., and Sutcliffe, J.V.: River flow forecasting through conceptual models: Part 1.  
1169 A discussion of principles, *J. Hydrology*, 10(3), 282–290, 1970.  
1170
- 1171 Nielsen, O.-K., Mikkelsen, M.H., Hoffmann, L., Gyldenkærne, S., Winther, M., Nielsen,  
1172 M., Fauser, P., Thomsen, M., Plejdrup, M.S., Albrektsen, R., Hjelgaard, K., Bruun, H.G.,  
1173 Johannsen, V.K., Nord-Larsen, T., Bastrup-Birk, A., Vesterdal, L., Møller, I.S.,  
1174 Rasmussen, E., Arfaoui, K., Baunbæk, L. & Hansen, M.G.: Denmark's National Inventory  
1175 Report 2012. Emission Inventories 1990-2010 - Submitted under the United Nations  
1176 Framework Convention on Climate Change and the Kyoto Protocol. Aarhus University,  
1177 DCE – Danish Centre for Environment and Energy, 1168 pp. Scientific Report from DCE  
1178 – Danish Centre for Environment and Energy No. 19 <http://www.dmu.dk/Pub/SR19.pdf>,  
1179 2012.  
1180
- 1181 NIR 2010: National Emission Inventory Report (NIR) 2010 for 2008 – Calculation of  
1182 Emissions from German Agriculture, Ed. Haenel, H.D., vTI Agriculture and Forestry  
1183 Research, Special Issue 334, p. 428, 2010.  
1184
- 1185 Petersen, S.O., Hoffmann, C.C., Schäfer, C.-M., Bilcher-Mathiesen, G., Elsgaard, L.,  
1186 Kristensen, K., Larsen, S.E., Torp, S.B., and Greve, M.H.: Annual emissions of CH<sub>4</sub> and  
1187 N<sub>2</sub>O, and ecosystem respiration, from eight organic soils in Western Denmark managed  
1188 by agriculture, *Biogeosciences*, 9, 403–422, 2012.  
1189
- 1190 R Development Core Team: R: A language and environment for statistical computing, R  
1191 Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, available at:  
1192 <http://www.R-project.org>, 2013.  
1193
- 1194 Reiche, M., Gleixner, G., and Küsel, K.: Effect of peat quality on microbial greenhouse  
1195 gas formation in an acidic fen, *Biogeosciences*, 7, 187–198, 2010.  
1196
- 1197 Renou-Wilson, F., Barry, C., Müller, C., and Wilson, D.: The impacts of drainage, nutrient  
1198 status and management practice on the full carbon balance of grasslands on organic  
1199 soils in a maritime temperate zone, *Biogeosciences*, 11, 4361–4379, 2014.

- 1200  
1201 Rochette, P., Angers, D.A., Belanger, G., Chantigny, M.H., Prevost, D., and Levesque,  
1202 G.: Emissions of N<sub>2</sub>O from alfalfa and soybean crops in eastern Canada, *Soil Sci. Soc.*  
1203 *Am. J.*, 68, 493–506, 2004.
- 1204  
1205 Schäfer, C. M., Elsgaard, L., Hoffmann, C. C., and Petersen, S. O.: Seasonal methane  
1206 dynamics in three temperate grasslands on peat, *Plant Soil*, 357, 339–353, 2012.
- 1207  
1208 Schober, H.M., Stein, Ch., and Prösl, K.-H: Interkommunales Flächenmanagement  
1209 Schlussbericht, LEADER+-Projekt Freisinger Moos, p. 56, 2008.
- 1210  
1211 Schothorst, C.J.: Subsidence of low moor peat soils in the Western Netherlands,  
1212 *Geoderma*, 17, 265–291, 1977.
- 1213  
1214 Sey, B.K., Manceur, A.M., Wahlen, J.K., Gregorich, E.G, and Rochette, P.: Root-derived  
1215 respiration and nitrous oxide production as affected by crop phenology and nitrogen  
1216 fertilization, *Plant Soil*, 326, 369–379, 2010.
- 1217  
1218 Silvan, N., Tuittila, E.-S., Kitunen, V., Vasander, H., and Laine, J.: Nitrate uptake by  
1219 *Eriophorum vaginatum* controls N<sub>2</sub>O production in a restored peatland, *Soil Biol.*  
1220 *Biochem.*, 37, 1519–1526, 2005.
- 1221  
1222 Silvola, J., Alm, J., Ahlholm, U., Nykänen, H., and Martikainen, P.J.: CO<sub>2</sub> fluxes from peat  
1223 in boreal mires under varying temperature and moisture conditions, *Journal of Ecology*,  
1224 84, 219–228, 1996.
- 1225  
1226 Sonneveld, M.P.W., and Lantinga, E.A.: The contribution of mineralization to grassland  
1227 N uptake on peatland soils with anthropogenic A horizons, *Plant Soil*; 340, 357–368,  
1228 2011.
- 1229  
1230 Stolk, P.C., Hendriks, R.F.A., Jacobs, C.M.J., Moors, E.J., and Kabat, P.: Modeling the  
1231 effect of aggregates on N<sub>2</sub>O emission from denitrification in an agricultural peat soil,  
1232 *Biogeosciences*, 8, 2649–2663, 2011.
- 1233  
1234 Svensson, B.H., and Sundh, I.: Factors affecting methane production in peat soils. *Suo.*,  
1235 43, 183–190, 1992.
- 1236  
1237 Tiemeyer, B., Freibauer, A., Drösler, M., Albiac-Borraz, E., Augustin J., Bechtold, M.,  
1238 Beetz, S., Belting, S., Bernrieder, M., Beyer, C., Eberl, J., Eickenscheidt, T., Fell, H.,  
1239 Fiedler, S., Förster, C., Frahm, E., Frank, S., Giebels, M., Glatzel, S., Grünwald, T.,  
1240 Heinichen, J., Hoffmann, M., Hommeltenberg, J., Höper, H., Laggner, A., Leiber-Sauheitl,  
1241 K., Leppelt, T., Metzger, C., Peichl-Brak, M., Röhling, S., Roskopf, N., Rötzer, T.,  
1242 Sommer, M., Wehrhan, M., Werle, P., and Zeitz, J.: Klimarelevanz von Mooren und  
1243 Anmooren in Deutschland: Ergebnisse aus dem Verbundprojekt "Organische Böden in  
1244 der Emissionsberichterstattung", Thünen Working Paper, No. 15, [http://nbn-](http://nbn-resolving.de/urn:nbn:de:gbv:253-201311-dn052806-7)  
1245 [resolving.de/urn:nbn:de:gbv:253-201311-dn052806-7](http://nbn-resolving.de/urn:nbn:de:gbv:253-201311-dn052806-7), 2013.
- 1246  
1247 Tiemeyer, B., Borraz, E.A, Augustin, J., Bechtold, M., Beetz, S., Beyer, C., Eickenscheidt,  
1248 T., Drösler, M., Förster C., Freibauer, A., Giebels, M., Glatzel, S., Heinichen, J.,  
1249 Hoffmann, M., Höper, H., Leiber-Sauheitl, K., Roskopf, N., and Zeitz, J.: Greenhouse  
1250 gas budgets for grasslands on peatlands and other organic soils, *Geophysical Research*

- 1251 Abstracts, Vol. 16, EGU2014-14825, 2014, EGU General Assembly, 2014.  
1252
- 1253 Tietema, A., Warmerdam, B., Lenting, E., and Riemer, L.: Abiotic factors regulating  
1254 nitrogen transformations in the organic layer of acid forest soils: Moisture and pH, *Plant  
1255 and Soil*, 147, 69–78, 1992.  
1256
- 1257 Tjoelker, M.G., Oleksyn, J., and Reich, P.B.: Modeling respiration of vegetation:  
1258 evidence for a general temperature-dependent  $Q_{10}$ , *Global Change Biology*, 7, 223–230,  
1259 2001.  
1260
- 1261 Veenendaal, E.M., Kolle, O., Leffelaar, P.A., Schrier-Uijl, A.P., Huissteden van, J.,  
1262 Walsem van, J., Möller, F., and Berendse, F.: CO<sub>2</sub> exchange and carbon balance in two  
1263 grassland sites on eutrophic drained peat soils, *Biogeosciences*, 4, 1027–1040, 2007.  
1264
- 1265 Velthof, G.L., Brader, A.B., and Oenema, O.: Seasonal variations in nitrous oxide losses  
1266 from managed grasslands in the Netherlands, *Plant and Soil*, 181, 263–274, 1996.  
1267
- 1268 VDLUFA: Bestimmung von mineralischem (Nitrat-)Stickstoff in Bodenprofilen (Nmin-  
1269 Labormethode), in: *Methodenbuch Teil 2*, VDLUFA, Speyer, Germany, 1997.  
1270
- 1271 Vuichard, N., Soussana, J.-F., Ciais, P., Viovy, N., Ammann, C., Calanca, P., Clifton-  
1272 Brown, J., Fuhrer, J., Jones, M., and Martin, C.: Estimating the greenhouse gas fluxes  
1273 of European grasslands with a process-based model: 1. Model evaluation from in situ  
1274 measurements, *Global Biogeochem. Cycles*, 21, GB1004, doi:10.1029/2005GB002611,  
1275 2007.  
1276
- 1277 Whalen, S.C.: Biogeochemistry of methane exchange between natural wetlands and the  
1278 atmosphere, *Environmental Engineering Science*, 22 (1), 73–94, 2005.  
1279
- 1280 Worrall, F., Burt, T. P., Rowson, J. G., Warburton, J., and Adamson, J. K.: The multi-  
1281 annual carbon budget of a peat-covered catchment, *Sci. Total Environ.*, 407, 4084–4094,  
1282 2009.  
1283
- 1284 WRB, 2006 – IUSS Working Group: World Reference Base for Soil Resources 2006,  
1285 2nd edition, World Soil Resources Reports No. 103. Rome. 2006.  
1286
- 1287 Zehlius-Eckert, W., Schwaiger, H., and Beckmann, A.: Monitoring und Erfolgskontrolle  
1288 im Freisinger Moos, Bayer. Akad.f. Naturschutz u. Landschaftspflege - Laufen /Salzach  
1289 2003, *Laufener Seminarbeitr.*, 1/03, 147–170, 2003.  
1290

**Table 1** Physical and chemical properties of the investigated plots.

Site	Soil type	Organic carbon [%]		C/N ratio 0–20 cm	pH (CaCl <sub>2</sub> ) 0–20 cm	Bulk density [g cm <sup>-3</sup> ]		Mean GW level above surface [cm]	
		0–10 cm	10–20 cm			0–10 cm	10–20 cm	2010	2011
A1C <sub>medium</sub>	molic Gleysol	9.6 ± 0.1	9.3 ± 0.2	10	5.24	0.72 ± 0.03	0.85 ± 0.08	-56 (-86/0)	-67 (-86/-4)
A1C <sub>high</sub>	sapric Histosol	16.9 ± 0.2	17.2 ± 0.2	12	5.61	0.63 ± 0.05	0.67 ± 0.04	-45 (-90/7)	-49 (-76/5)
A2C <sub>medium</sub>	molic Gleysol	9.4 ± 0.0	9.2 ± 0.1	10	5.24	0.83 ± 0.06	0.90 ± 0.06	-56 (-86/0)	-67 (-86/-4)
A2C <sub>high</sub>	sapric Histosol	16.1 ± 0.9	16.8 ± 0.2	12	5.61	0.67 ± 0.11	0.77 ± 0.08	-45 (-90/7)	-49 (-76/5)
G1C <sub>medium</sub>	molic Gleysol	10.5 ± 0.2	9.4 ± 0.1	10	4.10	0.71 ± 0.09	0.90 ± 0.06	-65 (-91/-2)	-72 (-92/0)
G1C <sub>high</sub>	sapric Histosol	17.2 ± 0.0	16.7 ± 0.1	11	4.24	0.53 ± 0.09	0.64 ± 0.05	-45 (-64/-1)	-52 (-66/-3)
G2C <sub>medium</sub>	molic Gleysol	10.9 ± 0.2	10.1 ± 0.1	10	4.10	0.81 ± 0.09	0.88 ± 0.03	-63 (-92/0)	-72 (-97/0)
G2C <sub>high</sub>	sapric Histosol	16.4 ± 0.1	15.6 ± 0.1	11	4.24	0.57 ± 0.08	0.67 ± 0.03	-45 (-67/-1)	-50 (-65/-3)

Values present means ± SD

Values in brackets are minimum and maximum values

A, arable land; G, grassland;

**Table 2** Date and type of conducted management events.

Date	Julian day	Management events		
		A1	A2	G
2009-09-24	–	seed sowing ( <i>Secale cereale</i> )	seed sowing ( <i>Secale cereale</i> )	–
2010-03-26	85	–	–	levelling
2010-03-30	89	–	plowing & seed sowing ( <i>Avena sativa</i> + 15% <i>Vicia faba minor</i> )	–
2010-04-07	97	–	–	rolling
2010-04-13	103	–	harrowing	–
2010-04-28	118	plowing	–	–
2010-04-30	120	seed sowing ( <i>Zea mays</i> )	–	–
2010-05-24	144	grubbing	–	harvesting
2010-06-11	162	grubbing	–	–
2010-06-14	165	–	–	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
2010-07-06	187	grubbing & hilling	–	–
2010-08-20	232	–	–	harvesting
2010-08-22	234	–	harvesting	–
2010-08-25	237	–	–	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
2010-08-28	240	–	milling	–
2010-09-04	247	–	–	–
2010-09-23	266	–	–	herbicide against common sorrel ( <i>Rumex acetosa</i> )
2010-10-15	288	harvesting	–	–
2010-10-30	303	mulching	–	–
2011-03-16	440	–	–	levelling
2011-04-01	456	plowing & seed sowing ( <i>Avena sativa</i> + 20% <i>Vicia sativa</i> )	–	–
2011-04-18	473	–	plowing	–
2011-04-26	481	–	grubbing + seed sowing ( <i>Zea mays</i> )	–
2011-04-30	485	harrowing	harrowing	–
2011-05-08	493	–	harrowing	–
2011-05-19	504	–	mattocks	–
2011-05-23	508	–	–	harvesting
2011-05-27	512	–	–	manuring [25 m <sup>3</sup> ha <sup>-1</sup> ]
2011-06-14	530	–	hilling	–
2011-08-01	578	–	–	harvesting
2011-08-16	593	harvesting	–	–
2011-08-18	595	milling	–	–
2011-08-27	604	plowing & seed sowing ( <i>Secale cereale</i> )	–	–
2011-09-13	621	–	–	harvesting
2011-09-22	630	–	–	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
2011-09-28	636	–	harvesting	–

**Table 3** Cumulative  $R_{ECO}$ , GPP, NEE,  $CH_4$  and  $N_2O$  exchange rates as well as C import through fertilizer and C export due to crop/grass yield.

Plot/year	$R_{ECO}$ [g C m <sup>-2</sup> yr <sup>-1</sup> ]	GPP [g C m <sup>-2</sup> yr <sup>-1</sup> ]	NEE [g C m <sup>-2</sup> yr <sup>-1</sup> ]	Fertilizer input* [g C m <sup>-2</sup> yr <sup>-1</sup> ]	Crop yield* [g C m <sup>-2</sup> yr <sup>-1</sup> ]	$CH_4^*$ [g C m <sup>-2</sup> yr <sup>-1</sup> ]	$N_2O^*$ [g N m <sup>-2</sup> yr <sup>-1</sup> ]
A1C <sub>medium</sub> / 10	2473 ± 272	-1454 ± 114	1019 ± 386	-	193 ± 53	-	-
A1C <sub>medium</sub> / 11	2992 ± 230	-1862 ± 126	1130 ± 356	-	74 ± 8	0.51 ± 0.17	0.27 ± 0.01
A1C <sub>high</sub> / 10	2012 ± 284	-873 ± 110	1139 ± 394	-	58 ± 23	-	-
A1C <sub>high</sub> / 11	2117 ± 123	-1302 ± 77	815 ± 200	-	135 ± 7	0.22 ± 0.04	0.23 ± 0.05
A2C <sub>medium</sub> / 10	2704 ± 544	-1449 ± 103	1255 ± 647	-	227 ± 27	-	-
A2C <sub>medium</sub> / 11	2354 ± 309	-2360 ± 237	-6 ± 546	-	457 ± 71	-0.03 ± 0.05	0.39 ± 0.06
A2C <sub>high</sub> / 10	2907 ± 482	-1200 ± 137	1707 ± 619	-	145 ± 19	-	-
A2C <sub>high</sub> / 11	2538 ± 329	-2188 ± 253	350 ± 582	-	330 ± 79	-0.10 ± 0.07	0.86 ± 0.21
G1C <sub>medium</sub> / 10	3954 ± 671	-2131 ± 180	1823 ± 851	126	297 ± 32	-	-
G1C <sub>medium</sub> / 11	4099 ± 300	-2414 ± 195	1685 ± 495	267	344 ± 63	-0.06 ± 0.09	0.12 ± 0.01
G1C <sub>high</sub> / 10	3736 ± 491	-2152 ± 140	1584 ± 631	126	325 ± 41	-	-
G1C <sub>high</sub> / 11	4026 ± 707	-2633 ± 138	1393 ± 845	267	455 ± 41	-0.07 ± 0.02	0.18 ± 0.02
G2C <sub>medium</sub> / 10	3683 ± 453	-2131 ± 213	1552 ± 666	76	342 ± 39	-	-
G2C <sub>medium</sub> / 11	4265 ± 379	-2880 ± 177	1385 ± 556	53	543 ± 58	-0.11 ± 0.05	0.19 ± 0.02
G2C <sub>high</sub> / 10	3521 ± 1041	-2093 ± 152	1428 ± 1193	76	380 ± 43	-	-
G2C <sub>high</sub> / 11	4316 ± 562	-2962 ± 178	1354 ± 740	53	593 ± 132	-0.02 ± 0.02	0.31 ± 0.09

\* Data from grassland plots derived from Eickenscheidt et al. (2014).  
A, arable land; G, grassland; 10, year 2010; 11, year 2011.

**Table 4** Model evaluation statistics from observed  $R_{ECO}$  versus modeled  $R_{ECO}$ .  $r$  = Pearson's correlation coefficient, NSE = Nash-Sutcliffe efficiency, PBIAS = percent bias, RSR = ratio of the root mean square error to the standard deviation of measured data.

Site	2010				2011			
	$r$	NSE	PBIAS	RSR	$r$	NSE	PBIAS	RSR
A1C <sub>medium</sub>	0.90	0.70	-7.93	0.55	0.98	0.95	-0.17	0.22
A1C <sub>high</sub>	0.98	0.96	0.44	0.19	0.98	0.97	1.79	0.18
A2C <sub>medium</sub>	0.93	0.81	-5.68	0.44	0.94	0.89	-0.23	0.33
A2C <sub>high</sub>	0.96	0.92	2.60	0.29	0.98	0.96	0.00	0.20
G1C <sub>medium</sub>	0.96	0.93	1.54	0.27	0.95	0.91	-2.40	0.31
G1C <sub>high</sub>	0.89	0.75	-6.27	0.50	0.97	0.95	0.03	0.23
G2C <sub>medium</sub>	0.93	0.86	0.80	0.37	0.98	0.96	0.06	0.19
G2C <sub>high</sub>	0.93	0.82	-4.65	0.42	0.97	0.94	0.92	0.25

**Table 5** Model evaluation statistics from observed NEE versus modeled NEE.  $r$  = Pearson's correlation coefficient, NSE = Nash-Sutcliffe efficiency, PBIAS = percent bias, RSR = ratio of the root mean square error to the standard deviation of measured data.

Site	2010				2011			
	$r$	NSE	PBIAS	RSR	$r$	NSE	PBIAS	RSR
A1C <sub>medium</sub>	0.94	0.87	-11.84	0.36	0.97	0.93	1.41	0.26
A1C <sub>high</sub>	0.94	0.88	-7.94	0.35	0.98	0.96	-4.94	0.21
A2C <sub>medium</sub>	0.85	0.72	3.03	0.53	0.96	0.92	-3.64	0.28
A2C <sub>high</sub>	0.79	0.61	3.63	0.63	0.96	0.91	-9.56	0.29
G1C <sub>medium</sub>	0.90	0.80	-10.98	0.45	0.92	0.84	-10.47	0.40
G1C <sub>high</sub>	0.91	0.82	-12.07	0.43	0.94	0.88	-10.04	0.35
G2C <sub>medium</sub>	0.95	0.89	-13.23	0.33	0.96	0.92	-5.43	0.28
G2C <sub>high</sub>	0.94	0.87	-10.71	0.36	0.94	0.89	-6.22	0.34

**Table 6** Estimated global warming potential for a time horizon of 100 years.

Site/periode	GWP <sub>100</sub> NEE <sub>corrected</sub> *	GWP <sub>100</sub> CH <sub>4</sub>	GWP <sub>100</sub> N <sub>2</sub> O	GWP <sub>100</sub> balance
	[g CO <sub>2</sub> eq. m <sup>-2</sup> yr <sup>-1</sup> ]	[g CO <sub>2</sub> eq. m <sup>-2</sup> yr <sup>-1</sup> ]	[g CO <sub>2</sub> eq. m <sup>-2</sup> yr <sup>-1</sup> ]	[g CO <sub>2</sub> eq. m <sup>-2</sup> yr <sup>-1</sup> ]
A1C <sub>medium</sub> / 11	4419 ± 1336	16.96 ± 5.65	126.32 ± 4.68	4562 ± 1346
A1C <sub>high</sub> / 11	3487 ± 760	7.32 ± 1.33	107.61 ± 23.39	3601 ± 785
A2C <sub>medium</sub> / 11	1655 ± 2264	-1.00 ± 1.33	182.47 ± 28.07	1837 ± 2293
A2C <sub>high</sub> / 11	2496 ± 2426	-3.33 ± 1.66	402.36 ± 98.25	2895 ± 2526
G1C <sub>medium</sub> / 11	6467 ± 2048	-2.00 ± 2.99	56.14 ± 4.68	6521 ± 2056
G1C <sub>high</sub> / 11	5802 ± 3252	-2.33 ± 0.67	84.21 ± 9.36	5884 ± 3262
G2C <sub>medium</sub> / 11	6881 ± 2253	-3.66 ± 1.66	88.89 ± 9.36	6967 ± 2264
G2C <sub>high</sub> / 11	6951 ± 3200	-0.67 ± 0.67	145.04 ± 42.11	7095 ± 3243

\* Corrected for C export and C import

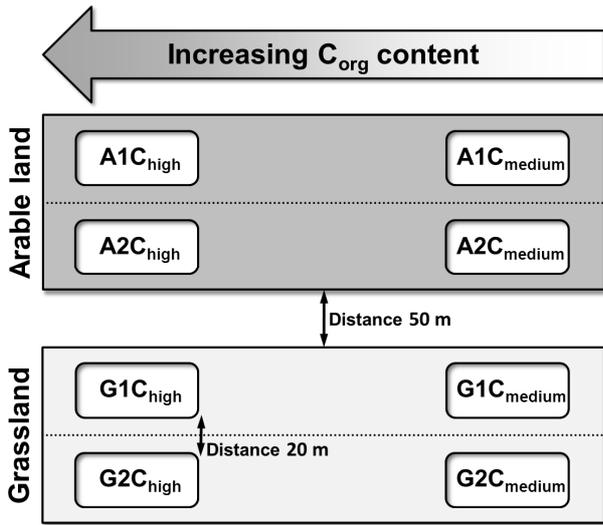


Fig. 1 Schema of the experimental design.

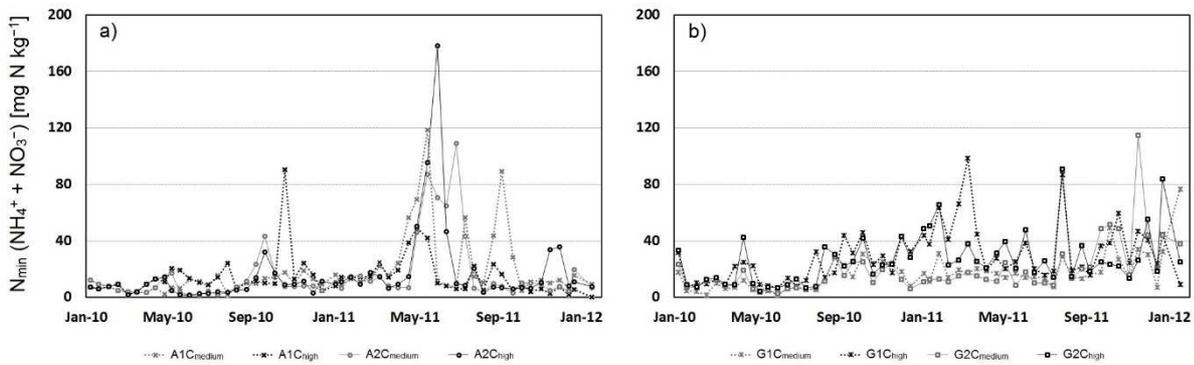


Fig. 2 Mineral nitrogen contents [ $\text{mg N kg}^{-1}$ ] for the arable land a) and the grassland b) of the soil depth 0–10 cm for the years 2010 and 2011.

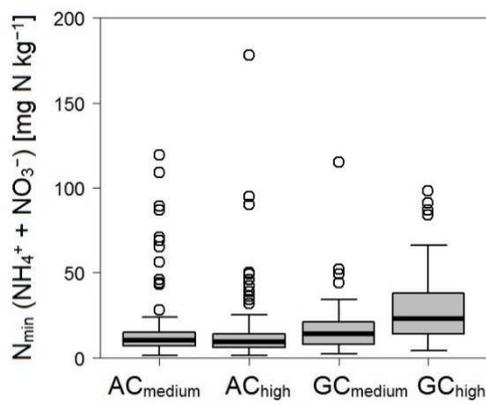
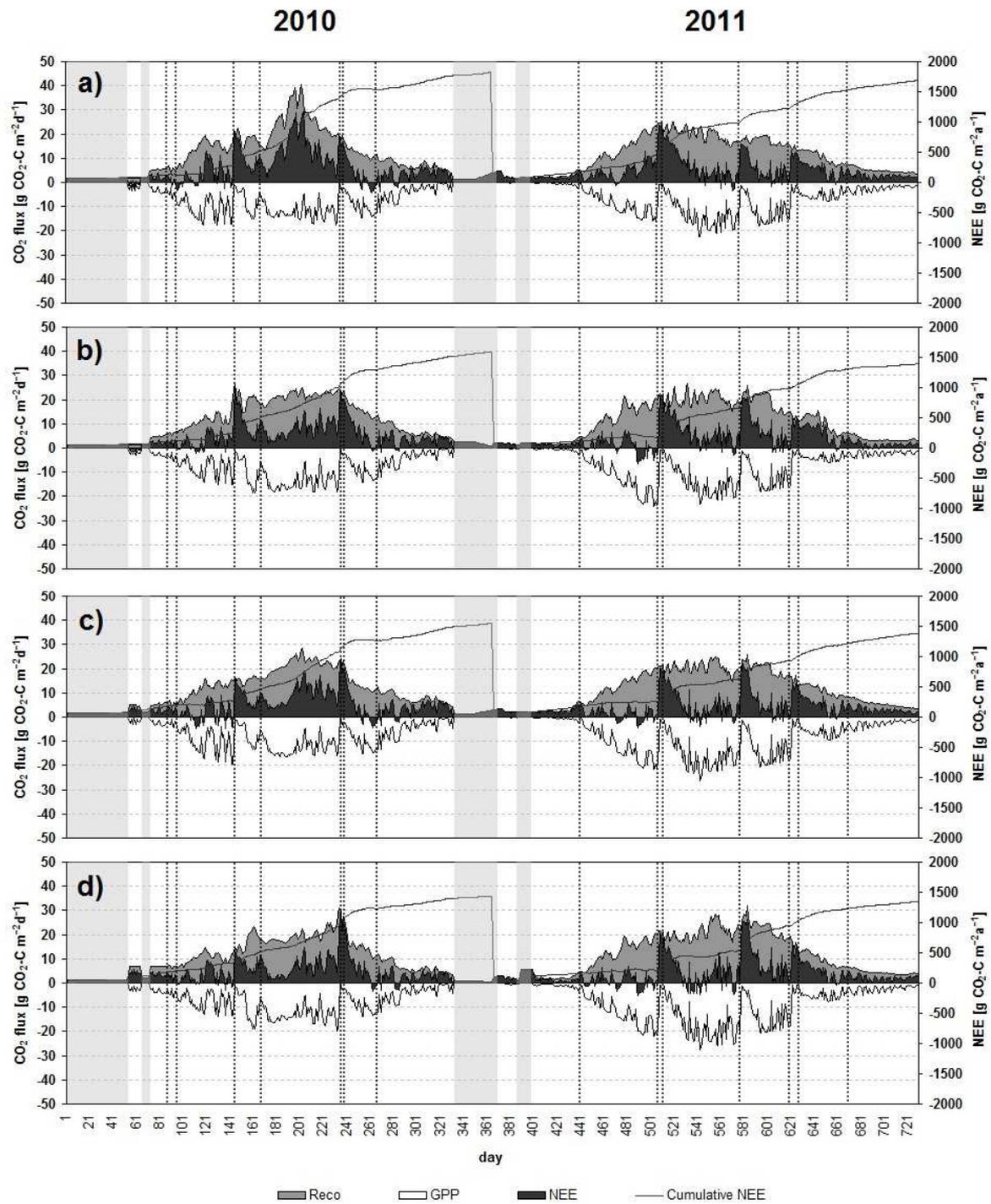
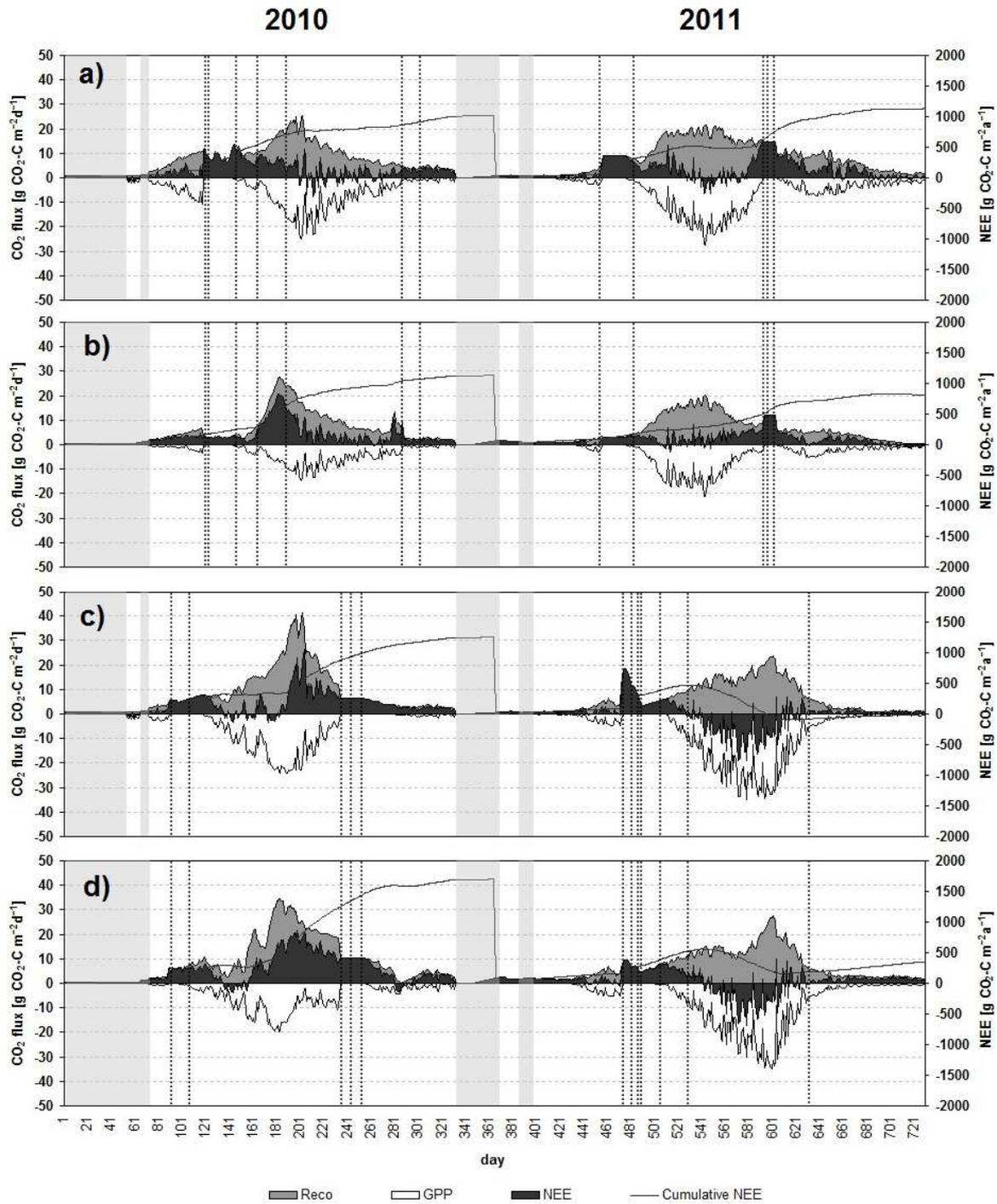


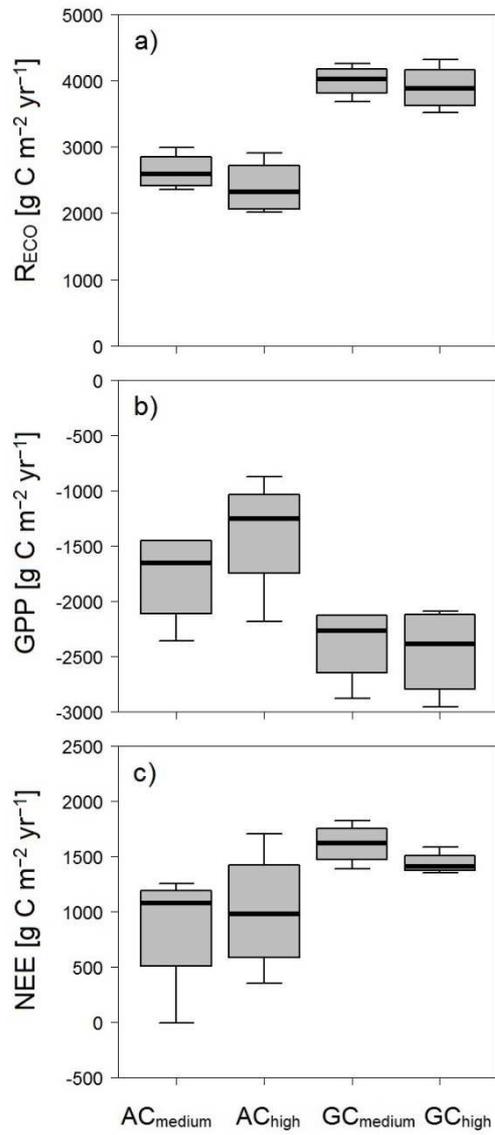
Fig. 3 Box plots of mineral nitrogen contents [ $\text{mg N kg}^{-1}$ ] of the soil depth 0–10 cm (A = arable land, G = grassland).



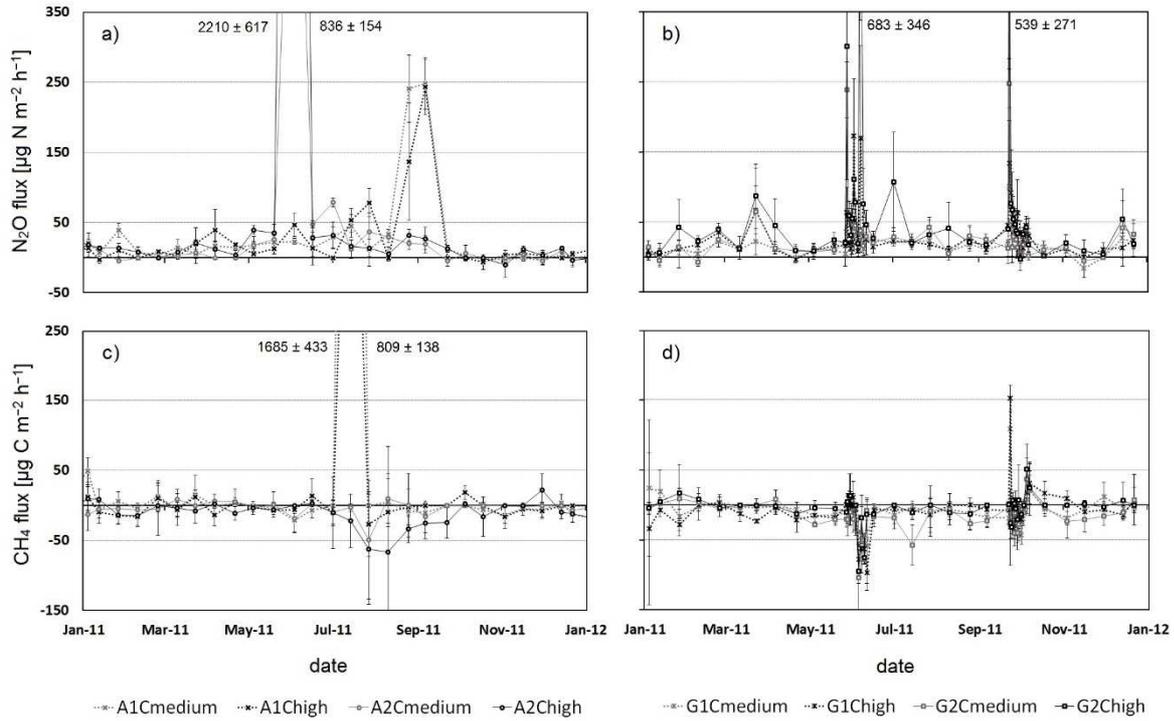
**Fig. 4** Time series of modeled CO<sub>2</sub> fluxes [g CO<sub>2</sub>-C m<sup>-2</sup> d<sup>-1</sup>; g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup>] for each site in 2010 and 2011; a) grassland, cattle slurry, C<sub>medium</sub>; b) grassland cattle slurry, C<sub>high</sub>; c) grassland biogas digestate C<sub>medium</sub>; d) grassland, biogas digestate, C<sub>high</sub>. Grey bars mark the period with snow cover. Dashed lines indicate management activities (see table 2).



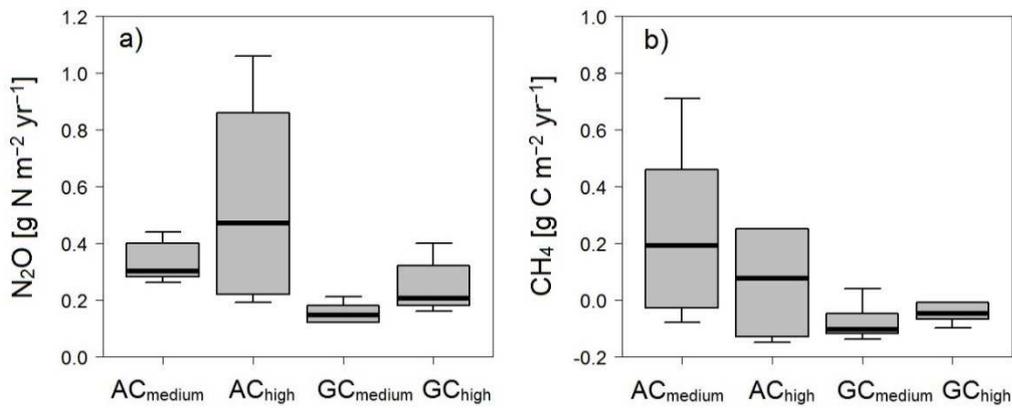
**Fig. 5** Time series of modeled CO<sub>2</sub> fluxes [g CO<sub>2</sub>-C m<sup>-2</sup> d<sup>-1</sup>; g CO<sub>2</sub>-C m<sup>-2</sup> yr<sup>-1</sup>] for each site in 2010 and 2011; a) arable land, 2010 maize, 2011 oat, C<sub>medium</sub>; b) arable land, 2010 maize, 2011 oat, C<sub>high</sub>; c) arable land, 2010 oat, 2011 maize, C<sub>medium</sub>; d) arable land, 2010 oat, 2011 maize, C<sub>high</sub>. Grey bars mark the period with snow cover. Dashed lines indicate management activities (see table 2).



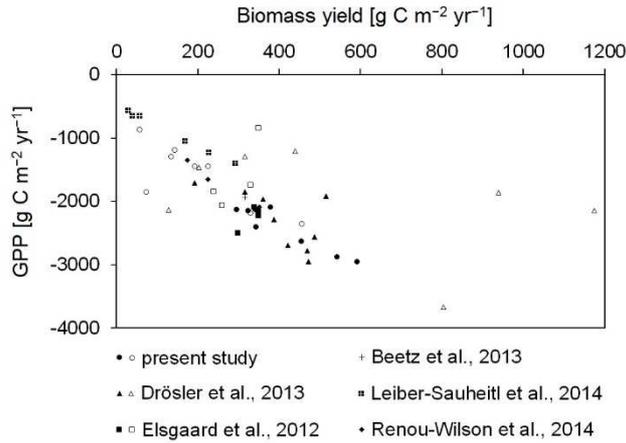
**Fig. 6** Box plots of  $R_{Eco}$  (a), GPP (b) and NEE (c) for the two soil types and land-use types.



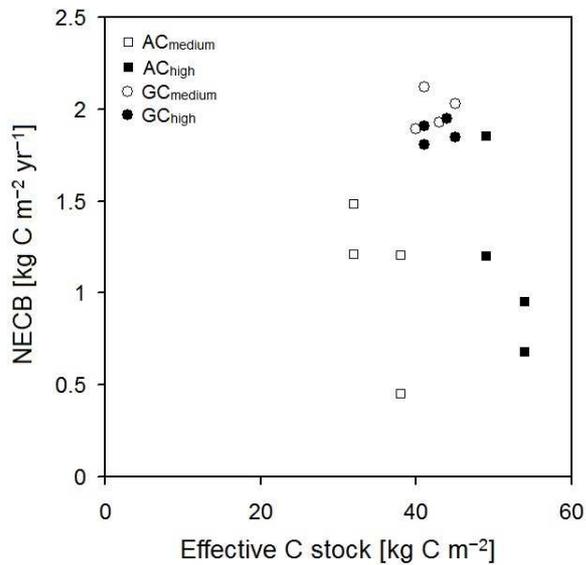
**Fig. 7** Time series of measured  $\text{N}_2\text{O}$  fluxes (a, arable land; b, grassland) and  $\text{CH}_4$  fluxes (c, arable land; d, grassland) for the year 2011.



**Fig. 8** Box plots of cumulative annual  $\text{N}_2\text{O}$  emissions (a), and cumulative annual  $\text{CH}_4$  emissions for the two soil types and land-use types.



**Fig. 9** Relationship of GPP and biomass export from temperate peatlands. Filled symbols represents grassland sites (intensive and extensive), unfilled symbols represents arable lands.



**Fig. 10** NECB plotted against the effective C stock, which is defined as the fraction of aerated carbon in the soil profile (according to Leiber-Sauheitl et al., 2014) (calculated NECB did not include CH<sub>4</sub> losses).

## SUPPLEMENT TO PUBLICATION I.

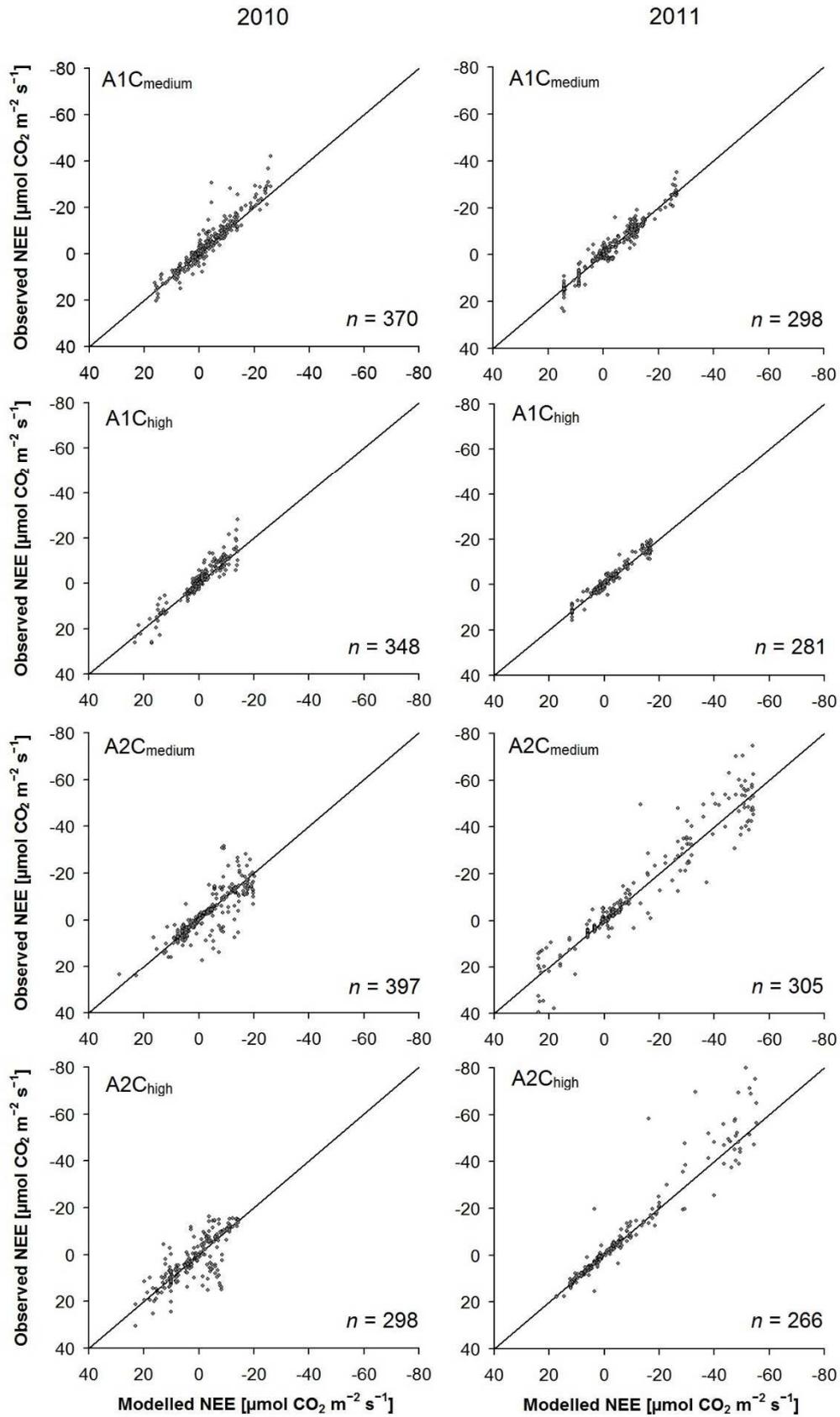


Fig. S1 Observed vs. modelled plots of NEE for the arable sites. Solid lines indicate the 1:1 line for a perfect fit.

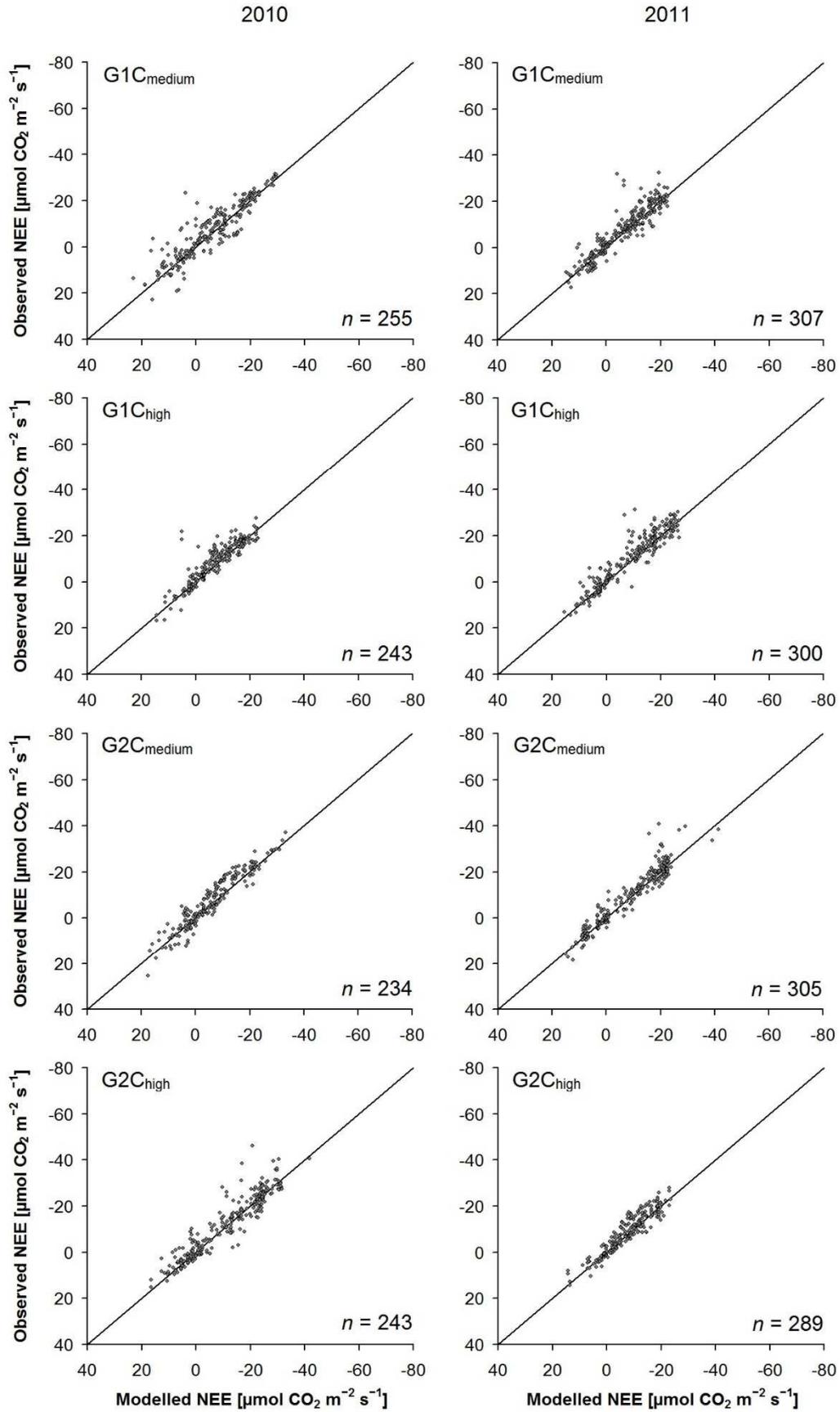


Fig. S2 Observed vs. modelled plots of NEE for the grassland sites. Solid lines indicate the 1:1 line for a perfect fit.

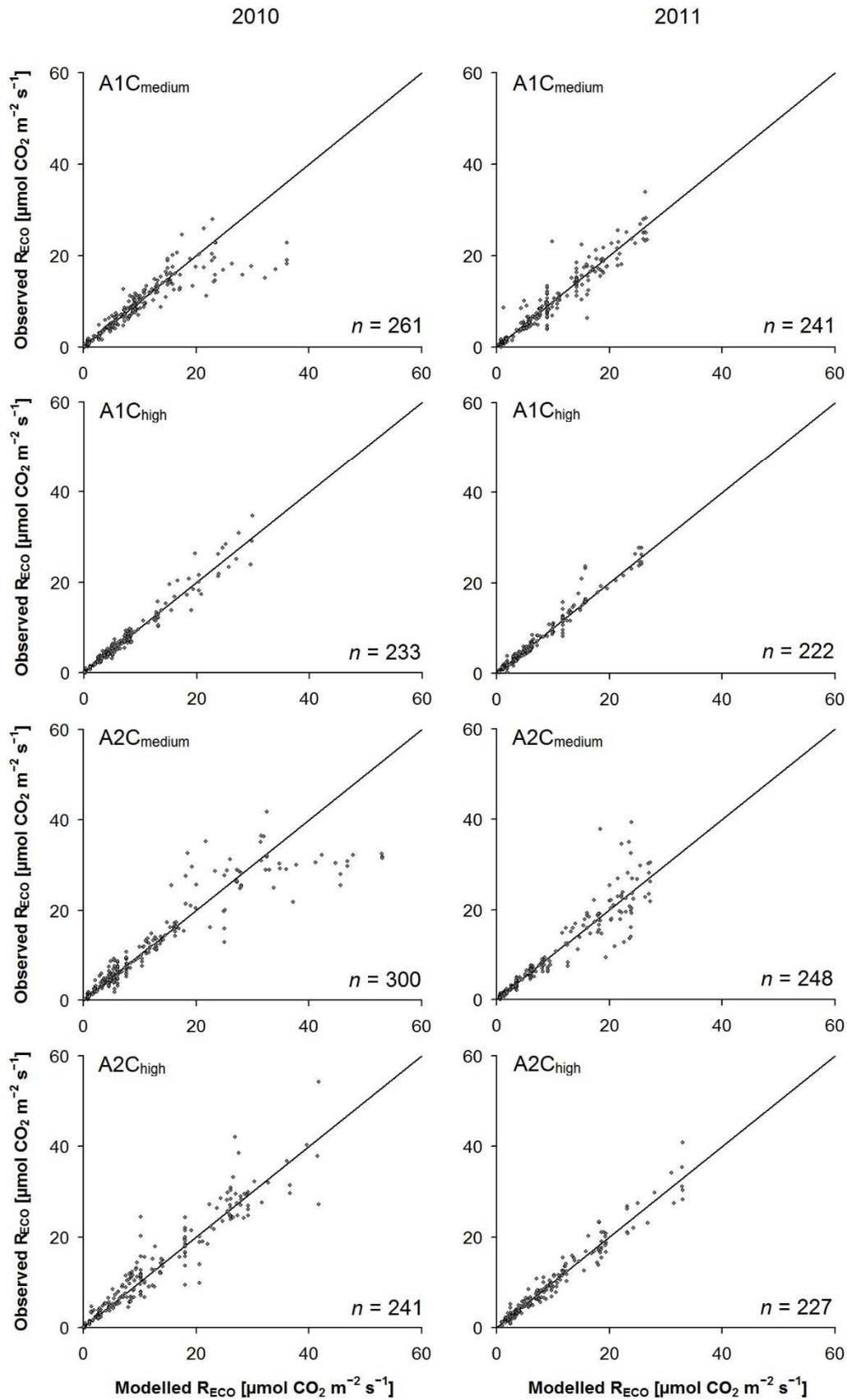


Fig. S3 Observed vs. modelled plots of  $R_{ECO}$  for the arable sites. Solid lines indicate the 1:1 line for a perfect fit.

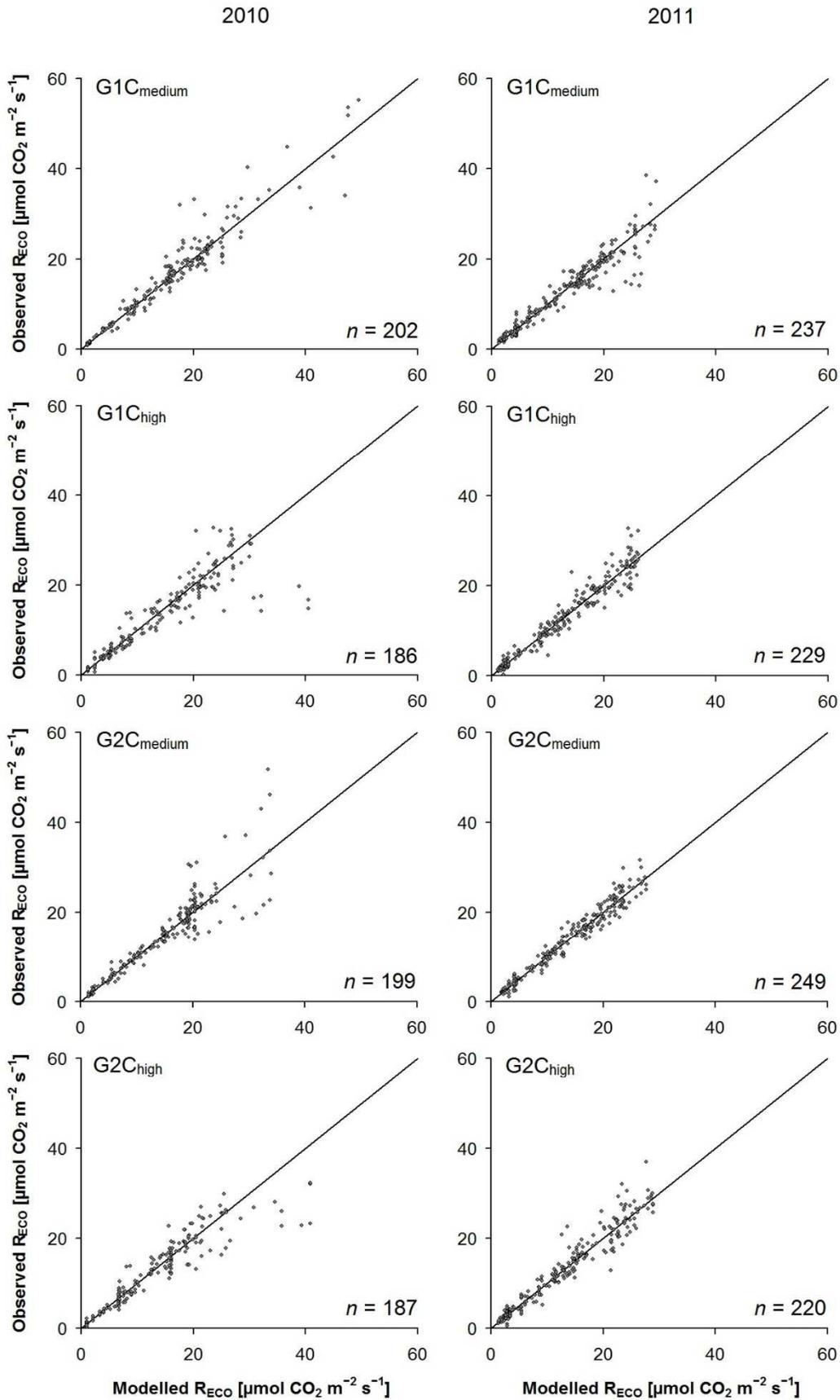


Fig. S4 Observed vs. modelled plots of  $R_{\text{Eco}}$  for the grassland sites. Solid lines indicate the 1:1 line for a perfect fit.



Table S2 Model parameters of the A1C<sub>high</sub> site.

Site	Date	$R_{CO_2}$										GPP										$R_{CO_2}$ without model								
		Std. Error					95% Confidence Limits					model based on					Std. Error					95% Confidence Limits					daily mean $R_{CO_2}$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )			
		$R_{min}$	$E_s$	$R_{max}$	$E_s$	Std. Error	lower $R_{CO_2}$	upper $R_{CO_2}$	lower $E_s$	upper $E_s$	n	model	based on	$\alpha$	GPP <sub>max</sub>	$\alpha$	Std. Error	lower $\alpha$	upper $\alpha$	lower GPP <sub>max</sub>	upper GPP <sub>max</sub>	n	lower $R_{CO_2}$	upper $R_{CO_2}$	lower 95% Confidence Limits	upper 95% Confidence Limits	n			
A1C <sub>high</sub>	2010-02-09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
A1C <sub>high</sub>	2010-02-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
A1C <sub>high</sub>	2010-03-08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
A1C <sub>high</sub>	2010-03-24	2.49	76.95	0.07	13.88	2.34	2.64	48.53	105.38	30	$T_{air}$	0.00	-2.46	0.00	0.12	-0.01	-0.01	0.00	-2.71	-2.21	44	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-04-06	4.59	81.94	0.20	23.27	4.16	5.02	32.85	131.03	20	$T_{air}$	0.00	-3.57	0.00	0.18	-0.01	0.00	0.00	-3.94	-3.19	30	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-04-28	5.84	155.65	0.34	33.27	5.11	6.57	84.29	227.01	16	$ST_5$	-0.01	-8.94	0.00	0.51	-0.01	0.00	0.00	-10.00	-7.89	24	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-05-23	2.95	106.80	0.23	27.68	2.45	3.45	47.82	165.79	17	$T_{air}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-06-10	1.39	404.93	0.19	36.87	0.98	1.79	327.15	482.70	19	$ST_2$	-0.01	-9.42	0.00	0.30	-0.01	-0.01	-0.01	-10.04	-8.80	29	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-07-02	23.46	42.87	1.83	21.10	19.33	27.59	4.86	90.60	11	$T_{air}$	-0.02	-17.50	0.01	1.43	-0.03	0.00	0.00	-20.50	-14.50	20	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-07-21	12.61	88.94	1.14	21.86	10.20	15.02	42.83	135.05	19	$T_{air}$	-0.04	-37.67	0.01	1.76	-0.05	-0.02	-0.02	-41.28	-34.06	30	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-08-21	6.66	146.95	0.47	18.09	5.65	7.67	107.88	186.02	15	$T_{air}$	-0.04	-24.30	0.01	1.27	-0.05	-0.02	-0.02	-26.99	-21.60	18	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-09-12	5.73	81.71	0.33	17.09	5.01	6.44	44.79	118.63	15	$T_{air}$	-0.01	-20.57	0.00	1.09	-0.02	-0.01	-0.01	-22.80	-18.34	30	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-10-04	4.54	203.09	0.39	36.90	3.67	5.40	120.88	285.29	12	$T_{air}$	-0.03	-20.40	0.01	1.25	-0.05	-0.02	-0.02	-23.12	-17.69	14	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-10-13	14.00	577.38	2.83	138.77	7.48	20.51	257.36	897.39	10	$ST_2$	-0.02	-15.84	0.01	8.05	-0.04	0.00	0.00	-33.23	1.56	15	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-10-29	2.76	87.44	0.07	12.46	2.60	2.92	60.30	114.59	14	$T_{air}$	-0.01	-10.84	0.00	3.14	-0.01	0.00	0.00	-17.57	-4.10	16	-	-	-	-	-	-			
A1C <sub>high</sub>	2010-12-13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-01-05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-01-27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-02-07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-03-08	1.20	64.75	0.04	13.73	1.11	1.29	35.10	94.41	15	$T_{air}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-03-29	3.06	250.34	0.19	35.10	2.65	3.47	175.52	325.16	17	$T_{air}$	-0.01	-10.48	0.00	0.46	-0.01	-0.01	-0.01	-11.45	-9.51	21	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-04-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-05-06	4.33	167.57	0.18	20.60	3.96	4.70	124.11	211.03	19	$ST_5$	-0.01	-5.85	0.00	0.27	-0.01	0.00	0.00	-6.39	-5.31	42	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-05-25	12.13	68.75	0.46	11.91	11.08	13.17	41.81	95.69	11	$T_{air}$	-0.08	-33.08	0.01	0.71	-0.10	-0.06	-0.06	-34.53	-31.62	31	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-06-28	13.41	150.82	0.49	10.04	12.37	14.45	129.64	171.99	19	$T_{air}$	-0.10	-41.08	0.01	0.82	-0.12	-0.07	-0.07	-42.80	-39.37	23	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-08-02	6.49	96.67	0.34	13.66	5.77	7.21	67.98	125.36	20	$T_{air}$	-0.01	-7.74	0.00	0.26	-0.02	-0.01	-0.01	-8.28	-7.21	22	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-08-24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-09-24	4.43	137.92	0.27	28.27	3.85	5.01	77.29	198.55	16	$T_{air}$	-0.03	-17.13	0.00	0.71	-0.04	-0.02	-0.02	-18.64	-15.63	19	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-10-16	5.71	86.06	0.14	12.31	5.42	6.00	59.82	112.29	17	$T_{air}$	-0.01	-14.30	0.00	0.89	-0.02	-0.01	-0.01	-16.16	-12.43	21	-	-	-	-	-	-			
A1C <sub>high</sub>	2011-12-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
A1C <sub>high</sub>	2012-01-12	1.03	301.93	0.11	68.91	0.79	1.27	153.06	450.81	15	$T_{air}$	-0.01	-11.43	0.00	3.50	-0.01	0.00	0.00	-18.86	-4.01	18	-	-	-	-	-	-			













## 7.2 PUBLICATION II.



**Eickenscheidt, T.**, Freibauer, A.; Heinichen, J., Augustin, J., and Drösler, M.: Short-term effects of biogas digestate and cattle slurry application on greenhouse gas emissions affected by N availability from grasslands on drained fen peatlands and associated organic soils, *Biogeosciences*, 11, 6187–6207, doi:10.5194/bg-11-6187-2014, 2014.

Biogeosciences, 11, 6187–6207, 2014  
www.biogeosciences.net/11/6187/2014/  
doi:10.5194/bg-11-6187-2014  
© Author(s) 2014. CC Attribution 3.0 License.



## Short-term effects of biogas digestate and cattle slurry application on greenhouse gas emissions affected by N availability from grasslands on drained fen peatlands and associated organic soils

T. Eickenscheidt<sup>1</sup>, A. Freibauer<sup>2</sup>, J. Heinichen<sup>1</sup>, J. Augustin<sup>3</sup>, and M. Drösler<sup>1</sup>

<sup>1</sup>University of Applied Sciences Weihenstephan-Triesdorf, Chair of Vegetation Ecology, Weihenstephaner Berg 4, 85354 Freising, Germany

<sup>2</sup>Thünen Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Braunschweig, Germany

<sup>3</sup>Leibniz Centre for Agricultural Landscape Research e.V., Institute of Landscape Matter Dynamics, Eberswalder Straße 84, 15374 Müncheberg, Germany

Correspondence to: T. Eickenscheidt (tim.eickenscheidt@hswt.de)

**Abstract.** A change in German energy policy has resulted in a strong increase in the number of biogas plants in Germany. As a consequence, huge amounts of nutrient-rich residues, the by-products of the fermentative process, are used as organic fertilizers. Drained peatlands are increasingly used to satisfy the huge demand for fermentative substrates (e.g., energy crops, grass silage) and the digestate is returned to the peatlands. However, drained organic soils are considered as hot spots for nitrous oxide (N<sub>2</sub>O) emissions and organic fertilization is additionally known to increase N<sub>2</sub>O emissions from managed grasslands. Our study addressed the questions (a) to what extent biogas digestate and cattle slurry application increase N<sub>2</sub>O and methane (CH<sub>4</sub>) fluxes as well as the mineral nitrogen use efficiency (NUE<sub>min</sub>) and grass yield, and (b) how different soil organic matter contents (SOMs) and nitrogen contents promote the production of N<sub>2</sub>O. In addition NH<sub>3</sub> volatilization was determined at one application event to obtain first clues with respect to the effects of soil and fertilizer types. The study was conducted at two sites within a grassland parcel, which differed in their soil organic carbon (SOC) and N contents. At each site (named C<sub>org-medium</sub> and C<sub>org-high</sub>) three plots were established: one was fertilized five times with biogas digestate, one with cattle slurry, and the third served as control plot. On each plot, fluxes of N<sub>2</sub>O and CH<sub>4</sub> were measured on three replicates over 2 years using the closed chamber method. For NH<sub>3</sub> measurements we used the calibrated dynamic chamber method. On an annual basis, the application of biogas digestate significantly enhanced the N<sub>2</sub>O fluxes compared to the application of cattle slurry and additionally increased the plant

N-uptake and NUE<sub>min</sub>. Furthermore, N<sub>2</sub>O fluxes from the C<sub>org-high</sub> treatments significantly exceeded N<sub>2</sub>O fluxes from the C<sub>org-medium</sub> treatments. Annual cumulative emissions ranged from  $0.91 \pm 0.49$  to  $3.14 \pm 0.91$  kg N ha<sup>-1</sup> yr<sup>-1</sup>. Significantly different CH<sub>4</sub> fluxes between the investigated treatments or the different soil types were not observed. Cumulative annual CH<sub>4</sub> exchange rates varied between  $-0.21 \pm 0.19$  and  $-1.06 \pm 0.46$  kg C ha<sup>-1</sup> yr<sup>-1</sup>. Significantly higher NH<sub>3</sub> losses, NUE<sub>min</sub> and grass yields from treatments fertilized with biogas digestate compared to those fertilized with cattle slurry were observed. The total NH<sub>3</sub> losses following the splash plate application were 18.17 kg N ha<sup>-1</sup> for the digestate treatments and 3.48 kg N ha<sup>-1</sup> for the slurry treatments (36 and 15 % of applied NH<sub>4</sub><sup>+</sup>-N). The observed linear increase of 16 days' cumulative N<sub>2</sub>O-N exchange or annual N<sub>2</sub>O emissions, with mean groundwater level and ammonium application rate, reveals the importance of site-adapted N fertilization and the avoidance of N surpluses in C<sub>org-rich</sub> grasslands.

### 1 Introduction

Germany has become the largest biogas producing country in the world since a change in German energy policy and the enactment of the German Renewable Energy Act (Weiland, 2010). At the end of 2012, more than 7500 agricultural biogas plants were operating in Germany (Fachverband Biogas, 2014). Heat and power from biogas substitute for fossil fuels and therefore can reduce greenhouse gas (GHG) emissions

(Weiland, 2010; Don et al., 2012). The strong increase in the number of biogas plants caused a land-use change towards agro-biomass production and additionally raised land-use intensity to satisfy the huge demand for fermentative substrates (Don et al., 2012). In 2011, grass silage accounted for 9 % of the total renewable resources for biogas production (DBFZ, 2012) and was the second most important fermentation substrate after maize silage.

During the fermentative process high amounts of nutrient-rich residues are produced as a by-product. Today, this new form of organic fertilizer is used instead of mineral fertilizers or animal slurries to maintain soil fertility and productivity. Several studies reported a significant increase in nitrous oxide ( $\text{N}_2\text{O}$ ) emissions due to the application of nitrogen fertilizers (e.g., Bouwman, 1996; Chadwick et al., 2000; Rodhe et al., 2006; Ruser, 2010). Liquid organic fertilizers such as animal slurry add easily degradable organic carbon (Christensen, 1983) and moisture, both further favoring  $\text{N}_2\text{O}$  losses through denitrification (Clayton et al., 1997). Enhanced  $\text{N}_2\text{O}$  emissions are of major concern due to the fact that  $\text{N}_2\text{O}$  acts as a radiative forcing GHG (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). In Germany, about 78 % of  $\text{N}_2\text{O}$  emissions originate from the agricultural sector (Umweltbundesamt, 2014). In particular, organic soils (e.g., drained peat soils and soils developed in wet conditions) are considered as hotspots of GHG emissions including  $\text{N}_2\text{O}$ , due to the very high mineralization rates of degrading peat (Kasimir-Klemetsson et al., 1997; Freibauer et al., 2004; Klemetsson et al., 2005; Goldberg et al., 2010) and to soil moisture conditions that favor anaerobic microsites. According to Maljanen et al. (2010),  $\text{N}_2\text{O}$  emissions from drained organic soils under agricultural use were on average four times as high as those from mineral soils. The few field studies of organic fertilization effects on annual  $\text{N}_2\text{O}$  emissions from drained organic grassland soils revealed very high  $\text{N}_2\text{O}$  emissions of up to  $41.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Velthof et al., 1996).

In Germany, 50 % of the drained peatlands are used as grasslands (Drösler et al., 2011), particularly in the smallholder structure of south Germany. Grassland soils in Europe and Germany produce more  $\text{N}_2\text{O}$  per unit of fertilizer-N than croplands, and emission factors further increase with soil organic carbon (SOC) and nitrogen content (Freibauer and Kaltschmitt, 2003; Dechow and Freibauer, 2011). Moreover, agricultural soils in the southern part of Germany emit about three times as much of the applied N as  $\text{N}_2\text{O}$  as soils in the rest of Germany, which is attributed to the more frequent frost–thaw cycles and enhanced precipitation rates (Jungkunst et al., 2006; Dechow and Freibauer, 2011). Thus, grasslands on organic soils in South Germany represent a widespread high-risk situation for high  $\text{N}_2\text{O}$  emissions after cattle slurry or biogas digestate application, which has not, to our knowledge, been studied before.

Biogas digestate is depleted in easily degradable C compounds and in organic dry matter content compared to fresh

slurry due to anaerobic digestion (Möller and Stinner, 2009). The pH value and the ammonium ( $\text{NH}_4^+$ ) content as well the  $\text{NH}_4^+ : \text{N}_{\text{org}}$  ratio are higher than in fresh slurry (Wulf et al., 2002b; Möller and Stinner, 2009). Since digested products are more recalcitrant than fresh slurry it could be assumed that microbial degradation is slow, resulting in fewer anoxic microsites and reduced  $\text{N}_2\text{O}$  emissions compared with fresh slurry application (Clemens and Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009). However, the few available field and laboratory experiments are contradictory regarding the effect of biogas digestate application on  $\text{N}_2\text{O}$  emissions (e.g., Clemens and Huschka, 2001; Wulf et al., 2002b; Clemens et al., 2006; Senbayram et al., 2009; Sängler et al., 2010), and very few studies exist for grasslands (e.g., Wulf et al., 2002b, Clemens et al., 2006).

The different properties of biogas digestate and cattle slurry (e.g., higher  $\text{NH}_4^+ - \text{N}$  concentrations, narrower C : N ratio, higher pH values) directly affect N transformation processes, plant N availability, and thus grass yield. Furthermore it can be assumed that the plant N-uptake and the  $\text{N}_2\text{O}$  emissions are closely interconnected since N-uptake can be considered as a proxy for N availability, affecting N gaseous losses as well. Currently, the effect of anaerobic digestates on crop growth after surface application under field conditions is contradictory, since some authors reported higher crop yields compared to undigested slurries (e.g., Odlare, 2005 cited in Möller and Müller, 2012) whereas others found no effects (e.g., Möller et al., 2008). Only a few studies exist for grassland but it seems that fertilization with biogas digestates positively affects grass yields, but only in single years (Elsässer et al., 1995; Rubæk et al., 1996; Möller et al., 2008; Möller and Müller, 2012).

As well as  $\text{N}_2\text{O}$ , slurry application leads to short-term methane ( $\text{CH}_4$ ) and ammonia ( $\text{NH}_3$ ) emissions. Methane acts as a strong GHG, whereas  $\text{NH}_3$  is considered an indirect GHG through ammonia deposition which could promote the formation of  $\text{N}_2\text{O}$  (Moiser, 2001). Moreover,  $\text{NH}_3$  deposition causes soil acidification and eutrophication of ecosystems (e.g., Fangmeier et al., 1994; Galloway, 1995, 2001; Smith et al., 1999). In Germany, agriculture is responsible for 95.3 % of anthropogenic  $\text{NH}_3$  emissions (Haenel et al., 2010). Particularly high  $\text{NH}_4^+$  contents and high pH values, which are typically for the biogas digestate, promote accelerated  $\text{NH}_3$  volatilization (Quakernack et al., 2011). High  $\text{NH}_3$  emissions particularly occur after splash plate application on grassland (Rubæk et al., 1996; Wulf et al., 2002a), which is still common practice in the smallholder farms of South Germany.

The objective of this study was to quantify short-term  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emissions after application of biogas digestate and cattle slurry on grassland on two types of organic soils in South Germany, which differed in their SOC and N contents. Additionally, to what extent biogas digestate and cattle slurry application affect N availability and grass yield should

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6189

**Table 1.** Summary of the grassland management for both vegetation periods.

Date	Management event
26 Mar 2010	leveling
7 Apr 2010	rolling
24 May 2010	mowing
14 Jun 2010	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
20 Aug 2010	mowing
25 Aug 2010	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
23 Sep 2010	herbicide against common sorrel ( <i>Rumex acetosa</i> )
16 Mar 2011	leveling
23 May 2011	mowing
27 May 2011	manuring [25 m <sup>3</sup> ha <sup>-1</sup> ]
1 Aug 2011	mowing
13 Sep 2011	mowing
22 Sep 2011	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
4 Nov 2011	manuring [25 m <sup>3</sup> ha <sup>-1</sup> ]

be tested. Furthermore, NH<sub>3</sub> volatilization was determined at one application event to obtain first clues with respect to the effects of soil and fertilizer types. We hypothesize the following: (a) more N<sub>2</sub>O is emitted after biogas digestate than after slurry application because of higher NH<sub>4</sub><sup>+</sup>-N concentrations in the substrate and, thus, higher NH<sub>4</sub><sup>+</sup>-N amounts when using equal volumetric application rates. The more recalcitrant nature of the carbon in the biogas digestate does not matter for GHG formation in high organic carbon soils. (b) N<sub>2</sub>O emissions increase with increasing soil C<sub>org</sub> and N content due to more favorable conditions for denitrification after organic fertilizer application. (c) Biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to cattle slurry due to the higher N availability of the digestate.

## 2 Materials and methods

### 2.1 Study site

The study was conducted on a permanent grassland at a drained fen peatland 30 km northeast of Munich (Freisinger Moos, 48°21' N, 11°41' E; 450 m a.s.l.). The dominant species were *Poa trivialis*, *Poa pratensis*, *Festuca pratensis*, *Dactylis glomerata*, and *Alopecurus pratensis*. The grassland was mown two and three times in 2010 and 2011 respectively, as is the usual practice in this region. A summary of the complete grassland management over both vegetation periods can be found in Table 1. The grass was used as silage or hay for cattle or as substrate for biogas plants. According to the climate station in Weißenstephan, located 10 km northeast of the site, the 30-year mean annual temperature was 7.5 °C and the mean annual precipitation was 787 mm (1961–1990). Annual atmospheric N deposition amounted to 6.22 and 7.20 kg N ha<sup>-1</sup> yr<sup>-1</sup>, with NH<sub>4</sub><sup>+</sup>-N : NO<sub>3</sub><sup>-</sup>-N ra-

tios of 46 : 54 and 49 : 51 in 2010 and 2011. Data of N deposition were collected by the Bavarian State Institute of Forestry at a German Level II monitoring area (Forest Intensive Monitoring Programme of the UNECE), located at 7 km distance from the investigated grassland. In October 2009 we selected two sites within the grassland parcel, which differed in their SOC contents in the topsoil (Table 2). According to the WRB (2006), soil types were classified as mollic Gleysol (named C<sub>org</sub>-medium) and as sapric Histosol (named C<sub>org</sub>-high; N. Roßkopf, personal communication, 2013).

### 2.2 Experimental design

At each site of the grassland parcel, three adjacent plots (plot dimension 12 × 12 m) were selected. At one plot biogas digestate and at another plot cattle slurry were applied; the third plot served as a control (without fertilization). Centrally at each plot, three PVC-collars for GHG measurements (inside dimension 75 × 75 cm; 0.5625 m<sup>2</sup>) were permanently inserted 10 cm into the soil with a distance of 1.5 m to each other. To prevent oscillations of the peat through movements during the measurements, boardwalks were installed. At each site a climate station was set up in March 2010 for the continuous recording (every 0.5 h; CR200X Datalogger, Campbell Scientific) of air temperature and humidity at 20 cm above soil surface (CS215-L, Campbell Scientific) and soil temperatures at depths of -2, -5 and -10 cm (109-L, Campbell Scientific). For NH<sub>3</sub> measurements, sensors for wind speed and wind direction (Kleinwindensor, Thies Clima) in 2 m height were additionally integrated from May to July 2011, with a logging frequency of 5 s (GP1, Delta-T Devices). For measuring the groundwater table, plastic perforated tubes (JK-casings DN 50, 60 mm diameter, 1 m length) were inserted close to each collar to obtain individual groundwater tables for all repetitions during each gas flux measurement. In April 2010, we equipped one tube per plot with a water level logger (Type MiniDiver, Schlumberger water services), which logged the water tables every 15 min. Additionally to the recorded data, plot-specific soil temperatures at three soil depths (-2, -5 and -10 cm) were determined with penetration thermometers at the beginning and end of each gas flux measurement.

In 2010 and 2011, organic fertilizers were applied via splash plate (swiveling slurry spreader for biogas digestate; gooseneck scatterer for cattle slurry) on 14 June 2010, 25 August 2010, 27 May 2011, 22 September 2011, and 4 November 2011 by the landowners (see Table 1). The surface application technique via splash plate is the most common application technique in the smallholder structure of the region. The organic fertilizer was applied on the basis of equal volumetric rates per application event (20 or 25 m<sup>3</sup> ha<sup>-1</sup>). This method is typical for farming practices, but produces diverging N application rates per event between slurry and digestate based on NH<sub>4</sub><sup>+</sup> or N<sub>tot</sub> applications. It is known that the splash plate application technique can result in very uneven

## 6190 T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

Table 2. Soil properties of the study site.

	Sampling depth	C <sub>org</sub> -medium	C <sub>org</sub> -high	<i>n</i>
Soil type (WRB, 2006) <sup>1</sup>		mollic Gleysol	sapric Histosol	
Soil type (German classification KA5)		GMq	KV-KM	
Peat depth [cm] <sup>1</sup>		80	70	1
pH value <sup>2</sup>		4.1	4.2	
Total nitrogen [%] <sup>2</sup>		1.0	1.5	
Organic carbon [%]	0–10 cm	10.3 ± 0.2	17.0 ± 0.1	9
	10–20 cm	9.3 ± 0.2	16.3 ± 0.2	9
Bulk density [g cm <sup>-3</sup> ]	0–10 cm	0.79 ± 0.02	0.54 ± 0.02	18
	10–20 cm	0.90 ± 0.01	0.64 ± 0.01	18
Porosity [%]	0–10 cm	71 ± 1	78 ± 1	18
	10–20 cm	67 ± 1	72 ± 0	18

Values present means ± SE. <sup>1</sup> World Reference Base for Soil Resources. <sup>2</sup> Relative to the upper horizon (C<sub>org</sub>-medium 0–20 cm; C<sub>org</sub>-high 0–15 cm); N. Roßkopf, personal communication, 2013.

spreading regarding the application rate and/or the evenness. Both chosen spreading devices are known for the higher precision in their application evenness compared to conventional splash plates (approximately 15 and 18–27 % application variability for swiveling slurry spreader and gooseneck scatterer and up to 47 % for conventional splash plate; Frick, 1999). In the present study, the application of an equal volumetric slurry rate was controlled via the barrel content and the tractor speed. At all plots, the tractor lane was 1 m in front of the collars, which were placed in a row with a distance of 1.5 m to each other. Both spreading systems had a spreading width of 12 m and no overlapping zones occurred. Nevertheless we cannot give any estimation of the precision of application evenness that was actually achieved.

The physical and chemical composition of the slurries and digestates varied between the four application events (Table 3). Composition of organic fertilizers was analyzed from 1 L samples which were taken from the slurry tank in the field. Slurries were immediately frozen at –20 °C until analysis was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). Due to technical problems at the first application event, cattle slurry was applied by watering cans on the ground of the collars and on a 120 m<sup>2</sup> adjacent area. To ensure an equal volumetric amount of organic fertilizer a 1 × 1 m grid, fabricated from cords, was previously installed. The same method was used at the fourth application event for the digestate.

### 2.3 N<sub>2</sub>O and CH<sub>4</sub> flux measurements

As a background, we measured fluxes of N<sub>2</sub>O and CH<sub>4</sub> every second week from January 2010 to January 2012 using the static manual chamber method (volume 309 L) (Livingston

and Hutchinson; 1995). We removed, however, the gas fluxes measured in 2010 from the data set due to errors in the gas chromatography analysis and due to long vial storage. Intensive measurement campaigns were performed after the four fertilization events on 14 June 2010, 25 August 2010, 27 May 2011, and 22 September 2011. Immediately after fertilization flux measurements were carried out daily for a week and on every second day for another 8–9 days. To minimize diurnal variation in the flux pattern, sampling was always carried out between 09.00 and 11.30 a.m. A detailed description of chamber dimensions and configuration is given in Drösler (2005). Four gas samples were taken at regular time intervals after chamber closure (enclosure time 60 min). The samples were collected in 20 mL glass vials, each sealed with a butyl rubber septum. The vials were flushed with chamber air for 30 s using a portable micro pump (KNF Neuberger GmbH, NMP015B), so that the air in the vials was exchanged 32 times. In addition the pump was used to build up an overpressure of approximately 550 mbar to protect the sample against fluctuations in atmospheric pressure during storage. Gas analyses were carried out with a gas chromatograph (Perkin and Elmer, Clarus 400 GC respectively Clarus 480 GC) equipped with a headspace auto sampler (Perkin & Elmer, TurboMatrix 110), a PoraPack 80/100 mesh column, an electron capture detector (ECD) for N<sub>2</sub>O (ECD temperature 380 °C) and a flame ionization detector (FID) for CH<sub>4</sub> analyses (FID temperature 310 °C). Gas samples from the first fertilization event (14–30 June 2010) were immediately analyzed at the Max Planck Institute for Biogeochemistry in Jena, whereas samples from the second fertilization event (25 August–10 September 2010) were analyzed at the Thünen Institute in Braunschweig with a Varian CP-3800 GC-FID/-

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6191

**Table 3.** Physical and chemical properties of the applied digestates and slurries.

	1. Application (14 Jun 2010)	2. Application (25 Aug 2010)	3. Application (27 May 2011)	4. Application (22 Sep 2011)	5. Application (4 Nov 2011)
Cattle slurry					
Fertilizer quantity [m <sup>3</sup> ha <sup>-1</sup> ]	20	20	25	20	20
Total carbon [kg ha <sup>-1</sup> ]	579	676	798	797	1073
Organic carbon [kg ha <sup>-1</sup> ]	410	573	655	706	960
Total nitrogen [kg ha <sup>-1</sup> ]	47	64	70	85	97
NO <sub>3</sub> <sup>-</sup> [kg N ha <sup>-1</sup> ]	0	0	0	0	0
NH <sub>4</sub> <sup>+</sup> [kg N ha <sup>-1</sup> ]	20	28	23	33	38
NH <sub>4</sub> <sup>+</sup> : N <sub>tot</sub> ratio	0.42	0.44	0.33	0.38	0.39
C : N ratio	12	11	11	9	11
pH (CaCl <sub>2</sub> )	–	–	6.8	7.0	7.0
Dry matter content [%]	5	7	7	9	10
Biogas digestate					
Fertilizer quantity [m <sup>3</sup> ha <sup>-1</sup> ]	20	20	25	20	20
Total carbon [kg ha <sup>-1</sup> ]	384	373	167	184	178
Organic carbon [kg ha <sup>-1</sup> ]	306	337	148	161	178
Total nitrogen [kg ha <sup>-1</sup> ]	49	52	78	35	61
NO <sub>3</sub> <sup>-</sup> [kg N ha <sup>-1</sup> ]	0	0	0	0	0
NH <sub>4</sub> <sup>+</sup> [kg N ha <sup>-1</sup> ]	22	28	51	17	40
NH <sub>4</sub> <sup>+</sup> : N <sub>tot</sub> ratio	0.45	0.53	0.65	0.49	0.66
C : N ratio	8	7	2	5	3
pH (CaCl <sub>2</sub> )	–	–	7.7	7.4	7.7
Dry matter content [%]	4	4	2	2	3

ECD using a headspace autosampler (QUMA Elektronik & Analytik GmbH, Germany) and similar conditions. Gas flux rates were calculated from the linear change in gas concentration over time considering chamber air temperature and atmospheric pressure. Gas fluxes were accepted when the linear regression was significant ( $P \leq 0.05$ ). In case of small N<sub>2</sub>O or CH<sub>4</sub> fluxes, fluxes were also accepted if the coefficient of determination was  $\geq 0.90$  and the regression slope was between  $-1$  and  $1$  ppb min<sup>-1</sup>. The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

#### 2.4 NH<sub>3</sub> flux measurements

Ammonia volatilization was measured at the third organic fertilizer application event on 27 May 2011. Measurements were performed immediately after fertilizer application and thereafter at irregular time intervals of a few hours (in total 96 measurements). For NH<sub>3</sub> measurements we used the calibrated dynamic chamber method (“Dräger-Tube Method”; DTM) which was described in detail by Pacholski et al. (2006). One day before application, eight stainless steel rings (104 cm<sup>2</sup>) were inserted into the upper soil (3 cm) at each plot, of which four were grouped close together. Ambient air was sucked with a defined flow rate (1 L min<sup>-1</sup>) through four connected (via Teflon tubes) conical stainless

steel chambers to an ammonia indicator tube (Drägerwerk AG, Lübeck, Germany). The NH<sub>3</sub> volume concentration was corrected for air temperature and air pressure (Pacholski et al., 2006). To prevent overestimation of NH<sub>3</sub> volatilization through NH<sub>3</sub> enriched ambient air from surrounding area, ammonia concentration from the control treatments was subtracted from the fertilized treatments prior to NH<sub>3</sub> flux calculation. Different studies report a distinct underestimation of up to one order of magnitude of NH<sub>3</sub> fluxes determined by the DTM, mainly due to the low air exchange rate in the chambers (Roelcke et al., 2002; Pacholski et al., 2006). To avoid underestimation of cumulative NH<sub>3</sub>-N losses determined by the DTM, Pacholski et al. (2006) developed the following calibration formula to correct the NH<sub>3</sub> fluxes:

$$\ln(\text{NH}_3 \text{ flux}_{\text{IHF}}) = 0.444 \cdot \ln(\text{NH}_3 \text{ flux}_{\text{DTM}}) + 0.590 \cdot \ln(v_{2\text{m}}), \quad (1)$$

where NH<sub>3</sub> flux<sub>IHF</sub> is NH<sub>3</sub> flux measured by the integrated horizontal flux method (kg N ha<sup>-1</sup> h<sup>-1</sup>); NH<sub>3</sub> flux<sub>DTM</sub> is NH<sub>3</sub> flux measured by the DTM (kg N ha<sup>-1</sup> h<sup>-1</sup>);  $v_{2\text{m}}$  is wind speed at 2 m height (m s<sup>-1</sup>). Quakernack et al. (2011) compared the DTM method with the frequently used micrometeorological method, concluding that the corrected DTM method also allows quantitative NH<sub>3</sub>-loss measurements. The total cumulative NH<sub>3</sub> volatilization was estimated by curve fitting and integration of the area obtained by the fit-

ted curve between time zero and the time point where the  $\text{NH}_3$  flux was zero.

### 2.5 Grass yield, apparent N use efficiency, and N-balances

The annual yield was determined by harvesting the grass inside the PVC-collars with a pair of scissors at each mowing event (same cutting height as the farmer, at about 5 cm; sample area = 0.5625 m<sup>2</sup>). There was no visible disturbance from trace gas measurements in the collars. The grassland parcel showed a strong spatial heterogeneity in grass yield so that only sampling inside the collars allowed grass yield and N uptake to be related with  $\text{N}_2\text{O}$  emissions. Mowing events took place on 24 May 2010, 20 August 2010, 23 May 2011, 1 August 2011, and 13 September 2011 (see Table 1). To determine the dry mass (DM), grass samples were oven dried at 60 °C for 48 h. To determine the total carbon ( $C_{\text{tot}}$ ) and total nitrogen ( $N_{\text{tot}}$ ) concentrations of plant biomass, dried grass samples were milled (0.5 mm) and mixed subsamples were analyzed according to DIN ISO 10694 and DIN ISO 13878 by the AGROLAB Labor GmbH (Bruckberg, Germany). The apparent  $N_{\text{tot}}$  or  $N_{\text{min}}$  use efficiency (NUE,  $\text{NUE}_{\text{min}}$ ) was calculated as follows:

$$\text{NUE or } \text{NUE}_{\text{min}} = \left( \frac{N_{\text{uptake}_{\text{treatment}}} - N_{\text{uptake}_{\text{control}}}}{\text{total N applied}} \right) \cdot 100\%, \quad (2)$$

where  $N_{\text{uptake}_{\text{treatment}}}$  is the amount of N taken up by the plants in the fertilized treatments,  $N_{\text{uptake}_{\text{control}}}$  is the amount of N taken up by the plants in the unfertilized control, and “total N applied” is the amount of  $N_{\text{tot}}$  or  $N_{\text{min}}$  applied, corrected by  $\text{NH}_3$ -N losses. Emission factors for  $\text{NH}_3$  were taken from the German national GHG inventory (see Haenel et al., 2014, Table 4.6 – broadcast, grassland, emission factor (EF) of 0.60 kg kg<sup>-1</sup> related to applied  $\text{NH}_4^+$ -N), whereas for the third application event our own estimated values based on our measurements were used.

Based on the measured gaseous N fluxes and the N uptake by plants and soil  $N_{\text{min}}$  contents, a simple N balance was calculated:

$$\text{N balance} = (\text{N applied} + (\text{N min}_{t_2} - \text{N min}_{t_1}) + \text{N}_{\text{dep}}) - (\text{N uptake} + \text{N}_2\text{O}_{\text{cum}} + \text{NH}_3_{\text{cum}}), \quad (3)$$

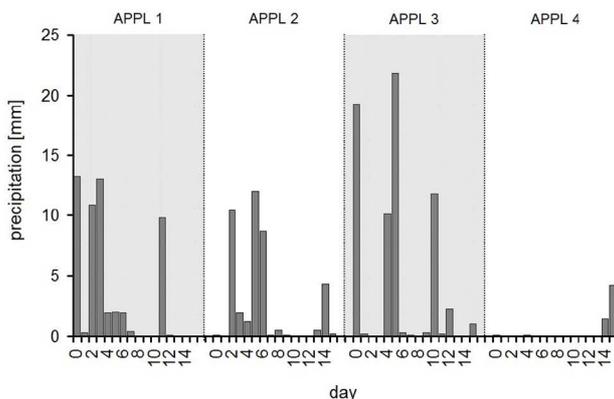
where “N applied” is the amount of  $N_{\text{tot}}$  applied,  $\text{N min}_{t_1}$  and  $\text{N min}_{t_2}$  are the amounts of  $N_{\text{min}}$  at time 1 (6 April 2011; early April represents the beginning of the vegetation period in 2011) and time 2 (18 October 2011; end of October represents the end of the vegetation period in 2011) for the soil depth 0–20 cm,  $\text{N}_{\text{dep}}$  is the annual atmospheric N deposition, “N uptake” is the amount of N taken up by the plants (quantified in harvested biomass),  $\text{N}_2\text{O}_{\text{cum}}$  is the amount of the annual cumulative  $\text{N}_2\text{O}$ -N losses, and  $\text{NH}_3_{\text{cum}}$  is the amount of the annual cumulative  $\text{NH}_3$ -N losses.

### 2.6 Soil sampling and laboratory analyses

For the determination of mineral N ( $N_{\text{min}} = \text{NH}_4^+ - \text{N} + \text{NO}_3^- - \text{N}$ ) contents, one mixed soil sample consisting of nine individual samples was collected at two soil depths (0–10, 10–20 cm) at each plot during every gas flux measurement. Samples were immediately cooled and stored in an ice box before analyses. Mineral N was extracted after shaking 40 g of fresh soil with 160 mL  $\text{CaCl}_2$  (0.0125 M) for 1 hour. The extracts were filtered through a 4–7  $\mu\text{m}$  filter paper (Whatman 595 1/2) and the first 20 mL of the extract were discarded. The solution was frozen at –20 °C until analysis, which was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). A subsample of 20–30 g was used to determine the gravimetric water content, which was taken into account for the calculation of mineral N concentrations. For determination of  $C_{\text{tot}}$  and organic carbon ( $C_{\text{org}}$ ) a mixed soil sample of nine individual samples was collected close to each collar at two soil depths (0–10, 10–20 cm) using a 3 cm diameter auger. After drying for 72 h at 40 °C, soil samples were sieved to 2 mm to remove stones and living roots. Analyses were conducted at the Division of Soil Science and Site Science (Humboldt Universität zu Berlin, Germany). For the determination of bulk density and porosity, three undisturbed core cutter samples (100 cm<sup>3</sup>) were randomly taken at four depths (0–5, 5–10, 10–15, 15–20 cm) for each plot.

### 2.7 Statistical analysis

Statistical analyses were conducted using R 2.12.1 (R Development Core Team, 2010). We used analysis of variance (ANOVA; for grass yield, 16 days’ cumulative  $\text{N}_2\text{O}$  emissions and treatment  $\text{NO}_3^-$  comparison) or the nonparametric Kruskal–Wallis rank sum test (for GW level) to compare means of samples. In case of significant differences among the means, we used Tukey’s honest significant differences (Tukey HSD) or the non-parametric pairwise Wilcoxon rank sum test with Bonferroni correction for multiple comparisons. For testing two independent sample means, we use the Welch two-sample *t* test (for soil type  $\text{NO}_3^-$  comparison in 2010) or the nonparametric Mann–Whitney *U* test (for soil type  $\text{NO}_3^-$  comparison in 2011). For time series data ( $\text{N}_2\text{O}$ ,  $\text{CH}_4$  field measurements) we applied linear mixed effects models (Crawley, 2007; Eickenscheidt et al., 2011; Hahn-Schöfl et al., 2011). We set up a basic model with soil type and fertilizer treatment as fixed effects and the spatial replication (individual collar) nested in time as random effect. Non-significant terms were removed from the fixed structure. We extended the basic model by a variance function when heteroscedasticity was observed. In case of significant serial correlation in data, a moving average or a first-order temporal autoregressive function was included in the model. Autocorrelation was tested using the Durbin–Watson test and by plotting the empirical autocorrelation structure. The model extension was proved by the Akaike information criterion



**Figure 1.** Daily sums of precipitation following the organic fertilizer application events (APPL).

(AIC). For multiple comparisons we conducted Tukey contrasts using the General Linear Hypotheses function from the “multcomp” package (Hothorn et al., 2013).

The assumption of normality of residuals was tested using the Lilliefors or Shapiro–Wilk test and the quantile–quantile plots. Homogeneity of variances of residuals was checked using the Levene or Breusch–Pagan test and by plotting the residuals against the fitted values. Where necessary, data were box-cox transformed prior to analyses. We used simple and multiple linear or non-linear regression models to explain  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{NH}_3$  fluxes. We accepted significant differences if  $P \leq 0.05$ . Results in the text are given as means  $\pm 1$  SD.

### 3 Results

#### 3.1 Environmental drivers

Temperatures between the two investigated soil types did not differ. In 2010 and 2011, air temperature at 20 cm height ranged from  $-17.5$  to  $39.5$  °C, with an annual mean of  $8.6$  °C in 2011 at both investigated areas. Soil temperature in  $-2$  cm soil depth averaged  $10.3$  °C at the  $\text{C}_{\text{org}}$ -medium site and was slightly higher with  $10.5$  °C at the  $\text{C}_{\text{org}}$ -high site in 2011. Air temperature at 20 cm height 15 or 16 days after fertilization averaged  $16.0$ ,  $13.1$ ,  $15.4$ , and  $11.5$  °C for application events 1 to 4 at both investigated soil types. Soil temperature in  $-2$  cm soil depth was approximately  $2$  °C above the mean air temperature in the same periods at both soil types. In 2010 and 2011 annual precipitation was 850 and 841 mm, which was slightly above the 30-year mean of the period 1961–1990. Figure 1 shows the precipitation following the fertilizer application. With the exception of the third application event, no rainfall occurred during the application of the organic fertilizers. However, precipitation during and after the third application event was weak and amounted to 3 mm in the time span between 16:00 and 00:00 LT.

All treatments showed similar dynamics in their annual hydrographs (Fig. 2a), but mean annual groundwater levels of the  $\text{C}_{\text{org}}$ -high treatments were significantly higher (all  $P < 0.001$ ) compared to the  $\text{C}_{\text{org}}$ -medium treatments in 2010 and 2011 (Table 4). Mean groundwater levels following the fertilizer applications are shown in Table 4.

#### 3.2 N input and N availability

The amount of N applied was 111 and  $252 \text{ kg N ha}^{-1}$  for slurry treatments and 101 and  $174 \text{ kg N ha}^{-1}$  for digestate treatments in 2010 and 2011, respectively. However, due to the distinctly higher  $\text{NH}_4^+ - \text{N} : \text{N}_{\text{tot}}$  ratio of the biogas digestate, total  $\text{NH}_4^+ - \text{N}$  input was comparable to (2010) or slightly higher than (15 % more  $\text{NH}_4^+ - \text{N}$ ; 2011) that for the slurry treatments (Table 3). Additional physical and chemical properties of the slurry and digestate are shown in Table 3.

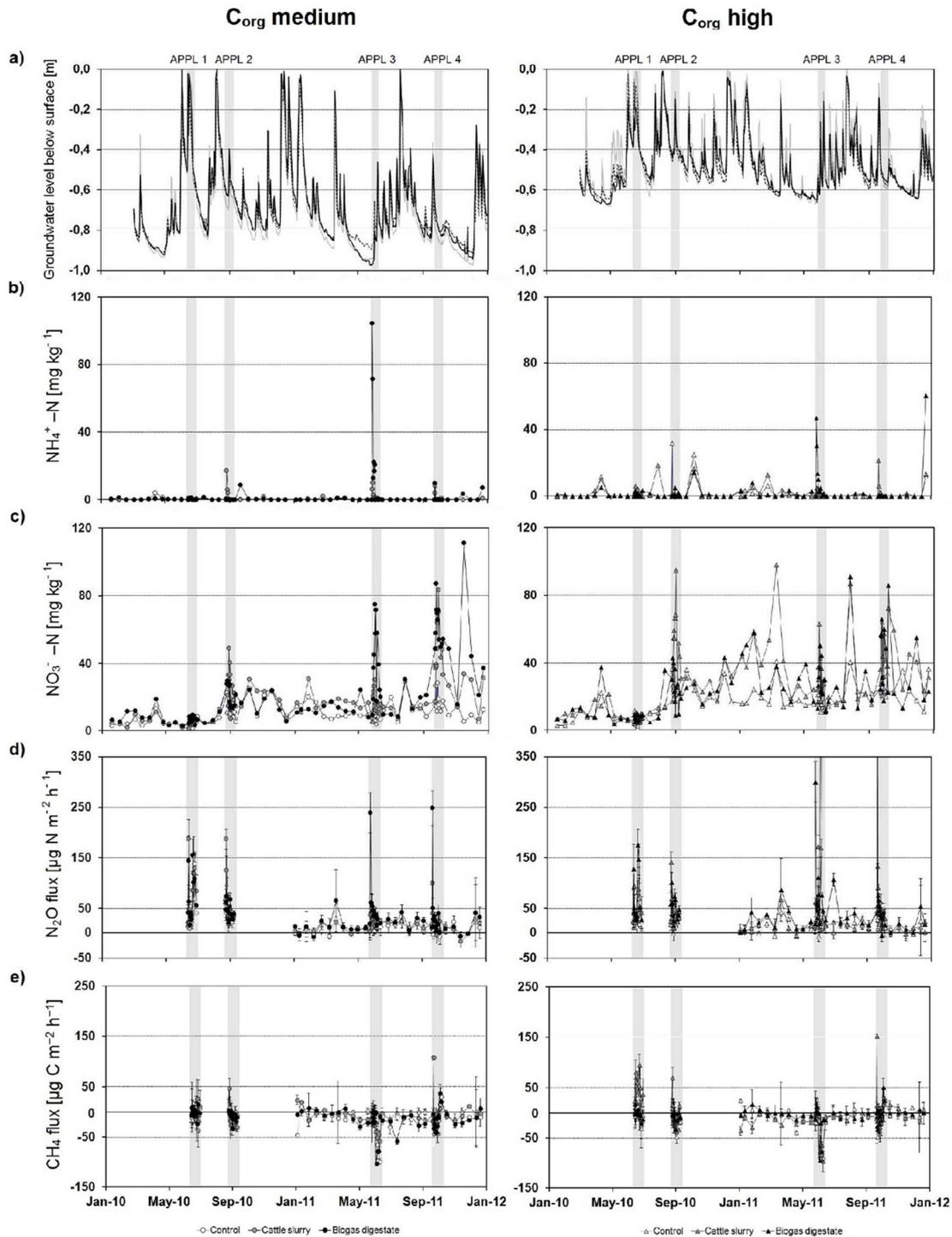
The extractable  $\text{N}_{\text{min}}$  contents of the soils were dominated by  $\text{NO}_3^-$  whereas  $\text{NH}_4^+$  was only of minor importance, especially at the  $\text{C}_{\text{org}}$ -medium treatments (Fig. 2b and c). The  $\text{NO}_3^-$  content was significantly higher ( $P < 0.001$ ) at the  $\text{C}_{\text{org}}$ -high treatments than at the  $\text{C}_{\text{org}}$ -medium treatments in 0–10 cm soil depth in both years and in 10–20 cm soil depth in 2010 ( $P < 0.01$ ) (Table 4). With the exception of the first application event, all fertilization events increased the  $\text{NO}_3^-$  contents of the soil for a short period (Fig. 2c, Table 4). However, only in 2011 did the fertilized sites show significantly ( $P < 0.01$ ) higher  $\text{NO}_3^-$  contents compared to the control treatments, but differences between digestate and slurry were generally not significant (except for 0–10 cm soil depth at the  $\text{C}_{\text{org}}$ -medium site; Table 4).

#### 3.3 $\text{N}_2\text{O}$ emissions

$\text{N}_2\text{O}$  fluxes were generally low for all treatments (Fig. 2d). Background emissions rarely exceeded  $50 \mu\text{g N m}^{-2} \text{ h}^{-1}$ . Highest  $\text{N}_2\text{O}$  fluxes were found immediately after fertilizer application (Figs. 2d and 3), sometimes followed by a second phase of higher emissions after 6 to 12 days. In the case of the  $\text{C}_{\text{org}}$ -medium treatments  $\text{N}_2\text{O}$  fluxes returned to background emission level within 3 to 7 days, whereas the  $\text{C}_{\text{org}}$ -high treatments had longer lasting increased  $\text{N}_2\text{O}$  emissions, particularly for the digestate treatment.

Short-term (16 days)  $\text{N}_2\text{O}$  fluxes of fertilized treatments significantly ( $P < 0.01$ ) exceeded  $\text{N}_2\text{O}$  fluxes of control treatments at all fertilization events. However, only in one out of four fertilization events were short-term  $\text{N}_2\text{O}$  fluxes significantly ( $P < 0.001$ ) higher for the digestate treatments compared to the slurry treatments. Additionally, significantly ( $P < 0.001$ ) higher short-term  $\text{N}_2\text{O}$  fluxes were observed at the  $\text{C}_{\text{org}}$ -high treatments compared to the  $\text{C}_{\text{org}}$ -medium treatments in 2011, but the opposite was observed at the second fertilization event in 2010.

However, due to the high variability and the partially fast return to the background emission level, short-term (16 days)



**Figure 2.** Variation in groundwater level (a), extractable  $\text{NH}_4^+$  (b) and  $\text{NO}_3^-$  (c) contents for the soil depth 0–10 cm,  $\text{N}_2\text{O}$  (d) and  $\text{CH}_4$  fluxes (e) (mean  $\pm$  SD,  $n = 3$ ) of the  $\text{C}_{\text{org}}$ -medium and  $\text{C}_{\text{org}}$ -high sites from January 2010 to January 2012. Gray bars mark the 15 or 16 days period of intensive gas flux measurements following organic fertilizer application.

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6195

**Table 4.** Mean (minimum/maximum) groundwater level (GW), NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> content in the soil following organic fertilizer application and for the investigated years 2010 and 2011.

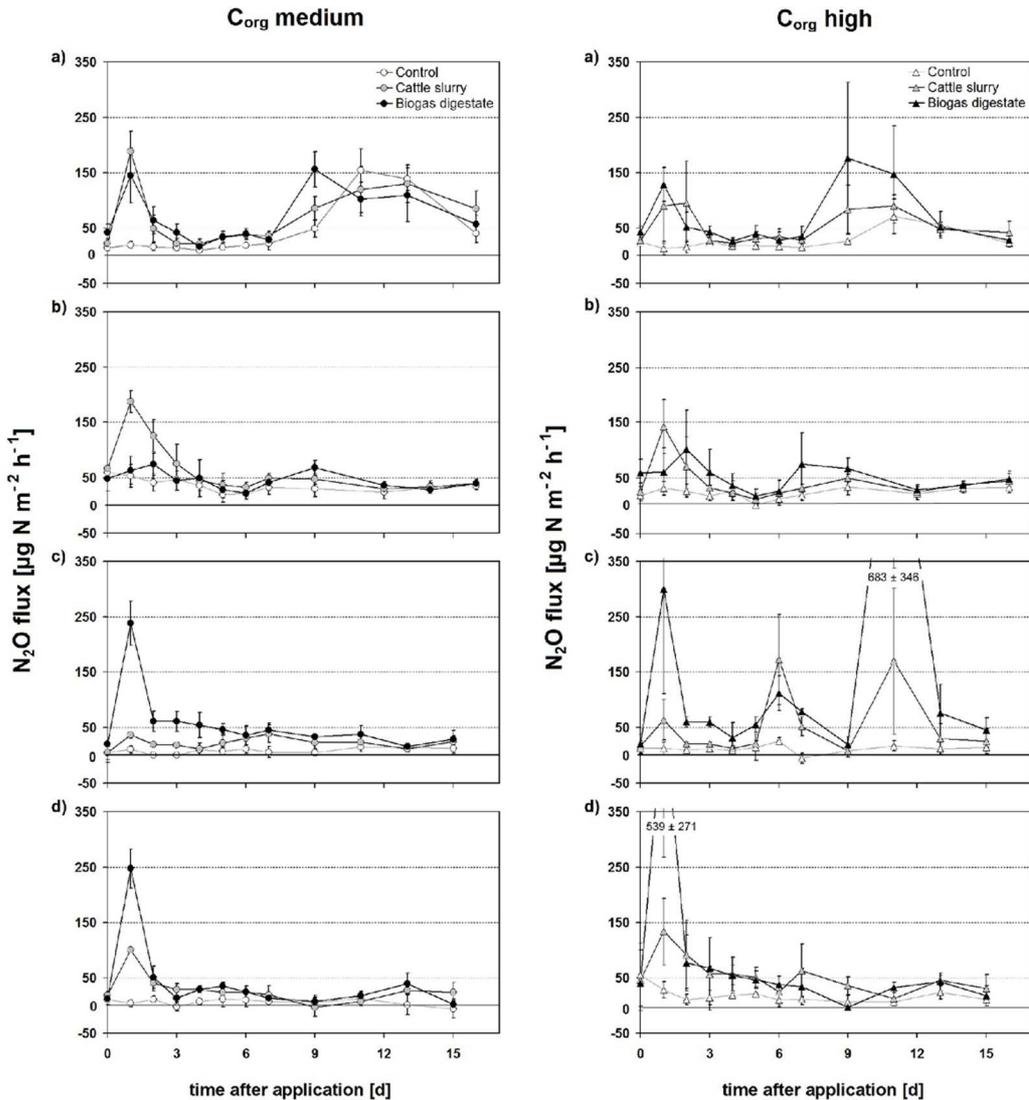
Sampling depth [cm]	C <sub>org</sub> -medium			C <sub>org</sub> -high			n
	Control	Cattle slurry	Biogas digestate	Control	Cattle slurry	Biogas digestate	
1 Application (14 Jun–30 Jun 2010)							
GW level [cm]	-32 (-62/-2)	-39 (-60/-5)	-31 (-58/-2)	-21 (-46/-1)	-26 (-45/-7)	-33 (-45/-19)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 5 (1/9)	5 (1/7)	7 (3/10)	6 (1/12)	8 (3/11)	8 (5/10)	12
	10–20 9 (6/12)	9 (5/13)	11 (8/15)	11 (8/15)	12 (7/15)	14 (6/19)	12
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/1)	0 (0/1)	0 (0/1)	1 (0/2)	1 (0/6)	1 (0/3)	12
	10–20 0 (0/1)	0 (0/1)	0 (0/1)	0 (0/2)	1 (0/11)	1 (0/2)	12
2 Application (25 Aug–10 Sep 2010)							
GW level [cm]	-64 (-70/-49)	-58 (-63/-42)	-57 (-63/-40)	-36 (-40/-37)	-40 (-46/-22)	-37 (-43/-15)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 13 (6/23)	27 (7/49)	21 (14/30)	25 (17/37)	50 (17/95)	25 (9/43)	12
	10–20 22 (17/28)	28 (19/37)	27 (17/38)	31 (26/35)	34 (11/45)	31 (12/48)	12
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/0)	2 (0/17)	0 (0/0)	3 (0/32)	0 (0/1)	1 (0/5)	12
	10–20 1 (0/10)	0 (0/0)	0 (0/1)	0 (0/1)	0 (0/1)	1 (0/3)	12
3 Application (27 May–11 Jun 2011)							
GW level [cm]	-82 (-94/-57)	-76 (-89/-52)	-80 (-97/-46)	-41 (-60/-11)	-47 (-62/-16)	-49 (-62/-16)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 9 (4/17)	17 (5/30)	40 (10/75)	17 (11/26)	29 (12/63)	29 (11/50)	12
	10–20 17 (11/22)	31 (18/44)	45 (18/75)	24 (18/30)	28 (18/40)	45 (21/148)	12
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/2)	2 (0/10)	21 (0/104)	0 (0/1)	1 (0/5)	10 (0/47)	12
	10–20 0 (0/1)	1 (0/2)	6 (0/26)	1 (0/2)	1 (0/3)	4 (0/12)	12
4 Application (22 Sep–7 Oct 2011)							
GW level [cm]	-83 (-87/-72)	-77 (-81/-70)	-76 (-83/-58)	-54 (-60/-33)	-55 (-58/-46)	-53 (-57/-41)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 18 (12/28)	48 (18/83)	62 (49/87)	23 (20/34)	43 (28/73)	45 (18/86)	12
	10–20 32 (18/46)	50 (21/79)	53 (35/66)	24 (20/30)	30 (22/39)	38 (23/86)	12
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/0)	1 (0/8)	1 (0/10)	0 (0/0)	3 (0/21)	0 (0/0)	12
	10–20 0 (0/0)	0 (0/0)	0 (0/1)	0 (0/1)	1 (0/3)	0 (0/0)	12
2010							
GW level [cm]*	-67 (-94/-2)	-65 (-91/-2)	-63 (-92/0)	-41 (-68/2)	-45 (-64/-1)	-45 (-67/-1)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 9 (1/26)	14 (1/49)	12 (3/30)	15 (1/37)	24 (3/95)	17 (4/43)	45
	10–20 14 (5/34)	17 (5/38)	17 (4/38)	19 (7/47)	23 (6/64)	21 (6/49)	45
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/4)	1 (0/17)	0 (0/9)	2 (0/32)	2 (0/19)	1 (0/14)	45
	10–20 0 (0/10)	0 (0/1)	0 (0/1)	0 (0/8)	1 (0/11)	1 (0/5)	45
2011							
GW level [cm]	-76 (-98/-3)	-72 (-92/0)	-72 (-97/0)	-47 (-67/1)	-52 (-66/-3)	-50 (-65/-3)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	0–10 13 (4/31)	25 (5/83)	36 (8/111)	21 (11/41)	36 (12/98)	34 (11/91)	47
	10–20 24 (9/46)	34 (15/79)	40 (18/120)	27 (14/52)	33 (18/78)	37 (10/148)	47
NH <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	0–10 0 (0/2)	1 (0/10)	6 (0/104)	1 (0/12)	2 (0/21)	4 (0/60)	47
	10–20 0 (0/3)	0 (0/4)	2 (0/26)	1 (0/7)	1 (0/27)	2 (0/12)	47

cumulative N<sub>2</sub>O emissions were not significantly different from the control treatments in 2010 (Fig. 4), but for 2011 short-term cumulative N<sub>2</sub>O emissions had a clear trend in the order digestate > slurry > control (although not significant in one case).

On an annual basis organic fertilization led to significantly ( $P < 0.001$ ) higher N<sub>2</sub>O fluxes compared to unfertilized treatments. Additionally, the application of biogas digestate significantly ( $P < 0.01$ ) enhanced the N<sub>2</sub>O fluxes compared to the application of cattle slurry. Furthermore, N<sub>2</sub>O fluxes from the C<sub>org</sub>-high treatments significantly ( $P < 0.001$ ) exceeded N<sub>2</sub>O fluxes from the C<sub>org</sub>-medium treat-

ments. Annual cumulative emissions ranged from  $0.91 \pm 0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (control treatment, C<sub>org</sub>-medium site) to  $3.14 \pm 0.91 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (digestate treatment, C<sub>org</sub>-high site; Table 5). Calculated EFs based on the amount of N<sub>tot</sub> ranged from 0.12 to 0.23 for the slurry treatments and from 0.55 to 1.13 for the digestate treatments (Table 5).

Observed collar-specific cumulative annual N<sub>2</sub>O fluxes were strongly related to collar-specific annual plant N-uptake (Fig. 5a and b). Of the temporal and spatial variation in the 16 days' cumulative N<sub>2</sub>O–N exchange rates, 53 % was explained by the amounts of applied NH<sub>4</sub><sup>+</sup>-N and the mean groundwater levels below surface during the same time



**Figure 3.** Mean ( $\pm$ SD,  $n = 3$ )  $\text{N}_2\text{O}$  fluxes following organic fertilizer application events (a) 14–30 June 2010; (b) 25 August–10 September 2010; (c) 27 May–11 June 2011 and (d) 22 September–7 October 2011.

(Fig. 6). A similar trend was observed for the annual cumulative  $\text{N}_2\text{O}$  emissions, but regression analysis was not possible due to the small sample size ( $n = 6$ ).

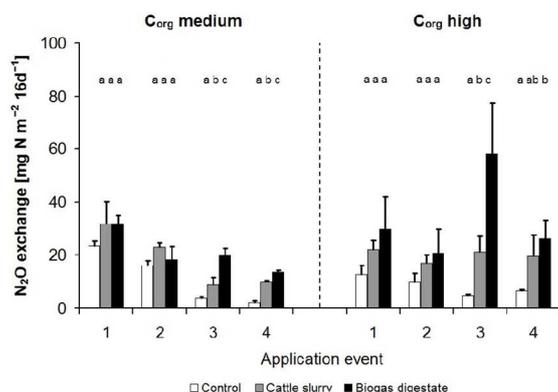
### 3.4 $\text{CH}_4$ emissions

Most of the time,  $\text{CH}_4$  emissions could not be detected (Fig. 2e). Occasionally  $\text{CH}_4$  peaks were only found immediately after cattle slurry application. However, with the exception of the slurry treatment of the  $\text{C}_{\text{org}}$ -high site at the first application event, the organic fertilization did not result in significantly different short-term (15 or 16 days)  $\text{CH}_4$  fluxes between the treatments or the investigated soil types. The observed weak  $\text{CH}_4$  emissions or uptakes amounted to cumulative annual  $\text{CH}_4$  exchange rates of  $-0.21 \pm 0.19$

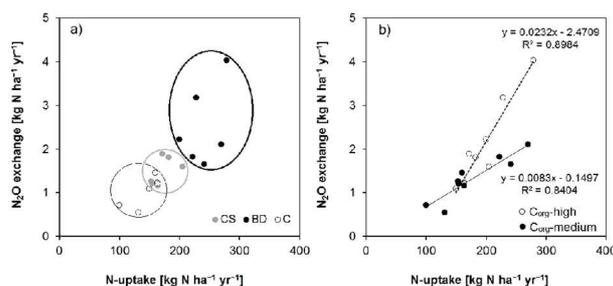
to  $-1.06 \pm 0.46 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ . Significantly different  $\text{CH}_4$  fluxes between the investigated treatments or the different soil types could not be observed regarding the annual fluxes in 2011.

### 3.5 $\text{NH}_3$ volatilization

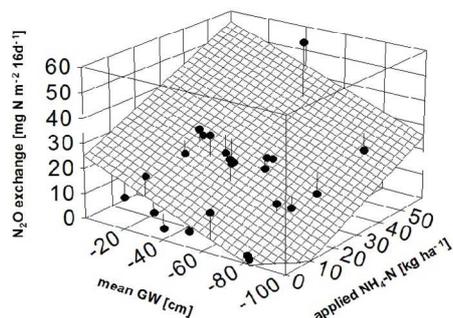
Highest  $\text{NH}_3$  losses were observed immediately after fertilization (Fig. 7). During the first 24 h, 64 and 100 % of total  $\text{NH}_3$  losses occurred at the digestate and slurry treatments, respectively. Since differences in the response of  $\text{NH}_3$  volatilization were not significant, treatment data were pooled by soil type prior to regression analysis. The total  $\text{NH}_3$  loss following application was  $18.17 \text{ kg N ha}^{-1}$  for the digestate treatments and  $3.48 \text{ kg N ha}^{-1}$  for the slurry



**Figure 4.** Cumulative  $\text{N}_2\text{O}$  exchange during 16 days following organic fertilizer application. Bars indicate mean values  $\pm$  SD ( $n = 3$ ). Means with the same letter indicated no significant differences between treatments at a single application event for sites  $\text{C}_{\text{Org-medium}}$  and  $\text{C}_{\text{Org-high}}$  respectively (ANOVA, Tukey HSD test at  $P \leq 0.05$ ).



**Figure 5.** Relationship between cumulative annual  $\text{N}_2\text{O}$  emissions and annual plant N uptake for the treatments (a) and for the investigated soil types (b). Dots represent mean annual values of each PVC collar; CS, cattle slurry; BD, biogas digestate; C, control.



**Figure 6.** Relationship of plot-wise mean 16 days' cumulative  $\text{N}_2\text{O}$ -N emissions of the four application events ( $y$ ) to mean groundwater level ( $x_1$ ) and the amount of applied  $\text{NH}_4\text{-N}$  ( $x_2$ ). The regression equation is  $y = 24.98 (\pm 4.98) + x_1 \cdot 0.30 (\pm 0.09) + x_2 \cdot 0.51 (\pm 0.11)$ ;  $R^2 \text{ adj.} = 0.53$ ,  $P < 0.001$ ,  $df = 21$ . Solid lines indicate the deviation of measured data from the model surface.

**Table 5.** Calculated EFs for the year 2011 and for single application events (16 days; Appl. 1–Appl. 4). The EF is based on the amount of total nitrogen ( $\text{N}_{\text{tot}}$ ) without consideration of  $\text{NH}_3\text{-N}$  losses.

	Control	Cattle slurry	Biogas digestate
$\text{C}_{\text{Org-medium}}$			
$\text{N}_2\text{O}$ exchange [ $\text{kg N ha}^{-1} \text{ yr}^{-1}$ ]	$0.91 \pm 0.49$	$1.21 \pm 0.05$	$1.86 \pm 0.23$
Annual EF		0.12	0.55
EF Appl. 1		0.18	0.17
EF Appl. 2		0.11	0.05
EF Appl. 3		0.08	0.21
EF Appl. 4		0.09	0.33
$\text{C}_{\text{Org-high}}$			
$\text{N}_2\text{O}$ exchange [ $\text{kg N ha}^{-1} \text{ yr}^{-1}$ ]	$1.18 \pm 0.07$	$1.77 \pm 0.15$	$3.14 \pm 0.91$
Annual EF		0.23	1.13
EF Appl. 1		0.20	0.35
EF Appl. 2		0.11	0.21
EF Appl. 3		0.23	0.68
EF Appl. 4		0.15	0.56

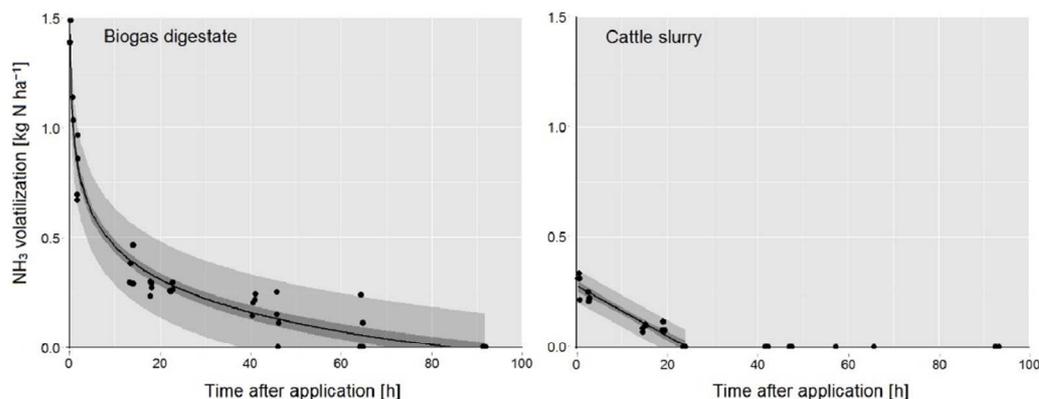
treatments. The relative N loss was 36 and 15 % of applied  $\text{NH}_4\text{-N}$ , or 23 and 5 % of total applied N for the digestate and slurry treatments, respectively.

### 3.6 Grass yield, apparent N use efficiency and estimated N balances

In 2010 and 2011, the mean annual grass yield ranged from 4.5 (control  $\text{C}_{\text{Org-medium}}$ ) to 13.1 t DM  $\text{ha}^{-1} \text{ yr}^{-1}$  (digestate  $\text{C}_{\text{Org-high}}$ ; Table 6). In both years the mean annual grass yield from the digestate treatments was significantly ( $P < 0.05$ ) higher compared to the slurry treatments. This pattern was also found in the annual plant N-uptake, which showed a clear partitioning between the treatments investigated (Fig. 5a). Additionally, the mean annual grass yield from the  $\text{C}_{\text{Org-high}}$  treatments exceeded yields from the  $\text{C}_{\text{Org-medium}}$  treatments of both years, but differences were not significant.

The application of biogas digestate markedly increased apparent NUE and  $\text{NUE}_{\text{min}}$  compared to cattle slurry treatments (Table 6). NUE values were on average  $115 \pm 136 \%$  for biogas digestate treatments and  $24 \pm 23 \%$  for cattle slurry.  $\text{NUE}_{\text{min}}$  values were always  $> 100 \%$  for biogas digestate treatments, whereas for cattle slurry  $\text{NUE}_{\text{min}}$  values averaged  $74 \pm 68 \%$  in 2011 but were  $> 100 \%$  in 2010. Besides fertilizer type effects, higher NUE and  $\text{NUE}_{\text{min}}$  were observed at the  $\text{C}_{\text{Org-medium}}$  treatments compared to the  $\text{C}_{\text{Org-high}}$  treatments.

The estimated N balances revealed N surpluses of up to  $70 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  for cattle slurry treatments but deficits of



**Figure 7.** Ammonia ( $\text{NH}_3$ ) volatilization following organic fertilizer application at event 3 (27 May 2011). Dots present single  $\text{NH}_3$  measurements for a time period of 94 h. Black lines show the estimated  $\text{NH}_3$  volatilization with 95 % confidence band (dark gray) and 95 % prediction band (light gray). The model function for biogas digestate is  $y = -0.2619 (\pm 0.025) \cdot \ln(x) + 0.9605 (\pm 0.008)$ ;  $r^2 = 0.96$ ;  $P < 0.0001$ ; the model function for cattle slurry is  $y = 0.2818 (\pm 0.012) - 0.0114(x) (\pm 0.001)$ ;  $r^2 = 0.92$ ;  $P < 0.0001$ .

**Table 6.** Grass yields, N uptake and N use efficiency for the years 2010 and 2011.

Treatment	Cutting date	Fertilization date	N content plant [%]	DM [ $\text{t ha}^{-1} \text{yr}^{-1}$ ]	N uptake [ $\text{kg N ha}^{-1}$ ]	N applied [ $\text{kg N ha}^{-1}$ ] <sup>b</sup>	$N_{\min}$ applied [ $\text{kg N ha}^{-1}$ ] <sup>b</sup>	N use efficiency [%]	$N_{\min}$ use efficiency [%]
Control $C_{\text{org}}$ -medium	24 May 2010	–	2.04 <sup>a</sup>	2.52	51	–	–	–	–
Control $C_{\text{org}}$ -high	24 May 2010	–	2.14	2.93	63	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	24 May 2010	N.A.	2.37	3.19	76	–	–	–	–
Cattle slurry $C_{\text{org}}$ -high	24 May 2010	N.A.	2.14	3.58	77	–	–	–	–
Biogas digestate $C_{\text{org}}$ -medium	24 May 2010	N.A.	2.04	4.17	85	–	–	–	–
Biogas digestate $C_{\text{org}}$ -high	24 May 2010	N.A.	2.27	4.39	100	–	–	–	–
Control $C_{\text{org}}$ -medium	20 Aug 2010	–	2.03	2.02	41	–	–	–	–
Control $C_{\text{org}}$ -high	20 Aug 2010	–	2.00	2.63	53	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	20 Aug 2010	14 Jun 2010	2.19	3.06	67	45	17	58	153
Cattle slurry $C_{\text{org}}$ -high	20 Aug 2010	14 Jun 2010	1.93	3.23	62	45	17	22	57
Biogas digestate $C_{\text{org}}$ -medium	20 Aug 2010	14 Jun 2010	2.03	2.99	61	38	14	52	140
Biogas digestate $C_{\text{org}}$ -high	20 Aug 2010	14 Jun 2010	2.00	3.51	70	38	14	47	125
Control $C_{\text{org}}$ -medium	23 May 2011	–	1.96	2.66	52	–	–	–	–
Control $C_{\text{org}}$ -high	23 May 2011	–	1.70	3.82	65	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	23 May 2011	25 Aug 2010	2.01	2.58	52	61	24	0	0
Cattle slurry $C_{\text{org}}$ -high	23 May 2011	25 Aug 2010	1.70	4.20	71	61	24	11	27
Biogas digestate $C_{\text{org}}$ -medium	23 May 2011	25 Aug 2010	1.96	3.97	78	40	18	64	144
Biogas digestate $C_{\text{org}}$ -high	23 May 2011	25 Aug 2010	1.83	4.54	83	40	18	45	101
Control $C_{\text{org}}$ -medium	1 Aug 2011	–	1.71	2.06	35	–	–	–	–
Control $C_{\text{org}}$ -high	1 Aug 2011	–	1.48	2.88	43	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	1 Aug 2011	27 May 2011	1.71	2.73	47	67	20	17	58
Cattle slurry $C_{\text{org}}$ -high	1 Aug 2011	27 May 2011	1.51	3.19	48	67	20	8	28
Biogas digestate $C_{\text{org}}$ -medium	1 Aug 2011	27 May 2011	1.78	4.88	87	60	33	86	158
Biogas digestate $C_{\text{org}}$ -high	1 Aug 2011	27 May 2011	1.48	5.34	79	60	33	61	112
Control $C_{\text{org}}$ -medium	13 Sep 2011	–	2.53	1.71	43	–	–	–	–
Control $C_{\text{org}}$ -high	13 Sep 2011	–	2.26	2.27	51	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	13 Sep 2011	27 May 2011	2.57	2.28	59	(55) <sup>c</sup>	(8) <sup>c</sup>	28	189
Cattle slurry $C_{\text{org}}$ -high	13 Sep 2011	27 May 2011	2.53	2.64	67	(61) <sup>c</sup>	(14) <sup>c</sup>	25	110
Biogas digestate $C_{\text{org}}$ -medium	13 Sep 2011	27 May 2011	2.53	3.15	80	(8) <sup>c</sup>	(0) <sup>c</sup>	436	–
Biogas digestate $C_{\text{org}}$ -high	13 Sep 2011	27 May 2011	2.26	3.25	74	(24) <sup>c</sup>	(0) <sup>c</sup>	94	–

<sup>a</sup> N contents from control treatments were estimated from fertilized treatments. <sup>b</sup> Applied  $N_{\text{tot}}$  and  $N_{\min}$  were corrected by  $\text{NH}_3$ -N losses (23 and 5 % from  $N_{\text{tot}}$ , or 36 and 15 % from  $N_{\min}$  for biogas digestate and cattle slurry, respectively). <sup>c</sup> Hypothetically remaining  $N_{\text{tot}}$  and  $N_{\min}$  from the application event 3 (27 May 2011). N.A. = not available.

**Table 7.** Estimated nitrogen balance for the year 2011.

Treatment	N applied [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N <sub>min</sub> t <sub>1</sub> <sup>a</sup> [kg N ha <sup>-1</sup> ]	N <sub>min</sub> t <sub>2</sub> <sup>a</sup> [kg N ha <sup>-1</sup> ]	N deposition [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N uptake [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N <sub>2</sub> O [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	NH <sub>3</sub> <sup>b</sup> [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N balance [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]
Control C <sub>org</sub> -medium	0	27.5	29.4	7.2	130	0.9	0.0	-122.4
Control C <sub>org</sub> -high	0	22.8	27.7	7.2	159	1.2	0.0	-148.0
Cattle slurry C <sub>org</sub> -medium	252	35.7	51.2	7.2	157	1.2	46.1	70.4
Cattle slurry C <sub>org</sub> -high	252	27.3	68.1	7.2	186	1.8	46.1	66.1
Biogas digestate C <sub>org</sub> -medium	174	29.8	83.3	7.2	244	1.9	52.4	-64.1
Biogas digestate C <sub>org</sub> -high	174	26.2	28.4	7.2	236	3.1	52.4	-108.1

<sup>a</sup> Reference date for t<sub>1</sub> is 6 April 2011 and for t<sub>2</sub> 18 October 2011. <sup>b</sup> NH<sub>3</sub>-N losses at the fourth and fifth application event were estimated based on EF taken from the German national greenhouse gas inventory (EF = 0.6 related to applied NH<sub>4</sub><sup>+</sup>; Haenel et al., 2014).

up to 108 kg N ha<sup>-1</sup> yr<sup>-1</sup> for biogas digestate treatments, for the year 2011 (Table 7).

## 4 Discussion

### 4.1 Drainage and fertilizer effects on N-availability and N-transformation

Mineral nitrogen contents were consistently higher at the C<sub>org</sub>-high treatments than at the C<sub>org</sub>-medium treatments, in line with the considerably higher amount of SOC and N at this site. It is well known that drainage enhances the degradation of soil organic matter (SOM) and thus stimulates net nitrogen mineralization and N transformation processes (Kasimir Klemedtsson et al., 1997; Freibauer et al., 2004; Klemedtsson et al., 2005; Goldberg et al., 2010). Various studies reported an annual N supply through peat mineralization of 70 to 292 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Schothorst, 1977; Flessa et al., 1998; Sonneveld and Lantinga, 2011). It can be assumed that at a comparable aeration status and temperature, mineralization processes are more intensive at peatlands that were recently drained (Hacin et al., 2001; Renger et al., 2002; Sonneveld and Lantinga, 2011) or contain higher amounts of SOM.

As expected from the literature, the biogas digestates differed in their physical and chemical properties from the cattle slurries. In the present study, the biogas digestates had narrower C:N ratios (see also, e.g., Tambone et al., 2009), higher pH values (see also Wulf et al., 2002b and Quakernack et al., 2011), wider NH<sub>4</sub><sup>+</sup>:N<sub>tot</sub> ratios and thus relatively higher NH<sub>4</sub><sup>+</sup> contents than the cattle slurries (see also Möller and Stinner 2009). The amounts of NH<sub>4</sub><sup>+</sup>-N were not distinctly different between the applied organic fertilizers but in 2011 biogas treatments received 15 % more NH<sub>4</sub><sup>+</sup>-N compared to cattle slurry treatments.

We observed an unexpected small change in the NH<sub>4</sub><sup>+</sup> content of the soil immediately after fertilizer application, which can be attributed to different reasons. Firstly, the fertilizers partly remained on the plant canopy after splash plate application and therefore soil contact and infiltration were limited (Quakernack et al., 2011). Secondly, a significant fraction of NH<sub>4</sub><sup>+</sup> from the organic fertilizer was lost in a few hours after splash plate application via NH<sub>3</sub> volatilization. Thirdly,

and probably most importantly, in well aerated soils applied NH<sub>4</sub><sup>+</sup> underwent rapid nitrification, as was indicated by the increasing soil NO<sub>3</sub><sup>-</sup> contents in the upper soil layer after fertilizer application. In general, the continuously observed absent or low NH<sub>4</sub><sup>+</sup> contents with simultaneously high extractable NO<sub>3</sub><sup>-</sup> in the soil indicate that net nitrification entirely controlled net nitrogen mineralization at all treatments of the investigated study sites. Nitrification requires sufficient oxygen (O<sub>2</sub>) availability in the soil (Davidson et al., 1986), hence we can assume well aerated soil conditions, at least in the upper soil layer, for most of the time at the study sites.

Several studies (e.g., Gutser et al., 2005; Jones et al., 2007) reported that the infiltration of organic fertilizer may enhance the soil N pool and further stimulates SOM mineralization, leading to additional N<sub>min</sub>. This becomes evident in the observed significantly higher NO<sub>3</sub><sup>-</sup> contents of the fertilized treatments compared to the unfertilized control treatments, especially in the 0–10 cm soil layer. However, significant differences in the N<sub>min</sub> contents between the two investigated organic fertilizers were not found in 2010 and 2011. This may be due to the fact that the N uptake by plants at the digestate treatments was on average 27 % higher and that marked differences in the amount of N<sub>tot</sub> and NH<sub>4</sub><sup>+</sup> of the applied organic fertilizers were only observed in the second study year.

To maintain soil fertility and yield and to reduce harmful side effects (e.g., N<sub>2</sub>O losses, NO<sub>3</sub><sup>-</sup> leaching), site-adapted fertilization is necessary. The estimated negative N balances for biogas treatments are in line with Andres et al. (2013), who reported that positive N balances could only be achieved when the amount of applied digestate contains more than 200 kg N ha<sup>-1</sup> yr<sup>-1</sup>. However, the strong negative N balances of the control treatments reveal that large amounts of up to 148 kg N ha<sup>-1</sup> yr<sup>-1</sup> originate from peat mineralization, demonstrating the unsustainable agricultural use of drained peatlands. Assuming that the fertilized treatments received equal amounts of N from peat mineralization, all N balances of these treatments were strongly positive. N surpluses as estimated for the cattle slurry treatments enhance the soil N pool, but the gradual release of N at a non-predictable stage from the soil N pool carries the risk of leaching or gaseous losses (Amon et al., 2006). Particularly in wintertime, high amounts of available NO<sub>3</sub><sup>-</sup> in the soil, as observed especially at the fertilized treatments of the C<sub>org</sub>-high sites, carry the

6200

T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

risk of N leaching due to the reduced N demand by plant uptake and by the microbial community during this period (Merino et al., 2002; Sanger et al., 2010).

#### 4.2 Fertilizer effect on N-use efficiency and grass yield

In line with investigations from Schils et al. (2008) most of the applied and produced  $N_{\min}$  was probably rapidly absorbed by the grassland as the soil  $N_{\min}$  content usually decreased within a few days after fertilizer application (Fig. 2b and c). This becomes evident also in the apparent  $NUE_{\min}$ , especially from biogas digestate treatments. A significant effect of biogas digestate on crop yields and apparent  $NUE_{\min}$  as observed in the present study was also reported from pot experiments (e.g., de Boer, 2008; Moller and Muller, 2012), but not for field applications without incorporation of the digestate into the soil (Moller and Muller, 2012). According to de Boer (2008), the higher  $NUE_{\min}$  at digestate treatments can be attributed to the wider  $NH_4^+/N_{\text{tot}}$  ratio as well as to the narrower C/N ratio of the applied digestate. Thus more N was immediately available for plant growth after fertilization (Amon et al., 2006; Sanger et al., 2010), whereas the lower C/N ratio reduced the potential for microbial immobilization of applied N (Velthof et al., 2003, de Boer, 2008). We hypothesized that the application of biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to the application of cattle slurry due to the higher N availability of the digestate. This could partly be confirmed, but the much higher grass yields from biogas digestate treatments cannot solely be explained by differences in applied  $NH_4^+$ , since differences were small. However, the much higher N-uptake at the digestate treatments (Fig. 5a) indicated that much more N must have been available at these treatments. Many studies have shown that the utilization of N derived from organic fertilizer is relatively small in the year of application, due to the slow release of organically bound N (Jensen et al., 2000; Sorensen and Amato, 2002; Gutser et al., 2005). The consistently higher  $NUE_{\min}$  of > 100 % at the digestate treatments indicates that some organic N derived from the fertilizer or from the SOM pool has been mineralized (Gunnarsson et al., 2010). Since the digestate is considered as more recalcitrant (Clemens and Huschka, 2001; Oenema et al., 2005; Moller and Stinner, 2009), it can be assumed that the digestate enhanced SOM mineralization more than cattle slurry, or that N mineralized from SOM or fertilizer had a larger share in the uptake by the plants due to lower competition of microbial immobilization as was reported by Gutser et al. (2010). Probably the assumed higher SOM mineralization at the digestate treatments could partly be related to a priming effect since the higher biomass production probably caused a higher release of root exudates, containing easily available C and N that enhanced microbial activity (Mounier et al., 2004; Henry et al., 2008), promoting SOM mineralization. However, further investigations

are needed to prove this explanation. The lower NUE at the  $C_{\text{org}}$ -high treatments compared to  $C_{\text{org}}$ -medium treatments reveals that plants are more independent of N input by fertilizer with increasing SOM at drained fen peatlands due to the extra  $N_{\min}$  derived from enhanced mineralization processes, as mentioned above.

#### 4.3 Fertilizer- and site-induced $N_2O$ emissions

The observed annual  $N_2O$  emissions were markedly lower than the actual default emission factor from the Tier 1 approach for temperate, deep drained, nutrient-rich grassland of  $8.2 \text{ kg } N_2O\text{-N ha}^{-1} \text{ yr}^{-1}$  (IPCC, 2014) and at the lower end of literature values from other organic soils. Studies from Germany reported much higher  $N_2O$  emissions, ranging from  $1.15$  to  $19.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Flessa et al., 1997; Augustin et al., 1998; Flessa et al., 1998; Beetz et al., 2013). Also investigations from other European countries showed that much higher  $N_2O$  emissions can be released from grasslands on drained peatlands. For example, Velthof et al. (1996) and van Beek et al. (2010, 2011) reported  $N_2O$  emissions ranging from  $4.2$  to  $41.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  for the Netherlands, whereas at boreal regions  $N_2O$  emissions of up to  $9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  were measured (Nykanen et al., 1995; Maljanen et al., 2004; Regina et al., 2004). The observed  $N_2O$  emissions were also in the range of those reported from grasslands on mineral soils in Germany, summarized by Jungkunst et al. (2006). In line with our results, Flessa et al. (1998) also found that  $N_2O$  losses from peat soils are not always larger than from nearby mineral soils, but in contrast, Maljanen et al. (2010) found on average four times higher  $N_2O$  emissions from cultivated organic soils than from mineral soils. The  $N_2O$  emissions from the  $C_{\text{org}}$ -high site significantly exceeded those from the  $C_{\text{org}}$ -medium site in all treatments, which was in line with higher  $N_{\min}$  contents and higher groundwater levels. Additionally, the observed markedly stronger increase of cumulative annual  $N_2O$  emissions with increasing N-uptake by plants (Fig. 5b) reveals that with increasing N availability a higher proportion is lost as  $N_2O$  at the  $C_{\text{org}}$ -high treatments compared to the  $C_{\text{org}}$ -medium treatments. This probably could be attributed to the more favorable soil conditions for denitrification, due to higher C and N mineralization rates and alternating groundwater levels, promoting anaerobicity (Koops et al., 1996). Moreover, as mentioned above, net nitrification entirely controls net nitrogen mineralization, promoting also  $N_2O$  losses, but probably to a lesser extent. However, the source of  $N_2O$  production in soils is often uncertain because aerobic and anaerobic microsites can occur within close proximity and thus nitrification and denitrification as well as other abiotic processes producing  $N_2O$  (e.g., nitrifier–denitrification, coupled nitrification–denitrification) can run simultaneously (Davidson et al., 1986; Butterbach-Bahl et al., 2013). Despite surprisingly low  $N_2O$  emission levels, we confirmed our hypothesis that  $N_2O$  emissions increase with increasing

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6201

soil  $C_{\text{org}}$  content, probably due to more favorable conditions for denitrification.

The observed background emissions on the two organic soils correspond well to those on mineral agricultural soils (Bouwman, 1996). However, calculated emission factors as a percentage of applied N without consideration of the  $\text{NH}_3$  losses were lower for all treatments than the IPCC default value. Several other studies also reported emission factors < 1 % of applied N (Chadwick et al., 2000; Velthof et al., 2003; Clemens et al., 2006; Jones et al., 2007; Möller and Stinner, 2009), but so far not for organic soils. Indeed,  $\text{N}_2\text{O}$  studies on organic soils rarely differentiate between fertilizer and soil derived N sources by unfertilized control plots as we do in this study. In line with Möller and Stinner (2009), the application of biogas digestate resulted in a markedly higher percentage of  $\text{N}_2\text{O}$  produced from applied N compared to cattle slurry, yet at a low level.

One reason of generally low  $\text{N}_2\text{O}$  emissions observed in the present study could be the small number of frost–thaw cycles in 2011. In general frost–thaw cycles are considered to favor high  $\text{N}_2\text{O}$  emissions (Flessa et al., 1998; Jungkunst et al., 2006) but these observations seem to be more pronounced for croplands than for grasslands in Germany (Dechow and Freibauer, 2011). Denitrification activity is strongly related to the  $\text{NO}_3^-$  content close to the groundwater level (van Beek et al., 2004). Given the high  $\text{NO}_3^-$  contents, in particular in the  $C_{\text{org}}$ -high soil, the evidence for fast nitrification and high net nitrogen mineralization, we argue that frequent but low dosage application of fertilizer and quick N uptake by plants avoid conditions favorable for high  $\text{N}_2\text{O}$  emissions. Moreover, through the splash plate application technique high amounts of  $\text{NH}_4^+$  were rapidly lost as  $\text{NH}_3$ , and therefore reduced the proportion of immediately available N for nitrification and denitrification.

As expected from the literature, highest  $\text{N}_2\text{O}$  fluxes were found immediately after fertilizer application. The initial  $\text{N}_2\text{O}$  peak could mainly be attributed to the denitrification of available soil  $\text{NO}_3^-$ , presumably due to the more favorable conditions for denitrification through the addition of easily degradable organic C and water (Comfort et al., 1990; Chadwick et al., 2000; Velthof et al., 2003). Additionally, a probably smaller part of initial  $\text{N}_2\text{O}$  could be ascribed to the rapid nitrification (Chadwick et al., 2000) or to nitrifier denitrification of slurry  $\text{NH}_4^+$ . In contrast, the partially observed second  $\text{N}_2\text{O}$  peak, mostly found a week after fertilizer application, can be attributed to the denitrification of mineralized and nitrified organic components of fertilizer N (Velthof et al., 2003).

Several authors proposed that the more recalcitrant digestate might reduce the rate of microbial degradation and oxygen consumption in the soil, resulting in reduced  $\text{N}_2\text{O}$  emissions through less anaerobic soil conditions (Clemens and Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009). In contrast, our study on organic soils found signif-

icantly higher  $\text{N}_2\text{O}$  emissions from the digestate treatments compared to the slurry treatments. Higher  $\text{N}_2\text{O}$  emissions derived from biogas digestates were also reported by a few other authors (e.g. Senbayram et al., 2009; Sanger et al., 2010), whereas Clemens et al. (2006) found no differences between untreated and digested slurry.

It can be assumed that in drained organic soils, as in the present study, sufficient metabolizable C is generally widely available in the upper soil profile (e.g. van Beek et al., 2004). Thus, as hypothesized, labile carbon is not limiting on organic soils. This was in line with Velthof et al. (2003), who supposed that the application of available C with the organic fertilizer has a larger effect on denitrification activity at soils with a lower  $C_{\text{org}}$  content compared to  $C_{\text{org}}$  rich soils. However, contrary to our hypothesis, the significantly higher  $\text{N}_2\text{O}$  emissions from the digestate treatments cannot solely be explained by the higher content of available N in the biogas digestate, since the amount of applied  $\text{NH}_4^+-\text{N}$  in the substrate was not markedly different. Nevertheless, as mentioned above, the much higher N-uptake at the biogas treatments (Fig. 5a) indicates that the application of this fertilizer resulted in a markedly higher N availability, promoting  $\text{N}_2\text{O}$  production. It could be assumed that the high pH and the lower C:N ratio of the biogas digestate obviously slightly enhanced SOM mineralization, probably due to increased microbial activity compared to cattle slurry fertilizer, leading to extra N for nitrification and denitrification. Moreover, as proposed above, it is also conceivable that the higher biomass production at these treatments itself is related to the increased  $\text{N}_2\text{O}$  emissions, due to the stimulating effect of plant roots on denitrification activity (Klemmedtsson et al., 1987; Bakken, 1988). Considering that increasing biomass production means increasing root growth and activity, it could be assumed that exudation of easily available organic C and N (Hailer and Stolp, 1985), as well as the  $\text{O}_2$  demand due to root respiration, is higher for the digestate treatments, promoting more anaerobic microsites and thus denitrification compared to cattle slurry (Erich et al., 1984; Klemmedtsson et al., 1987). Furthermore, several authors have suggested that root exudates may increase bacterial metabolism (Klemmedtsson, 1987; Mounier et al., 2004; Henry et al., 2008), further lowering the oxygen concentration and thus increasing denitrification (Klemmedtsson et al., 1987). However, the enhanced biomass production simultaneously should have depleted mineral N in the soil and thus reduced available N for nitrification and denitrification processes. Obviously, despite the negative apparent N balance of the biogas digestate treatment, there was no real nitrogen competition between plants and microbes. However, further investigations are required to prove whether digestates enhanced SOM mineralization or to what extent increased biomass production favors  $\text{N}_2\text{O}$  emissions and which N pathways and processes are involved.

The observed linear increase in the cumulative  $\text{N}_2\text{O}-\text{N}$  emissions during the first 16 days or annual  $\text{N}_2\text{O}$  emissions,

due to a higher mean groundwater level and a higher application rate of  $\text{NH}_4^+-\text{N}$ , reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of  $\text{C}_{\text{org}}$ -rich grasslands. The same was postulated for mineral soils by Ruser (2010).

#### 4.4 Fertilizer- and site-induced $\text{CH}_4$ emissions

The observed consumption rates of  $\text{CH}_4$  were in the range of  $\text{CH}_4$  uptakes reported by Flessa et al. (1998) for two different meadows in a southern German fen peatland. Slightly higher  $\text{CH}_4$  emissions of up to  $1.46 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$  were reported from Beetz et al. (2013) for a drained intensive grassland in northern Germany and from Nykänen et al. (1995) for a drained grassland in Finland. It is known that drainage turns peatlands from a significant source back to a sink of  $\text{CH}_4$  (Crill et al., 1994). In peatlands the position of the groundwater table is considered the key factor regulating methanogenic and methanotrophic processes (Whalen, 2005). In line with this, Flessa et al. (1998) showed that the consumption rate of  $\text{CH}_4$  increased with lowering of the groundwater level. Nevertheless, significant differences in the amount of the annual  $\text{CH}_4$  uptake capacity between the two study sites  $\text{C}_{\text{org}}$ -medium and  $\text{C}_{\text{org}}$ -high could not be seen, although distinct differences in the groundwater table were observed.

The occasionally observed  $\text{CH}_4$  peak emissions were only found immediately after cattle slurry application. This was in line with several other studies that reported short-term  $\text{CH}_4$  emissions immediately after organic fertilizer application, due probably to volatilization of dissolved  $\text{CH}_4$  from the applied substrate (Sommer et al., 1996; Chadwick et al., 2000; Wulf et al., 2002b; Jones et al., 2005; Amon et al., 2006). The longer lasting  $\text{CH}_4$  emissions observed after the first application event at the slurry treatment of the  $\text{C}_{\text{org}}$ -high site might result from the degradation of volatile fatty acids by methanogenic bacteria (Chadwick et al., 2000; Wulf et al., 2002b). Furthermore, the high groundwater level promotes the formation of  $\text{CH}_4$  during this time period. However, we could not find any significant differences in the short term or annual  $\text{CH}_4$  emissions between the two investigated fertilizers. According to Chadwick et al. (2000) more than 90 % of total  $\text{CH}_4$  emissions occur during the first 24 h following fertilizer application. Therefore, we must assume that we have missed most of the fertilizer-induced  $\text{CH}_4$  emissions. However, all studies from literature confirm the minor importance of  $\text{CH}_4$  emissions from applied organic fertilizers in the GHG balance of agricultural grasslands (Wulf et al., 2002b; Amon et al., 2006; Dietrich et al., 2012).

#### 4.5 N-losses by $\text{NH}_3$ volatilization

The  $\text{NH}_3$  losses measured after splash plate application at the third application event followed the typical pattern of lost ammonia (Clemens et al., 2006), particularly at the digestate treatments. Significantly higher  $\text{NH}_3$  losses from treatments

fertilized with biogas digestate were observed compared to those fertilized with cattle slurry. This is in line with several other studies (Messner, 1988, Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Amon et al., 2006; Möller and Stinner, 2009; Pacholski et al., 2010; Ni et al., 2011), whereas Pain et al. (1990), Rubæk et al. (1996), Wulf et al. (2002a) and Clemens et al. (2006) found no differences between anaerobic digested slurries and other animal slurries. However, it has to be taken into account that the present results are based only on measurements from a single application event. The observed relative N losses of 36 % of applied  $\text{NH}_4^+-\text{N}$  at the biogas digestate treatments were in the range reported for liquid slurries and digestates applied via surface application, whereas the significantly lower relative N losses (15 %) at the cattle slurry treatments stand in strong contrast to those reported in the literature (e.g., Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Smith et al., 2000; Wulf et al., 2002a; Chantigny et al., 2004). However, compared to the EF of 60 % used in the German national GHG inventory, both estimated  $\text{NH}_3$  loss rates were rather low (Haenel et al., 2014). It can be assumed that the higher concentration of  $\text{NH}_4^+$  ( $\text{NH}_4^+/\text{N}_{\text{tot}}$  ratio 0.65 vs. 0.33) and the markedly higher pH value (7.7 vs. 6.8) of the applied digestate compared to the cattle slurry caused the observed differences in the current study, since temperature and wind speed were equal. According to Sommer and Hutchings (2001) a change in the pH value from 7.7 to 8.0 will double the emission. However, the factors controlling the rise in pH are complex (Sommer and Husted, 1995 cited in Sommer and Hutchings, 2001) and the pH value was not determined after fertilization in the present study. Several authors propose that a lower dry matter content of slurries favors the infiltration into the soil with a subsequent faster decrease of  $\text{NH}_3$  losses (Sommer et al., 1996; Ni et al., 2011). There over a limited range (slurry DM of 2–5 %),  $\text{NH}_3$  losses increase by approximately 6 % for every 1 % DM content (Smith et al., 2000). Although the observed dry matter content of the biogas digestates was very low and at the lower end of values reported in the literature (e.g., Gutser et al., 2005; Möller et al., 2008; Quarkernack et al., 2011), no corresponding effect was found in the present study, as was also reported by Möller and Stinner (2009). According to Döhler and Horlacher (2010) and Smith et al. (2000), water-saturated grassland soils as well as very dry grassland soils high in organic matter lead to higher  $\text{NH}_3$ -losses due to the reduced infiltration of slurries. Thus it could be assumed that the infiltration of the slurries was possibly hampered in the current study, removing the effect of the different DM contents, due to the strong rain event that took place before the fertilizer application. The cattle slurry in our experiment had very favorable characteristics for crust formation (high DM content, grass silage diet; Smith et al., 2007). Warm weather also supported crust formation after application of cattle slurry, which can effectively inhibit  $\text{NH}_3$  exchange with the atmosphere and has been proposed as an  $\text{NH}_3$  mitigation measure for slurry

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6203

storage (Smith et al., 2007). The emission pattern observed in our study on soil with limited infiltration capacity supports the effectiveness of crusts for low  $\text{NH}_3$  losses. Additionally, at low dosage applications a large part of the organic fertilizer remained on the plant canopy and thus soil contact and infiltration was limited after spreading. We conclude that this was also the main reason why no significant differences in the pattern of  $\text{NH}_3$  volatilization between the soil types were found in the present study. Nevertheless, the markedly lower relative N losses from cattle slurry compared to literature values could not be explained in this way, but  $\text{NH}_3$  volatilization reported in literature showed a high variability in respect to climatic and soil conditions, slurry composition, and application technique.

The observed relative N losses of 15–36% of applied  $\text{NH}_4^+$ -N demonstrates that  $\text{NH}_3$  volatilization is quantitatively the most important N loss from slurry application, as was also proposed by Flessa and Beese (2000). Besides the negative effects of eutrophication and acidification of ecosystems (e.g., Fangmeier et al., 1994; Galloway, 1995; Smith et al., 1999; Galloway, 2001), marked  $\text{NH}_3$  volatilization decreases N fertilizer use efficiency. One of the most effective measures to reduce  $\text{NH}_3$  emissions from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several studies reported a considerable increase of GHGs, mainly  $\text{N}_2\text{O}$ , after injection of slurries and biogas digestates (Dosch and Gutser, 1996; Flessa and Beese, 2000; Wulf et al., 2002b). To date no study has examined the effect of the injection technique on organic soils.

## 5 Conclusions

We studied  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  fluxes after splash plate application of biogas digestate and cattle slurry in a region known for its risk of high  $\text{N}_2\text{O}$  and  $\text{NH}_3$  emissions and we were the first to study digestate application on high organic carbon soils with 10 to 17%  $\text{C}_{\text{org}}$  content in the topsoil. To our surprise,  $\text{N}_2\text{O}$  emissions and EFs were lower than generally observed on mineral soils in the vicinity of the sites. We attributed the low  $\text{N}_2\text{O}$  emissions to a mild winter without clear freeze–thaw cycles, but maybe also to frequent application with low dosage of N, which was quickly taken up by the grass vegetation, as was indicated by the apparent  $\text{NUE}_{\text{min}}$ .  $\text{N}_2\text{O}$  emissions increased with  $\text{C}_{\text{org}}$  content and fertilization. As hypothesized,  $\text{N}_2\text{O}$  levels were markedly higher after digestate than after slurry fertilization, which probably could be attributed to a priming effect caused by increased SOM mineralization or other sources of labile carbon triggered by digestate application. Due to the deep drainage,  $\text{CH}_4$  emissions were of minor importance and were independent of fertilizer type. Estimated N balances were negative for the control and the digestate treatments, but strongly positive in all cases when the net N supply from SOM mineralization was considered. The observed linear increase in cumulative  $\text{N}_2\text{O}$

emissions with increasing  $\text{NH}_4^+$  fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of  $\text{C}_{\text{org}}$ -rich grasslands.

*Acknowledgements.* We thank the two anonymous referees for their careful reading of the manuscript and suggestions which have greatly improved the paper. We thank the landowners Ludwig Büchler and Josef Pellmeyer for the opportunity to conduct the measurements during the regular land management as well for their excellent cooperation and help. We thank Caroline Müller, Michael Schlapp, Susanne Köstner, Melissa Mayer, Phillip Metzner, and Lukas Aberl for their help during field and laboratory work; Nadine Eickenscheidt (Thünen Institute) for helpful discussion and critical review; Niko Roßkopf (Humboldt University of Berlin) for soil description and providing  $\text{N}_{\text{tot}}$  and pH values; as well as Stephan Raspe from the Bavarian State Institute of Forestry for providing the N deposition data. This study was part of the joint research project “Organic soils”: Acquisition and Development of Methods, Activity Data and Emission Factors for the Climate Reporting under LULUCF/AFOLU, founded by the Thünen Institute.

Edited by: T. Laurila

## References

- Amon, B., Kryvoruchko, G. M., and Amon, T.: Greenhouse gas and ammonia emission abatement by slurry treatment, *International Congress Series*, 1293, 295–298, 2006.
- Andres, M., Hagemann, U., Seidel, A., and Augustin, J.: Gasförmige N-Verluste ( $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ) und N-Bilanzsalden beim Anbau von Energiemais mit Gärrestapplikation, in: Böden – Lebensgrundlage und Verantwortung, Jahrestagung der DBG, Symposium AG Bodengase, 7–12 September 2013, Rostock, 2013 (in German).
- Augustin, J., Merbach, W., Steffens, L., and Snelinski, B.: Nitrous Oxide Fluxes of Disturbed Minerotrophic Peatlands, *Agribiol. Res.*, 51, 47–57, 1998.
- Bakken, L. R.: Denitrification under different cultivated plants: effects of soil moisture tension, nitrate concentration, and photosynthetic activity, *Biol. Fertil. Soils*, 6, 271–278, 1988.
- Beetz, S., Liebersbach, H., Glatzel, S., Jurasinski, G., Buczko, U., and Höper, H.: Effects of land use intensity on the full greenhouse gas balance in an Atlantic peat bog, *Biogeosciences*, 10, 1067–1082, doi:10.5194/bg-10-1067-2013, 2013.
- Bouwman, A. F.: Direct emissions of nitrous oxide from agricultural soils, *Nutr. Cycl. Agroecosys.*, 45, 53–70, 1996.
- Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., and Zechmeister-Boltenstern, S.: Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, *Philos. T. R. Soc. B.*, 368, 1621, 2013.
- Chadwick, D. R., Pain, B. F., and Brookman, S. K. E.: Nitrous oxide and Methane Emissions following Application of Animal Manures to Grassland, *J. Environ. Qual.*, 29, 277–287, 2000.
- Chantigny, M. H., Rochette, P., Angers, D. A., Massé, D., and Côté, D.: Ammonia volatilization and selected soil characteristics fol-

6204 T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

- lowing application of anaerobically digested pig slurry, *Soil Sci. Soc. Am. J.*, 68, 306–312, 2004.
- Christensen, S.: Nitrous oxide emission from a soil under permanent grass: Seasonal and diurnal fluctuations as influenced by manuring and fertilisation, *Soil Biol. Biochem.*, 15, 531–536, 1983.
- Clayton, H., McTaggart, I. P., Parker, J., and Swan, L.: Nitrous oxide emissions from fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental conditions, *Biol. Fert. Soils*, 25, 252–260, 1997.
- Clemens, J. and Huschka, A.: The effect of biological oxygen demand of cattle slurry and soil moisture on nitrous oxide emissions, *Nutr. Cycling Agroecosyst.*, 59, 193–198, 2001.
- Clemens, J., Trimborn, M., Weiland, P., and Amon, B.: Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry, *Agr. Ecosyst. Environ.*, 112, 171–177, 2006.
- Comfort, S. D., Kelling, K. A., Keeney, D. R., and Converse, J. C.: Nitrous oxide production from injected dairy manure, *Soil Sci. Soc. Am.*, 1, 421–427, 1990.
- Crawley, M. J.: *The R Book*, John Wiley and Sons Ltd, Chichester, p. 942, 2007.
- Crill, P. M., Martikainen, P. J., Nykänen, H., and Silvola, J.: Temperature and fertilization effects on methane oxidation in a drained peatland soil, *Soil Biol. Biochem.*, 26, 1331–1339, 1994.
- Crutzen, P. J.: The role of NO and NO<sub>2</sub> in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Pl. Sc.*, 7, 443–472, 1979.
- Davidson, E. A., Swank, W. T., and Perry, T. O.: Distinguishing between nitrification and denitrification as sources of gaseous nitrogen production in soil, *Appl. Environ. Microb.*, 52, 1280–1286, 1986.
- DBFZ (Deutsches BiomasseForschungsZentrum gemeinnützige GmbH): Monitoring zur Wirkung des Erneuerbare-Energien-Gesetz (EEG) auf die Entwicklung der Stromerzeugung aus Biomasse – Endbericht zur EEG-Periode 2009 bis 2011, p. 120, 2012 (in German).
- De Boer, H. C.: Co-digestion of animal slurry can increase short-term nitrogen recovery by crops, *J. Environ. Qual.*, 37, 1968–1973, 2008.
- Dechow, R. and Freibauer, A.: Assessment of German nitrous oxide emissions using empirical modelling approaches, *J. Nutr. Cycl. Agroecosyst.*, 91, 235–254, 2011.
- Dietrich, B., Finnan, J., Frost, P., Gilkinson, S., and Müller, C.: The extent of methane (CH<sub>4</sub>) emissions after fertilisation of grassland with digestate, *Biol. Fert. Soils*, 48, 981–985, 2012.
- Don, A., Osborne, B., Hastings, A., Skiba, U., Carter, M. S., Drewer, J., Flessa, H., Freibauer, A., Hyvönen, N., Jones, M. B., Lanigan, G. J., Mander, Ü., Monti, A., Djomo, S. N., Valentine, J., Walter, K., Zegada-Lizarazu, W., and Zenone, T.: Land-use change to bioenergy production in Europe: implications for the greenhouse gas balance and soil carbon, *GCB Bioenergy*, 4, 372–391, doi:10.1111/j.1757-1707.2011.01116.x, 2012.
- Dosch, P. and Gutser, R.: Reducing N losses (NH<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>) and immobilization from slurry through optimized application techniques, *Fer. Res.*, 43, 165–171, 1996.
- Döhler, H. and Horlacher, D.: Ammoniakemissionen organischer Düngemittel, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems, Southern Germany, PhD thesis, Chair of Vegetation Ecology, Department of Ecology, Technical University Munich, p. 179, 2005.
- Drösler, M., Freibauer, A., Adelman, W., Augustin, J., Bergman, L., Beyer, C., Chojnicki, B., Förster, C., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H., Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P., Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz in der Praxis – Ergebnisse aus dem BMBF-Verbundprojekt “Klimaschutz – Moornutzungsstrategien” 2006–2010, 2011 (in German).
- Eickenscheidt, N., Brumme, R., and Veldkamp, E.: Direct contribution of nitrogen deposition to nitrous oxide emissions in a temperate beech and spruce forest – a <sup>15</sup>N tracer study, *Biogeosciences*, 8, 621–635, doi:10.5194/bg-8-621-2011, 2011.
- Elsässer, R. M., Kunz, H. G., and Briemle, G.: Unterschiedliche technische Behandlung von Gülle und deren Auswirkungen auf intensiv genutztes Grünland, *J. Agron. Crop. Sci.*, 174, 253–264, 1995 (in German).
- Erich, M. S., Bekerie, A., and Duxbury, J. M.: Activities of denitrifying enzymes in freshly sampled soils, *Soil Sci.*, 138, 25–32, 1984.
- Fachverband Biogas e.V.: Branchenzahlen – Prognosen 2013/2014, Entwicklung des jährlichen Zubaus von neuen Biogasanlagen in Deutschland, available at: [http://www.biogas.org/edcom/webfbv.nsf/id/DE\\_Branchenzahlen](http://www.biogas.org/edcom/webfbv.nsf/id/DE_Branchenzahlen), last access: November 2013.
- Fangmeier, A., Hadwiger-Fangmeier, A., van der Eerden, L., and Jäger, H. J.: Effects of atmospheric ammonia on vegetation – a review, *Environ. Pollu.*, 86, 43–82, 1994.
- Flessa, H. and Beese, F.: Laboratory Estimates of Trace Gas Emissions following Surface Application and Injection of Cattle Slurry, *J. Environ. Qual.*, 29, 262–268, 2000.
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: C- und N-Stoffflüsse auf Torfstichsimulationsflächen im Donaumoos, *Z. f. Kulturtechnik und Landentwicklung*, 38, 11–17, 1997 (in German).
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: Nitrous oxide and methane fluxes from organic soils under agriculture, *Eur. J. Soil Sci.*, 49, 327–335, 1998.
- Freibauer, A. and Kaltschmitt, M.: Nitrous oxide emissions from agricultural mineral soils in Europe – controls and models, *Biogeochemistry*, 63, 93–115, 2003.
- Freibauer, A., Rounsevell, M. D. A., Smith, P., and Verhagen, J.: Carbon sequestration in the agricultural soils of Europe, *Geoderma*, 122, 1–23, 2004.
- Frick, R.: Verteilgeräte an Güllefässern – Grosse Unterschiede bezüglich Arbeitsbreite und Verteilgenauigkeit, *FAT Berichte*, 531, 1–37, 1999 (in German).
- Galloway, J. N.: Acid deposition: Perspectives in time and space, *J. Water, Air Soil Poll.*, 85, 15–24, 1995.
- Galloway, J. N.: Acidification of the world: natural and anthropogenic, *J. Water, Air, Soil Poll.*, 130, 17–24, 2001.
- Goldberg, S. D., Knorr, K. H., Blodau, C., Lischeid, G., and Gebauer, G.: Impact of altering the water table height of an acidic fen on N<sub>2</sub>O and NO fluxes and soil concentrations, *Global Change Biol.*, 16, 220–233, 2010.

## T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

6205

- Gunnarsson, A., Bengtsson, F., and Caspersen, S.: Use efficiency of nitrogen from biodigested plant material by ryegrass, *J. Plant Nutr. Soil Sci.*, 173, 113–119, 2010.
- Gutser, R., Ebertseder, Th., Weber, A., Schraml, M., and Schmidhalter, U.: Short-term and residual availability of nitrogen after long-term application of organic fertilizers on arable land, *J. Plant Nutr. Soil Sci.*, 168, 439–446, 2005.
- Gutser, R., Ebertseder, T., Schraml, M., Tucher von, S., and Schmidhalter, U.: Stickstoffeffiziente und umweltschonende organische Düngung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Hacin, J., Cop, J., and Mahne, I.: Nitrogen mineralization in marsh meadows in relation to soil organic matter content and watertable level, *J. Plant Nutr. Soil Sci.*, 164, 503–509, 2001.
- Haenel, H. D., Freibauer, A., Rösemann, C., Poddey, E., Gensior, A., Menden, B. M., and Döhler, H.: Emissionen landwirtschaftlich genutzter Böden im Rahmen der deutschen Klimaberichterstattung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Haenel, H. D., Rösemann, C., Dämmgen, U., Poddey, E., Freibauer, A., Wulf, S., Eurich-Menden, B., Döhler, H., Schreiner, C., Bauer, B., and Osterburg, B.: Calculations of gaseous and particulate emissions from German agriculture 1990–2012, *Johann Heinrich von Thünen-Institut, Braunschweig*, 348 pp., Thünen Rep 17, 2014.
- Hahn-Schöfl, M., Zak, D., Minke, M., Gelbrecht, J., Augustin, J., and Freibauer, A.: Organic sediment formed during inundation of a degraded fen grassland emits large fluxes of CH<sub>4</sub> and CO<sub>2</sub>, *Biogeosciences*, 8, 1539–1550, doi:10.5194/bg-8-1539-2011, 2011.
- Hailer, T. and Stolp, H.: Quantitative estimation of root exudation of maize plants, *Plant Soil*, 86, 207–216, 1985.
- Henry, S., Texier, S., Hallet, S., Bru, D., Dambreville, C., Chêneby, D., Bizouard, F., Germon, J. C., and Philippot, L.: Disentangling the rhizosphere effect on nitrate reducers and denitrifiers: insight into the role of root exudates, *Environ. Microbiol.*, 10, 3082–3092, 2008.
- Hothorn, T., Bretz, F., Westfall, P., Heiberger, R. M., and Schuetzenmeister, A.: Simultaneous Inference in General Parametric Models: R package version 1.2-17, 2013.
- IPCC: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- IPCC: 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands, edited by: Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M. and Troxler, T. G., Published: IPCC, Switzerland, 2014.
- Jensen, L. S., Pedersen, I. S., Hansen, T. B., and Nielsen, N. E.: Turnover and fate of <sup>15</sup>N-labelled cattle slurry ammonium-N applied in the autumn to winter wheat, *Eur. J. Agron.*, 12, 23–35, 2000.
- Jones, S. K., Rees, R. M., Skiba, U. M., and Ball, B. C.: Greenhouse gas emissions from managed grassland, *Global Planet. Change*, 47, 201–211, 2005.
- Jones, S. K., Rees, R. M., Skiba, U. M., and Ball, B. C.: Influence of organic and mineral N fertiliser on N<sub>2</sub>O fluxes from temperate grassland, *Agriculture, Ecosystems Environ.*, 121, 74–83, 2007.
- Jungkunst, H. F., Freibauer, A., Neufeldt, H., and Bareth, G.: Nitrous oxide emissions from agricultural land use in Germany – a synthesis of available annual field data, *J. Plant Nutr. Soil Sci.*, 169, 341–351, 2006.
- Kasimir Klemedtsson, Å., Klemedtsson, L., Berglund, K., Martikainen, P., Silvola, J., and Oenema, O.: Greenhouse gas emissions from farmed organic soils: a review, *Soil Use Manage.*, 13, 1–6, 1997.
- Klemedtsson, L., Svensson, B. H., and Rosswall, T.: Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants, *Plant Soil*, 99, 303–319, 1987.
- Klemedtsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, *Glob. Change Biol.*, 11, 1142–1147, 2005.
- Koops, J. G., Oenema, O., and van Beusichem, M. L.: Denitrification in the top soil of grassland on peat soil, *Plant Soil*, 184, 1–10, 1996.
- Livingston, G. P. and Hutchinson, G. L.: Enclosure-based measurement of trace gas exchange: application and sources of error, in: *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by: Matson, P. A. and Harriss, R. C., Blackwell Science, Cambridge, 14–50, 1995.
- Maljanen, M., Komulainen, V. M., Hytönen, J., Martikainen, P. J., and Laine, J.: Carbon dioxide, nitrous oxide and methane dynamics in boreal organic agricultural soils with different soil characteristics, *Soil Biol. Biochem.*, 36, 1801–1808, 2004.
- Maljanen, M., Sigurdsson, B. D., Gudmundsson, J., Óskarsson, H., Huttunen, J. T., and Martikainen, P. J.: Greenhouse gas balances of managed peatlands in the Nordic countries – present knowledge and gaps, *Biogeosciences*, 7, 2711–2738, doi:10.5194/bg-7-2711-2010, 2010.
- Merino, P., Estavillo, J. M., Gracioli, L. A., Pinto, M., Lacuesta, M., Muñoz-Rueda, A., and Gonzalez-Murua, C.: Mitigation of N<sub>2</sub>O emissions from grassland by nitrification inhibitor and Actilith F2 applied with fertilizer and cattle slurry, *Soil Use Manage.*, 18, 135–141, 2002.
- Messner, H.: Düngewirkung anaerob fermentierter und unbehandelter Gülle, Dissertation, Fakultät für Landwirtschaft und Gartenbau, TU München, 1988 (in German).
- Möller, K. and Stinner, W.: Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and gaseous nitrogen losses (ammonia, nitrous oxide), *Eur. J. Agronomy*, 30, 1–16, 2009.
- Möller, K. and Müller, T.: Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review, *Eng. Life Sci.*, 12, 242–257, 2012.
- Möller, K., Stinner, W., Deuker, A., and Leithold, G.: Effects of different manuring systems with and without biogas digestion on nitrogen cycle and crop yield in mixed organic dairy farming systems, *Nutr. Cycl. Agroecosyst.*, 82, 209–232, doi:10.1007/s10705-008-9196-9, 2008.
- Moiser, A. R.: Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere, *Plant Soil*, 228, 17–27, 2001.
- Mounier, E., Hallet, S., Chêneby, D., Benizri, E., Gruet, Y., Nguyen, C., Piutti, S., Robin, C., Slezack-Deschaumes, S., Martin-

6206 T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application

- Laurent, F., Germon, J. C., and Philippot, L.: Influence of maize mulch on the diversity and activity of the denitrifying community, *Environ. Microbiol.*, 6, 301–312, 2004.
- Ni, K., Pacholski, A., Gericke, D., and Kage, H.: Analysis of ammonia losses after field application of biogas slurries by an empirical model, *J. Plant Nutr. Soil Sci.*, 175, 1–12, doi:10.1002/jpln.201000358, 2011.
- Nykänen H., Alm, J., Lång, K., Silvola, J., and Martikainen, P. J.: Emissions of CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub> from a virgin fen and a fen drained for grassland in Finland, *J. Biogeogr.*, 22, 351–357, 1995.
- Oenema, O., Wrage, N., Velthof, G. L., van Groenigen, J. W., Dolfing, J., and Kuikman, P. J.: Trends in global nitrous oxide emissions from animal production systems, *Nutr. Cycl. Agroecosyst.*, 72, 51–65, 2005.
- Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z., and Roelcke, M.: Calibration of a simple method for determining ammonia volatilization in the field – comparative measurements in Henan Province, China, *Nutr. Cycl. Agroecosyst.*, 74, 259–273, 2006.
- Pacholski, A., Gericke, D., Ni, K., and Kage, H.: Ammoniakemissionen nach Ausbringung von Gärresten im Vergleich zu Gülle, *KTBL-Schrift*, 483, p. 384, 2010 (in German).
- Pain, B. F., Misselbrook, T. H., Clarkson, C. R., and Rees, Y. J.: Odour and ammonia emissions following the spreading of anaerobically-digested pig slurry on grassland, *Biol. Wastes*, 34, 259–267, 1990.
- Quarkernack, R., Pacholski, A., Techow, A., Herrmann, A., Taube, F., and Kage, H.: Ammonia volatilization and yield response of energy crops after fertilization with biogas residues in a coastal marsh of Northern Germany, *Agric. Ecosyst. Environ.*, 160, 66–74, doi:10.1016/j.agee.2011.05.030, 2011.
- Regina, K., Syväsalo, E., Hannukkala, A., and Esala, M.: Fluxes of N<sub>2</sub>O from farmed peat soils in Finland, *Eur. J. Soil Sci.*, 55, 591–599, 2004.
- R Development Core Team: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, available at: <http://www.R-project.org> (last access: November 2013), 2010.
- Renger, M., Wessolek, G., Schwarzel, K., Sauerbrey, R., and Siewert, C.: Aspects of peat conservation and water management, *J. Plant Nutr. Soil Sci.*, 165, 487–493, 2002.
- Rodhe, L., Pell, M., and Yamulki, S.: Nitrous oxide, methane and ammonia emissions following slurry spreading on grassland, *J. Soil Use Manage.*, 22, 229–237, 2006.
- Roelcke, M., Li, S. X., Gao, Y. J., and Richter, J.: In situ comparisons of ammonia volatilization from N fertilizers in Chinese loess soils, *Nutr. Cycl. Agroecosyst.*, 62, 73–88, 2002.
- Rubæk, G. H., Henriksen, K., Petersen, J., Rasmussen, B., and Sommer, S. G.: Effects of application technique and anaerobic digestion on gaseous loss from animal slurry applied to ryegrass (*Lolium perenne*), *J. Agric. Sci. Camb.*, 126, 481–492, 1996.
- Ruser, R.: Möglichkeiten zur Minderung der Lachgasfreisetzung aus landwirtschaftlich genutzten Böden bei mineralischer Stickstoffdüngung, in: Emissionen landwirtschaftlich genutzter Böden, *KTBL-Schrift*, 483, p. 384, 2010 (in German).
- Sänger, A., Geisseler, D., and Ludwig, B.: Effects of rainfall pattern on carbon and nitrogen dynamics in soil amended with biogas slurry and composted cattle manure, *J. Plant Nutr. Soil Sci.*, 173, 692–698, 2010.
- Schils, R. L. M., van Groenigen, J. W., Velthof, G. L., and Kuikman, P. J.: Nitrous oxide emissions from multiple combined applications of fertiliser and cattle slurry to grassland, *Plant Soil*, 310, 89–101, 2008.
- Schothorst, C. J.: Subsidence of low moor peat soils in the Western Netherlands, *Geoderma*, 17, 265–291, 1977.
- Senbayram, M., Chen, R., Mühling, K. H., and Dittert, K.: Contribution of nitrification and denitrification to nitrous oxide emissions from soils after application of biogas waste and other fertilizers, *Rapid Commun. Mass Spectrom.*, 23, 2489–2498, 2009.
- Smith, V. H., Tilman, G. D., and Nekola, J. C.: Eutrophication: impacts of excess nutrient input on freshwater, marine, and terrestrial ecosystems, *Environ. Pollut.*, 100, 179–196, 1999.
- Smith, K. A., Jackson, D. R., Misselbrook, T. H., Pain, B. F., and Johnson, R. A.: Reduction of ammonia emission by slurry application techniques, *J. Agric. Engng. Res.*, 77, 277–287, 2000.
- Smith, K., Cumby, T., Lapworth, J., Misselbrook, T., and Williams, A.: Natural crusting of slurry storage as an abatement measure for ammonia emissions on dairy farms, *Biosyst. Eng.*, 97, 464–471, 2007.
- Sørensen, P. and Amato, M.: Remineralisation and residual effects of N after application of pig slurry to soil, *Eur. J. Agron.*, 16, 81–95, 2002.
- Sommer, S. G. and Husted, S.: A simple model of pH in slurry, *J. Agric. Sci. Camb.*, 124, 447–453, 1995.
- Sommer, S. G., Sherlock, R. R., and Khan, R. Z.: Nitrous oxide and methane emissions from pig slurry amended soils, *Soil Biol. Biochem.*, 28, 1541–1544, 1996.
- Sommer, S. G. and Hutchings, N. J.: Ammonia emission from field applied manure and its reduction – invited paper, *Eur. J. Agro.*, 15, 1–15, 2001.
- Sonneveld, M. P. W. and Lantinga, E. A.: The contribution of mineralization to grassland N uptake on peatland soils with anthropogenic A horizons, *Plant Soil*, 340, 357–368, 2011.
- Tambone, F., Genevini, P., D'Imporzano, G., and Adani, F.: Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW, *Bioresource Technol.*, 100, 3140–3142, 2009.
- Umweltbundesamt: Nationale Trendtabellen für die deutsche Berichterstattung atmosphärischer Emissionen seit 1990, available at: <http://www.umweltbundesamt.de/daten/klimawandel/treibhausgas-emissionen-in-deutschland/distickstoffoxid-emissionen>, 2014 (in German).
- van Beek, C. L., Hummelink, E. W. J., Velthof, G. L., and Oenema, O.: Denitrification rates in relation to groundwater level in a peat soil under grassland, *Biol. Fertil. Soils*, 39, 329–336, 2004.
- van Beek, C. L., Pleijter, M., Jacobs, C. M. J., Velthof, G. L., van Groenigen, J. W., and Kuikman, P. J.: Emissions of N<sub>2</sub>O from fertilized and grazed grassland on organic soil in relation to groundwater level, *Nutr. Cycl. Agroecosyst.*, 86, 331–340, 2010.
- van Beek, C. L., Pleijter, M., and Kuikman, P. J.: Nitrous oxide emissions from fertilized and unfertilized grasslands on peat soil, *Nutr. Cycl. Agroecosyst.*, 89, 453–461, 2011.
- Velthof, G. L., Brader, A. B., and Oenema, O.: Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands, *Plant Soil*, 181, 263–274, 1996.

**T. Eickenscheidt et al.: Short-term effects of biogas digestate and cattle slurry application****6207**

- Velthof, G. L., Kuikman, P. J., and Oenema, O.: Nitrous oxide emission from animal manures applied to soil under controlled conditions, *Biol. Fertil. Soils*, 37, 221–230, 2003.
- Weiland, P.: Biogas production: current state and perspectives, *Appl. Microbiol. Biotechnol.*, 85, 849–860, 2010.
- Whalen, S. C.: Biogeochemistry of methane exchange between natural wetlands and the atmosphere, *Environ. Eng. Sci.*, 22, 73–94, 2005.
- WRB, 2006 – IUSS Working Group: World Reference Base for Soil Resources 2006, 2nd edition, World Soil Resources Reports No. 103, Rome, 2006.
- Wulf, S., Maeting, M., and Clemens, J.: Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: I Ammonia Volatilization, *J. Environ. Qual.*, 31, 1789–1794, 2002a.
- Wulf, S., Maeting, M., and Clemens, J.: Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: II Greenhouse Gas Emissions, *J. Environ. Qual.*, 31, 1795–1801, 2002b.

### 7.3 PUBLICATION III.



**Eickenscheidt, T.**, Heinichen, J., Augustin, J., Freibauer, A., and Drösler, M.: Nitrogen mineralization and gaseous nitrogen losses from waterlogged and drained organic soils in a black alder (*Alnus glutinosa* (L.) Gaertn.) forest, *Biogeosciences*, 11, 2961–2976, doi:10.5194/bg-11-2961-2014, 2014.

Biogeosciences, 11, 2961–2976, 2014  
 www.biogeosciences.net/11/2961/2014/  
 doi:10.5194/bg-11-2961-2014  
 © Author(s) 2014. CC Attribution 3.0 License.



## Nitrogen mineralization and gaseous nitrogen losses from waterlogged and drained organic soils in a black alder (*Alnus glutinosa* (L.) Gaertn.) forest

T. Eickenscheidt<sup>1</sup>, J. Heinichen<sup>1</sup>, J. Augustin<sup>2</sup>, A. Freibauer<sup>3</sup>, and M. Drösler<sup>1</sup>

<sup>1</sup>University of Applied Sciences Weihenstephan-Triesdorf, Chair of Vegetation Ecology, Weihenstephaner Berg 4, 85354 Freising, Germany

<sup>2</sup>Leibniz Centre for Agricultural Landscape Research e. V., Institute of Landscape Matter Dynamics, Eberswalder Straße 84, 15374 Müncheberg, Germany

<sup>3</sup>Thünen Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Brunswick, Germany

Correspondence to: T. Eickenscheidt (tim.eickenscheidt@hswt.de)

Received: 25 September 2013 – Published in Biogeosciences Discuss.: 5 December 2013

Revised: 5 March 2014 – Accepted: 12 March 2014 – Published: 5 June 2014

**Abstract.** Black alder (*Alnus glutinosa* (L.) Gaertn.) forests on peat soils have been reported to be hotspots for high nitrous oxide (N<sub>2</sub>O) losses. High emissions may be attributed to alternating water tables of peatlands and to the incorporation of high amounts of easily decomposable nitrogen (N) into the ecosystem by symbiotic dinitrogen (N<sub>2</sub>)-fixation of alder trees. Our study addressed the question to what extent drainage enhances the emissions of N<sub>2</sub>O from black alder forests and how N turnover processes and physical factors influence the production of N<sub>2</sub>O and total denitrification. The study was conducted in a drained black alder forest with variable groundwater tables at a southern German fen peatland. Fluxes of N<sub>2</sub>O were measured using the closed chamber method at two drained sites (D-1 and D-2) and one undrained site (U). Inorganic N contents and net N mineralization rates (NNM) were determined. Additionally a laboratory incubation experiment was carried out to investigate greenhouse gas and N<sub>2</sub> fluxes at different temperature and soil moisture conditions. Significantly different inorganic N contents and NNM rates were observed, which however did not result in significantly different N<sub>2</sub>O fluxes in the field but did in the laboratory experiment. N<sub>2</sub>O fluxes measured were low for all sites, with total annual emissions of  $0.51 \pm 0.07$  (U),  $0.97 \pm 0.13$  (D-1) and  $0.93 \pm 0.08$  kg N<sub>2</sub>O–N ha<sup>-1</sup> yr<sup>-1</sup> (D-2). Only 37 % of the spatiotemporal variation in field N<sub>2</sub>O fluxes could be explained by peat temperature and groundwater level, demonstrating the complex interlinking of the

controlling factors for N<sub>2</sub>O emissions. However, temperature was one of the key variables of N<sub>2</sub>O fluxes in the incubation experiment conducted. Increasing soil moisture content was found to enhance total denitrification losses during the incubation experiment, whereas N<sub>2</sub>O fluxes remained constant. At the undrained site, permanently high groundwater level was found to prevent net nitrification, resulting in a limitation of available nitrate (NO<sub>3</sub><sup>-</sup>) and negligible gaseous N losses. N<sub>2</sub>O flux rates that were up to four times higher were measured in the incubation experiment. They reveal the potential of high N<sub>2</sub>O losses under changing soil physical conditions at the drained alder sites. The high net nitrification rates observed and high NO<sub>3</sub><sup>-</sup> contents bear the risk of considerable NO<sub>3</sub><sup>-</sup> leaching at the drained sites.

### 1 Introduction

Black alder (*Alnus glutinosa* (L.) Gaertn.) forests represent the natural vegetation in many semi-wet and wet regions, mostly on soils with high organic carbon contents (Dilly et al., 1999; Schäfer and Joosten, 2005; Kätzel, 2003). Unlike most other wetlands, alder forests on peatland represent non N-limited ecosystems, due to the ability of alder trees for symbiotic N<sub>2</sub>-fixation of up to 85 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Dittert, 1992; Augustin, 2003). To date, there are only a few studies on N turnover and N transformation processes

in black alder forests on peatland. First results indicate that these ecosystems show high N-transfer rates between the atmosphere, the alder trees and the soil (Augustin, 2003). Through the symbiotic N<sub>2</sub>-fixation high amounts of easily decomposable N enter the ecosystem and lead to a low C/N ratio of the soil organic matter (Löhmus et al., 2002). Semi-wet peat soils with low C/N ratios are known to be potential hotspots for gaseous and dissolved nitrogen losses via mineralization, nitrification, denitrification and nitrate leaching (Löhmus et al., 2002; Gundersen et al., 1998; Ollinger et al., 2002; Klemmedtsson et al., 2005). Enhanced N<sub>2</sub>O emissions, in particular, are of great interest due to the fact that N<sub>2</sub>O acts as a radiative forcing greenhouse gas (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). The few annual observations of N<sub>2</sub>O emissions from *Alnus* forest ecosystems on drained or undrained peatlands range between 0.1 and 72.0 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Augustin et al., 1998; Brumme et al., 1999; Merbach et al., 2001; von Arnold et al., 2005). Most emissions exceed by far the IPCC default emission factor of 0.6 (0.16–2.4) kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> (IPCC, 2006) for boreal and temperate nutrient-rich forest peatlands. The high range requires in-depth process understanding to narrow down the uncertainty and better understand N<sub>2</sub>O formation, not least because of the attempt to reduce the climate impact of drained fen peatland by rewetting and afforestation with black alder trees (*Alnus glutinosa* (L.) Gaertn.) (Schäfer and Joosten, 2005; Wichtmann and Joosten, 2007).

The production of N<sub>2</sub>O depends mainly on the two microbial processes of denitrification and nitrification (Davidson, 1986). Thus, the availability of soil mineral N and oxygen are the main controlling factors (Del Grosso et al., 2000; Jungkunst et al., 2004). Furthermore, soil temperature is known to be a key variable controlling both processes (Firestone and Davidson, 1989; Smith et al., 1998). Highest N<sub>2</sub>O fluxes are mainly related to incomplete denitrification. This requires the presence of efficient electron acceptors (e.g., NO<sub>3</sub><sup>-</sup>) to prevent the reduction of N<sub>2</sub>O to N<sub>2</sub> (Bremner and Blackmer, 1981; Speir et al., 1995; Jungkunst et al., 2004). Due mainly to analytical difficulties in the determination of microbially produced N<sub>2</sub>, to date the denitrification potential from waterlogged peat soils has rarely been estimated (Watts and Seitzinger, 2000; Mander et al., 2003; Teiter and Mander, 2005; Wray and Bayley, 2007; Roobroeck et al., 2010; Soosaar et al., 2011; Uri et al., 2011). The substitution of ambient N<sub>2</sub> by Helium (He) in laboratory studies possibly represents the most reliable method for the direct and simultaneous determination of N<sub>2</sub>O and N<sub>2</sub> exchange rates (Butterbach-Bahl et al., 2002; Roobroeck et al., 2010; Butterbach-Bahl et al., 2013).

The objectives of our study were to quantify (i) the nitrogen mineralization and nitrogen transformation processes, and (ii) N<sub>2</sub>O emissions and the factors regulating the N<sub>2</sub>O emissions and N<sub>2</sub>O/N<sub>2</sub> ratio from waterlogged and drained black alder forest on organic soil.

We hypothesize that (1) in drained black alder forests high N<sub>2</sub>O emissions occur due to accelerated N turnover and N mineralization, and (2) N<sub>2</sub>O is replaced by N<sub>2</sub> losses during periods of temporarily high water levels. In contrast, NO<sub>3</sub><sup>-</sup> limitation in permanently waterlogged peat soils results in negligible N<sub>2</sub>O and N<sub>2</sub> losses. To investigate our hypotheses, we selected three sites in an alder forest along a groundwater table gradient, representative of the small-scale heterogeneity of the forest stand.

## 2 Materials and methods

### 2.1 Study area and experimental design

The study was carried out in a drained 45-year-old black alder (*Alnus glutinosa* (L.) Gaertn.) forest stand (2.2 ha) on organic soil (Freisinger Moos, 48°22' N, 11°40' E; 449 m a.s.l.). According to the climate station in Weihestephan, located 10 km northeast of the site, the 30-year mean annual temperature was 7.5 °C and the mean annual precipitation was 787 mm (1961–1990). At a German Level II monitoring area, located at 5 km distance from the alder forest, annual stand N deposition amounted to 17.67 kg N ha<sup>-1</sup> yr<sup>-1</sup> with a NH<sub>4</sub><sup>+</sup>-N:NO<sub>3</sub><sup>-</sup>-N ratio of 46:54 in 2011 (data were collected and analyzed by the Bavarian State Institute of Forestry). The black alder stand was planted on grassland in 1965 and has not been managed. In 2009, stem density was approximately 1031 trees per hectare, with a mean height of 19.7 m and a mean diameter at breast height of 21 cm (S. Röhling, personal communication, 2012). Approximately 15 % of the forest area consists of undrained hollows whereas most parts are drained by ditches. In October 2009, we selected three sites which differed in groundwater table (Table 1) as well as in their physical and chemical soil properties relevant for N<sub>2</sub>O processes (e.g., bulk density, carbon and nitrogen content) (Table 2). One site was situated in an undrained hollow (named U). The other two sites were situated in the drained part of the forest (named D-1 and D-2) along a gradient of drainage depth. Soils at the drained sites were classified as sapric histosols whereas the undrained site was classified as fluvisol (according to the World Reference Base for Soil Resources (WRB), 2006). The surface organic layer at the drained sites was a L-mull humus, and at the undrained site a submerged mud layer. At the site U, the dominant species in the herb layer were *Phragmites australis* and *Carex acutiformis*. Site D-1 was dominated by *Impatiens glandulifera*, *Impatiens parviflora*, *Deschampsia cespitosa* and *Circaea x intermedia*, whereas site D-2 was dominated by *Carex acutiformis*, *Circaea x intermedia*, *Rubus caesius* and *Carex elongata*.

At each site, three PVC-collars for greenhouse gas (GHG) measurements (inside dimensions 75 × 75 cm) were permanently inserted 10 cm into the soil. The collars of a site were grouped closely to each other (distance of 0.8 to

## T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

2963

**Table 1.** Groundwater level, water-filled pore space (WFPS), extractable nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) contents of the three sites for the year 2011.

	Soil depth [cm]	U	D-1	D-2	<i>n</i>
Groundwater level [cm]		4 (−26/28) <sup>a</sup>	−41 (−71/−3)	−47 (−77/−5)	
		3 (−20/22) <sup>b</sup>	−42 (−65/−22)	−44 (−68/−25)	81
WFPS [Vol %]	0–10	97 (79/100) a	70 (56/87) b	63 (51/73) c	26
	10–20	99 (92/100) a	81 (65/95) b	78 (66/88) c	26
$\text{NO}_3^-$ [mg N kg <sup>−1</sup> ]	0–10	7 (0/57) a	103 (36/196) b	60 (24/106) c	26
	10–20	4 (0/21) a	109 (55/193) b	62 (28/109) c	26
$\text{NH}_4^+$ [mg N kg <sup>−1</sup> ]	0–10	73 (0/209) a	18 (0/88) b	10 (0/58) b	26
	10–20	68 (0/169) a	11 (0/57) b	6 (0/24) b	26

Values are given as mean with minimum and maximum in parentheses. Means followed by the same lower-case letters indicate no significant differences between the sites within the year 2011. (Pairwise Wilcoxon rank sum test with Bonferroni correction for WFPS,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at  $P \leq 0.05$ ). <sup>a</sup> Values give the mean data from the water level loggers (15 min log interval). <sup>b</sup> Values give the mean groundwater level during the gas flux measurements conducted.

**Table 2.** Soil properties of the sites.

	Soil depth [cm]	U	D-1	D-2	<i>n</i>
Soil type (WRB* 2006)		Fluvisol	Sapric histosol	Sapric histosol	
Soil type (German classification KA5)		DY	KV-KM	KV-KM	
Peat depth [cm]		60	90	90	1
Organic carbon [%]	0–10	35.2 ± 1.4	14.6 ± 0.1	9.7 ± 0.4	3
	10–20	30.2 ± 0.6	13 ± 0.1	8.3 ± 0.2	3
Total nitrogen [%]	0–10	2.8 ± 0.1	1.8 ± 0.1	1.1 ± 0.0	3
	10–20	2.0 ± 0.0	1.5 ± 0.1	0.9 ± 0.0	3
C/N ratio	0–10	12 ± 0.2	8 ± 0.2	9 ± 0.6	3
	10–20	15 ± 0.1	9 ± 0.5	9 ± 0.3	3
Bulk density [g cm <sup>−3</sup> ]	0–10	0.14 ± 0.01	0.36 ± 0.02	0.47 ± 0.04	6
	10–20	0.13 ± 0.00	0.43 ± 0.01	0.60 ± 0.03	6
Porosity [%]	0–10	89 ± 3	79 ± 2	74 ± 1	6
	10–20	92 ± 1	79 ± 1	75 ± 1	6

Values give means ± standard error. \*World Reference Base for Soil Resources.

2.5 m) due to large heterogeneity in soil properties. Boardwalks were installed to prevent oscillations of the peat through movements during the measurements. Plastic perforated tubes (JK-casings DN 50, Ø 60 mm, length 1 m) were installed close to each collar for plot-specific measurements of the groundwater table during gas flux measurements. We equipped one tube per site with a water level logger (Type Mini-Diver, Schlumberger water services), which logged the water table every 15 min. Additionally, climate stations were installed between the sites D-1 and D-2 at the beginning of March 2010 and at site U in April 2011. At each climate station, air temperature and humidity at 20 cm above soil sur-

face, soil temperatures at a depth of −2, −5 and −10 cm as well as soil moisture content at −5 cm were logged every 30 min. In addition to the recorded data, site-specific soil temperatures at three soil depths (−2, −5 and −10 cm) were determined with penetration thermometers at the beginning and end of each gas flux measurement. Moreover, plot-specific groundwater levels were measured inside the tubes without loggers during gas flux measurements.

2964

T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

## 2.2 Field measurements

### 2.2.1 N<sub>2</sub>O flux measurements

We measured fluxes of N<sub>2</sub>O every second week from December 2010 to January 2012 using the static manual chamber method with a chamber height of 0.5 m (Livingston and Hutchinson, 1995). At site U, in periods where the forest floor vegetation grew higher than the chamber height, extensions (same dimension as chamber) were installed between the collar and chamber (white, opaque; volume varied between 309 and 927 L). A detailed description of chamber dimension and configuration is given in Drösler (2005). Four gas samples were taken at four regular time intervals after chamber closure (enclosure time 60 min, in the case of two extensions 120 min). The samples were collected in 20 mL glass vials, each sealed with a butyl rubber septum. The vials were flushed with chamber air for 30 s using a portable micro pump (KNF Neuberger GmbH, NMP015B), so that the air in the vials was exchanged 32 times. In addition, the pump was used to build up an overpressure of approximately 550 mbar to protect the sample against fluctuations in atmospheric pressure during storage. Gas analyses were carried out with a gas chromatograph (Perkin and Elmer, Clarus 400 GC or Clarus 480 GC) equipped with a headspace auto sampler (Perkin and Elmer, TurboMatrix 110), a Poropack 80/100 mesh column and an electron capture detector (ECD) for N<sub>2</sub>O (ECD temperature 380 °C). Gas flux rates were calculated from the linear change in gas concentration over time considering chamber air temperature and atmospheric pressure. Gas fluxes were accepted when the linear regression was significant ( $P \leq 0.05$ ). In the case of small N<sub>2</sub>O fluxes, fluxes were also accepted if the coefficient of determination was  $\geq 0.90$  and the regression slope was between  $-1$  and  $1 \text{ ppb min}^{-1}$ . The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

### 2.2.2 Soil sampling and laboratory analysis

Total carbon ( $C_{\text{tot}}$ ), organic carbon ( $C_{\text{org}}$ ) and total nitrogen ( $N_{\text{tot}}$ ) were analyzed by the AGROLAB Labor GmbH (Bruckberg, Germany) on three mixed soil samples per site. Each sample was composed of nine individual samples collected close to each collar at two soil depths (0–10, 10–20 cm). After drying for 72 h at 40 °C, soil samples were sieved to 2 mm to remove stones and living roots.

For the determination of bulk density and porosity, three undisturbed core cutter samples ( $100 \text{ cm}^3$ ) were randomly taken at four depths (0–5, 5–10, 10–15, 15–20 cm) for each site.

During every gas flux measurement, one mixed soil sample consisting of nine individual samples was collected at two soil depths (0–10, 10–20 cm) for each site for the determination of mineral N ( $N_{\text{min}} = \text{NH}_4^+ - \text{N} + \text{NO}_3^- - \text{N}$ ) contents.

Samples were immediately cooled in an ice box until further processing. Mineral N was extracted after shaking 40 g of fresh soil with 160 mL CaCl<sub>2</sub> (0.0125 M) for one hour. The extracts were filtered through a 4–7 µm filter paper (Whatman 595 1/2) and the first 20 mL of the extract were discarded (VDLUFA, 1997). The solution was frozen at  $-20^\circ\text{C}$  until analysis, which was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). A subsample of 20–30 g was used to determine the gravimetric water content, which was taken into account for the calculation of mineral N concentrations.

### 2.2.3 Net N mineralization

In 2011, net ammonification, nitrification and N mineralization rates (NNM) were determined in situ in four different periods in time (March, June, September and December). At each study site and period, three pairs of intact soil cores were taken randomly from the upper 20 cm of the soil layer using a cylindrical auger (diameter of 45 mm). In the case of flooding at the undrained site, disturbed soil samples were used. One core of each pair was sealed in low density polyethylene (LDPE) bags (19 µm) and returned into the soil for incubation (t1), which lasted 21 days (20 days in December) (e.g., Adams et al., 1989). The other soil cores were used as initial samples (t0). Mineral N contents were determined as described above after soil cores were divided into 0–10 and 10–20 cm sections. Net ammonification, net nitrification and net N mineralization were calculated according to the method described by Uri et al. (2003)

## 2.3 Laboratory incubation experiment

To examine the magnitude of potential total denitrification losses from the undrained and drained alder forest, a laboratory incubation experiment was performed; the experimental conditions were supposed to reproduce field conditions as closely as possible in respect to their temperature range and mean WFPS.

### 2.3.1 Soil core sampling and WFPS adjustment

In June 2011, eight intact soil cores with a diameter of 7.3 cm and a height of 6 cm were collected from a soil depth of 9–15 cm close to each collar of site D-2 for incubation in the laboratory (in total, 24 soil cores per site). Four samples per collar were immediately weighed and stored at 4 °C. The remaining four intact soil cores per collar were used to estimate the actual water-filled pore space (WFPS). This information was used to adjust the WFPS to 70 % and 100 % in the cores stored for laboratory incubation (six cores for 70 % and six cores for 100 % per site).

For the soil core sampling at site U, it had to be considered that the drying of the soil cores in order to adjust a WFPS of 70 % would lead to distinct shrinking of the waterlogged organic soil in the cores. To avoid this, three cubic blocks

(dimensions 40 × 25 cm, height 20 cm) were collected with plastic containers from which the bottom plate was removed beforehand. For transport, storage and drying to 70 % WFPS, the containers were placed on perforated metal plates. Six intact soil cores for site U were collected from these soil blocks after they reached the required WFPS level. Additionally, six soil cores per collar were directly collected in the field and treated in the same way as the samples from site D-2 (four samples for determining actual WFPS and two samples for incubation at 100 % WFPS level per collar). All soil cores were stored at 4 °C until they were placed in the incubation vessels.

After incubation the WFPS of the soil cores was determined to test the accuracy of the adjusted WFPS. The samples from site U and D-2 had exactly 100 % WFPS as well as 70 % WFPS at D-2 (on average  $70.4 \pm 2.2$  % WFPS). For site U, however, WFPS had been adjusted to  $83.0 \pm 0.5$  % instead of 70 %. We suspect that, due to the shrinking of the soil sample blocks, the bulk density must have changed; therefore the calculation of the required water content was not as accurate as needed to adjust a WFPS of 70 %.

### 2.3.2 Determination of gas fluxes

For measurements of N<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> fluxes, we applied the helium–oxygen (He–O) method (Butterbach-Bahl et al., 2002; Mander et al., 2003; Roobroeck et al., 2010; Uri et al., 2011) using four different incubation temperatures (0, 5, 15 and 25 °C). Five replications per site and moisture content were simultaneously placed in special gas-tight incubation vessels inside a climate chamber. The sixth one served as a reserve. Analyses were conducted in the laboratory of the Institute of Landscape Matter Dynamics, Leibniz Centre for Agricultural Landscape Research (ZALF), Müncheberg, Germany. Four substitution sequences with moderate evacuation (0.047 bar), followed by flushing the vessels with an artificial He/O<sub>2</sub> gas mixture (20.58 % O<sub>2</sub>, 347.8 ppm CO<sub>2</sub>, 1.780 ppm CH<sub>4</sub>, 0.290 ppm N<sub>2</sub>O, 3.04 ppm N<sub>2</sub>, rest He), were conducted to remove ambient N<sub>2</sub>. Subsequently, the air temperature of the climate chamber was set to 0 °C and a continuous He/O<sub>2</sub> gas flow rate of 15 mL per minute was adjusted to the vessel headspaces, followed by a 24 h period to establish a new flow equilibrium. From each vessel, we measured the N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> headspace concentration once and the N<sub>2</sub> concentration three times. After gas flux measurements were done, we immediately increased the incubation temperature to the next level for 20 h and continued the measurements. Soil core samples lost approximately  $5.0 \pm 0.9$  % and  $2.7 \pm 0.3$  % of their initial water content at 100 % and 70/83 % WFPS during the incubation procedure of five days. Concentration of N<sub>2</sub> were analyzed by a micro-GC (Agilent Technologies, 3000 Micro GC), equipped with a thermal conductivity detector (TCD). Gas chromatograph settings were as follows: TCD temperature 60 °C, sample inlet 60 °C, molsieve capillary column (14 m), oven tempera-

ture 60 °C, carrier gas He 6.0 (1 mL min<sup>-1</sup>). Concentrations of trace gases were analyzed by a GC (Shimadzu, Duisburg, Germany, GC-14B) equipped with a flame ionization detector (FID) for CH<sub>4</sub> and an ECD for N<sub>2</sub>O and CO<sub>2</sub>. GC settings were as follows: FID temperature 310 °C, ECD temperature 310 °C, column Porapack 80/100 mesh, oven temperature 60 °C, carrier gas N<sub>2</sub> 6.0 (13 mL min<sup>-1</sup>). Background N<sub>2</sub> concentrations varied between 3.5 and 4.5 ppm (ca. 3 ppm originated from the artificial He/O<sub>2</sub> gas mixture and 1 ppm from diffusion into the incubation measuring device). Flux rates were calculated from the actual gas concentration of the continuous flow rate from the vessels' headspaces after subtraction of a blank value from a vessel without a soil core, which is equivalent to concentrations from the artificial He/O<sub>2</sub> gas mixture. The lowest detectable flux rates were 200 µg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>, 0.2 µg CH<sub>4</sub>-C m<sup>-2</sup> h<sup>-1</sup>, 0.5 µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>, and 0.04 mg N<sub>2</sub>-N m<sup>-2</sup> h<sup>-1</sup>.

In order to obtain the temperature effect on gas flux rates,  $Q_{10}$  values were calculated from the following equation:

$$Q_{10} = \left( \frac{R_2}{R_1} \right)^{\left( \frac{10}{T_2 - T_1} \right)}, \quad (1)$$

where  $Q_{10}$  is the temperature quotient;  $R_1$  and  $R_2$  are gas flux (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, N<sub>2</sub>) rates (mg C or N m<sup>-2</sup> h<sup>-1</sup>; µg C or N m<sup>-2</sup> h<sup>-1</sup>); and  $T_1$  and  $T_2$  are temperature (°C).

### 2.3.3 Estimation of available N<sub>min</sub> and NO<sub>3</sub><sup>-</sup> consumption

According to Schaufler et al. (2010) laboratory incubation experiments are limited by the fact that sample storage and incubation procedure decrease the substrate (e.g., NO<sub>3</sub><sup>-</sup>) supply and thereby falsify the results. The amount of N<sub>min</sub> in the solution from soil cores was not ascertained in the present study. However, a rough estimation of available NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> was performed on the basis of t<sub>0</sub> samples from the net N mineralization experiment conducted, which started three days before soil core samples were taken (Table 3). In the present study, significant amounts of gaseous N losses are only expected in the case of complete denitrification with N<sub>2</sub> as the end product. Thus only samples incubated at 100 % WFPS were potentially affected by NO<sub>3</sub><sup>-</sup> limitation. According to our estimation, samples from site U at 100 % WFPS were presumably permanently NO<sub>3</sub><sup>-</sup> limited at each temperature level during the incubation procedure, which reflects the natural site conditions. However, for samples from site D-2 at 100 % WFPS no NO<sub>3</sub><sup>-</sup> limitation was expected. For soil core samples with 70/83 % WFPS, it has to be kept in mind that not only N consumption but also nitrification takes place. However, we can not totally rule out that reduced NO<sub>3</sub><sup>-</sup> availability lowered the gaseous N fluxes at a later stage of incubation for samples from site D-2 at 100 % and 70 % as well as for site U at 83 % WFPS.

**Table 3.** Estimation of available  $N_{\min}$  and  $NO_3^-$  consumption during sample storage and incubation time at 100 % WFPS.

	Time [h]	Site U	Site D-2
Mean bulk density from soil samples 9–16 cm soil depth [ $g\ cm^{-3}$ ]		0.13	0.56
Estimated $NO_3^-$ content [ $mg\ N\ kg^{-1}$ ] <sup>a</sup>		5.90	68.33
Estimated $NH_4^+$ content [ $mg\ N\ kg^{-1}$ ]		23.30	0.00
Soil mass 250 $cm^3$ soil core [kg]		0.03	0.14
Estimated amount of $NO_3^-$ per soil core [mg N]		0.19	9.57
Estimated amount of $NH_4^+$ per soil core [mg N]		0.76	0.00
Surface soil core [ $m^2$ ]		0.00407	0.00407
Estimated mean $N_2$ flux during storage at 4 °C [ $mg\ N\ m^{-2}\ h^{-1}$ ]		1.40	0.82
Mean $N_2$ flux at 0 °C [ $mg\ N\ m^{-2}\ h^{-1}$ ]		1.55	1.03
Mean $N_2$ flux at 5 °C [ $mg\ N\ m^{-2}\ h^{-1}$ ]		1.24	0.60
Mean $N_2$ flux at 15 °C [ $mg\ N\ m^{-2}\ h^{-1}$ ]		1.36	1.37
Mean $N_2$ flux 25 °C [ $mg\ N\ m^{-2}\ h^{-1}$ ]		1.27	6.02
Estimated mean $N_2$ exchange from soil cores at 4 °C [mg N]	264/432 <sup>b</sup>	2.4527	0.8757
Mean $N_2$ exchange from soil cores at 0 °C [mg N]	24	0.1514	0.1006
Mean $N_2$ exchange from soil cores at 5 °C [mg N]	20	0.1009	0.0488
Mean $N_2$ exchange from soil cores at 15 °C [mg N]	20	0.1107	0.1115
Mean $N_2$ exchange from soil cores at 25 °C [mg N]	20	0.1034	0.4900
Sum $N_2$ exchange during sample preparation and incubation [mg N]		2.92	1.63
Proportion from estimated available $NO_3^-$ [%]		> 100	17

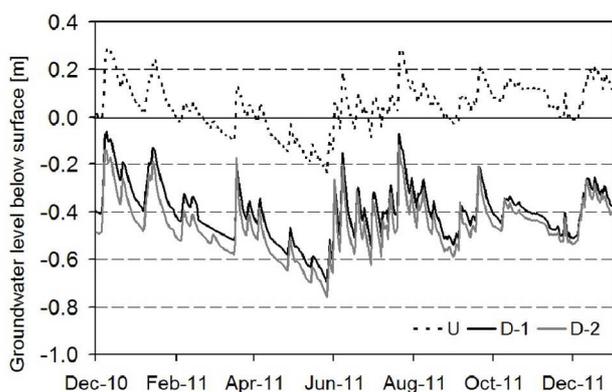
<sup>a</sup>Values give start concentrations from the net N mineralization experiment, which started on the 7 June 2011. Soil core samples for incubation were taken on the 10 June 2011. <sup>b</sup>Samples from site D-2 (100 % WFPS) were stored for 264 h before the incubation experiment started. Samples from site U (100 % WFPS) were stored 432 h before the incubation started.

## 2.4 Statistical analysis

Statistical analyses were conducted using R 2.12.1 (R Development Core Team, 2013). The assumption of normality of residuals was tested using the Lilliefors or Shapiro–Wilk test and by plotting the quantile–quantile plots. Homogeneity of variances of residuals was checked with the Levene or Breusch–Pagan test and by plotting the residuals against the fitted values. If necessary, data were transformed (Box–Cox) prior to analyses. We used analysis of variance (ANOVA) (for NNM rates) or the nonparametric Kruskal–Wallis rank sum test (for WFPS,  $NO_3^-$ ,  $NH_4^+$ ) to compare means of samples. In case of significant differences between the means, we used Tukey’s honest significant differences (TukeyHSD) or the nonparametric pairwise Wilcoxon rank sum test with Bonferroni correction for multiple comparisons. For testing two independent sample means (for WFPS,  $NO_3^-$ ,  $NH_4^+$ ), we used the nonparametric Mann–Whitney  $U$  test.

Due to temporal pseudoreplication of time series data ( $N_2O$  field measurements) and repeated measurements of vessels in the incubation experiment, we applied linear mixed effect models (Crawley 2007; Eickenscheidt et al., 2011; Hahn–Schöfl et al., 2011). For  $N_2O$  field measurements we set up a basic model with site type as a fixed effect and the spatial replication (individual plot) nested in time as a random effect. For the incubation experiment ( $N_2O$ ,  $N_2$ ,  $CO_2$ ,  $CH_4$ ), the fixed structure included the temperature, the site type and the soil water-filled pore space as well as all possible

interaction terms. Non significant terms were removed from the fixed structure. The individual vessel was set as a random effect. We extended the respective basic model by a variance function when heteroscedasticity was observed. In case of significant serial correlation in data, a first-order temporal autoregressive function was included in the model. Autocorrelation was tested with the Durbin–Watson test and by plotting the empirical (partial) autocorrelation structure (Eickenscheidt et al., 2011). The model extension was proven by the Akaike information criterion (AIC). For multiple comparisons, we conducted Tukey contrasts using the general linear hypothesis function from the “multcomp” package (Hothorn et al., 2013). We used nonlinear regressions to explain field  $N_2O$  fluxes and NNM rates. The model structure for mean  $N_2O$  fluxes included a linear term for the soil temperature in –2 cm soil depth and a cubic term for the mean groundwater (GW) level. Serial autocorrelation were not taken into account in the regression model. The nonlinear model for NNM rates was optimized by using the program Table Curve 3-D (version 4.0) (nonlinear equation is shown in Fig. 4). We accepted significant differences if  $P \leq 0.05$ . Results in the text are given as means  $\pm 1$  standard error.



**Figure 1.** Annual variation in the groundwater level (U=undrained; D-1=drained site 1; D-2=drained site 2). Please note that the *x* axis starts on 1 December 2010.

### 3 Results

#### 3.1 Site characteristics

In 2011, the forest air temperature in 20 cm height ranged from  $-12.3$  to  $27.8$  °C with an annual mean of  $9.1$  °C. Soil temperature in  $-2$  cm soil depth averaged  $9.6$  °C at the drained sites and was slightly lower with  $9.2$  °C at the undrained site. The topsoil at the undrained site U consisted of a mud sediment while the topsoil at the drained sites D-1 and D-2 consisted of highly degraded fen peat. Total organic carbon and the total nitrogen concentrations in the 0–10 cm and 10–20 cm soil layers were two to three times higher at site U than at sites D-1 and D-2 (Tables 1 and 2). Due to much higher bulk density, however, the total N stock in the upper 20 cm of the soil was more than 50 % higher at D-1 and D-2 than at U. The C/N ratios of all sites were narrow (between 11 and 16), indicating nitrogen-rich conditions. No relation between soil properties and N fluxes was determined so that the results and discussion focus on groundwater table and climate variables.

The three sites showed similar dynamics in their annual hydrographs but on different levels (Fig. 1). The mean annual groundwater level was +4 cm at U,  $-40$  cm at D-1, and  $-47$  cm at D-2. At site U, WFPS remained permanently close to 100 %. At the drained sites, WFPS was close to 70 % (D-1) and 63 % (D-2) in the 0–10 cm layer and around 80 % in the 10–20 cm layer with some temporal variation (Table 1).

#### 3.2 Nitrogen availability and net N mineralization

In 2011, extractable  $\text{NO}_3^-$  contents in both soil depths investigated differed significantly among the three sites (all  $P < 0.03$ ) (Table 1). At the undrained site, nitrate was not detectable most of the time, whereas the drained sites showed high  $\text{NO}_3^-$  contents (Fig. 2a), in particular for the soil depth

of 10–20 cm. However, differences between the two soil depths were not significant.

In contrast to  $\text{NO}_3^-$ , significantly higher  $\text{NH}_4^+$  contents were measured at the undrained site than at the drained sites (Table 1).  $\text{NH}_4^+$  contents did not significantly vary between soil depths.

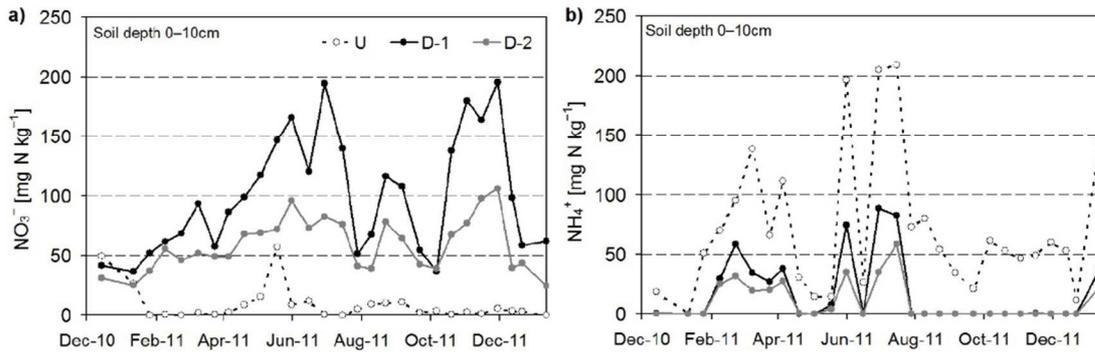
In line with the high contents of extractable inorganic N compounds, NNM rates were also high at the drained sites (Fig. 3a and b). For both soil depths, the drained sites had significantly (all  $P < 0.005$ ) higher NNM rates than the undrained site, whereas differences between the drained sites were not significant. The NNM rates decreased with soil depth, but differences were not statistically significant. The mean NNM rates of the four time periods investigated and the upper 20 cm of the soil were  $23 \pm 7$   $\text{mg N m}^{-2} \text{d}^{-1}$  (U),  $179 \pm 35$   $\text{mg N m}^{-2} \text{d}^{-1}$  (D-1) and  $142 \pm 32$   $\text{mg N m}^{-2} \text{d}^{-1}$  (D-2). Assuming that the time periods are representative of the annual dynamics, mean annual NNM rates are estimated to be  $84 \pm 26$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (U),  $653 \pm 128$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (D-1) and  $518 \pm 117$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (D-2). The NNM rates of the upper 10 cm displayed a clear seasonality with high rates during the summer months and low rates during the winter months. However, only in June a significantly (all  $P < 0.001$ ) higher NNM rate was observed compared to December and March. At the drained sites, net nitrification amounted to nearly 100 % of the NNM, whereas ammonification was the dominating process at the undrained site. Negative net nitrification rates ( $\text{NO}_3^-$  consumption) were detected at the undrained site in June and September in 0–10 cm soil depth. The NNM in the upper 10 cm of the soil depended on the WFPS and the mean temperature in  $-5$  cm soil depth (Fig. 4).

#### 3.3 Field $\text{N}_2\text{O}$ fluxes

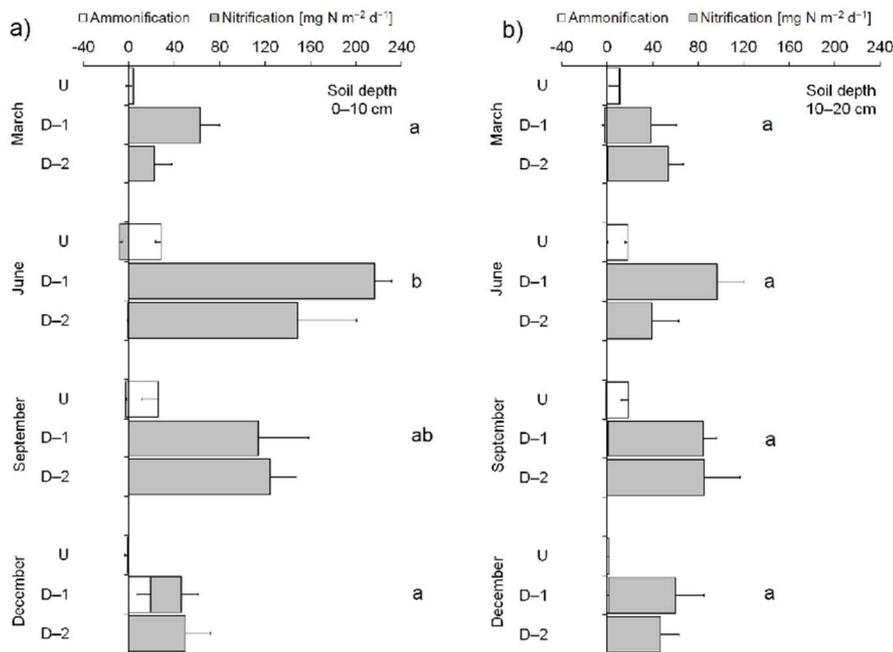
Annual  $\text{N}_2\text{O}$  emissions were unexpectedly low at all three sites (Fig. 5) with  $0.51 \pm 0.07$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (U),  $0.97 \pm 0.13$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (D-1) and  $0.93 \pm 0.08$   $\text{kg N ha}^{-1} \text{yr}^{-1}$  (D-2). The differences in  $\text{N}_2\text{O}$  fluxes between the sites were not statistically significant. At the drained sites the highest  $\text{N}_2\text{O}$  emissions were observed during the late summer and autumn, whereas at the undrained site highest emissions occurred during the dry period in May (Figs. 1 and 5). The temperature at  $-2$  cm soil depth and the mean groundwater level represented the best explanation for mean  $\text{N}_2\text{O}$  fluxes; nevertheless only 37 % of the spatiotemporal variation could be explained ( $P < 0.001$ ) (Fig. 6). Site-specific regression analyses explained 55 % of temporal  $\text{N}_2\text{O}$  variation at D-1 ( $P < 0.001$ ), 32 % at D-2 ( $P < 0.01$ ) and 20 % at U ( $P < 0.04$ ).

2968

T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses



**Figure 2.** Annual variation in the extractable  $\text{NO}_3^-$  (a) and  $\text{NH}_4^+$  (b) contents for the soil depth of 0–10 cm (U = undrained; D-1 = drained site 1; D-2 = drained site 2). Please note that the x axis starts on 1 December 2010.



**Figure 3.** Net ammonification, net nitrification and net N mineralization rates (sum of net ammonification and net nitrification rate) for the soil depth of 0–10 cm (a) and 10–20 cm (b). Means ( $\pm$ SE;  $n = 3$ ) followed by the same letter indicates no significant differences in the net N mineralization rate between the months within one soil depth (two-way ANOVA, TukeyHSD test at  $P \leq 0.05$ ). Differences between both soil depths are not significant.

### 3.4 Effect of temperature and soil moisture on greenhouse and dinitrogen gas exchange under laboratory conditions

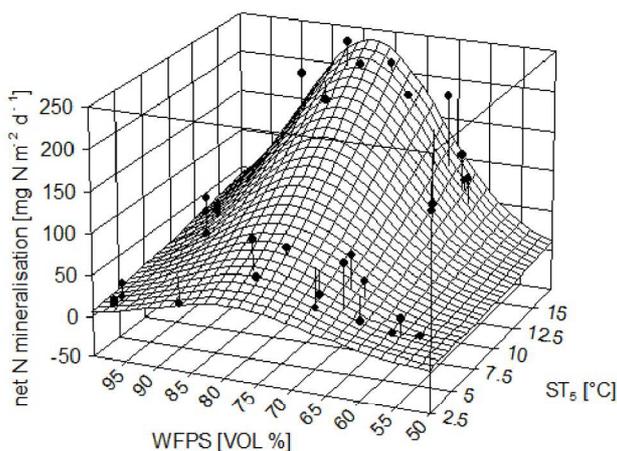
#### 3.4.1 $\text{CO}_2$ exchange

$\text{CO}_2$  exchange indicates heterotrophic soil respiration in the incubation. No significant effect of soil moisture and site type on  $\text{CO}_2$  exchange was detected (Fig. 7a), indicating comparable soil microbial activity in all incubated treatments. A statistically significant ( $P < 0.0001$ ) quadratic effect of tem-

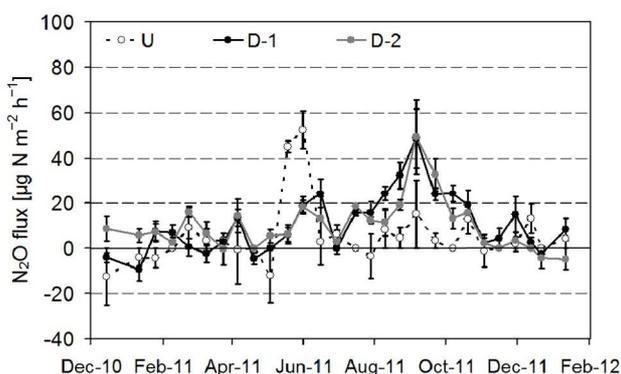
perature on  $\text{CO}_2$  emissions was observed in all treatments with  $Q_{10}$  values between 1.82 and 17.80  $\text{mg C m}^{-2} \text{h}^{-1} 10^\circ\text{C}^{-1}$ .

#### 3.4.2 $\text{CH}_4$ exchange

No significant  $\text{CH}_4$  emissions were observed in any treatment (Fig. 7b). Incubations at 100% WFPS showed consistent near zero  $\text{CH}_4$  fluxes or slight  $\text{CH}_4$  uptake without significant effects of site type and temperature. At 70/83% WFPS the uptake of  $\text{CH}_4$  was significantly ( $P < 0.0001$ ) higher at all temperature levels and for both sites compared



**Figure 4.** Relationship of net N mineralization in 0–10 cm soil depth (y) to mean water-filled pore space (x1) and mean soil temperature in 5 cm soil depth (x2) over 21 days of in situ incubation. Equation formula is  $y = 304.28 (\pm 85.27) \cdot \exp(-0.5 \cdot (((WFPS - 25.72 (\pm 4.46)) / 11.47 (\pm 1.14))^2)) + (((ST_5 - 78.60 (\pm 1.15)) / 11.47 (\pm 1.14))^2))$ . ( $n = 36$ ;  $adj-R^2 = 0.75$ ;  $P < 0.0001$ ).

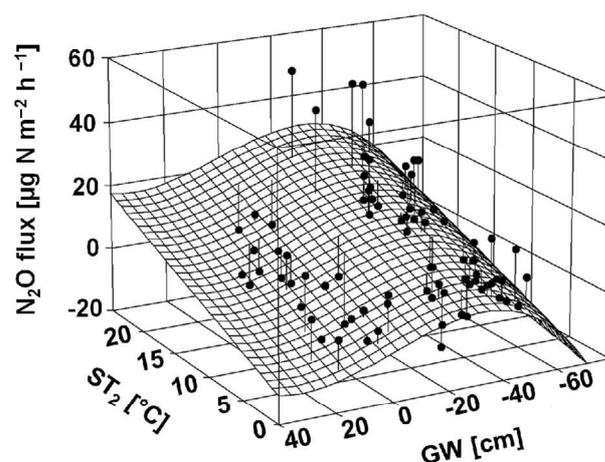


**Figure 5.** Mean ( $\pm$ SE,  $n = 3$ )  $N_2O$  fluxes of the undrained (U), drained 1 (D-1) and drained 2 (D-2) sites. Please note that the x axis starts on 1 December 2010.

to 100 % WFPS.  $CH_4$  uptake increased significantly with temperature only in incubated samples of the drained site ( $P < 0.001$ ).

### 3.4.3 $N_2O$ exchange

$N_2O$  exchange differed in response to site type, WFPS and temperature. Significantly ( $P < 0.0001$ ) higher  $N_2O$  fluxes at both WFPS levels were measured from samples of the drained site (D-2) compared to samples from the undrained site (U) (Fig. 7c). At the drained site,  $Q_{10}$  of  $N_2O$  emissions was  $2.17 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 70 % WFPS for the temperature range of 0 to 25 °C and  $2.12 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 100 % WFPS for 0 to 15 °C.



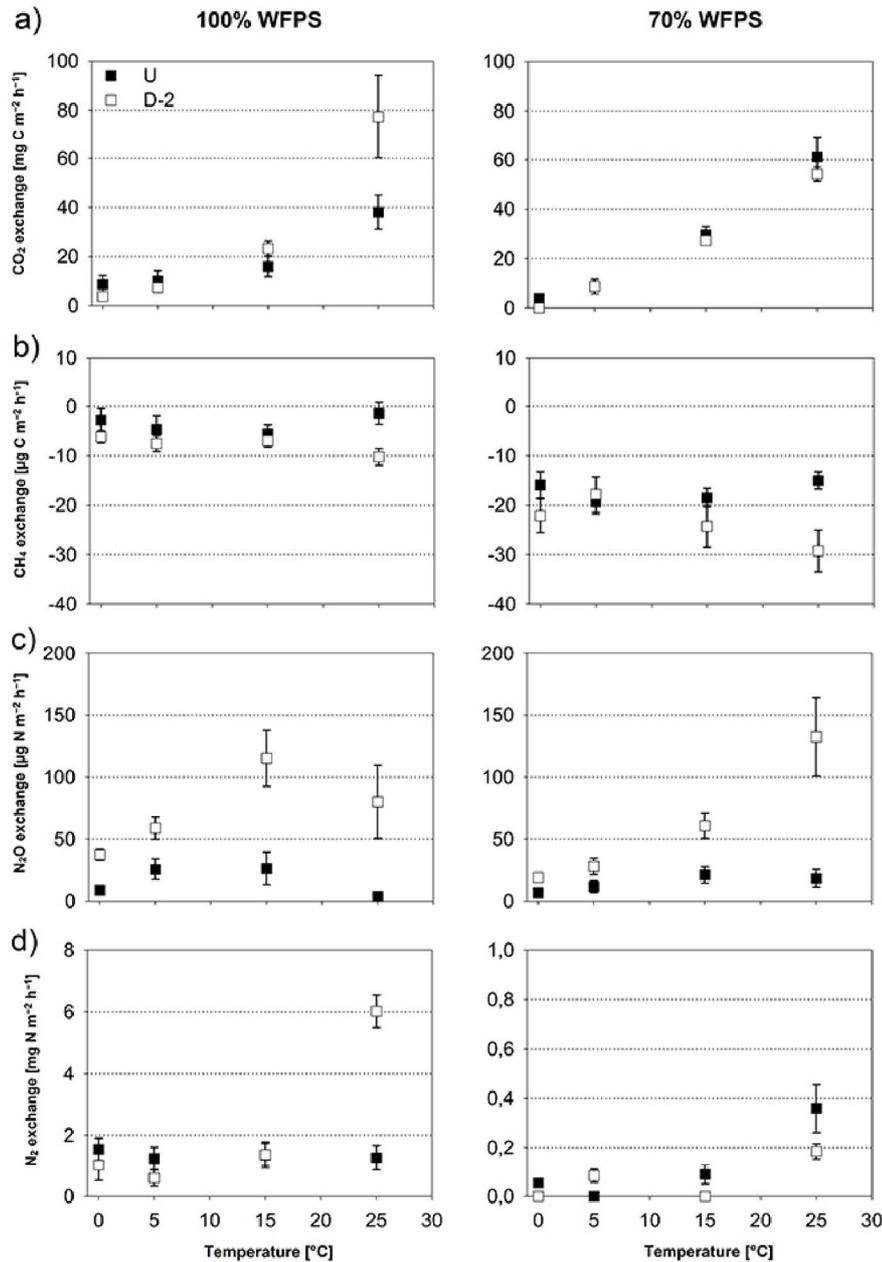
**Figure 6.** Relationship of mean  $N_2O$  flux (y) to mean soil temperature in 2 cm soil depth (x1) and to mean groundwater level (x2). Equation formula is  $y = -4.884 (\pm 2.409) + 1.128 (\pm 0.179) \cdot ST_2 + (-0.322) (\pm 0.086) \cdot GW + 0.0004 (\pm 0.000) \cdot GW^3$  ( $n = 80$ ;  $adj-R^2 = 0.37$ ;  $P < 0.001$ ).

For both WFPS levels, samples of the undrained site (U) only showed a weak, but significant (all  $P < 0.03$ ) temperature response for the temperature range of 0 to 15 °C. The  $Q_{10}$  values of  $N_2O$  emissions for the undrained site are  $2.07 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 100 % WFPS for 0 to 15 °C and  $1.51 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 83 % WFPS for 0 to 25 °C.

For both sites a decline in nitrous oxide emissions at 25 °C and 100 % WFPS was observed. However, this pattern was also detected at 83 % WFPS for the undrained site.  $N_2O$  emissions observed at the undrained site U were on the same order of magnitude as the field measurements, whereas the drained site D-2 samples showed up to four times higher  $N_2O$  fluxes during the laboratory incubation than in the field at 70 % WFPS.

### 3.4.4 $N_2$ exchange

$N_2$  emissions were near zero at 70/83 % WFPS at low temperatures and never exceeded  $0.4 mg N m^{-2} h^{-1}$  at high temperatures (Fig. 7d).  $N_2$  emissions at 100 % WFPS were consistently at least 10 times higher than at 70/83 % WFPS ( $P < 0.0001$ ).  $N_2$  exchange also reacted to site type at 25 °C and to temperature. At the drained site,  $Q_{10}$  of  $N_2$  emissions was  $2.03 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 70 % WFPS for the temperature range of 0 to 25 °C and  $1.48 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 100 % WFPS for the temperature range of 5 to 25 °C. At the undrained site,  $Q_{10}$  of  $N_2$  emissions was  $2.13 \mu g N m^{-2} h^{-1} 10^\circ C^{-1}$  at 83 % WFPS for the temperature range of 0 to 25 °C.  $N_2$  emissions of the undrained site did not respond to temperature at 100 % WFPS.  $N_2$  emissions increased most strongly from 15 to 25 °C in samples of



**Figure 7.** Mean ( $\pm$ SE,  $n = 5$ ) of  $\text{CO}_2$  (a),  $\text{CH}_4$  (b),  $\text{N}_2\text{O}$  (c) and  $\text{N}_2$  (d) exchange rates per water-filled pore space (vol. %; 70 % for D-2 and 83 % for U), temperature ( $^\circ\text{C}$ ) and site treatment. U = undrained; D-2 = drained 2. Please note the different scales for the  $\text{N}_2$  exchange rates.

the drained site at 70 % and in particular 100 % WFPS and in samples of the undrained site at 83 % WFPS.

The high  $\text{N}_2$  emissions observed at 100 % WFPS resulted in low  $\text{N}_2\text{O}/\text{N}_2$  ratios, with mean values of  $0.03 \pm 0.01$  (U) and  $0.10 \pm 0.02$  (D-2). A similarly low  $\text{N}_2\text{O}/\text{N}_2$  ratio (mean value of  $0.12 \pm 0.03$ ) were found at 83 % WFPS for the samples from the U site, as a result of the low  $\text{N}_2\text{O}$  emissions. In contrast, the samples from the drained site D-2 showed a considerably higher  $\text{N}_2\text{O}/\text{N}_2$  ratio, with a mean value of

$0.62 \pm 0.11$  (note that in the case of zero  $\text{N}_2$  fluxes no ratio was calculated). No relationship between temperature and  $\text{N}_2\text{O}/\text{N}_2$  ratio was observed for either soil moisture contents.

## 4 Discussion

### 4.1 Nitrogen mineralization and transformation processes

For both drained sites, the NNM rates observed (518–653 kg N ha<sup>-1</sup> yr<sup>-1</sup>) are at the high end of NNM rates given in the literature. Janiesch (1978) and Janiesch et al. (1991) reported NNM rates of up to 500 kg ha<sup>-1</sup> yr<sup>-1</sup> (0–15 cm soil depth) and of up to 321.2 kg ha<sup>-1</sup> yr<sup>-1</sup> (0–10 cm soil depth) for different *Alnus glutinosa* forests from degraded fen peatlands in northern Germany. The significantly lower NNM rates from the undrained site are in the range of NNM rates reported for other seminatural black alder forests (Janiesch, 1978; Janiesch et al., 1991).

The compiled values from the literature and the results of the present study indicate an increasing NNM rate in black alder forests with increasing degradation of the fen peatland. In forest soils, high NNM rates are generally related to narrow C/N ratios (Gundersen et al., 1998; Ollinger et al., 2002), which are also characteristic for alder swamps (Mäkinen, 1979) and which were observed in the present study. Typically NNM rates for deciduous stands range between 50 to 150 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Aber et al., 1989). The considerably higher NNM rates measured in the present study compared to those of other deciduous forests can partly be attributed to the high amount of easily decomposable organic nitrogen which becomes incorporated into the forest ecosystem through symbiotic atmospheric N<sub>2</sub> fixation by *Frankia* actinomycetes (Kätzel, 2003). Dittert (1992) estimated N<sub>2</sub> fixation rates of between 40 to 85 kg N ha<sup>-1</sup> yr<sup>-1</sup> for a black alder stand in northern Germany. Comparable and even higher values have also been reported for grey alder stands (e.g., Rytter et al., 1991; Löhmus et al., 2002; Mander et al., 2005; Uri et al., 2011). Additionally, drainage of histosols supplies large amounts of N through mineralization of ancient organic matter (Klemedtsson et al., 2005). However, the distinct differences in the C and N contents of the drained sites did not result in significantly different NNM rates in the present study. Low retranslocation of nitrogen from senescing leaves to the alder tree (Mander et al., 1997; Löhmus et al., 2002; Uri et al., 2011) causes high contents of N and narrow C/N ratios of the foliage, favoring the fast decomposition of the leaf litter (Struwe and Kjølner, 1990; Rytter et al., 1991; Löhmus et al., 2002; Uri et al., 2011). The organic surface layer at the drained sites was classified as L-mull humus type, indicating the fast decomposition of the incorporated alder leaves.

Beside substrate chemistry, moisture content together with temperature are considered as the most important abiotic factors influencing biogeochemical transformation processes (Tietema et al., 1992). In general, increasing moisture contents stimulate the biogeochemical processes up to a threshold value where anaerobicity can limit microbial activity (Tietema et al., 1992). Temperature has a similar effect

on microbial activity, due to the fact that rates of enzymatic processes generally increase with increasing temperature (Michaelis and Menten, 1913). This finding becomes apparent in the Gaussian relationship observed between NNM rates in 0–10 cm soil depth, mean WFPS and mean temperature in –5 cm soil depth during the incubation period (Fig. 4). Significant effects of soil moisture and temperature on NNM or nitrification rates were also reported by other studies (e.g., Kowalenko and Cameron, 1976; Goodroad and Keeney, 1984; Gonçalves and Carlyle, 1994). The minor reduction in N turnover observed with increasing soil depth furthermore reflects the influence of aeration and temperature on mineralization processes. We attributed the significantly lower NNM rates at the undrained site to the limitation of microorganisms by anaerobicity due to the permanently high water levels. The oxygen deficit at the undrained site also explained why NNM was solely determined by net ammonification. Events of NO<sub>3</sub><sup>-</sup> presence and NO<sub>3</sub><sup>-</sup> consumption in the upper soil layer suggest that in periods of low water level net nitrification also occurs at the undrained site. In contrast, at the well-aerated drained sites, the NH<sub>4</sub><sup>+</sup> produced becomes immediately oxidized to NO<sub>3</sub><sup>-</sup>, hence net nitrification entirely controls the NNM. However, using NNM rates as indicators of soil N dynamics bears the risk of considerably underestimating the intensity and complexity of the real N fluxes (Augustin, 2003); thus, further investigation should rather use the <sup>15</sup>N isotope dilution method (e.g., Davidson et al., 1991) for measuring gross rates of all relevant N turnover processes.

The permanently high mineral N contents detected in the probed soil depth probably indicate that the alder forest investigated has reached N saturation, due to the fact that the availability of N exceeds the biotic uptake capacity of the system (Aber et al., 1989). High contents of available NO<sub>3</sub><sup>-</sup> in the soil carry the risk of leaching or gaseous losses (Robertson, 1982). Several studies reported NO<sub>3</sub><sup>-</sup> losses by leaching from soils under alder stands (e.g., Binkley et al., 1992; Van Miegroet et al., 1992; Compton et al., 2003; Uri et al., 2011). The slightly higher NO<sub>3</sub><sup>-</sup> contents but lower NNM rates observed in the soil depth of 10–20 cm compared to the soil depth of 0–10 cm at the drained sites probably indicate leaching of NO<sub>3</sub><sup>-</sup> into deeper soil layers. Analysis of groundwater samples from the sites investigated showed nitrate contents of up to 36.2 mg L<sup>-1</sup> and dissolved organic nitrogen (DON) contents of up to 2.8 mg L<sup>-1</sup> (B. Tiemeyer, personal communication, 2013), confirming the earlier assumption of N leaching. Nitrate leaching into the anaerobic peat profile can result in enhanced denitrification (Regina et al., 1996), wherein the ratio of N<sub>2</sub>O/N<sub>2</sub> depends on the residence time of N<sub>2</sub>O on its way from the production site in the anaerobic subsoil to the atmosphere (van Groenigen et al., 2005).

2972

T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

#### 4.2 Factors controlling temporal and site-specific variation in N<sub>2</sub>O and N<sub>2</sub> fluxes

In the present study, field N<sub>2</sub>O fluxes observed at the drained sites are very low. Different studies reported considerably higher values for N<sub>2</sub>O emissions from drained black alder stands, varying from 5 to 75 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Mogge et al., 1998; Augustin, 1998; Brumme et al., 1999; Merbach et al., 2001; Hefting et al., 2003; von Arnold et al., 2005). According to Klemmedtsson et al. (2005), NO<sub>3</sub><sup>-</sup> availability is the main driver of N<sub>2</sub>O emissions from drained histosols. However, despite distinct differences in the NO<sub>3</sub><sup>-</sup> contents and NNM rates, significantly different N<sub>2</sub>O emissions between the three sites were not found in the present study. This was in contrast to our hypothesis that accelerated N turnover and N mineralization leads to significantly increased amounts of N<sub>2</sub>O emissions. We cannot rule out, however, that we may have missed high N<sub>2</sub>O events on the drained sites due to our regular measurement intervals. In addition many wetland adapted trees such as alder can mediate N<sub>2</sub>O fluxes from the soil to the atmosphere through the stem (Rusch and Rennenberg, 1998; Pangala et al., 2012; Machacova et al., 2013). This flux was not taken into account in the present study so that this study may underestimate the N<sub>2</sub>O emissions from the alder ecosystem.

In the alder forest investigated, temperature in -2 cm soil depth and the GW level best explained field N<sub>2</sub>O flux rates, whereas no relationship was found between field N<sub>2</sub>O fluxes and the amount of NO<sub>3</sub><sup>-</sup> in the soil. It is well known that temperature is a key variable affecting the emission rates of N<sub>2</sub>O because both nitrification and denitrification are microbial processes (Firestone and Davidson, 1989; Maag and Vinther, 1996; Smith et al., 1998; Dobbie and Smith, 2001). Higher soil moisture content increases N<sub>2</sub>O emissions through higher denitrification rates (Wolf and Russow, 2000). In our study, however, temperature and GW only explained 37 % of the spatiotemporal variation of mean N<sub>2</sub>O flux rates. This demonstrates the complex interlinkage of the controlling factors for N<sub>2</sub>O emissions, as reported for agricultural soils by Jungkunst et al. (2006). According to Couwenberg et al. (2011), mean annual GW levels below -15 cm show a wide range of N<sub>2</sub>O emissions in fens; in contrast, Jungkunst et al. (2004) found highest annual N<sub>2</sub>O emissions in a Norway spruce stand (black forest, southwest Germany) at a GW level of -20 cm, whereas higher or lower GW levels decreased the emissions. However in the present study, differences observed in the GW levels were only small between the drained sites, resulting in comparable annual N<sub>2</sub>O emissions. The observed cubic response to the GW level in our N<sub>2</sub>O model reveals maximum N<sub>2</sub>O emissions at a certain GW level. Perhaps it could be assumed that a mean GW level between the levels measured at the observed sites D-1 and U would result in enhanced N<sub>2</sub>O emissions at the present black alder forest. Indeed, Brumme et al. (1999) reported that small

seasonal fluctuations of the GW level seem to be more important than the mean GW level.

The overall results from the laboratory experiment lead to the conclusion that the incorrect setting of the WFPS to 83 % only marginally affected the responsiveness of samples from site U compared to 100 % WFPS treatments as well as to the samples from site D-2. Nevertheless, we cannot totally exclude the possibility that the incorrect adjustment lowered the gaseous N losses from these samples. However, in the laboratory experiment, significantly different N<sub>2</sub>O emissions were not observed between the two adjusted soil moisture contents, but total denitrification was considerably higher at 100 % WFPS compared to 70/83 % WFPS for both sites. This was in line with investigations by Scholefield et al. (1997), who found a greater than 50-fold increase in denitrification activity with increasing WFPS from 70 % to 90 %. Beside soil moisture, the dependency of denitrification activity on temperature, as found for field N<sub>2</sub>O fluxes, becomes even more apparent regarding the results from the incubation experiment, particularly for samples from site D-2. Additionally, our results reveal that the production of N<sub>2</sub> increased more with increasing temperature than the production of N<sub>2</sub>O, which was in line with Maag and Vinther (1996). Higher denitrification activity with increasing temperature was also reported by several other studies (e.g., Dobbie and Smith, 2001; Schindlbacher et al., 2004; Schaufler et al., 2010). Butterbach-Bahl et al. (2013) reported that the  $Q_{10}$  of denitrification exceeds the  $Q_{10}$  of soil respiration and attributed this to a tight coupling between the microbial C and N cycles. Additionally, denitrification is indirectly affected by the temperature-induced respiratory depletion of soil oxygen concentration (Butterbach-Bahl et al., 2013).

The proportion of N<sub>2</sub>O emissions at 100 % WFPS amounted to ~1 to 6 % and to ~0.7 to 2 % of total N release from denitrification for samples from site D-2 and U, indicating that in the present alder stand losses of N<sub>2</sub>O are only of minor importance compared to N<sub>2</sub> losses at water-saturated conditions. This agrees with findings that, with increasing anoxic conditions, the percentage of N<sub>2</sub> increases until it becomes the major gas evolved (Rolston et al., 1978; Davidson, 1991). Indeed several studies reported that high contents of available NO<sub>3</sub><sup>-</sup> result in the inhibition of N<sub>2</sub>O reductase activity (Blackmer and Bremner, 1978; Firestone et al., 1979; Weier et al., 1993; Regina et al., 1996). However, for the present study it is not possible to state conclusively to what extent the probably higher NO<sub>3</sub><sup>-</sup> availability inhibits the conversion of N<sub>2</sub>O to N<sub>2</sub> at samples from site D-2. N<sub>2</sub>O fluxes only declined in D-2 samples at water-saturated conditions and 25 °C with simultaneously exponentially increasing N<sub>2</sub> fluxes. While this mechanism supports our hypothesis that N<sub>2</sub>O release is displaced by N<sub>2</sub> losses during periods of temporarily high water levels, the field observations never reached the point in which the decreasing N<sub>2</sub>O : N<sub>2</sub> ratio overcompensated the increasing denitrification rate.

## T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

2973

In contrast to the field observations, significant differences in the  $\text{N}_2\text{O}$  fluxes between the two sites investigated were found at both soil moisture contents in the incubation experiment conducted, mainly due to the distinct differences in the  $\text{N}_2\text{O}$  reaction to temperature. Our data have shown that denitrification was limited by temperature at the drained site, but limited by other factors at the undrained site, like the availability of labile organic carbon, available  $\text{NO}_3^-$  or soil moisture (Letey et al., 1980; Knowles, 1982; Weier et al., 1993; Klemmedtsson et al., 2005). We can rule out that redox conditions are too anaerobic or microbial activity is less favorable for denitrification in samples from the undrained site in the incubation experiment because no  $\text{CH}_4$  emissions were detected from water-saturated soil cores and aerobic and anaerobic  $\text{CO}_2$  production was comparable and showed a distinct temperature response at both sites. However, at 100 % WFPS and 25 °C, the  $\text{CO}_2$  to N gas emission ratio was 30 for site U and 13 for site D-2, indicating that anaerobic  $\text{CO}_2$  production at site U was significantly more decoupled from denitrification activity than at the drained sites (Wang et al., 2011). Thus we attribute the small temperature response of  $\text{N}_2\text{O}$  and denitrification of the undrained site to  $\text{NO}_3^-$  limitation. The amount of  $\text{NO}_3^-$  in the solution from soil cores was not ascertained, but in the field net nitrification could never be detected at the undrained site. However,  $\text{N}_2\text{O}$  fluxes measured temporarily confirm our assumption that in periods of low water level net nitrification also occurs at the undrained site, albeit at a low level. Thus, we conclude that for most of the year denitrification activity is  $\text{NO}_3^-$  limited at the undrained site, confirming our hypothesis that  $\text{NO}_3^-$  limitation in permanently waterlogged peat soils results in negligible  $\text{N}_2\text{O}$  and  $\text{N}_2$  losses.

For  $\text{N}_2$  fluxes no comparable values from the field are available in the literature, but  $\text{N}_2$  fluxes observed in the incubation experiment are in the range of other studies from drained and undrained fen ecosystems (e.g., Teiter and Mander, 2005; Wray and Bayley, 2007; Mander et al., 2008; Roobroeck et al., 2010; Soosaar et al., 2011).

In the present study less than 0.2 % of the nitrified N was emitted as  $\text{N}_2\text{O}$ -N at the drained sites. Similar or slightly higher values were reported by Klemmedtsson et al. (1988) and Maag and Vinther (1996). In the incubation experiment  $\text{N}_2\text{O}$  fluxes that were up to four times higher were measured in samples for site D-2 compared to the field fluxes. This indicates the potential of high  $\text{N}_2\text{O}$  emissions from the drained alder sites under different soil physical conditions.

The low  $\text{N}_2\text{O}$  and  $\text{N}_2$  losses, despite very high N mineralization rates, perhaps indicate that, for most of the year, aerobic or only slightly anaerobic soil conditions are predominant at the drained sites. Thus, a certain proportion of the gaseous N may have been lost as nitric oxide (NO), a by-product of nitrification and an intermediate product of denitrification (Davidson, 1991). Several studies reported that net nitrification rates and  $\text{NO}_3^-$  in the soil solution are positively

correlated to NO fluxes in well-aerated soils (Skiba et al., 1998, 1999; Gasche and Papen, 1999; Venterea et al., 2003; Eickenscheidt and Brumme, 2012).

## 5 Conclusions

We studied N turnover processes in organic soils along a water table gradient in a nitrogen-saturated alder forest characterized by high mineral N concentrations. Drainage considerably increased net N mineralization and N turnover processes and shifted the dominant process from net ammonification to net nitrification, resulting in nitrate leaching. Surprisingly,  $\text{N}_2\text{O}$  emissions in the field remained low at the drained sites, but we cannot rule out that we have missed  $\text{N}_2\text{O}$  emission peaks. The incubation experiment supported the potential for high  $\text{N}_2\text{O}$  emissions at the drained alder sites. Temporarily water-saturated conditions enhanced  $\text{N}_2$  emissions, whereas  $\text{N}_2\text{O}$  emissions remained unchanged. In contrast, the permanently high groundwater level at the undrained site prevented net nitrification and resulted in negligible gaseous N losses.

*Acknowledgements.* We thank N. Eickenscheidt (Thünen Institute) for helpful discussion and a critical review as well as B. Gusovius for technical support in the lab at the ZALF. Further, the authors thank S. Raspe from the Bavarian State Institute of Forestry for providing the N deposition data and B. Tiemeyer from the T. Institute for providing nitrate and dissolved organic nitrogen concentration data of the groundwater. Furthermore we thank S. Röhling from the Chair of Forest Yield Science at the Technical University Munich for providing forest growth data. This study was part of the joint research project “Organic soils: Acquisition and development of methods, activity data and emission factors for the climate reporting under LULUCF/AFOLU”, funded by the Thünen Institute.

Edited by: T. Laurila

## References

- Aber, J. D., Nadelhoffer, K. J., Steudler, P., and Melillo, J. M.: Nitrogen saturation in northern forest ecosystems – Excess nitrogen from fossil fuel combustion may stress the biosphere, *BioScience*, 39, 378–386, 1989.
- Adams, M. A., Polglase, P. J., Attiwill, P. M., and Weston, C. J.: In situ studies of nitrogen mineralization and uptake in forest soils; some comments on methodology, *Soil Biol. Biochem.*, 21, 423–429, 1989.
- Augustin, J.: Erlenstandorte als Quelle und Senke klimarelevanter Spurengase. (Alder forests as a source and sink of Greenhouse gases), in: Die Schwarz-Erle (*Alnus glutinosa* [L.] GAERTN.) im nordostdeutschen Tiefland, Eberswalder Forstliche Schriftenreihe, 17, 46–59, 2003.
- Augustin, J., Merbach, W., and Rogasik, J.: Factors influencing nitrous oxide and methane emissions from minerotrophic fens in northeast Germany, *Biol. Fert. Soils*, 28, 1–4, 1998.

2974

T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

- Binkley, D., Sollins, P., Bell, R., Sachs, D., and Myrold, D.: Biogeochemistry of adjacent conifer and alder-conifer stands, *Ecology*, 73, 2022–2033, 1992.
- Blackmer, A. M. and Bremner, J. M.: Inhibitory effect of nitrate on reduction of  $N_2O$  to  $N_2$  by soil microorganisms, *Soil Biol. Biochem.*, 10, 187–191, 1978.
- Bremner, J. M. and Blackmer, A. M.: Terrestrial nitrification as a source of atmospheric nitrous oxide, in: *Denitrification, Nitrification and Nitrous Oxide*, edited by: Delwiche, P. P., 151–170, Wiley, New York, 1981.
- Brumme, R., Borken, W., and Finke, S.: Hierarchical control on nitrous oxide emission in forest ecosystems, *Global Biogeochem. Cy.*, 13, 1137–1148, 1999.
- Butterbach-Bahl, K., Willibald, G., and Papen, H.: Soil core method for direct simultaneous determination of  $N_2$  and  $N_2O$  emissions from forest soils, *Plant Soil*, 240, 105–116, 2002.
- Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., and Zechmeister-Boltenstern, S.: Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, *P. T. R. Soc. B*, 368, 20130122, doi:10.1098/rstb.2013.0122, 2013.
- Compton, J. E., Church, M. R., Larned, S. T., and Hogsett, W. E.: Nitrogen export from forested watershed in the Oregon Coast Range: The role of  $N_2$ -fixing red alder, *Ecosystems*, 6, 773–785, 2003.
- Couwenberg, J., Thiele, A., Tannenberger, F., Augustin, J., Bärtsch, S., Dubovik, D., Liashchynskaya, N., Michaelis, D., Minke, M., Skuratovich, A., and Joosten, H.: Assessing greenhouse gas emissions from peatlands using vegetation as a proxy, *Hydrobiologia*, 674, 67–89, 2011.
- Crawley, M. J.: *The R Book*, John Wiley and Sons Ltd, Chichester, 942 pp., 2007.
- Crutzen, P. J.: the role of  $NO$  and  $NO_2$  in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Pl. Sc.*, 7, 443–472, 1979.
- Davidson, E. A.: Fluxes of nitrous and nitric oxide from terrestrial ecosystems. in: *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*, edited by: Rogers, J. E. and Whitman, W. P., American Society for Microbiology, Washington, D.C., 219–235, 1991.
- Davidson, E. A., Swank, W. T., and Perry, T. O.: Distinguishing between nitrification and denitrification as sources of gaseous nitrogen production in soil, *Appl. Environ. Microb.*, 52, 1280–1286, 1986.
- Del Grosso, S. J., Parton, W. J., Mosier, A. R., Ojima, D. S., Kulkarni, A. E., and Phongpan, S.: General model for  $N_2O$  and  $N_2$  gas emissions from soils due to denitrification, *Global Biogeochem. Cy.*, 14, 1045–1060, 2000.
- Dilly, O., Blume, H. P., Kappen, L., Kutsch, W. L., Middelhoff, U., Wötzel, J., Buscot, F., Dittert, K., Bach, H. J., Mogge, B., Pritsch, K., and Munch, J. C.: Microbial processes and features of the microbiota in histosols from a black alder forest, *Geomicrobiol. J.*, 16, 65–78, 1999.
- Dittert, K.: Die stickstofffixierende Schwarzerle-Frankia-Symbiose in einem Erlenbruch der Bornhöveder Seenkette, *EcoSys. Suppl.*, 5, 1–98, 1992.
- Dobbie, K. E. and Smith, K. A.: The effects of temperature, water-filled pore space and land use on  $N_2O$  emissions from an imperfectly drained gleysol, *Eur. J. Soil Sci.*, 52, 667–673, 2001.
- Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems, Southern Germany, PhD thesis, Chair of Vegetation Ecology, Department of Ecology, Technical University Munich, 179 pp., 2005.
- Eickenscheidt, N. and Brumme, R.:  $NO_x$  and  $N_2O$  fluxes in a nitrogen-enriched European spruce forest soil under experimental long-term reduction of nitrogen depositions, *Atmos. Environ.*, 60, 51–58, 2012.
- Eickenscheidt, N., Brumme, R., and Veldkamp, E.: Direct contribution of nitrogen deposition to nitrous oxide emissions in a temperate beech and spruce forest – a  $^{15}N$  tracer study, *Biogeosciences*, 8, 621–635, doi:10.5194/bg-8-621-2011, 2011.
- Firestone, M. K. and Davidson, E. A.: Microbial basis of  $NO$  and  $N_2O$  production and consumption in soil, in: *Exchange of trace gases between terrestrial ecosystems and the atmosphere*, edited by: Andreae, M. O. and Schimel, D. S., John Wiley and Sons Ltd., Chichester, U.K., 7–21, 1989.
- Firestone, M. K., Smith, M. S., Firestone, R. B., and Tiedje, J. M.: The influence of nitrate, nitrite, and oxygen on the composition of the gaseous products of denitrification in soil, *Soil Sci. Soc. Am. J.*, 43, 1140–1144, 1979.
- Gasche, R. and Papen, H.: A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany – 2.  $NO$  and  $NO_2$  fluxes, *J. Geophys. Res.-Atmos.*, 104, 18505–18520, 1999.
- Gonçalves, J. L. M. and Carlyle, J. C.: Modelling the influence of moisture and temperature on net nitrogen mineralization in a forested sandy soil, *Soil Biol. Biochem.*, 26, 1557–1564, 1994.
- Goodroad, L. L. and Keeney, D. R.: Nitrous oxide production in aerobic soils under varying pH, temperature and water content, *Soil Biol. Biochem.*, 16, 39–43, 1984.
- Gundersen, P., Emmett, B. A., Kjønås, O. J., Koopmans, C. J., and Tietema, A.: Impact of nitrogen deposition on nitrogen cycling: a synthesis of NITREX-data, *Forest Ecol. Manag.*, 101, 37–55, 1998.
- Hahn-Schöfl, M., Zak, D., Minke, M., Gelbrecht, J., Augustin, J., and Freibauer, A.: Organic sediment formed during inundation of a degraded fen grassland emits large fluxes of  $CH_4$  and  $CO_2$ , *Biogeosciences*, 8, 1539–1550, doi:10.5194/bg-8-1539-2011, 2011.
- Hefting, M. M., Bobbink, R., and Caluwe, H.: Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones, *J. Environ. Qual.*, 32, 1194–1203, 2003.
- Hothorn, T., Bretz, F., Westfall, P., Heiberger, R. M., and Schuetzenmeister, A.: Simultaneous Inference in General Parametric Models: R package version 1.2-17, <http://cran.rproject.org/web/packages/multcomp/index.html>, 2013.
- IPCC: Chapter 11:  $N_2O$  Emissions from managed soils, and  $CO_2$  emissions from lime and urea application, in: *IPCC guidelines for national greenhouse gas inventories*, edited by: Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T., and Tanabe, K., IGES, Hayama, Japan, 2006.
- IPCC: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by:

## T. Eickenscheidt et al.: Nitrogen mineralization and gaseous nitrogen losses

2975

- Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- Janiesch, P., Mellin, C., and Müller, E.: Die Stickstoff-Netto-Mineralisierung in naturnahen und degradierten Erlenbruchwäldern als Kenngröße zur Beurteilung des ökologischen Zustandes, Poster zu Verhandlungen der Gesellschaft für Ökologie (Freising-Weihenstephan 1990), Band 20, 353–359, 1991.
- Jungkunst, H. F., Fiedler, S., and Stahr, K.: N<sub>2</sub>O emissions of a mature Norway spruce (*Picea abies*) stand in the Black Forest (southwest Germany) as differentiated by soil pattern, *J. Geophys. Res.*, 108, D07302, doi:10.1029/2003JD004344, 2004.
- Jungkunst, H. F., Freibauer, A., Neufeldt, H., and Bareth, G.: Nitrous oxide emissions from agricultural land use in Germany – a synthesis of available annual field data, *J. Plant Nutr. Soil Sc.*, 169, 341–351, 2006.
- Kätzel, R.: Zum physiologischen Anpassungspotenzial der Schwarz-Erle, In: Die Schwarz-Erle (*Alnus glutinosa* [L.] GAERTN.) im nordostdeutschen Tiefland, Eberswalder Forstliche Schriftenreihe, 17, 39–45, 2003.
- Klemetsson, L., Svensson, B. H., and Rosswall, T.: A method of selective inhibition to distinguish between nitrification and denitrification as sources of nitrous oxide in soil, *Biol. Fert. Soils*, 6, 112–119, 1988.
- Klemetsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, *Glob. Change Biol.*, 11, 1142–1147, 2005.
- Knowles, R.: Denitrification, *Microbiol. Rev.*, 46, 43–70, 1982.
- Kowalenko, C. G. and Cameron, D. R.: Nitrogen transformations in an incubated soil as affected by combinations of moisture content and temperature and adsorption – fixation of ammonium, *Can. J. Soil Sci.*, 56, 63–70, 1976.
- Leteý, J., Valoras, N., Hadas, A., and Focht, D. D.: Effect of air-filled porosity, nitrate concentration, and time on the ratio of N<sub>2</sub>O/N<sub>2</sub> evolution during denitrification, *J. Environ. Qual.*, 9, 227–231, 1980.
- Livingston, G. P. and Hutchinson, G. L.: Enclosure-based measurement of trace gas exchange: application and sources of error, in: Biogenic Trace Gases: Measuring Emissions from Soil and Water, edited by: Matson, P. A. and Harriss, R. C., Blackwell Science, Cambridge, 14–50, 1995.
- Löhmus, K., Kuusemets, V., Ivask, M., Teiter, S., Augustin, J., and Mander, Ü.: Budgets of nitrogen fluxes in riparian grey alder forests, *Arch. Hydrobiol. Suppl.*, 141, 321–332, 2002.
- Maag, V. and Vinther, F. P.: Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures, *Appl. Soil Ecol.*, 4, 5–14, 1996.
- Machacova, K., Papeň, H., Kreuzwieser, J., and Rennenberg, H.: Inundation strongly stimulates nitrous oxide emissions from stems of the upland tree *Fagus sylvatica* and the riparian tree *Alnus glutinosa*, *Plant Soil*, 364, 287–301, doi:10.1007/s11104-012-1359-4, 2012.
- Mäkinen, A.: Peat quality and peat formation in Finnish alder swamps, in: Classification of Peat and Peatlands, edited by: Kivinen, E., Heikurainen, L., and Pakarinen, P., International Peat Society, Helsinki, 171–183, 1979.
- Mander, Ü., Kuusemets, V., Löhmus, K., and Mauring, T.: Efficiency and dimensioning of riparian buffer zones in agricultural catchments, *Ecol. Eng.*, 8, 299–324, 1997.
- Mander, Ü., Kuusemets, V., Löhmus, K., Mauring, T., Teiter, S., and Augustin, J.: Nitrous oxide, dinitrogen, and methane emission in a subsurface flow constructed wetland, *Water Sci. Technol.*, 4, 135–142, 2003.
- Mander, Ü., Löhmus, K., Kuusemets, V., Ivask, M., Teiter, S., and Augustin, J.: Budgets of nitrogen and phosphorus fluxes in riparian grey alder forests, Natural and Constructed Wetlands: Nutrients, Metals and Management, 1–19, 2005.
- Mander, Ü., Löhmus, K., Teiter, S., Mauring, T., Nurk, K., and Augustin, J.: Gaseous fluxes in the nitrogen and carbon budgets of subsurface flow constructed wetlands, *Sci. Total Environ.*, 404, 343–353, 2008.
- Merbach, W., Augustin, J., and Gans, W.: Nitrous oxide emissions from fen mires in dependence of anthropogenic activities, *J. Appl. Bot.*, 75, 118–123, 2001.
- Michaelis, L. and Menten, M. L.: Die Kinetik der Invertinwirkung, *Biochem. Z.*, 49, 333–369, 1913.
- Mogge, B., Kaiser, E. A., and Munch, J. C.: Nitrous oxide emissions and denitrification N-losses from forest soils in the Bornhöved lake region (northern Germany), *Soil Biol. Biochem.*, 30, 703–710, 1998.
- Ollinger, S. V., Smith, M. L., Martin, M. E., Hallett, R. A., Goodale, C. L., and Aber, J. D.: Regional variation in foliar chemistry and N cycling among forests of diverse history and composition, *Ecology*, 83, 339–355, 2002.
- Pangala, S. R., Moore, S., Hornibrook, E. R. C., and Gauci, V.: Trees are major conduits for methane egress from tropical forested wetlands, *New Phytol.*, 197, 524–531, 2012.
- R Development Core Team: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, available at: <http://www.R-project.org>, 2010.
- Regina, K., Nykänen, H., Silvola, J., and Martikainen, P. J.: Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity, *Biogeochemistry*, 35, 401–418, 1996.
- Robertson, G. P.: Nitrification in forested ecosystems, *Philos. T. R. Soc. Lond.*, 296, 445–457, 1982.
- Rolston, D. E., Hoffman, D. L., and Toy, D. W.: Field measurements of denitrification: 1. Flux of N<sub>2</sub> and N<sub>2</sub>O, *Soil Sci. Soc. Am. J.*, 42, 863–869, 1978.
- Roobroeck, D., Butterbach-Bahl, K., Brüggemann, N., and Boeckx, P.: Dinitrogen and nitrous oxide exchanges from an undrained monolith fen: short-term responses following nitrate addition, *Eur. J. Soil Sci.*, 61, 662–670, 2010.
- Rusch, H. and Rennenberg, H.: Black alder (*Alnus glutinosa* (L.) Gaertn.) trees mediate methane and nitrous oxide emission from the soil to the atmosphere, *Plant Soil*, 201, 1–7, 1998.
- Rytter, L., Arveby, A. S., and Granhall, U.: Dinitrogen (C<sub>2</sub>H<sub>2</sub>) fixation in relation to nitrogen fertilization of grey alder [*Alnus incana* (L.) Moench.] plantations in a peat bog, *Biol. Fert. Soils*, 10, 233–240, 1991.
- Schäfer, A. and Joosten, H. (Eds.): Erlenaufforstung auf wiedervernässten Niedermooren. (*Alnus* afforestation on restored fen peatlands), Greifswald: Institute for Sustainable Development of Landscapes of the Earth, 68 pp. 2005.

- Schauffler, G., Kitzler, A., Schindlbacher, A., Skiba, U., Sutton, M. A., and Zechmeister-Boltenstern, S.: Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature, *Eur. J. Soil Sci.*, 61, 683–696, 2010.
- Schindlbacher, A., Zechmeister-Boltenstern, S., and Butterbach-Bahl, K.: Effects of soil moisture and temperature on NO, NO<sub>2</sub>, and N<sub>2</sub>O emissions from European forest soils, *J. Geophys. Res.*, 109, D17302, doi:10.1029/2004JD004590, 2004.
- Scholefield, D., Hawkins, J. M. B., and Jackson, S. M.: Use of a flowing helium atmosphere incubation technique to measure the effects of denitrification controls applied to intact cores of a clay soil, *Soil Biol. Biochem.*, 29, 1337–1344, 1997.
- Skiba, U., Sheppard, L., Pitcairn, C. E. R., Leith, I., Crossley, A., van Dijk, S., Kennedy, V. H., and Fowler, D.: Soil nitrous oxide and nitric oxide emissions as indicators of elevated atmospheric N deposition rates in seminatural ecosystems, *Environ. Pollut.*, 102, 457–461, 1998.
- Skiba, U., Sheppard, L. J., Pitcairn, C. E. R., van Dijk, S., and Rossall, M.: The effect of N deposition on nitrous oxide and nitric oxide emissions from temperate forest soils, *Water Air Soil Poll.*, 116, 89–98, 1999.
- Smith, K. A., Thomson, P. E., Clayton, H., McTaggart, I. P., and Conen, F.: Effects of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soil, *Atmos. Environ.*, 32, 3301–3309, 1998.
- Soosaar, K., Mander, Ü., Maddison, M., Kanal, A., Kull, A., Löhmus, K., Truu, J., and Augustin, J.: Dynamics of gaseous nitrogen and carbon fluxes in riparian alder forests, *Ecol. Eng.*, 37, 40–53, 2011.
- Speir, T. W., Kettles, H. A., and More, R. D.: Aerobic emissions of N<sub>2</sub>O and N<sub>2</sub> from soil cores: factors influencing production from <sup>13</sup>N-labelled NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, *Soil Biol. Biochem.*, 27, 1299–1306, 1995.
- Struwe, S. and Kjoller, A.: Seasonality of denitrification in waterlogged alder stands, *Plant Soil*, 128, 109–113, 1990.
- Teiter, S. and Mander, Ü.: Emission of N<sub>2</sub>O, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> from constructed wetlands for wastewater treatment and from riparian buffer zones, *Ecol. Eng.*, 25, 528–541, 2005.
- Tietema, A., Warmerdam, B., Lenting, E., and Riemer, L.: Abiotic factors regulating nitrogen transformations in the organic layer of acid forest soils: Moisture and pH, *Plant Soil*, 147, 69–78, 1992.
- Uri, V., Löhmus, K., and Tullus, H.: Annual net nitrogen mineralization in a grey alder (*Alnus incana* (L.) Moench) plantation on abandoned agricultural land, *Forest Ecol. Manag.*, 184, 167–176, 2003.
- Uri, V., Löhmus, K., Mander, Ü., Ostonen, I., Aosaar, J., Maddison, M., Helmsaari, H. S., and Augustin, J.: Long-term effects on the nitrogen budget of a short-rotation grey alder (*Alnus incana* (L.) Moench) forest on abandoned agricultural land, *Ecol. Eng.*, 37, 920–930, doi:10.1016/j.ecoleng.2011.01.016, 2011.
- van Groenigen, J. W., Zwart, K. B., Harris, D., and van Kessel, C.: Vertical gradients of δ<sup>15</sup>N and δ<sup>18</sup>O in soil atmospheric N<sub>2</sub>O – temporal dynamics in a sandy soil, *Rapid Commun. Mass Sp.*, 19, 1289–1295, 2005.
- van Miegroet, H., Homann, P. S., and Cole, D. W.: Soil nitrogen dynamics following harvesting and conversion of red alder and Douglas fir stands, *Soil Sci. Soc. Am. J.*, 56, 1311–1318, 1992.
- VDLUFA: Bestimmung von mineralischem (Nitrat-)Stickstoff in Bodenprofilen (Nmin-Labormethode), in: *Methodenbuch Teil 2*, edited by: VDLUFA, Speyer, Germany, 1997.
- Venterea, R. T., Groffman, P. M., Verchot, L. V., Magill, A. H., Aber, J. D., and Steudler, P. A.: Nitrogen oxide gas emissions from temperate forest soils receiving long-term nitrogen inputs, *Glob. Change Biol.*, 9, 346–357, 2003.
- von Arnold, K., Nilsson, M., Hånell, B., Weslien, P., and Klemmedtsen, L.: Fluxes of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O from drained organic soils in deciduous forests, *Soil Biol. Biochem.*, 37, 1059–1071, 2005.
- Wang, R., Willibald, G., Feng, Q., Zheng, X., Liao, T., Brüggemann, N., and Butterbach-Bahl, K.: Measurement of N<sub>2</sub>, N<sub>2</sub>O, NO and CO<sub>2</sub> Emissions from Soil with the Gas-Flow-Soil-Core Technique, *Environ. Sci. Technol.*, 45, 6066–6072, 2011.
- Watts, S. and Seitzinger, S. P.: Denitrification rates in organic and mineral soils from riparian sites: a comparison of N<sub>2</sub> flux and acetylene inhibition methods, *Soil Biol. Biochem.*, 32, 1383–1392, 2000.
- Weier, K. L., Doran, J. W., Power, J. F., and Walters, D. T.: Denitrification and dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate, *Soil Sci. Soc. Am. J.*, 57, 66–72, 1993.
- Wichtmann, W. and Joosten, H.: Paludiculture: peat formation and renewable resources from rewetted peatlands, in: *IMCG-Newsletter 3/2007*, 24–28, 2007.
- Wolf, I. and Russow, R.: Different pathways of formation of N<sub>2</sub>O, N<sub>2</sub> and NO in black earth soil, *Soil Biol. Biochem.*, 32, 229–239, 2000.
- Wray, H. E. and Bayley, S. E.: Denitrification rates in marsh fringes and fens in two boreal peatlands in Alberta, Canada, *Wetlands*, 27, 1036–1045, 2007.
- WRB, 2006 – IUSS Working Group: World Reference Base for Soil Resources 2006, 2nd Edn., World Soil Resources Reports No. 103, Rome, 2006.

## 7.4 CALCULATION APPROACH TO ESTIMATE NET GHG FLUXES OF THE ALDER FOREST

NEE estimation of the alder forest based on two different calculation approaches. The first calculation method based on the approach of von Arnold et al. (2005), who used dark forest floor CO<sub>2</sub> fluxes from static chamber measurements, which were also determined simultaneously to N<sub>2</sub>O fluxes in the present study (unpublished data). It must be pointed out that several studies (e.g. Venterea, 2010) have shown that the static chamber measurement method significantly underestimate CO<sub>2</sub> exchange of ecosystems. However, despite of high uncertainty the site-specific mean CO<sub>2</sub> flux rates observed for U, D-1 and D-2 amounted to  $56 \pm 10 \text{ mg C m}^{-2} \text{ h}^{-1}$ ,  $81 \pm 14 \text{ mg C m}^{-2} \text{ h}^{-1}$  and  $76 \pm 13 \text{ mg C m}^{-2} \text{ h}^{-1}$ , respectively. In the present study, referred CO<sub>2</sub> fluxes represent the sum of heterotrophic respiration (R<sub>h</sub>), autotrophic respiration (R<sub>a</sub>) from forest floor vegetation and autotrophic respiration from tree roots. Based on literature values, von Arnold (2005) assumed that 50% of the measured soil CO<sub>2</sub> released originated from root-based activity. Thus, in average  $245 \text{ g C m}^{-2} \text{ yr}^{-1}$  and approximately  $344 \text{ g C m}^{-2} \text{ yr}^{-1}$  are presumed to be mineralized at the undrained and drained site, respectively. Based on the conducted incubation experiment, collected annual leaf litter fall (unpublished data) and mineralization rates derived from a litterbag study, which lasted 374 days (unpublished data), a second calculation was accomplished to roughly estimate heterotrophic CO<sub>2</sub> release. There, R<sub>h</sub> derived from the incubation experiment was determined assuming an annual average temperature of 10°C and a mean annual WFPS of 100% for the undrained site and 70% for the drained sites. According to these assumptions, estimated CO<sub>2</sub> flux rates amounted to approximately  $15 \text{ mg C m}^{-2} \text{ h}^{-1}$  and  $20 \text{ mg C m}^{-2} \text{ h}^{-1}$  for the undrained and drained site, respectively. These values are distinctly lower than values determined from forest floor measurements, even after considering R<sub>a</sub>. However, it has to be kept in mind that mineralization rates from soil cores are solely representative for the soil depth 9–15 cm. From monitored leaf litter fall ( $4593 \pm 764 \text{ kg DM ha}^{-1} \text{ yr}^{-1}$ ) and the litterbag study, it was found that litter decay rates observed at the drained sites of the alder forest approximately doubled decay rates from the undrained sites ( $11.54 \text{ vs } 6.88 \text{ kg DM ha}^{-1} \text{ d}^{-1}$ ). This result is in line with Bragazza et al. (2009), who reported that the percentage of mass losses from vascular plant litter and *Sphagnum* litter was on average 2.3 times higher in oxic than anoxic layers. The average C content of collected leaf litter was 47%, leading to a mineralization rate of

approximately  $118 \text{ g C m}^{-2} \text{ yr}^{-1}$  at the undrained site and  $198 \text{ g C m}^{-2} \text{ yr}^{-1}$  at the drained sites. Taking together both,  $R_h$  determined from soil cores and leaf litter decay, annual mineralization rates amount to approximately  $249 \text{ g C m}^{-2} \text{ yr}^{-1}$  and  $373 \text{ g C m}^{-2} \text{ yr}^{-1}$  for the undrained and drained sites, respectively, which fits well with mineralization rates derived from forest floor release. Estimated net primary productivity (NPP) of the alder forest was  $-260.7 \text{ g C m}^{-2} \text{ yr}^{-1}$  and originated from tree biomass data and simulations of forest growth by the models BALANCE (Grote and Pretzsch, 2002) and SILVA (Pretzsch et al., 2002) (S. Röhling and T. Rötzer personal communication, 2013). Carbon accumulation from forest floor vegetation has not been considered in NPP calculation. However, the estimated NECB of the alder forest revealed a small C uptake ranging between  $-6.8$  and  $-2.8 \text{ g C m}^{-2} \text{ yr}^{-1}$  at the undrained site and a small C release ranging between  $83.1$  and  $112.1 \text{ g C m}^{-2} \text{ yr}^{-1}$  at the drained sites. For the drained sites the estimated values of C release seems quite low, considering that NNM rates revealed distinctly higher SOM turnover rates (e.g.  $\text{NNM} = 653 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ; C/N ratio = 8.5 for the soil depth 0–20 cm; resulting in a C turnover of at least  $556 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), but this can probably be attributed to the high uncertainty of estimated  $R_h$ . To assess the  $\text{GWP}_{100}$  (reference period 100 years; IPCC, 2007) of the alder sites, net emissions of carbon equivalents of NECB and  $\text{N}_2\text{O}$  were summed, considering radiative forcing factors of 25 and 298 for the conversion of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  to  $\text{CO}_2$  equivalents (Forster et al., 2007).

## 8 EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich die der Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt der Technischen Universität München zur Promotionsprüfung vorgelegten Arbeit mit dem Titel

„Assessment and modeling of greenhouse gas emissions (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) from different land use types and management practices on drained fen peatlands and associated organic soils – case study Freisinger Moos “

am Fachgebiet für Renaturierungsökologie unter der Anleitung und Betreuung durch Prof. Dr. Matthias Drösler ohne sonstige Hilfe erstellt und bei der Abfassung nur die gemäß § 6 Abs. 5 angegebenen Hilfsmittel benutzt habe.

Ich habe die Dissertation in keinem anderen Prüfungsverfahren als Prüfungsleistung vorgelegt.

Ich habe den angestrebten Doktorgrad noch nicht erworben und bin nicht in einem früheren Promotionsverfahren für den angestrebten Doktorgrad endgültig gescheitert.

Die Promotionsordnung der Technischen Universität München ist mir bekannt.

Freising, den \_\_\_\_\_

\_\_\_\_\_  
Tim Eickenscheidt

## 9 CURRICULUM VITAE

Tim Eickenscheidt  
 Born on 04.01.1982 in Leverkusen, Germany  
 Alte Poststr. 101  
 85356 Freising

### EDUCATION

---

Since 03/2009	Ph.D. study, Chair of Restoration ecology, Faculty of Landscape Architecture and Landscape Planning, Research Department Ecology and Ecosystem Management, School of Life Sciences Weihenstephan, Technical University Munich.
2003–2008	Diplom-Ingenieur (FH) in Forestry, University of Applied Forest Sciences Rottenburg, Germany. Main focus: Geographic Information System and Landscape Management. Diploma thesis: "Quantifizierung der Kohlenstoff- und Humusvorräte der Encosta Atlântica im Waldforschungsgebiet Pró-Mata, Mata Atlântica, Rio Grande do Sul".
2002–2003	Civilian service, Protection Centre for Birds of Prey, Erftkreis.
2001–2002	School further education, Vocational College Märkischer Kreis, Iserlohn.
1998–2001	Vocational training forestry, National Forest Department, Arnsberg.
1992–1998	Comprehensive school, Fröndenberg.

### RESEARCH EXPERIENCE

---

Since 09/2011	Scientist, Chair of Vegetation ecology, University of Applied Sciences Weihenstephan-Triesdorf.
03/2009–08/2011	Scientist, Chair of Restoration ecology, Research Department Ecology and Ecosystem Management, Technical University Munich.
02/2009	Scientific helper, Georg-August-University Göttingen; Department of Soil Science of Tropical and Subtropical Ecosystems.
03/2007–05/2007	Project thesis, Regional council Tübingen, Department of environment/nature conservation and University of Applied Forest Science Rottenburg, Project Titel: "Habitatsanalyse beim Weißstorch ( <i>Ciconia ciconia</i> ) im Donautal".
03/2006–09/2006	Data acquisition - Diploma thesis, Forest conservation and research area Pró-Mata, in Rio Grande do Sul, Brazil in cooperation with the Pontificia Universidade Católica do Rio Grande do Sul in Porto Alegre, Brazil and the Eberhard-Karls- University in Tübingen, Germany.
09/2004–11/2004	Internship, Swiss Federal Institut for Snow and Avalanche Research, Department of Alpine Environment in Davos/Schweizerland.