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**Assessment and modeling of greenhouse gas emissions (CO₂, CH₄, N₂O) from different land-use types and management practices on drained fen peatlands and associated organic soils – case study
Freisinger Moos**

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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 (CO₂) and nitrous oxide (N₂O). 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_{org}), whereas former peatlands and associated organic soils containing <12% C_{org} 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_{org} in 0–10 cm soil depth) and a sapric Histosol (16.1–17.2% C_{org} 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 (CO₂, N₂O and methane (CH₄)) were measured and modeled over a period of two years. No differences were found in the estimated net CO₂ 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 CO₂ eq. m⁻² yr⁻¹. 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 (NUE_{min}) and grass yields. It is well known that organic fertilization can enhance N_2O 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 N_2O and CH_4 fluxes as well as the NUE_{min} and grass yield, and ii) to what extent different soil organic matter (SOM) and nitrogen (N) contents influence on production of N_2O . Furthermore, ammonia (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 N_2O and NH_3 emissions and additionally increased the plant N-uptake and NUE_{min} , leading to significantly higher grass yields. This could partly be attributed to the higher ammonium (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 N_2O fluxes significantly increase with increasing SOM content, probably due to the more favourable soil conditions for denitrification. 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 N_2O 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 (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 N₂O from black alder forests and ii) how N turnover processes and physical factors influence the production of N₂O 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 N₂ 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 N₂O emissions in the field remained low at the drained sites, but the incubation experiment revealed the potential for high N₂O emissions under changing soil physical conditions at the drained alder sites. Temporally water-saturated conditions were found to enhance N₂ emissions, whereas N₂O 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 N₂O 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 CO₂ 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- (CO_2) und Distickstoffmonoxid-Emissionen (N_2O). 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 (C_{org}) aufweisen, wohingegen rezente Moore und mit Mooren vergesellschaftete organische Böden mit C_{org} -Gehalten von weniger als 12% C_{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% C_{org} in 0–10 cm Bodentiefe) sowie ein sapric Histosol (16.1–17.2% C_{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 (CO_2 , N_2O und Methan (CH_4)) gemessen und modelliert. Es konnten keine Unterschiede zwischen den zwei Bodentypen bezüglich der Netto- 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 CO₂ eq. m⁻² a⁻¹. 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_{min}) 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 N₂O 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 N₂O- und CH₄-Flüsse, sowie die NUE_{min} und den Grasertrag beeinflussen, und ii) welchen Einfluss unterschiedliche Bodenhumus- (SOM) und Bodenstickstoffgehalte (N) auf die Entstehung von N₂O haben. Zudem wurde im Zuge eines Düngeereignisses die Ammoniakverflüchtigung (NH₃) 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 N₂O- und NH₃-Emissionen sowie der Stickstoffaufnahme und NUE_{min} der Pflanzen führte, was wiederum eine signifikante Steigerung der Graserträge zur Folge hatte. Dies könnte zum Teil auf den höheren Ammoniumgehalt (NH₄⁺) 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 N₂O-Flüsse mit zunehmendem SOM-Gehalt signifikant ansteigen, was wahrscheinlich auf günstigere Bedingungen für Denitrifikation im Boden zurückzuführen ist. Zudem hat sich gezeigt, dass die CH₄-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 N₂O-Verluste angesehen, was auf die stark schwankenden Grundwasserflurabstände von Mooren sowie den Eintrag großer Mengen leicht verfügbaren organischen Stickstoffs durch die symbiotische Distickstoff(N₂)-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 N₂O-Emissionen führt und ii) wie Stickstoffumsetzungsprozesse und physikalische Einflussfaktoren die Bildung von N₂O 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 N₂-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 N₂O-Austauschraten beobachtet wurden, konnte im Rahmen des Inkubationsexperiments nachgewiesen werden, dass veränderte bodenphysikalische Bedingungen im entwässerten Erlenwald zu hohen N₂O Emissionen führen können. Temporär wassergesättigte Bedingungen verursachten einen Anstieg der N₂-Emissionen, wohingegen kein Einfluss auf die N₂O-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 N₂O-Bildungspotenzial bergen. Die in dieser Studie vorgenommene grobe Abschätzung des GWPs macht deutlich, dass weitere Untersuchungen vor allem bezüglich des Nett-CO₂-Austauschs erforderlich sind, um zu überprüfen inwieweit Erlenwälder eine Option zur Verminderung von THG-Emissionen darstellen.

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List of Abbreviations and Acronyms

AFOLU	Agriculture, Forestry and Other Land Uses
AIC	Akaike Information Criterion
Ar	Argon
C	Carbon
CaCl ₂	Calcium dichloride
CH ₄	Methane
CO ₂	Carbon dioxide
C _{org}	Organic carbon
C _{tot}	Total soil carbon
DM	Dry matter
DTM	Dräger-Tube Method
E ₀	Activation energy
ECD	Electron capture detector
EF	Emission factor
FID	Flame ionization detector
GC	Gas chromatograph
GHG	Greenhouse gases
GPP	Gross primary production
GPP ₂₀₀₀	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 ₂	Dinitrogen
N ₂ O	Nitrous oxide
NECB	Net Ecosystem Carbon Balance
NEE	Net ecosystem exchange of CO ₂
N _{dep}	Nitrogen deposition
Nr	Reactive nitrogen (Nr includes inorganic reduced forms of N (e.g., NH ₃ ⁻ , NH ₄ ⁺), inorganic oxidized forms (e.g., NO _x , HNO ₃ , N ₂ O, NO ₃ ⁻), and organic compounds (e.g., urea, amines, proteins, nucleic acids)).
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NH ₂ OH	Hydroxylamine
N _{org} /R-NH ₂	Monomeric organically bound N forms
N _{min}	Mineral soil nitrogen
NNM	Net nitrogen mineralization
NO	Nitric oxide
NO ₂ ⁻	Nitrite
NO ₂	Nitrogen dioxide
NO ₃ ⁻	Nitrate
NO _x	Nitric oxide + nitrogen dioxide
NPP	Net primary production
NSE	Nash-Sutcliffe efficiency

N_{tot}	Total soil nitrogen
NUE	Nitrogen use efficiency
NUE_{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_{ECO}	Ecosystem respiration
RF	Radiative Forcing
R_h	Heterotrophic respiration
R_{ref}	Respiration at T_{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_{air}	Air temperature in 20 cm above soil surface
TCD	Thermal conductivity detector
T_{ref}	Reference temperature: 283.15 [K]
UNFCCC	United Nation Framework Convention on Climate Change
VDS	Volatile dry solid
WFPS	Water filled pore space
α	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.: CO₂ 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 (CO₂, CH₄, N₂O) 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 CO₂, 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 NH₃, 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 N₂, N₂O, CH₄ and CO₂ 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 CO₂ measurements, soil sampling and sample preparation, data preparation and calculations as well as the modeling of CO₂.

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 CO₂ 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 CO₂ 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 km² 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 characteristic for bogs (Göttlich, 1990).

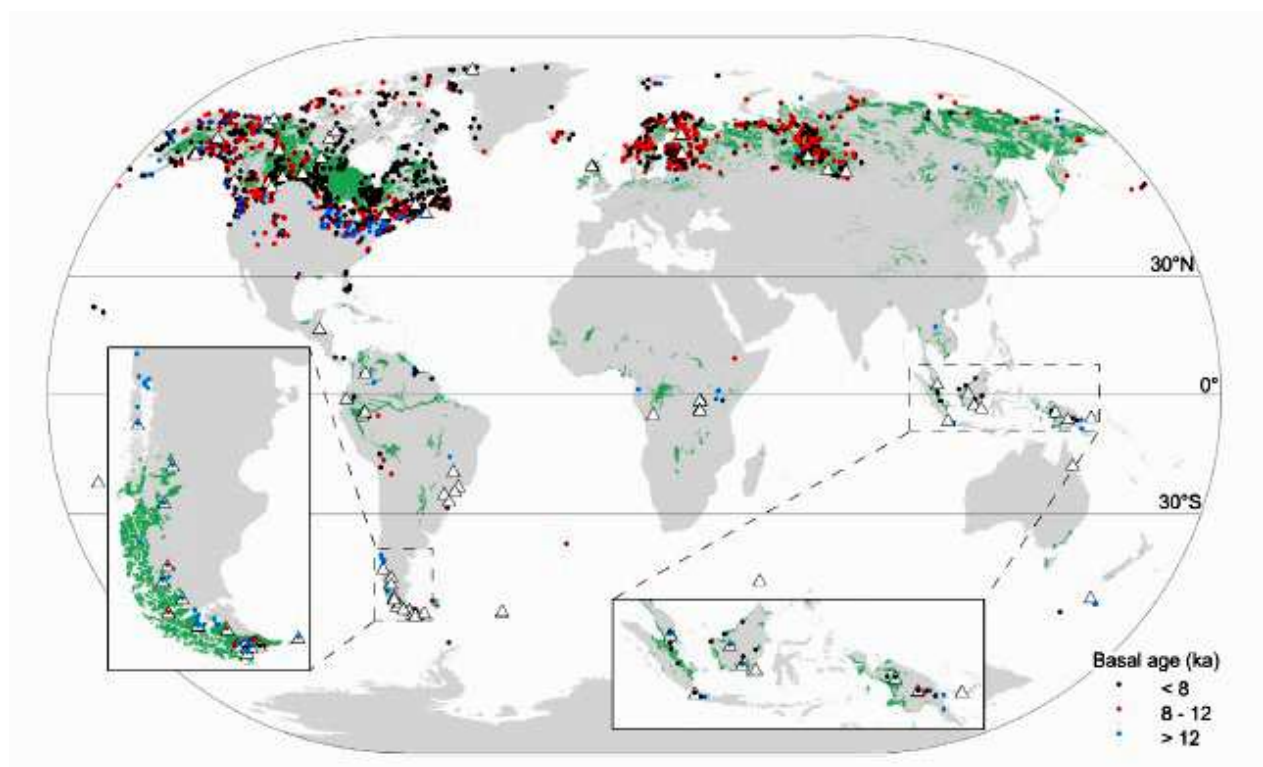


Figure 1 Global peatland distribution (green areas). Dots showing peatland study sites with basal peat age (colors showing the ages of peatland initiation: black <8 ka (ka =1000 yr), red 8-12 ka, and blue >12 ka) (Source: Yu et al., 2010).

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.

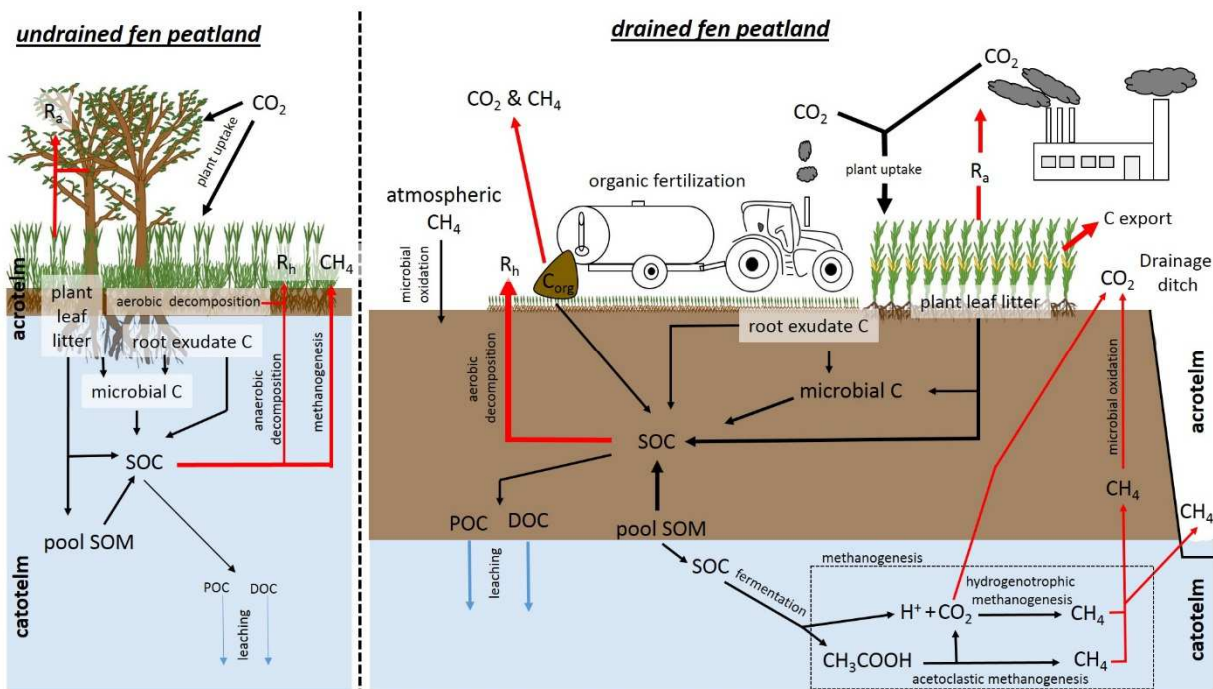
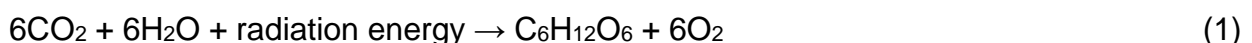


Figure 2 Simplified carbon cycle of a pristine and drained fen peatland.

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 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 CO_2 , which is referred as autotrophic respiration (R_a ; reverse

function of Eq.1). The amount of C converted to CO₂ by R_a is estimated to be half of the C fixed by GPP (Larcher, 2001). The sum of GPP (positive flow) and R_a (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_{max}) range from 5.2 to 12.4 μmol m⁻² s⁻¹) and a lower apparent quantum yield at low light (α values range from 0.017 to 0.027 μmol CO₂ μmol⁻¹ PAR) compared to croplands and forest ecosystems on mineral soils (GP_{max} up to 82.9 μmol m⁻² s⁻¹ and α up to 0.056 μmol CO₂ μmol⁻¹ PAR; Frohking et al., 1998). According to Blodau (2002), the NPP of peatlands range between 5 g DM m⁻² yr⁻¹ in northern regions and more than 1000 g DM m⁻² yr⁻¹ in the tropics with most common values between 100 and 400 g DM m⁻² yr⁻¹. This is in accordance with Gorham (1995) and Schulze et al. (2010), who reported NPP values of about 230 g C m⁻² yr⁻¹ and 295 g C m⁻² yr⁻¹, 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⁻² yr⁻¹ and 550 g C m⁻² yr⁻¹, respectively. However, depending on crop, dry matter yields of up to 1650 g DM m⁻² yr⁻¹ for winter wheat and up to 2500 g DM m⁻² yr⁻¹ 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⁻² yr⁻¹ 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 CO₂ 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 CO₂ 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⁻ 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 CO₂. 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 CO₂ (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, CH₄ is produced either through the reduction of acetate (acetoclastic methanogenesis), with the simultaneous release of CO₂, or through the reduction of CO₂ with H₂ (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 CH₄ production originate from this process (Artz, 2009). Once CH₄ 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 CH₄ passes through an oxic layer at the soil surface, aerobic methanotrophs, particularly alpha- and gamma-proteobacteria take it up and oxidize it to CO₂. Thus the amount of CH₄ that reaches the atmosphere depends mainly on the thickness of the acrotelm. Nevertheless, aerenchymatic vascular transport of CH₄ from an anaerobic layer to the atmosphere, bypassing the oxic zone at the soil surface, can account for up to 90% of total CH₄ emissions (Grosse et al., 1992; Svensson and Sundh, 1992; Wahlen, 2005). In turn, also O₂ can be transported within the plant into an anoxic zone, leading to the oxidation of CH₄ in close vicinity of the root (Wahlen, 2005). Recently, there has been growing evidence that beside aerobic CH₄ oxidation also anaerobic CH₄ 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 NO_3^- , SO_4^{3-} or 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 CH_4 fluxes from peatlands all over the world. Observed 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 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 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 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 O_2 availability in the upper soil profile. Simultaneously, anaerobic decomposition distinctly decreases and peatlands turn from a significant CH_4 source to a small sink of atmospheric CH_4 (Crill et al., 1994; Flessa et al., 1998). Water table manipulation experiments show that heterotrophic CO_2 emission rates are 4 to 6 times larger when the water table is lowered to a depth of -40 to -50 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 CO₂ 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⁻² yr⁻¹ for boreal and temperate croplands and from 500 to 730 g C m⁻² yr⁻¹ for temperate nutrient-rich grasslands.

Beside CO₂-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⁻² yr⁻¹ 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 CO₂ 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.

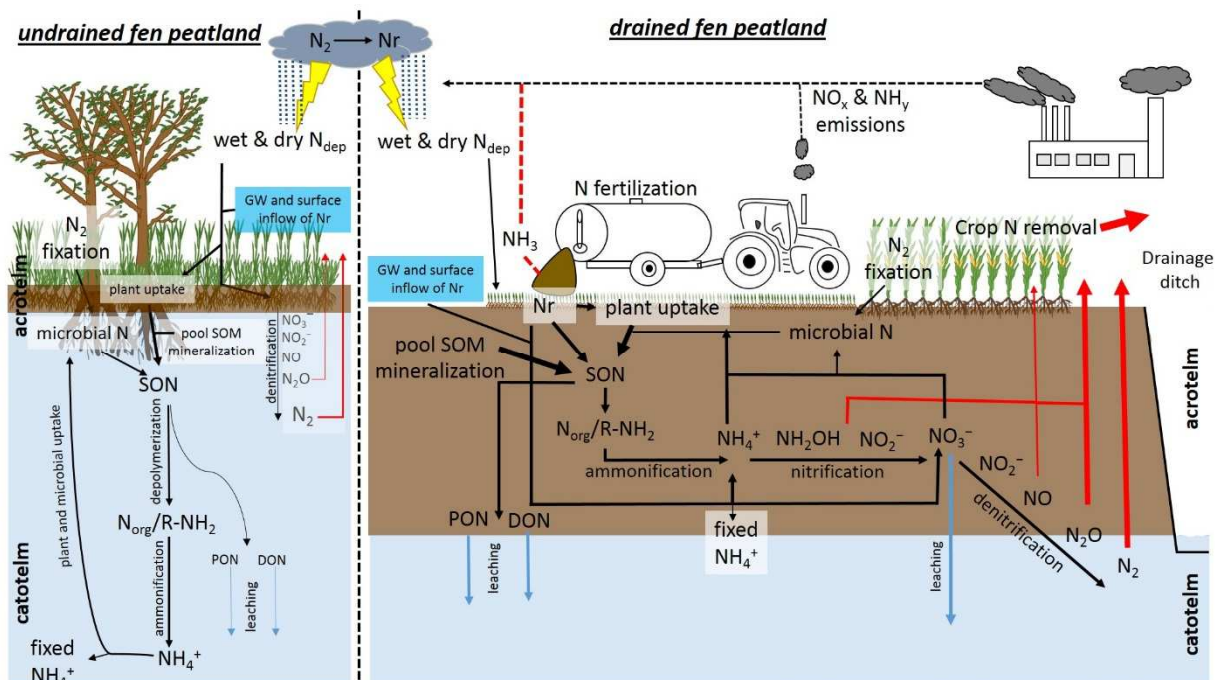


Figure 3 Simplified nitrogen cycle of a pristine and drained fen peatland.

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 (N₂), which makes up approximately 78% of the atmosphere (Galloway, 1998). Only a few genera of specialized microorganisms (diazotrophs) are able to incorporate atmospheric N₂ into organic molecules through the reduction of N₂ to 2NH₃, using the enzyme complex *nitrogenase* (McNeill and Unkovich, 2007). The reduction of N₂ 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 N₂ to Nr additionally occurs naturally through lightning (N₂ → NO), leading to wet and dry deposition of Nr. Natural N deposition rates are in the range of < 6 kg N ha⁻¹ yr⁻¹ (Pitcairn and Fowler, 1995; Koopmans et al., 1998) depending on latitude. In contrast, the annual N supply through biological N₂-fixation ranges between 0.3–62 kg N ha⁻¹ for bogs and 1.6–115 kg N ha⁻¹ for fen peatlands (Dittert, 1992; Succow and Joosten, 2012; Vile et al., 2014). Thus, it is assumed that the biological N₂-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_{dep} has drastically increased by a factor of >10 (Galloway et al., 2004). In Germany, prevailing total N_{dep} rates in open land are estimated to be on average 26 kg N ha⁻¹ yr⁻¹ (Wochele and Kiese, 2010). In contrast, critical N loads have been estimated to constitute 5–10 kg N ha⁻¹ yr⁻¹ (Bobbink and Roelofs, 1995; UNECE, 2004; Bobbink et al., 2010). It is well known that particularly NH₃ 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.

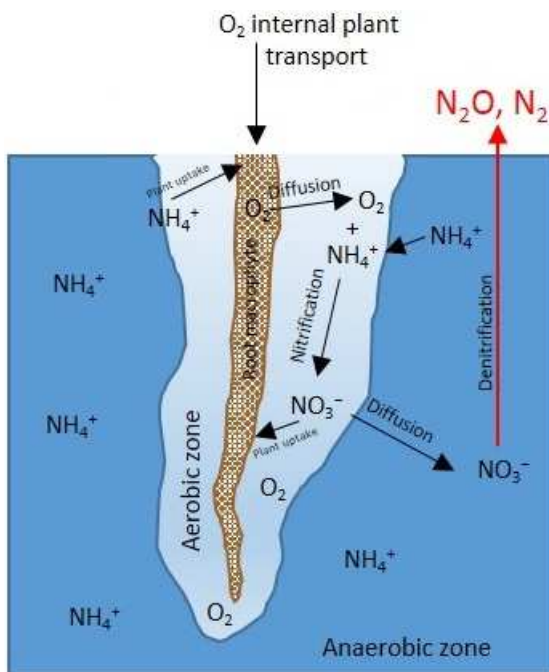


Figure 4 Simplified scheme of plant induced interactions of aerobic and anaerobic zones around a macrophyte root (modified after Cleemput van et al., 2007).

Therefore, these transformation processes only play a minor role for the N cycle of pristine peatlands and were therefore not included in Fig. 3.

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⁻¹ yr⁻¹ for intensively used crop- or grasslands, whereas under anaerobic conditions, net N mineralization rates are relatively low with

approximately 20 kg N ha⁻¹ yr⁻¹ (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

N, many peatland-adapted plants prefer NH_4^+ as N source (Succow and Joosten, 2012). Also, some plants are not able to utilize NO_3^- because they lack the enzyme *nitroreductase*, which is necessary for the reduction of NO_3^- to NH_4^+ (nitrate assimilation) (Succow and Joosten, 2012), and are thus restricted to NH_4^+ . To avoid NH_4^+ toxicity, absorbed or reduced 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 NH_4^+ , NO_2^- or 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, NH_4^+ is readily absorbed while the anion 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 (NH_3 , NO_x ($\text{NO} + \text{NO}_2$), N_2O or 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 (NO_3^- , NO_2^-) to the gaseous oxides NO_x and N_2O , which may themselves be further reduced to the inert atmospheric N_2 , is called biological denitrification (Knowles, 1982). Denitrification presupposes restricted 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 (NO_x , N_2O or 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 N_2O (Philipoot et al., 2011). It was found that with increasing anoxic conditions, the percentage of N_2 increases until it becomes the major gas evolved (Rolston et al., 1978; Davidson, 1991). Moreover, high contents of available NO_3^- inhibit N_2O reductase activity, the enzyme responsible for the conversion of N_2O to 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 NO_2^- , various purely abiotic reactions can lead to the formation of NO , N_2O and 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 NO and N_2O 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 NH_2OH can lead to N_2O and perhaps N_2 , with NO as precursor (Wrage et al., 2005; Frame and Casciotti, 2010), and secondly, N_2O can be produced during nitrifier-denitrification (Poth and Focht, 1985; Butterbach-Bahl et al.; 2013). Nitrifier-denitrification describes the oxidation of NH_4^+ (or NH_3) to NO_2^- and its subsequent stepwise reduction to NO , N_2O and perhaps N_2 by the same autotrophic ammonia oxidizers. This process requires conditions of high N availability but low organic C and 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 NO or N₂O, 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-Klemendtsen 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 N₂ or partially N₂O emissions due to denitrification. In contrast, drainage and fertilization have turned peatlands into a significant source of gaseous N emissions. Several studies reported N₂O emissions from drained organic soils ranging from 0 to 61 kg N₂O-N ha⁻¹ yr⁻¹ for arable lands (Kasimir-Klemendtsen 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 N₂O-N ha⁻¹ 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 NH₃ 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 NH₄⁺-N can be lost as NH₃ in a few hours (Vandre et al., 1997). Since NH₃ 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 N₂ in drained peatlands. Mainly due to analytical difficulties in the determination of microbial produced N₂, to date the total denitrification potential from peatlands has rarely been estimated. First results revealed annual N₂ emissions ranging between 15 and 650 kg N₂-N ha⁻¹ 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 CO₂, CH₄, N₂O, halocarbons; aerosols such as mineral dust, black carbon, SO₄²⁻, NO₃⁻; 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⁻²), 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 CO₂ (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 CO₂ (according to Forster et al., 2007).

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

a The CO₂ response function is based on the revised version of the Bern Carbon cycle model using a background CO₂ concentration value of 378 ppm. The decay of a pulse of CO₂ 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 CH₄ is 12 years. The GWP for CH₄ includes indirect effects from enhancements of ozone and stratospheric water vapor.

Global atmospheric concentrations of CO₂, CH₄ and N₂O have increased markedly since 1750, mainly due to human activities (Figure 5; IPCC, 2007). In April 2014, for the first time monthly concentrations of CO₂ in the atmosphere topped 400 parts per million (ppm) throughout the northern hemisphere (WMO, 2014). Also atmospheric CH₄ and N₂O 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⁻² 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).

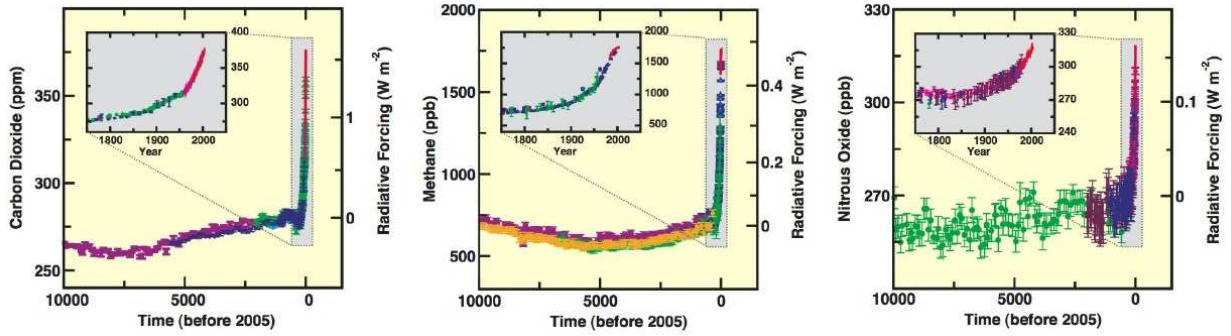


Figure 5 Atmospheric concentrations of the three important greenhouse gases CO₂, CH₄ and N₂O over the last 10,000 years. Increases since about 1750 (inset panels) are attributed to human activities in the industrial era (source: IPCC, 2007).

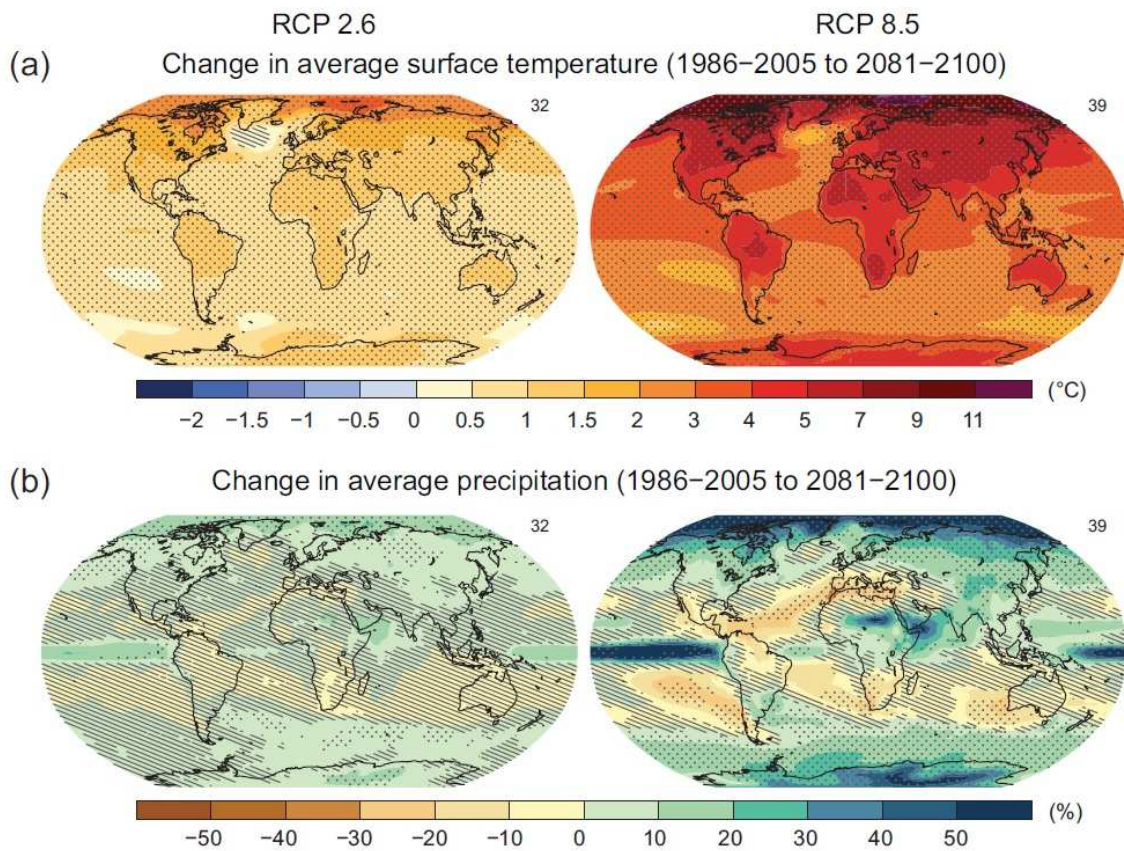


Figure 6 Maps of CMIP5 multi-model mean results for the scenarios RCP2.6 and RCP8.5 in 2081–2100 of (a) annual mean surface temperature change, (b) average percent change in annual mean precipitation, For the Fifth Assessment Report of IPCC, the scientific community has defined a set of four new scenarios, 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⁻² for RCP2.6, 4.5 W m⁻² for RCP4.5, 6.0 W m⁻² for RCP6.0, and 8.5 W m⁻² 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 CO₂ (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 CO₂ by peatlands reduced atmospheric CO₂ 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 ± 4.5 Gt CO₂ eq. yr⁻¹ 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 CO₂ eq. yr⁻¹) and secondarily due to emissions from land-use change (deforestation, agricultural soil and nutrient management, livestock farming), which accounts for approximately 10–12 Gt CO₂ eq. yr⁻¹ (IPCC, 2014b). From 1750 to 2011, CO₂ 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 km² of peatland area are estimated to be drained, leading to approximately total annual GHG emissions of 0.9 Gt CO₂ eq. yr⁻¹ in 2010 (FAOSTAT, 2013). Furthermore, Joosten (2010) estimated worldwide 500,000 km² of degraded peatland, leading to annual CO₂ emissions of approximately 1.30 Gt CO₂ yr⁻¹ (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 CO₂ yr⁻¹ globally, which corresponds to 5.4% of global anthropogenic CO₂ 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).

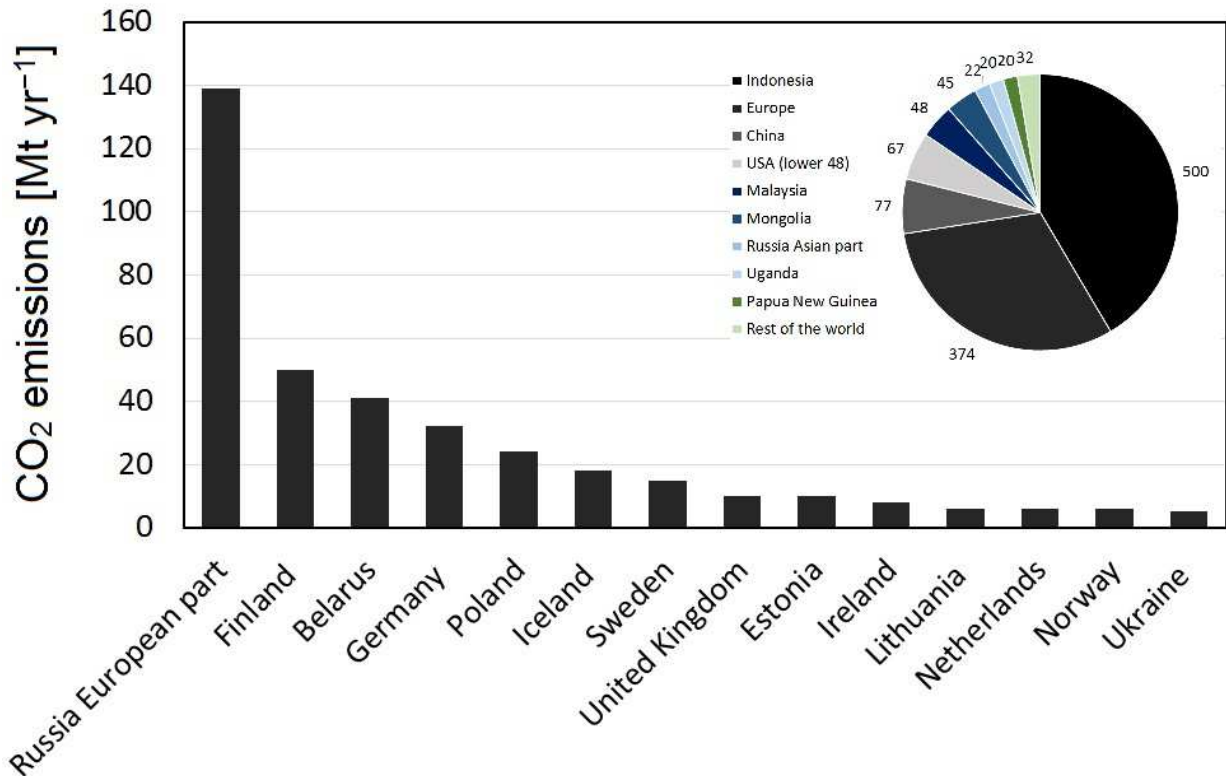


Figure 7 Estimated CO₂ emissions in Mt (10^6 t) from degrading peat for the year 2008. Bar chart shows European countries; pie chart shows total global emissions in Mt (Joosten, 2010).

Beside the uptake capacity of CO₂ since the last glaciation, peatland development has likewise significantly increased atmospheric CH₄ 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, CH₄ 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 CH₄ emissions. However, as previously pointed out, CH₄ 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 CH₄ sink (IPCC, 2014a).

N₂O 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 N₂O emissions (Kasimir-Klemetsson et al., 1997; Freibauer et al., 2004; Leppelt et al., 2014). According to Leppelt et al. (2014), direct N₂O emissions from organic soils in Europe amount up to 149.5 Gg N₂O-N yr⁻¹, which represents 13% of total European N₂O emissions reported in the European Union (EU) greenhouse gas inventory of 2011. Additionally, peatland cultivation can lead to NH₃ as well as NO_x (NO + NO₂) emissions. Besides acidification and eutrophication, NH₃ deposition promotes the formation of N₂O at the immission sites and therefore NH₃ is considered as indirect GHG (Moiser, 2001). However, the contribution of peatland cultivation to NH₃ emissions is still unclear, but overall agriculture is responsible for 95.3% of anthropogenic NH₃ emissions in Germany (Haenel et al., 2010). Due to high reactivity, NO and NO₂ 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 (O₃) and hydroxyl radicals (OH·) in the troposphere (IPCC, 2007). Additionally, NO_x also causes RF through NO₃⁻ formation, and via reaction with CH₄ 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 CH₄ (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 CO₂ and CH₄ 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 CO₂ and also N₂O 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 CO₂ emissions (Turetsky et al., 2004; Limpens et al., 2008). In contrast, several authors (e.g. Tarnocai, 2006; Arneeth et al., 2010; Charman et al., 2013) suggested that in the mid and high arctic latitudes, higher temperatures, longer growing seasons, and higher atmospheric CO₂ 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 CO₂ and N₂O, 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_{org}), whereas former peatlands and associated organic soils containing <12% C_{org} 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 N₂O and CH₄ 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 N₂O emissions and organic fertilization is known to increase N₂O 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 N₂O 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 N₂O is emitted after biogas digestate than after slurry application because of higher NH₄⁺-N concentrations in the substrate and, thus, higher NH₄⁺-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) N₂O emissions increase with increasing soil C_{org} 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, NH₃ 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 N₂O from black alder (*Alnus glutinosa* (L.) Gaertn.) forests and as to how N turnover processes and physical factors influence the production of N₂O 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 N₂O 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 N₂-fixation of the alder trees. The high magnitude of observed N₂O emissions from black alder forests, which exceed by far the IPCC default emission factor, requires in-depth process understanding of N₂O 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 N₂O emissions occur due to accelerated N turnover and N mineralization.
- (ii) N₂O losses are replaced by N₂ losses during periods of temporarily high water levels. In contrast, in permanently waterlogged peat soils NO₃⁻ limitation results in negligible N₂O and N₂ 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 simultaneous determination of N_2 , N_2O , CO_2 and CH_4 fluxes in a 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 NH_3 and N_2O in fertilizer applications studies or 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 ¹		Micrometeorological techniques	Mass balance methods ³	Backward Lagrangian stochastic dispersion technique
	manual systems	automatic systems	Eddy covariance ²		
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 ₂ , NH ₃ , N ₂ O, CH ₄	CH ₄ , N ₂ O, NH ₃	CH ₄ , N ₂ O, NH ₃
Workload	--	++	++	++	++
Straightforward application	++	+	-	+	-
Demands on infrastructure including power supply	++/-	-	--	-	-
Costs	++/--**	-/--**	-/--**	+/--**	+/--**

¹ including open and closed systems; closed systems contain static and dynamic gas detection.

² including eddy accumulation, relaxed eddy accumulation and flux-gradient methods.

³ including open and closed systems with adaption of open systems to circular source areas.

* e.g. CO₂, CH₄, N₂O, NH₃, 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 N₂O 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_{ECO} at these plots (Table 3, **Publication I.**). With the exception of the maize plot at the C_{medium} 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 ± 546 and 1707 ± 619 g CO₂-C m⁻² yr⁻¹ at the arable land and between 1354 ± 740 and 1823 ± 851 g CO₂-C m⁻² yr⁻¹ at the grassland. Generally, the annual CO₂ 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 CO₂ or CH₄ fluxes is difficult because no further studies exist concerning intensively used organic soils with SOC contents comparable to the C_{medium} 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ emission patterns.

Despite different SOC and groundwater levels, no differences in CH₄ fluxes were found between the two soil types investigated (**Publication I.** and **II.**). In contrast to literature (e.g. Maljanen et al., 2010) CH₄ 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 CH₄ 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 CH₄ exchange rates were low in the present study, ranging between -0.10 and 0.51 g C m⁻² yr⁻¹ at the arable plots and between -0.11 and -0.02 g C m⁻² yr⁻¹ 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 CH₄ exchange was only of minor importance, considering total GHG emissions.

In line with our hypotheses examined in **study I** and **study II** significantly higher N₂O emissions were found at the C_{high} sites compared to the C_{medium} sites, regardless of land-use type and management practices. Likewise, significantly higher NO₃⁻ 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 N₂O 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 N₂O production in soils is often uncertain since aerobic and anaerobic microsites occur within close proximity and thus different biotic and abiotic N₂O 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 N₂O emissions from the grasslands investigated. However, the **second study** demonstrated that NH₃ volatilization is quantitatively the most important N loss from surface application (Flessa and Beese, 2000), particularly when slurries contain high concentrations of NH₄⁺ and had high pH values. In line with our expectations, the **second study** revealed that the application of biogas digestate significantly enhances annual N₂O emissions as well as biomass production and NUE compared to the application of cattle slurry. Calculated harvest-related N₂O emissions averaged 0.20 kg N₂O-N t⁻¹ DM⁻¹ at the biogas treatments compared to 0.17 kg N₂O-N t⁻¹ DM⁻¹ at the cattle slurry treatments, demonstrating that the higher grass yield could not compensate for the significantly higher N₂O emissions at these treatments. However, contrary to our hypothesis, the significantly higher N₂O 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 NH₄⁺-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 N₂O 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 N₂O 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_{ECO} 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, N₂O 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_{min} 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 N₂O 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_{2eq.} m⁻² yr⁻¹ at the arable land and between 5884 and 7095 g CO_{2eq.} m⁻² yr⁻¹ 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_{2eq.} m⁻² yr⁻¹ with a 95% confidence interval of 2769 to 4292 g CO_{2eq.} m⁻² yr⁻¹, whereas the GWP of deep drained nutrient-rich grassland averaged 2662 g CO_{2eq.} m⁻² yr⁻¹ with a 95% confidence interval of 2070 to 3266 g CO_{2eq.} m⁻² yr⁻¹. 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 CO₂ exchange rates ranging from 800 to 11500 g CO₂ m⁻² yr⁻¹ for farmed organic soils, demonstrating the high bandwidth of measured CO₂-balances. Nevertheless, the question arises, to what extent model as well as measurement uncertainties triggered the magnitude of estimated GWPs. As mentioned above, N₂O and CH₄ contributed only negligible to total GWP but we cannot rule out that we may have missed at least high N₂O 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_{Eco} 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, NO_3^- availability is considered as the main driver of N_2O emissions from drained histosols (Klemetsson et al., 2005), but despite of significant differences in NNM rates and NO_3^- contents in the soil of the three sites, no differences were found regarding field N_2O fluxes. Generally, annual N_2O 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 N_2O 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 N_2O emissions occur due to accelerated N turnover and

transformation processes. However, in contrast to the field observations significant differences in the N_2O 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 N_2O 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 N_{min} contents were solely dominated by NH_4^+ at this site. In line with this observation, N_2O and N_2 flux pattern observed in the incubation experiment demonstrated that denitrification was limited by NO_3^- availability, confirming our hypothesis that NO_3^- limitation in permanently waterlogged peat soils results in negligible N_2O and N_2 losses.

In contrast, the very high NNM rates at the drained sites revealed that NH_4^+ produced becomes immediately oxidized to NO_3^- . Nevertheless, no relationship was found between field N_2O fluxes and NO_3^- availability, and less than 0.2% of nitrified N was emitted as N_2O -N at these sites. However, the **third study** gave evidence that field N_2O 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 N_2O 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°C to $115.2 \pm 22.6 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ at 15°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°C , whereas at 70% WFPS, N_2O fluxes increase from $19.1 \pm 3.1 \mu\text{g N m}^{-2} \text{ h}^{-1}$ at 0°C to $132.4 \pm 31.7 \mu\text{g N m}^{-2} \text{ h}^{-1}$ at 25°C . Furthermore, considering soil core samples from the drained site separately, it was found that N_2O 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 N_2O 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 N_2O emissions of total N release from denitrification indicated that in the present alder stand losses of N_2O are only of minor importance compared to N_2 losses at water saturated conditions. Moreover, the observed decline of N_2O fluxes at water-saturated conditions and 25°C with simultaneously exponentially increasing or at least constant N_2 fluxes supports our hypothesis that N_2O release is displaced by 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 N₂O emissions measured in the incubation experiment at 70% WFPS compared to the field fluxes revealed the potential of high N₂O emissions under changing soil physical conditions. This assumption was confirmed by continued N₂O gas flux measurements for the time period 2012–2013 at these sites (unpublished data), where annual N₂O 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 N₂O emissions, despite of distinctly different C and N contents, observed at the drained alder sites contrasts the findings of **study I** and **II**. Enhanced N₂O emissions at the C_{org} high sites in study **I** and **II** are related to more favorable conditions for denitrification. However, high net nitrification rates in combination with low N₂O and N₂ 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 O₂ diffusion into deeper soil layers of the alder forest compared to the intensively used grassland and cropland.

Besides N₂O, particularly CO₂ 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 CH₄ emissions are responsible for the climate impact. Unpublished data of determined CH₄ fluxes from the alder forest investigated, revealed annual CH₄ 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 CO₂ 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 CO₂ 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

GWP₁₀₀ values indicated that both sites slightly contributed to global warming with GWP₁₀₀ values of about 72–76 g CO₂-C_{equ.} m⁻² yr⁻¹ for the undrained site and about 98–127 g CO₂-C_{equ.} m⁻² yr⁻¹ for the drained sites. The estimated GWP₁₀₀ 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 N₂O emissions increase with increasing C_{org} content, whereas CH₄ exchanges were of only minor importance at the intensively drained and cropped organic soils. However, CO₂ 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_{org}. However, further investigations are needed to define the lower boundary for C_{org} limits.

Furthermore, the effects of biogas digestate application on short-term N₂O and CH₄ 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 N₂O 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 N₂O emissions at the biogas digestate treatments. Generally, the apparent NUE_{min} indicated that a frequent but low dosage application of fertilizer and quick N uptake by plants avoid conditions favorable for high N₂O emissions. However, the observed linear increase in cumulative N₂O emissions with increasing NH₄⁺ fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C_{org} rich grasslands.

In contrast to the intensively cropped drained organic soils, different SOC and N contents did not affect N₂O 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 N₂O 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 N₂ fluxes. Nevertheless, the laboratory study gave evidence that changing soil physical conditions can result in enhanced N₂O emissions at the drained alder sites. Continuous N₂O measurements in two subsequent years confirmed the findings from the incubation experiment, but it has to be pointed out that N₂O 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

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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
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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 (CO₂) and nitrous oxide (N₂O). 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_{medium}) as well as on
23 a sapric Histosol (named C_{high}). The two soil types significantly differed in their SOC
24 contents in the topsoil (C_{medium}: 9.4–10.9% SOC; C_{high}: 16.1–17.2% SOC). We
25 determined GHG fluxes (CO₂, N₂O and methane (CH₄)) over a period of 2 years. The
26 daily and annual net ecosystem exchange (NEE) of CO₂ was determined with the closed
27 dynamic chamber technique and by modeling the ecosystem respiration (R_{ECO}) and the
28 gross primary production (GPP). N₂O and CH₄ were determined by the close chamber
29 technique. Estimated NEE of CO₂ significantly differed between the two land-use types
30 with lower NEE values (–6 to 1707 g CO₂-C m⁻² yr⁻¹) at the arable sites and higher
31 values (1354 to 1823 g CO₂-C m⁻² yr⁻¹) at the grassland sites. No effect on NEE was
32 found regarding the SOC content. Significantly higher annual N₂O exchange rates were
33 observed at the arable sites (0.23–0.86 g N m⁻² yr⁻¹) compared to the grassland sites

34 (0.12–0.31 g N m⁻² yr⁻¹). Furthermore, N₂O fluxes from the C_{high} sites significantly
35 exceeded those of the C_{medium} sites. CH₄ fluxes were found to be close to zero at all plots.
36 Estimated global warming potential, calculated for a time horizon of 100 years (GWP₁₀₀)
37 revealed a very high release of GHGs from all plots ranging from 1837 to 7095 g CO₂ eq.
38 m⁻² yr⁻¹. 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 (CO₂) and as a source
49 for methane (CH₄) (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 CO₂ and nitrous oxide (N₂O) 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 (CO₂, CH₄ and N₂O) act as
56 climatic relevant greenhouse gases (IPCC, 2007). Additionally, N₂O 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 CO₂–C ha⁻¹ yr⁻¹ and 2 to 38 kg N₂O–N ha⁻¹ yr⁻¹ (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 ≥ 10 cm thickness of the soil/peat layer and a C_{org} content of $\geq 12\%$ in case of a soil thickness ≤ 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 CO₂ 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 CO₂ 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 CO₂ 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_{org} 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⁻¹ yr⁻¹ 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_{medium}) or as sapric Histosol (named C_{high}) (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_{air}) and humidity at 20 cm above soil surface, soil temperatures
166 at the depth –2, –5 and –10 cm (ST_{2, 5, 10}) 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_{tot}) and total nitrogen (N_{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_{tot} and organic carbon (C_{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 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 N_2O and 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). N₂O and CH₄ 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 N₂O or CH₄ fluxes, fluxes were
210 also accepted if the coefficient of determination was ≥ 0.90 and the regression slope
211 was between -1 and 1 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, N₂O and CH₄ 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 CO₂ flux measurements we used the closed dynamic manual chamber system which
219 was described in detail by Drösler (2005) and Elsgaard et al. (2012). CO₂ 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 N₂O and CH₄ 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_{ECO}) and the net ecosystem exchange (NEE). In total up to 55 NEE
228 measurements and 33 R_{ECO} measurements were conducted per measurement day and
229 plot (Table S1–S8 in the Supplement). As for N₂O and CH₄ 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 CO₂ 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 CO₂ 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). CO₂ 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_{ECO}) 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_{ECO} fluxes a minimum interval of 60 s was applied.

251

252 **6. Modeling of CO₂ net ecosystem exchange**

253 The net ecosystem exchange (NEE) of CO₂ is defined as the product of the gross
 254 primary production (GPP) and the ecosystem respiration (R_{ECO}) (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 CO₂ to the atmosphere (Elsgaard et al., 2012).

260

261 **7. Modeling of ecosystem respiration**

262 The measured R_{ECO} fluxes are the sum of autotrophic (R_a) and heterotrophic (R_h)
 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_{ECO} 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 CO₂-C m⁻² h⁻¹]

269 R_{ref} respiration at the reference temperature [mg CO₂-C m⁻² h⁻¹]

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	α	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		

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 α 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.) α
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 , α , 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. α 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 N₂O were summed according to Beetz et al (2013).
342 For the conversion of CH₄ and N₂O to CO₂ 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_{ECO} and NEE as well as for
352 annual yields and N_{min} 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 CO₂ 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_{org} contents, bulk density, yields) or the non
361 parametric Mann-Whitney U-test (for N_{min}). Due to temporal pseudoreplication of time
362 series data (N₂O, CH₄ field measurements) we applied linear mixed effects models
363 (Crawley 2007; Hahn-Schöfl et al., 2011; Eickenscheidt et al., 2014a and 2014b). For
364 N₂O 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 N₂O 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). CH₄ fluxes did not satisfy
373 the necessary requirements for the linear mixed effects model therefore CH₄ 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 ± 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°C with an annual mean of 8.6°C at both grassland sites in 2011. Soil temperature
382 in -2 cm soil depth averaged 10.3°C at the GC_{medium} site and 10.5°C at the GC_{high} site
383 in 2011. At the arable land air temperature in 20 cm height ranged from -15.0 to 39.5°C
384 in 2010 and 2011, with an annual mean of 8.8°C AC_{medium} and 8.7°C AC_{high} in 2011. Soil
385 temperature in -2 cm soil depth averaged 10.1°C at both arable land sites in 2011.
386 Longer periods of snow cover occurred in the period 1st of January to 12th of March 2010,
387 28th of November 2010 to 10th of January 2011 and from 24th of January to 5th 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 C_{high} sites were
392 significantly higher (all $P < 0.001$) compared to the C_{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 AC_{high} sites for the period from
396 1st to 17th 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 N_{min} contents of the soils ranged from 1 to 178 mg N kg⁻¹ at the arable sites
405 and from 2 to 115 mg N kg⁻¹ at the grassland sites (Fig. 2, Fig 3). In both years, the N_{min}
406 contents at the grassland sites significantly ($P < 0.001$) exceeded those from the arable
407 site (Fig. 3). Furthermore the N_{min} contents of the C_{high} sites were significantly ($P < 0.01$)

408 higher compared to the C_{medium} sites (Fig. 3), but this was not valid considering the arable
409 land separately. Slightly higher N_{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_{min} was mainly dominated by NO_3^- , whereas
412 NH_4^+ was only of minor importance. However, at the AC_{high} sites the proportion of NO_3^-
413 in the soil depth 0–10 cm was lower (approximately 80%) compared to the AC_{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 ± 0.5 to 10.2 ± 1.6 t DM ha⁻¹ yr⁻¹ at the
419 arable land and from 6.2 ± 0.7 to 13.1 ± 2.9 t DM ha⁻¹ yr⁻¹ 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_{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. CO₂ 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_{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_{air} , and only 12% on ST_2 , whereas at the grassland sites 54% of the
439 models based on T_{air} and 39% on ST_2 . Model evaluation statistics from observed R_{ECO}
440 versus modeled R_{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 $A2C_{medium}$ (oat) and $G1C_{medium}$ 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 $A2C_{high}$ (maize) plot and the $G2C_{high}$ plot, respectively (Fig. 4 and 5). At the grassland
450 sites, annual sums of modeled R_{ECO} ranged from 3521 ± 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 ± 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 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_{medium}) and up to -20 g
458 $\text{CO}_2\text{-C m}^{-2} \text{ d}^{-1}$ for the grassland ($G2C_{high}$), 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 $G2C_{high}$ plot (Fig. 4 and 5). At the grassland sites annual sums of GPP
461 ranged between -2093 ± 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 ± 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 ± 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 ± 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.N₂O and CH₄ fluxes

477 Nitrous oxide emissions were generally low at all plots (Fig 7). N₂O fluxes rarely
478 exceeded 50 µg N m⁻² h⁻¹. However, single N₂O peaks with maximum flux rates of up
479 to 2832 µg N m⁻² h⁻¹ were detected at the 3rd June at both maize plots as well as at the
480 6th of September at both oat plots with maximum flux rates of up to 289 µg N m⁻² h⁻¹. At
481 the grassland sites, highest N₂O fluxes of up to 992 µg N m⁻² h⁻¹ were found immediately
482 after fertilizer application (see Eickenscheidt et al., 2014b). In general, N₂O fluxes from
483 the arable sites were significantly ($P < 0.01$) higher compared to the grassland sites (Fig.
484 8a). Furthermore, N₂O fluxes from the C_{high} sites significantly ($P < 0.05$) exceeded N₂O
485 fluxes from the C_{medium} sites, but this was not valid considering the arable land separately.
486 Significant differences within the land-use types, regarding N₂O flux rates, were only
487 found between the grassland plots, where the application of biogas digestate
488 significantly ($P < 0.01$) enhanced the N₂O fluxes compared to the application of cattle
489 slurry (see Eickenscheidt et al., 2014b). At the arable land distinctly different N₂O 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 N₂O emissions at the maize plots
492 (Table 3, Fig 8a). N₂O peaks accounted for 75% and 87% of the annual N₂O balances
493 at the maize plots, whereas at the oat plots peaks account for 63% and 54% of the
494 annual N₂O sums (at C_{medium} and C_{high}, respectively). Annual cumulative N₂O emissions
495 ranged from 0.12 ± 0.01 g N m⁻² yr⁻¹ (G1C_{medium}) to 0.86 ± 0.21 g N m⁻² yr⁻¹ (A2C_{high})
496 (Table 3).

497 Most of the time, all sites showed a weak uptake of CH₄ or zero fluxes. CH₄ peaks up to
498 173 µg C m⁻² h⁻¹ were occasionally found immediately after fertilization at the G1 sites
499 (see Eickenscheidt et al., 2014b). Moreover, a high CH₄ peak event of up to 2177 µg C
500 m⁻² h⁻¹ occurred on the 14th of July 2011 at the oat plots. Generally, CH₄ fluxes of the
501 arable sites significantly ($P < 0.01$) exceeded CH₄ fluxes of the grassland sites, whereas
502 no differences were found between the two soil types investigated (Fig 7, and 8b).
503 Significantly different CH₄ 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, CH₄ emissions of the oat plots significantly ($P < 0.05$) exceeded those
506 of the maize plots. The observed weak CH₄ emissions or uptakes amounted to
507 cumulative annual CH₄ exchange rates ranging between -0.11 ± 0.05 g C m⁻² yr⁻¹
508 (G2C_{medium}) and 0.51 ± 0.17 g C m⁻² yr⁻¹ (A1C_{medium}) (Table 3). However, as previously
509 mentioned for N₂O, the single CH₄ peak event observed at the arable sites entirely

510 controls the cumulative sum of CH₄ and turns the plots from a sink into a source of CH₄.

511

512 **18.NECB and GWP**

513 Including the C export from harvested phytomass, C import from fertilization and CH₄

514 exchange to NEE, calculated NECB ranged from 451 ± 617 to 1894 ± 872 g C m⁻² yr⁻¹.

515 Estimated GWP's ranged from 1837 ± 2293 to 7095 ± 3243 g CO_{2eq.} m⁻² yr⁻¹, revealing

516 a very high release of greenhouse gases from all plots (Table 6). However, CO₂

517 dominated the GWP of all plot to nearly 100% (range between 97–99% and for maize

518 86–90%), whereas the contribution of N₂O and CH₄ were almost negligible, with

519 exception of the maize plots.

520

521 **19.Discussion**

522 **20.Magnitude of GHG fluxes**

523 The observed annual CO₂ emissions were in the upper range or partly higher than CO₂

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 CO₂ release of the C_{medium} and C_{high} sites were

530 found in the current study, and no information about CO₂ fluxes of comparable soils to

531 those of the C_{medium} sites were available in the literature. Observed CO₂ emissions from

532 the arable land were in the range or partly doubled (4.51 – 12.04 t CO₂-C ha yr⁻¹) the

533 IPCC default emission factor from the Tier 1 approach for drained boreal and temperate

534 arable lands (7.9 t CO₂-C ha yr⁻¹; IPCC, 2014) whereas more than three times higher

535 CO₂ emissions were observed at the grassland sites (15.81 – 18.94 t CO₂-C ha yr⁻¹)

536 compared to the IPCC default emission factor for deep-drained temperate grasslands

537 (6.1 t CO₂-C ha yr⁻¹; IPCC, 2014). However, comparison of CO₂ 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⁻¹

540 yr⁻¹, with a five year mean of 9.06 ± 6.64 t C ha⁻¹ yr⁻¹. 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 CO₂ exchange rates ranging from 2.2 to 31.3 t C ha⁻¹ yr⁻¹

544 for farmed organic soils, demonstrating the high bandwidth of measured CO₂-balances.
545 Observed cumulative annual N₂O 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 N₂O-N ha⁻¹ yr⁻¹; IPCC. 2014) and for temperate deep drained, nutrient rich
548 grassland (8.2 kg N₂O-N ha⁻¹ yr⁻¹; IPCC. 2014). In line with this, several other authors
549 reported much higher N₂O emissions from organic soils ranging from 0 to 61 kg N₂O-N
550 ha⁻¹ yr⁻¹ 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 N₂O-N ha⁻¹ yr⁻¹ 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 CH₄ 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 CH₄ 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 CH₄ 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 CH₄
563 ha⁻¹ yr⁻¹; IPCC, 2014). A distinctly higher emission factor however is given by the IPCC
564 for a temperate deep-drained, nutrient-rich grassland (16 kg CH₄ ha⁻¹ yr⁻¹; 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 CO₂ exchange rates.
569 Firstly, the R_{Eco} 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 CO₂ emissions, which we may have missed. Additionally, it can be
575 assumed that after harvesting at the grassland sites, R_{Eco} 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 CO₂ 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_{ECO} and NEE for both years (R_{ECO}
588 only in 2010). Thus, modeled R_{ECO} 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 N₂O 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 N₂O
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. N₂O 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 N₂O and CH₄ 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 N₂O, 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 CO₂ fluxes, the current findings are however in line with investigations from
617 Leiber-Sauheitl et al. (2014), who reported that CO₂ 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 CO₂ 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⁻²), probably explaining the equal CO₂ loss rates from this
630 land-use type. Temperature and soil moisture are considered to be the primary
631 regulators for CO₂ 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_{high} and C_{medium} sites mainly
636 according to the GW oscillation. It is well known that the water level height has a strong
637 influence on CO₂ 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 CO₂ 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 CO₂ and CH₄ 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 CO₂, CH₄ 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_{medium} and C_{high}
666 sites. It is known that the availability and quality of organic substrates influences the
667 amount of produced CH₄. Nevertheless, several studies indicate that high CH₄ 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 CO₂ and CH₄ fluxes, N₂O fluxes from the C_{high} sites significantly exceeded
672 N₂O fluxes from the C_{medium} sites. This can probably be attributed to the more favorable
673 soil conditions for denitrification, supported by higher N_{min} contents and higher
674 groundwater levels at these sites (Eickenscheidt et al., 2014b). In both years N_{min} was
675 mainly dominated by NO₃⁻, 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 N₂O production. In general,
678 N₂O 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⁻¹ and 9.05 t DM ha⁻¹ 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_{ECO} significantly differed between the two land-use
706 types with distinctly higher R_{ECO} values at the grassland sites. As mentioned above, R_{ECO}
707 is strongly controlled by temperature since it stimulates both R_a and R_h, as can be seen
708 in the pronounced seasonality of R_{ECO}. From the model fits it can be concluded that the
709 more frequent model adaptation with T_{air} (88%) reveals a higher share of R_a at the arable
710 site compared to the grassland sites. At the later, approximately 40% of the R_{ECO} models
711 based on ST₂, perhaps demonstrating a more balanced ratio of R_a and R_h. Nevertheless,
712 the proportion of the different respiration compartments of R_{ECO} 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 CH₄ compared to permanent grasslands. This
749 contrasted our results, where the CH₄ fluxes from the arable plots significantly exceeded
750 CH₄ fluxes from the grassland plots. However, all measured CH₄ fluxes were very low
751 and CH₄ 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 N₂O fluxes at the
757 grassland sites, where the application of biogas digestate led to significantly higher N₂O
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 N₂O fluxes from grasslands, whereas
761 no significant relationship between N fertilization and N₂O fluxes from arable lands were
762 found. Nevertheless, N₂O 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 N₂O 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 N₂O 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_{min} 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⁻¹ yr⁻¹ (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⁻¹ yr⁻¹. 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 N₂ fixing
783 leguminoses further increase the soil N_{min} 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_{org} 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_{org} 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_{org} 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_{org} 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_{org}. 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_{org} 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

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863

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Table 1 Physical and chemical properties of the investigated plots.

Site	Soil type	Organic carbon [%]		C/N ratio 0–20 cm	pH (CaCl ₂) 0–20 cm	Bulk density [g cm ⁻³]		Mean GW level above surface [cm]	
		0–10 cm	10–20 cm			0–10 cm	10–20 cm	2010	2011
A1C _{medium}	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 _{high}	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 _{medium}	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 _{high}	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 _{medium}	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 _{high}	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 _{medium}	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 _{high}	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 ³ ha ⁻¹]
2010-07-06	187	grubbing & hilling	–	–
2010-08-20	232	–	–	harvesting
2010-08-22	234	–	harvesting	–
2010-08-25	237	–	–	manuring [20 m ³ ha ⁻¹]
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 ³ ha ⁻¹]
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 ³ ha ⁻¹]
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 ⁻² yr ⁻¹]	GPP [g C m ⁻² yr ⁻¹]	NEE [g C m ⁻² yr ⁻¹]	Fertilizer input* [g C m ⁻² yr ⁻¹]	Crop yield* [g C m ⁻² yr ⁻¹]	CH_4^* [g C m ⁻² yr ⁻¹]	N_2O^* [g N m ⁻² yr ⁻¹]
A1C _{medium} / 10	2473 ± 272	-1454 ± 114	1019 ± 386	-	193 ± 53	-	-
A1C _{medium} / 11	2992 ± 230	-1862 ± 126	1130 ± 356	-	74 ± 8	0.51 ± 0.17	0.27 ± 0.01
A1C _{high} / 10	2012 ± 284	-873 ± 110	1139 ± 394	-	58 ± 23	-	-
A1C _{high} / 11	2117 ± 123	-1302 ± 77	815 ± 200	-	135 ± 7	0.22 ± 0.04	0.23 ± 0.05
A2C _{medium} / 10	2704 ± 544	-1449 ± 103	1255 ± 647	-	227 ± 27	-	-
A2C _{medium} / 11	2354 ± 309	-2360 ± 237	-6 ± 546	-	457 ± 71	-0.03 ± 0.05	0.39 ± 0.06
A2C _{high} / 10	2907 ± 482	-1200 ± 137	1707 ± 619	-	145 ± 19	-	-
A2C _{high} / 11	2538 ± 329	-2188 ± 253	350 ± 582	-	330 ± 79	-0.10 ± 0.07	0.86 ± 0.21
G1C _{medium} / 10	3954 ± 671	-2131 ± 180	1823 ± 851	126	297 ± 32	-	-
G1C _{medium} / 11	4099 ± 300	-2414 ± 195	1685 ± 495	267	344 ± 63	-0.06 ± 0.09	0.12 ± 0.01
G1C _{high} / 10	3736 ± 491	-2152 ± 140	1584 ± 631	126	325 ± 41	-	-
G1C _{high} / 11	4026 ± 707	-2633 ± 138	1393 ± 845	267	455 ± 41	-0.07 ± 0.02	0.18 ± 0.02
G2C _{medium} / 10	3683 ± 453	-2131 ± 213	1552 ± 666	76	342 ± 39	-	-
G2C _{medium} / 11	4265 ± 379	-2880 ± 177	1385 ± 556	53	543 ± 58	-0.11 ± 0.05	0.19 ± 0.02
G2C _{high} / 10	3521 ± 1041	-2093 ± 152	1428 ± 1193	76	380 ± 43	-	-
G2C _{high} / 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 _{medium}	0.90	0.70	-7.93	0.55	0.98	0.95	-0.17	0.22
A1C _{high}	0.98	0.96	0.44	0.19	0.98	0.97	1.79	0.18
A2C _{medium}	0.93	0.81	-5.68	0.44	0.94	0.89	-0.23	0.33
A2C _{high}	0.96	0.92	2.60	0.29	0.98	0.96	0.00	0.20
G1C _{medium}	0.96	0.93	1.54	0.27	0.95	0.91	-2.40	0.31
G1C _{high}	0.89	0.75	-6.27	0.50	0.97	0.95	0.03	0.23
G2C _{medium}	0.93	0.86	0.80	0.37	0.98	0.96	0.06	0.19
G2C _{high}	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 _{medium}	0.94	0.87	-11.84	0.36	0.97	0.93	1.41	0.26
A1C _{high}	0.94	0.88	-7.94	0.35	0.98	0.96	-4.94	0.21
A2C _{medium}	0.85	0.72	3.03	0.53	0.96	0.92	-3.64	0.28
A2C _{high}	0.79	0.61	3.63	0.63	0.96	0.91	-9.56	0.29
G1C _{medium}	0.90	0.80	-10.98	0.45	0.92	0.84	-10.47	0.40
G1C _{high}	0.91	0.82	-12.07	0.43	0.94	0.88	-10.04	0.35
G2C _{medium}	0.95	0.89	-13.23	0.33	0.96	0.92	-5.43	0.28
G2C _{high}	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 ₁₀₀ NEE _{corrected} * [g CO ₂ eq. m ⁻² yr ⁻¹]	GWP ₁₀₀ CH ₄ [g CO ₂ eq. m ⁻² yr ⁻¹]	GWP ₁₀₀ N ₂ O [g CO ₂ eq. m ⁻² yr ⁻¹]	GWP ₁₀₀ balance [g CO ₂ eq. m ⁻² yr ⁻¹]
A1C _{medium} / 11	4419 ± 1336	16.96 ± 5.65	126.32 ± 4.68	4562 ± 1346
A1C _{high} / 11	3487 ± 760	7.32 ± 1.33	107.61 ± 23.39	3601 ± 785
A2C _{medium} / 11	1655 ± 2264	-1.00 ± 1.33	182.47 ± 28.07	1837 ± 2293
A2C _{high} / 11	2496 ± 2426	-3.33 ± 1.66	402.36 ± 98.25	2895 ± 2526
G1C _{medium} / 11	6467 ± 2048	-2.00 ± 2.99	56.14 ± 4.68	6521 ± 2056
G1C _{high} / 11	5802 ± 3252	-2.33 ± 0.67	84.21 ± 9.36	5884 ± 3262
G2C _{medium} / 11	6881 ± 2253	-3.66 ± 1.66	88.89 ± 9.36	6967 ± 2264
G2C _{high} / 11	6951 ± 3200	-0.67 ± 0.67	145.04 ± 42.11	7095 ± 3243

* Corrected for C export and C import

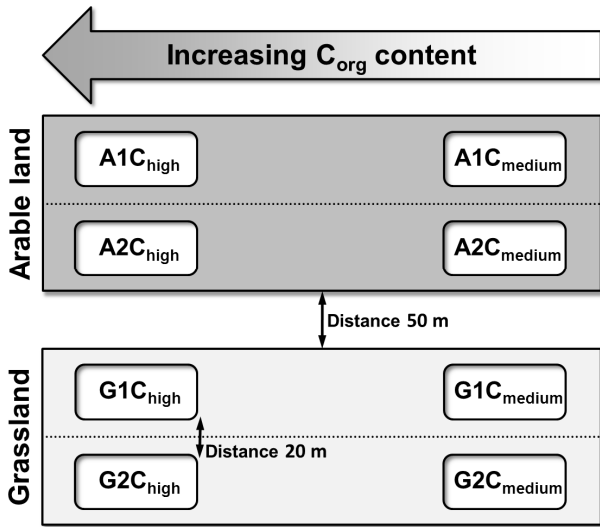


Fig. 1 Schema of the experimental design.

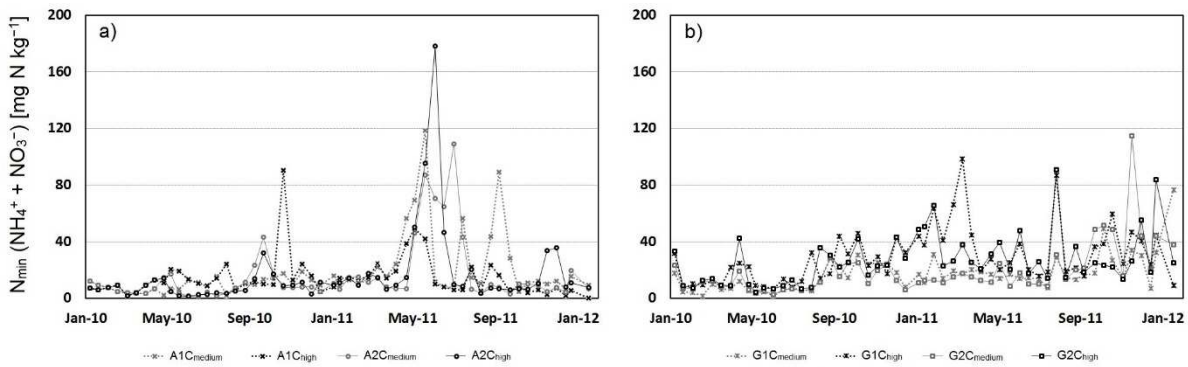


Fig. 2 Mineral nitrogen contents [mg N kg^{-1}] for the arable land a) and the grassland b) of the soil depth 0–10 cm for the years 2010 and 2011.

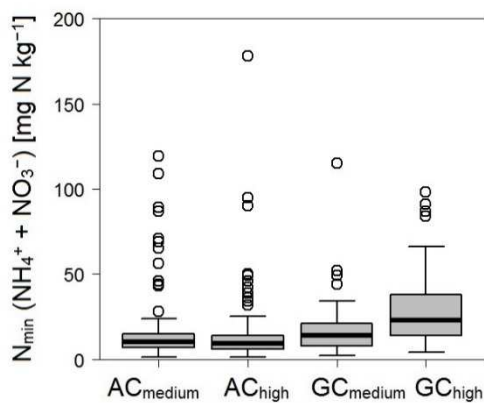


Fig. 3 Box plots of mineral nitrogen contents [mg N kg^{-1}] of the soil depth 0–10 cm (A = arable land, G = grassland).

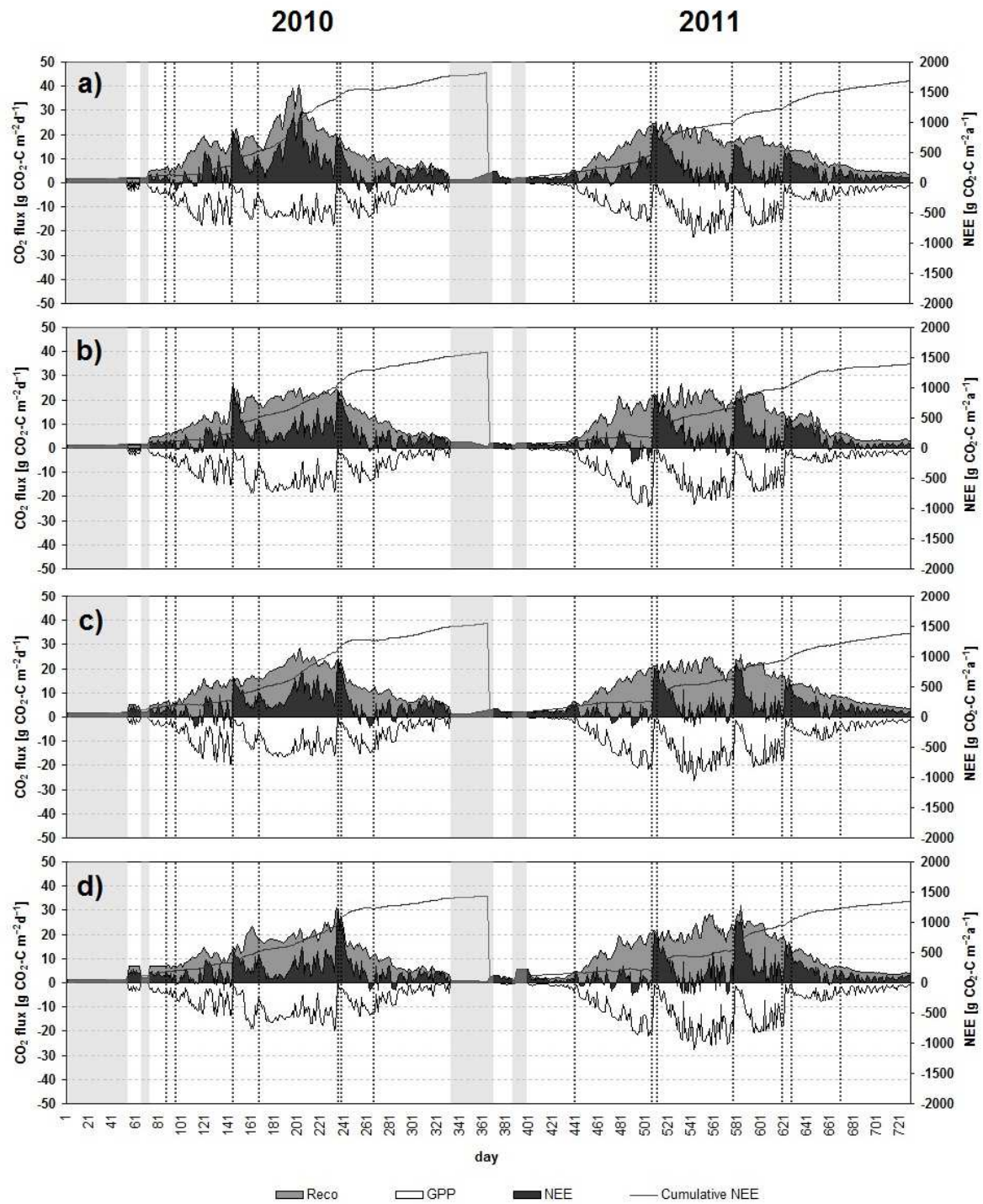


Fig. 4 Time series of modeled CO₂ fluxes [g CO₂-C m⁻² d⁻¹; g CO₂-C m⁻² yr⁻¹] for each site in 2010 and 2011; a) grassland, cattle slurry, C_{medium}; b) grassland cattle slurry, C_{high}; c) grassland biogas digestate C_{medium}; d) grassland, biogas digestate, C_{high}. Grey bars mark the period with snow cover. Dashed lines indicate management activities (see table 2).

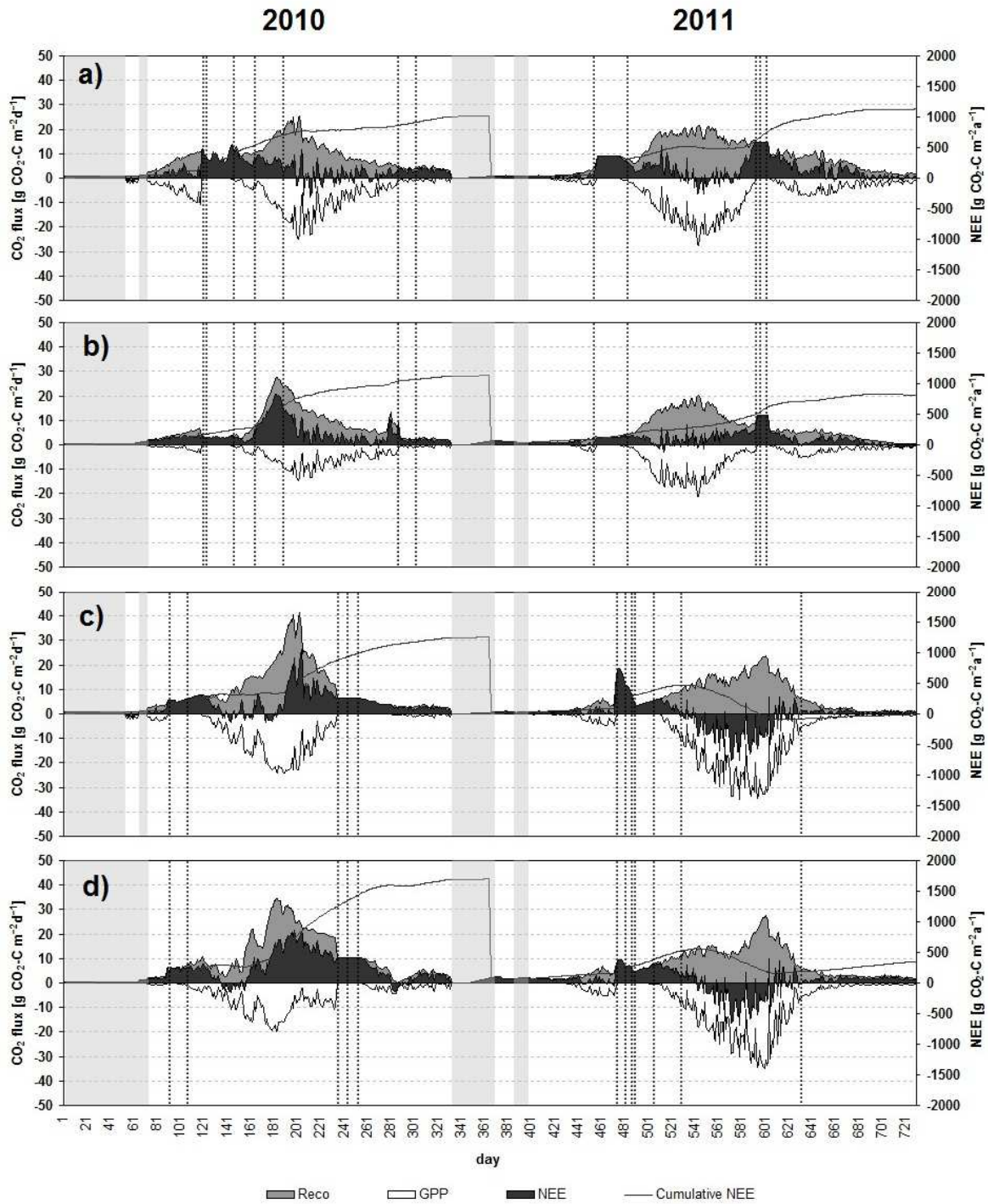


Fig. 5 Time series of modeled CO₂ fluxes [$\text{g CO}_2\text{-C m}^{-2} \text{d}^{-1}$; $\text{g CO}_2\text{-C m}^{-2} \text{yr}^{-1}$] for each site in 2010 and 2011; a) arable land, 2010 maize, 2011 oat, C_{medium} ; b) arable land, 2010 maize, 2011 oat, C_{high} ; c) arable land, 2010 oat, 2011 maize, C_{medium} ; d) arable land, 2010 oat, 2011 maize, C_{high} . Grey bars mark the period with snow cover. Dashed lines indicate management activities (see table 2).

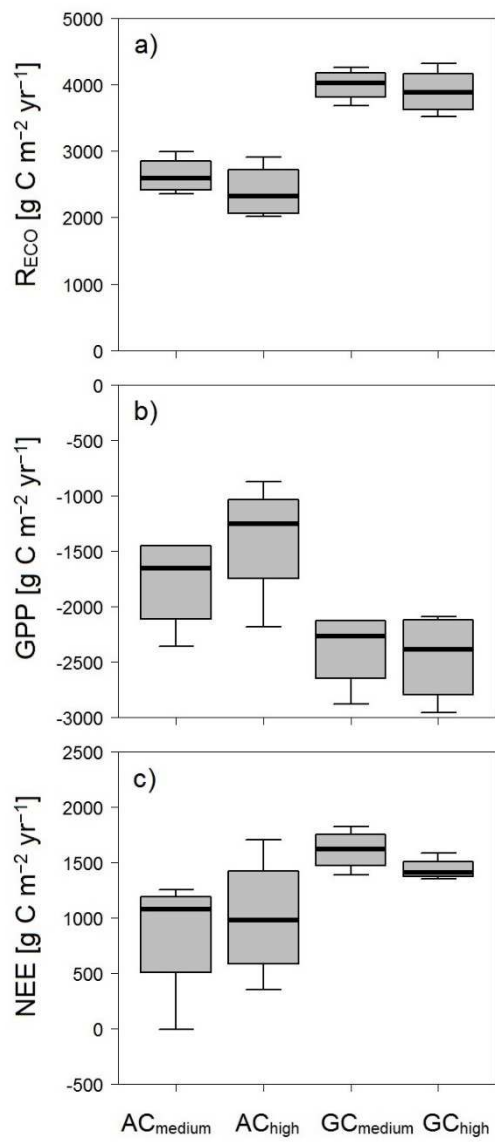


Fig. 6 Box plots of R_{Eco} (a), GPP (b) and NEE (c) for the two soil types and land-use types.

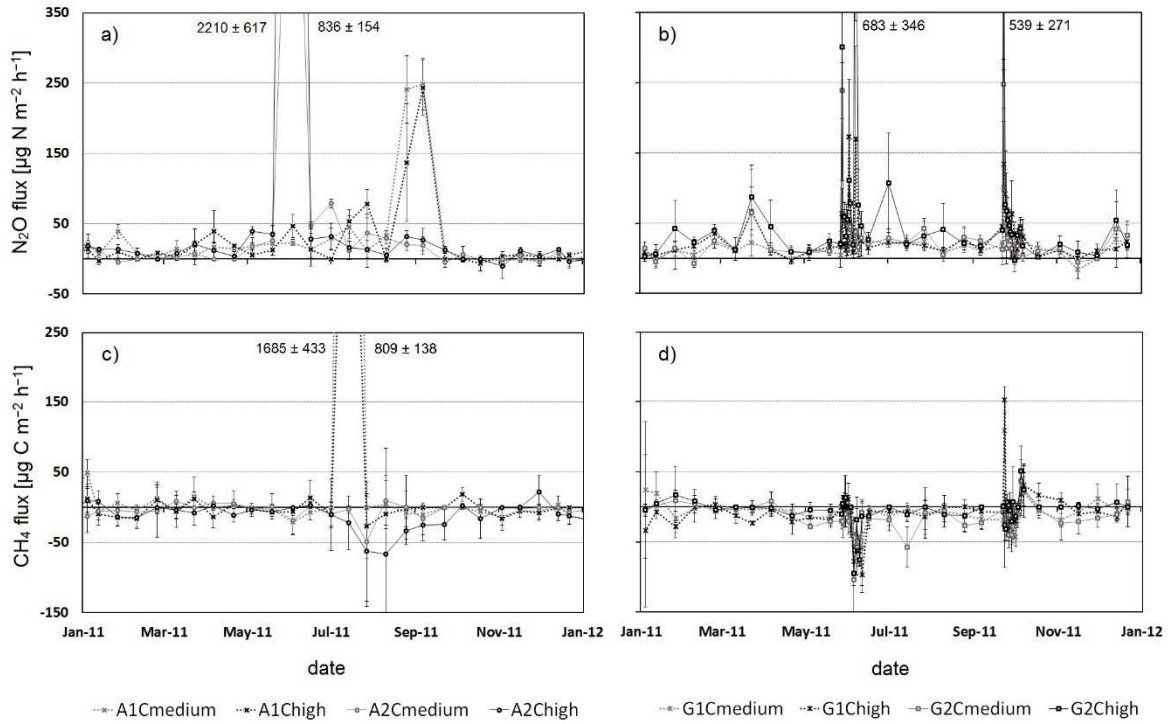


Fig. 7 Time series of measured N_2O fluxes (a, arable land; b, grassland) and CH_4 fluxes (c, arable land; d, grassland) for the year 2011.

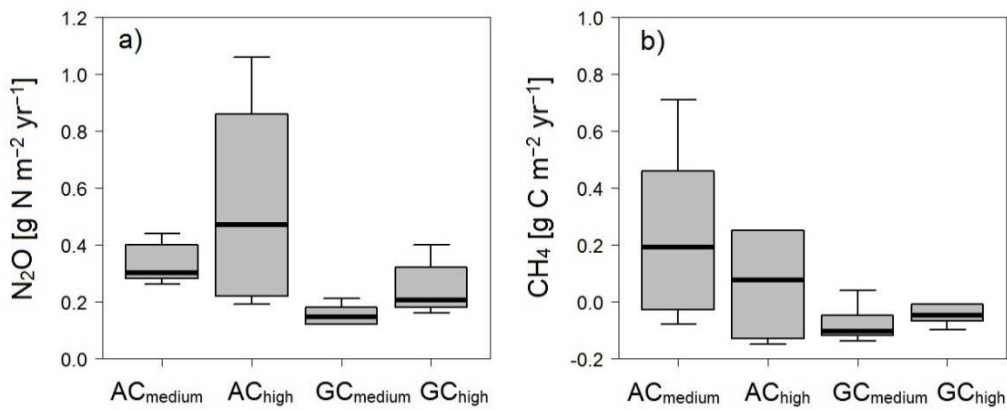


Fig. 8 Box plots of cumulative annual N_2O emissions (a), and cumulative annual CH_4 emissions for the two soil types and land-use types.

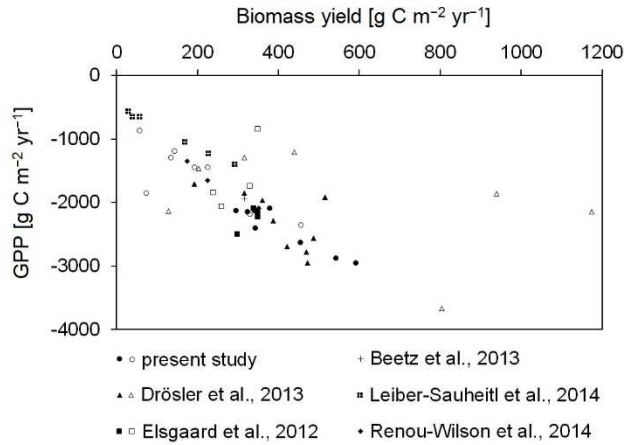


Fig. 9 Relationship of GPP and biomass export from temperate peatlands. Filled symbols represents grassland sites (intensive and extensive), unfilled symbols represents arable lands.

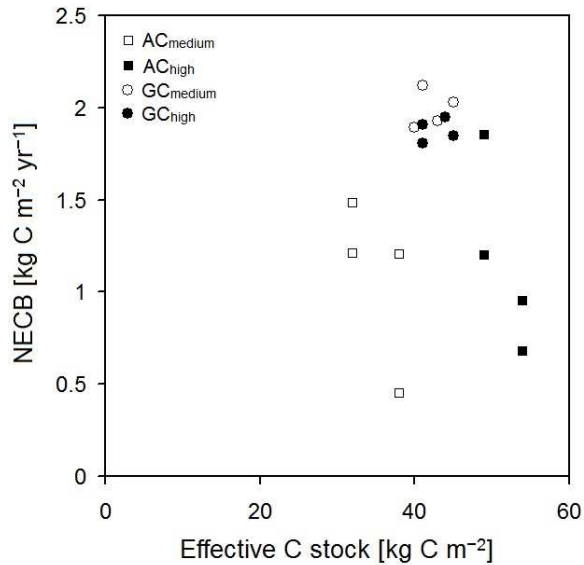


Fig. 10 NECB plotted against the effective C stock, which is defined as the fraction of aerated carbon in the soil profile (according to Leiber-Sauheitl et al., 2014) (calculated NECB did not include CH₄ losses).

SUPPLEMENT TO PUBLICATION I.

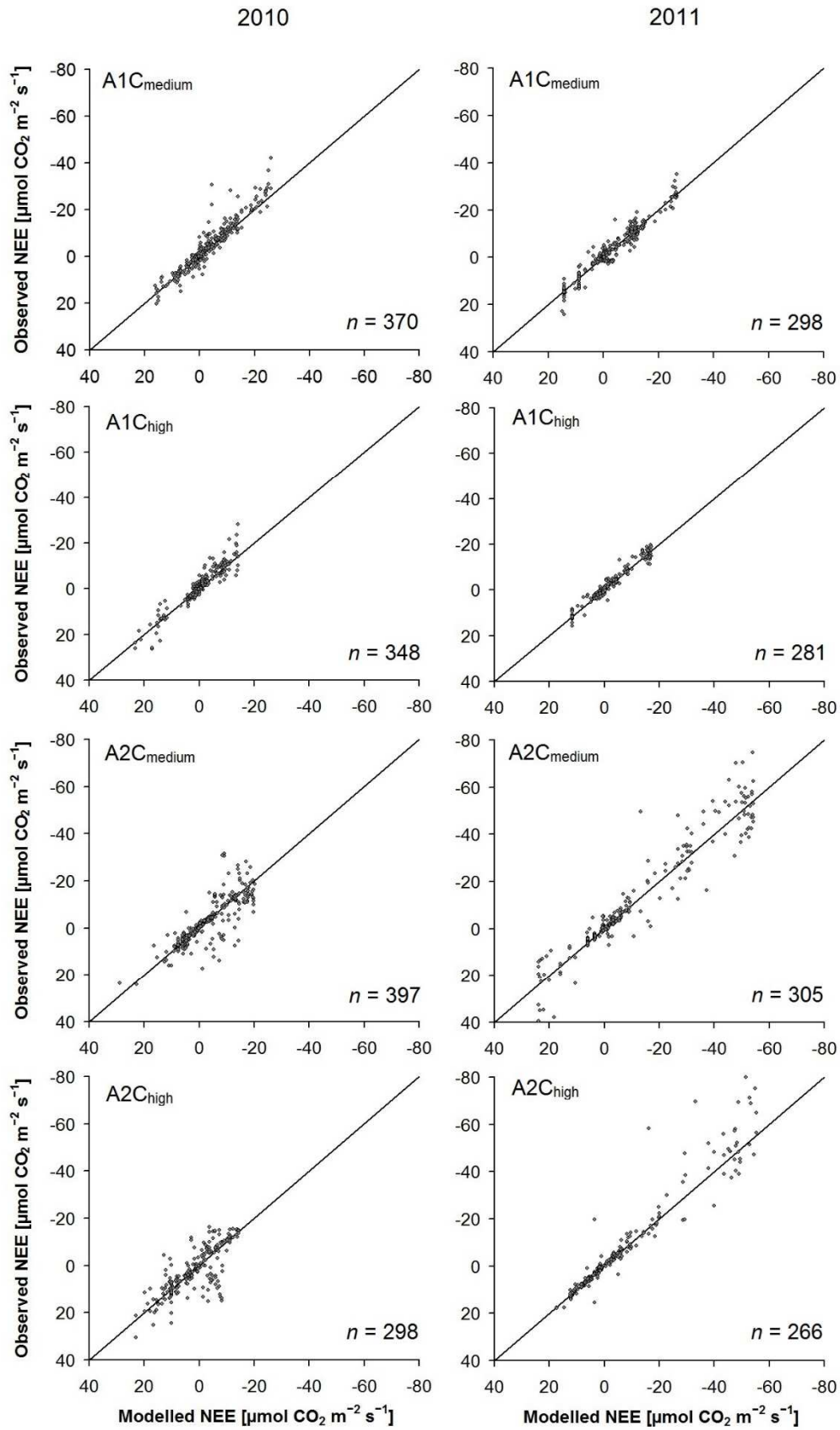


Fig. S1 Observed vs. modelled plots of NEE for the arable sites. Solid lines indicate the 1:1 line for a perfect fit.

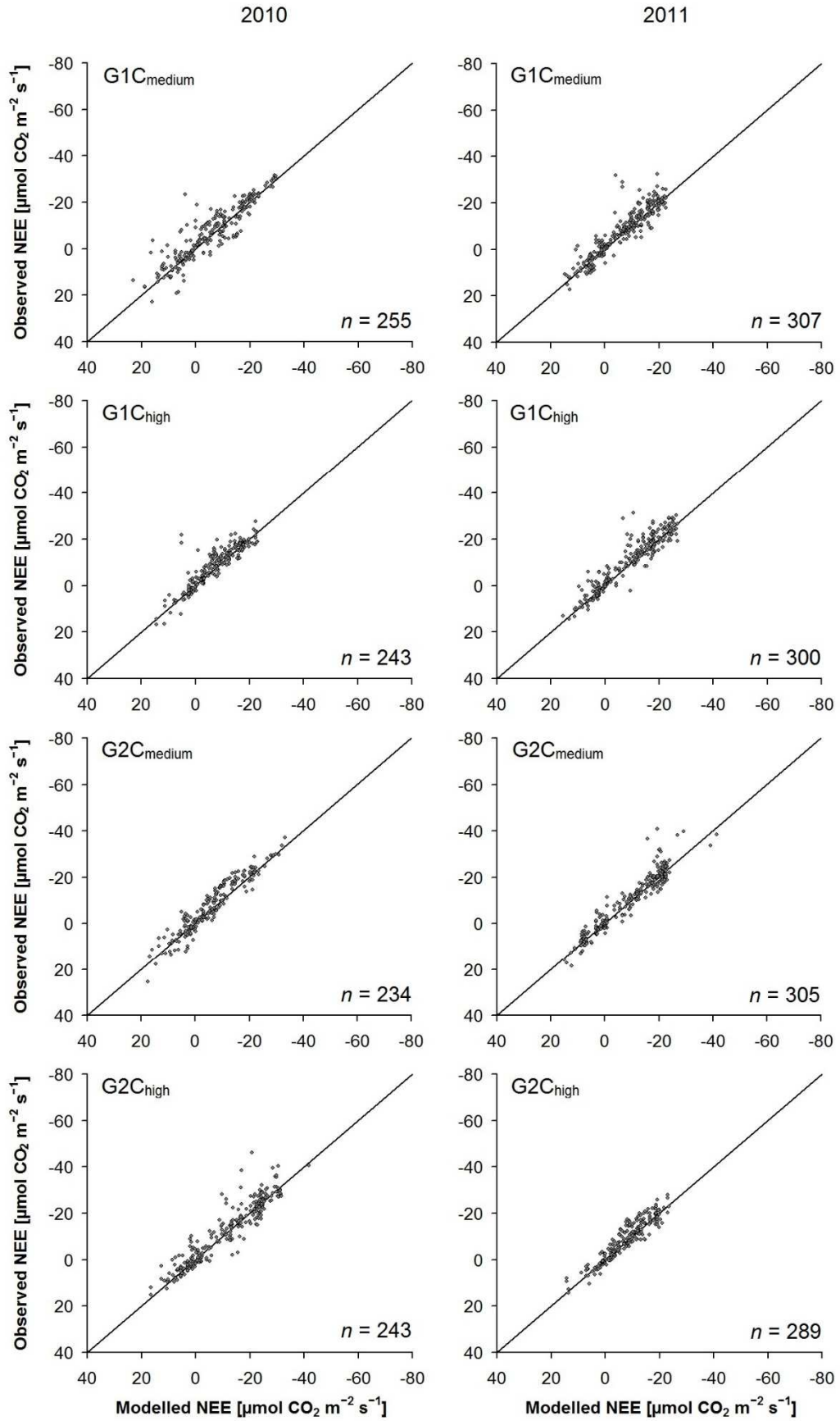


Fig. S2 Observed vs. modelled plots of NEE for the grassland sites. Solid lines indicate the 1:1 line for a perfect fit.

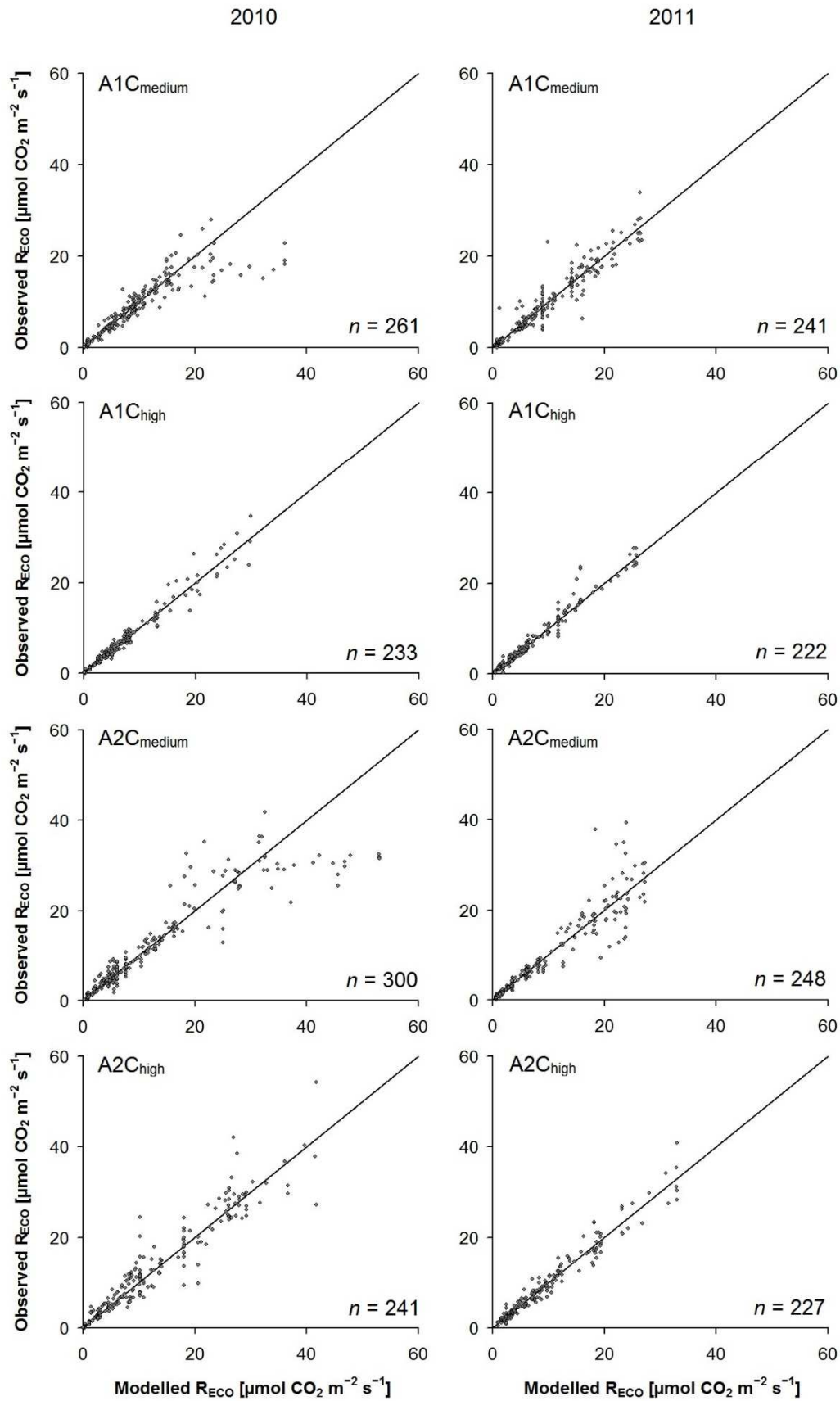


Fig. S3 Observed vs. modelled plots of R_{ECO} for the arable sites. Solid lines indicate the 1:1 line for a perfect fit.

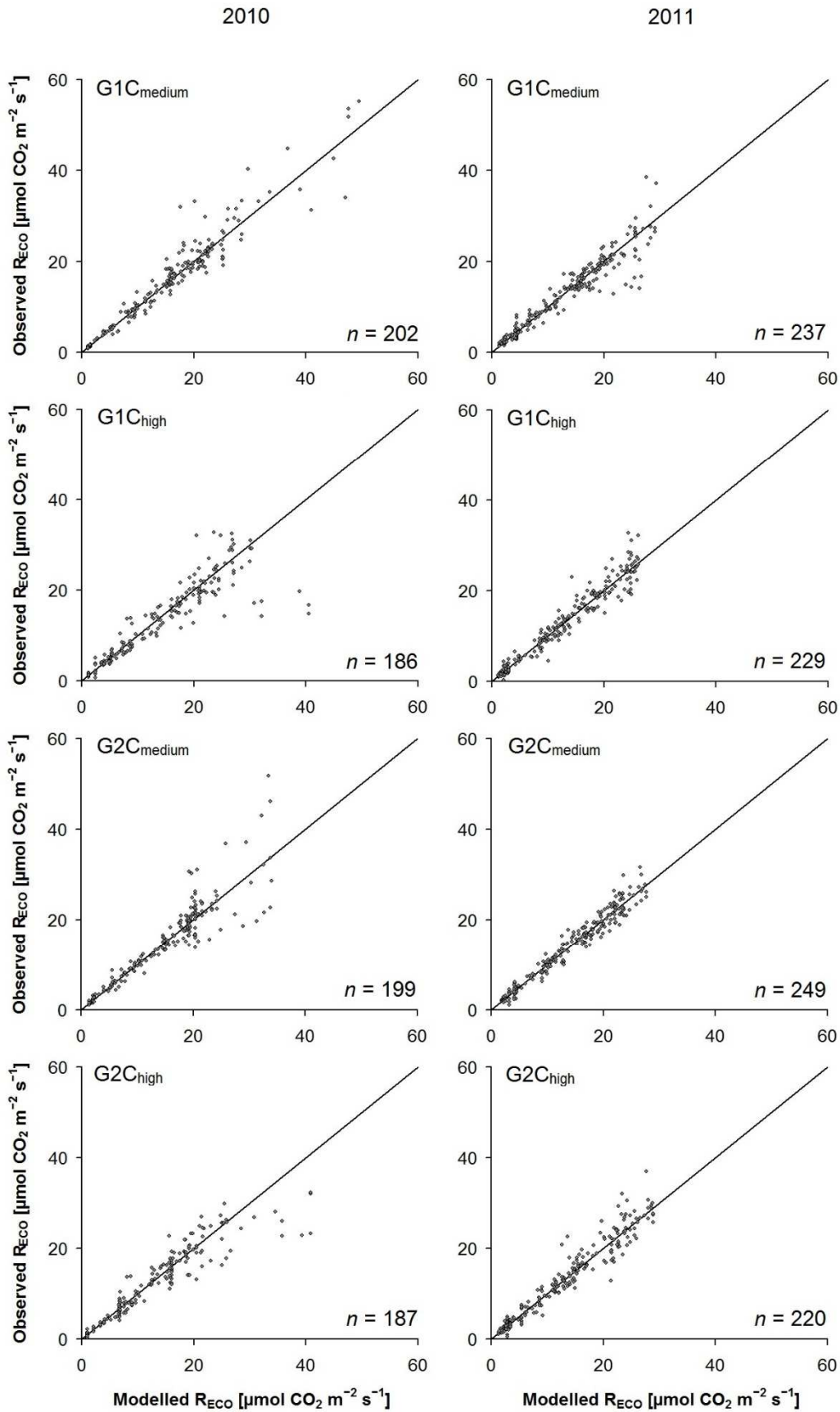


Fig. S4 Observed vs. modelled plots of R_{ECO} for the grassland sites. Solid lines indicate the 1:1 line for a perfect fit.

Table S1 Model parameters of the A1C_{medium} site.

Site	Date	R _{CO2}										GPP										R _{CO2} without model parameter				
		Std. Error		95% Confidence Limits				model based on				Std. Error		95% Confidence Limits				Std. Error		95% Confidence Limits						
		R _w	E _s	R _w	E _s	lower R _w	upper R _w	lower E _s	upper E _s	n	T _{far}	α	GPP _{CO2}	α	GPP _{CO2}	lower α	upper α	lower GPP _{CO2}	upper GPP _{CO2}	n	R _{CO2}	daily mean CO ₂ (μmole m ⁻² s ⁻¹)	Std. Error	lower R _{CO2}	upper R _{CO2}	n
A1C _{medium}	2010-02-09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.78	0.18	0.44	1.11	9
A1C _{medium}	2010-02-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.92	0.12	0.69	1.15	15
A1C _{medium}	2010-03-08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.11	0.09	0.95	1.28	9
A1C _{medium}	2010-03-24	3.43	138.31	0.06	7.64	3.32	3.55	122.73	153.89	33	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-	-	-	-	-
A1C _{medium}	2010-04-07	7.99	119.04	0.26	19.17	7.43	8.55	78.41	159.67	18	ST ₂	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-	-	-	-	-
A1C _{medium}	2010-04-28	9.62	103.31	0.40	17.69	8.77	10.47	65.60	141.02	17	ST ₂	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-	-	-	-	-
A1C _{medium}	2010-05-23	6.73	231.96	0.71	35.92	5.27	8.19	157.65	306.26	25	ST ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A1C _{medium}	2010-06-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.15	0.27	8.63	9.67	17
A1C _{medium}	2010-07-02	12.59	110.77	1.24	23.54	10.02	15.16	61.82	159.72	23	T _{far}	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-0.03	-	-	-	-	-
A1C _{medium}	2010-07-22	11.34	218.93	0.64	23.03	10.03	12.65	171.89	265.97	32	T _{far}	-0.06	-0.07	-0.05	-0.05	-0.07	-0.04	-0.07	-0.04	-0.07	-0.04	-	-	-	-	-
A1C _{medium}	2010-08-21	7.43	143.40	0.54	16.74	6.28	8.58	107.90	178.89	18	T _{far}	-0.04	-0.04	-0.04	-0.04	-0.05	-0.03	-0.05	-0.03	-0.05	-0.03	-	-	-	-	-
A1C _{medium}	2010-09-12	6.28	135.16	0.48	21.87	5.25	7.31	88.27	182.06	16	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01	-	-	-	-	-
A1C _{medium}	2010-10-04	4.62	202.38	0.18	14.43	4.23	5.01	171.21	233.55	15	T _{far}	-0.05	-0.05	-0.05	-0.05	-0.07	-0.02	-0.07	-0.02	-0.07	-0.02	-	-	-	-	-
A1C _{medium}	2010-10-13	6.10	175.57	0.54	46.50	4.83	7.37	65.62	285.52	9	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.02	0.00	-0.02	0.00	-0.02	0.00	-	-	-	-	-
A1C _{medium}	2010-10-29	4.70	104.79	0.36	36.38	3.93	5.47	26.77	182.81	16	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.01	0.00	-0.01	0.00	-0.01	0.00	-	-	-	-	-
A1C _{medium}	2010-12-13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	0.06	0.09	0.31	9
A1C _{medium}	2011-01-05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.82	0.14	0.56	1.09	9
A1C _{medium}	2011-01-27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.75	0.02	0.72	0.79	9
A1C _{medium}	2011-02-07	1.28	151.19	0.09	41.66	1.09	1.48	61.20	241.19	15	T _{far}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A1C _{medium}	2011-03-08	1.07	32.45	0.04	10.60	0.99	1.15	10.09	54.81	19	T _{far}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A1C _{medium}	2011-03-29	4.16	196.91	0.18	25.69	3.78	4.53	142.93	250.89	20	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.01	0.00	-0.01	0.00	-0.01	0.00	-	-	-	-	-
A1C _{medium}	2011-04-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A1C _{medium}	2011-05-06	5.90	79.18	0.24	15.44	5.39	6.41	47.06	111.29	23	T _{far}	-0.01	-0.01	-0.01	-0.01	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01	-	-	-	-	-
A1C _{medium}	2011-05-25	14.57	76.98	1.02	19.05	12.41	16.72	36.59	117.36	18	ST ₂	-0.03	-0.03	-0.03	-0.03	-0.04	-0.02	-0.04	-0.02	-0.04	-0.02	-	-	-	-	-
A1C _{medium}	2011-06-28	14.88	124.88	1.12	19.41	12.56	17.20	84.43	164.93	24	T _{far}	-0.16	-0.16	-0.16	-0.16	-0.20	-0.12	-0.20	-0.12	-0.20	-0.12	-	-	-	-	-
A1C _{medium}	2011-08-02	10.82	133.18	0.67	18.45	9.41	12.23	94.26	172.10	19	T _{far}	-0.15	-0.15	-0.15	-0.15	-0.21	-0.08	-0.21	-0.08	-0.21	-0.08	-	-	-	-	-
A1C _{medium}	2011-08-24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
A1C _{medium}	2011-09-24	7.30	177.34	0.30	20.51	6.66	7.94	133.64	221.05	17	T _{far}	-0.02	-0.02	-0.02	-0.02	-0.03	-0.02	-0.03	-0.02	-0.03	-0.02	-	-	-	-	-
A1C _{medium}	2011-10-16	9.69	207.95	0.37	22.25	8.90	10.49	160.52	255.38	17	ST ₂	-0.03	-0.03	-0.03	-0.03	-0.03	-0.02	-0.03	-0.02	-0.03	-0.02	-	-	-	-	-
A1C _{medium}	2011-12-15	2.42	168.70	0.20	31.97	1.95	2.89	93.11	244.28	9	T _{far}	-0.04	-0.04	-0.04	-0.04	-0.05	-0.03	-0.05	-0.03	-0.05	-0.03	-	-	-	-	-
A1C _{medium}	2012-01-12	4.53	302.37	0.55	59.54	3.28	5.78	167.69	437.06	11	T _{far}	-0.02	-0.02	-0.02	-0.02	-0.03	-0.01	-0.03	-0.01	-0.03	-0.01	-	-	-	-	-

Table S6 Model parameters of the G1C_{high} site.

Site	Date	R _{CO2}										GPP										R _{CO2} without model			
		R _{CO2}		Std. Error		95% Confidence Limits		model based on		GPP		Std. Error		95% Confidence Limits		lower R _{CO2}		upper R _{CO2}		daily mean R _{CO2} [μmol CO ₂ m ⁻² s ⁻¹]	R _{CO2}	Std. Error	95% Confidence Limits		
		R _{CO2}	E ₁	R _{CO2}	E ₁	lower R _{CO2}	upper R _{CO2}	lower E ₁	upper E ₁	n	model	α	GPP _{max}	α	GPP _{max}	lower α	upper α	lower R _{CO2}	upper R _{CO2}				n	lower R _{CO2}	upper R _{CO2}
G1C _{high}	2010-02-08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.26	0.88	1.02	1.50	6	
G1C _{high}	2010-03-08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.21	0.09	1.05	1.38	9	
G1C _{high}	2010-03-24	4.87	40.00	0.20	13.63	4.45	5.28	10.95	68.06	17	T _{air}	-0.02	-8.91	0.01	0.47	-0.03	-0.01	-9.88	-7.94	27	-	-	-	-	
G1C _{high}	2010-04-06	7.75	110.35	0.61	38.27	6.46	9.05	28.78	191.92	17	T _{air}	-0.02	-25.30	0.00	1.27	-0.02	-0.01	-27.94	-22.65	22	-	-	-	-	
G1C _{high}	2010-04-28	11.39	63.78	0.53	16.12	10.26	12.53	29.20	98.36	16	T _{air}	-0.03	-36.67	0.01	1.48	-0.04	-0.02	-39.79	-33.55	20	-	-	-	-	
G1C _{high}	2010-05-24	8.94	351.02	0.72	52.71	7.36	10.51	235.00	467.04	13	ST ₂	-0.04	-51.43	0.00	1.31	-0.05	-0.03	-54.17	-48.68	20	-	-	-	-	
G1C _{high}	2010-06-09	15.58	91.65	1.92	33.23	11.54	19.61	21.83	161.48	20	T _{air}	-0.10	-36.43	0.01	0.66	-0.12	-0.08	-37.78	-35.08	27	-	-	-	-	
G1C _{high}	2010-07-07	15.79	85.17	0.99	20.65	13.65	17.93	40.56	129.78	15	T _{air}	-0.06	-39.26	0.01	0.98	-0.07	-0.04	-41.32	-37.20	21	-	-	-	-	
G1C _{high}	2010-07-21	16.78	107.93	1.38	18.93	13.69	19.86	65.75	150.10	12	T _{air}	-0.07	-38.41	0.01	1.40	-0.09	-0.04	-41.43	-35.39	15	-	-	-	-	
G1C _{high}	2010-08-22	20.25	58.29	1.73	19.61	16.57	23.94	16.49	100.09	17	T _{air}	-0.08	-46.19	0.01	1.45	-0.11	-0.06	-49.20	-43.18	23	-	-	-	-	
G1C _{high}	2010-09-11	13.45	116.83	0.54	14.92	12.29	14.60	85.04	148.63	17	T _{air}	-0.10	-39.34	0.01	0.55	-0.11	-0.08	-40.47	-38.22	29	-	-	-	-	
G1C _{high}	2010-10-29	6.24	111.28	0.19	14.32	5.83	6.64	80.34	142.21	15	T _{air}	-0.02	-36.79	0.00	4.99	-0.03	-0.02	-47.56	-26.02	15	-	-	-	-	
G1C _{high}	2010-12-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.45	0.46	1.60	3.30	9	
G1C _{high}	2011-01-05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.13	0.45	1.35	2.91	9	
G1C _{high}	2011-01-27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.16	0.18	1.82	2.50	9	
G1C _{high}	2011-02-07	2.23	113.41	0.14	32.98	1.93	2.52	43.49	183.34	18	T _{air}	0.00	-5.11	0.00	0.73	0.00	0.00	-6.68	-3.54	15	-	-	-	-	
G1C _{high}	2011-03-08	2.45	82.00	0.16	21.30	2.10	2.80	35.61	127.40	17	T _{air}	0.00	-4.85	0.00	0.59	0.00	0.00	-6.10	-3.61	19	-	-	-	-	
G1C _{high}	2011-03-29	8.98	159.99	0.42	25.77	8.10	9.86	105.61	214.37	19	T _{air}	-0.03	-25.07	0.00	0.85	-0.04	-0.02	-26.83	-23.31	24	-	-	-	-	
G1C _{high}	2011-04-20	12.36	339.75	0.72	53.59	10.83	13.88	227.16	452.35	20	ST ₂	-0.04	-40.50	0.00	1.27	-0.05	-0.03	-43.11	-37.89	27	-	-	-	-	
G1C _{high}	2011-05-10	15.68	112.87	1.13	21.06	13.32	18.05	66.94	156.80	22	T _{air}	-0.10	-51.21	0.01	0.80	-0.11	-0.08	-52.85	-49.58	29	-	-	-	-	
G1C _{high}	2011-06-21	7.49	416.41	1.63	91.65	3.87	11.12	212.20	620.62	12	ST ₂	-0.07	-48.31	0.01	1.71	-0.09	-0.06	-51.96	-44.66	17	-	-	-	-	
G1C _{high}	2011-06-28	17.60	83.62	0.88	12.42	15.78	19.41	57.86	109.39	24	T _{air}	-0.13	-43.58	0.02	0.78	-0.16	-0.10	-45.18	-41.99	32	-	-	-	-	
G1C _{high}	2011-07-26	9.48	355.18	0.68	39.94	8.05	10.90	271.57	438.78	21	ST ₂	-0.09	-43.69	0.01	0.79	-0.11	-0.08	-45.29	-42.08	35	-	-	-	-	
G1C _{high}	2011-08-18	11.24	219.60	1.16	34.20	8.80	13.68	147.74	291.46	20	ST ₂	-0.09	-42.79	0.01	0.68	-0.11	-0.07	-44.19	-41.39	28	-	-	-	-	
G1C _{high}	2011-09-16	7.45	285.14	0.49	48.61	6.42	8.48	183.02	387.26	20	ST ₅	-0.01	-9.15	0.01	1.06	-0.03	0.00	-11.35	-6.95	24	-	-	-	-	
G1C _{high}	2011-10-16	8.24	437.52	0.60	113.76	6.85	9.62	175.19	699.84	10	ST ₅	-0.03	-27.09	0.00	1.05	-0.03	-0.02	-29.37	-24.81	14	-	-	-	-	
G1C _{high}	2011-12-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.98	0.31	2.40	3.55	9	
G1C _{high}	2012-01-12	13.31	525.53	3.73	127.91	5.18	21.45	246.82	804.23	14	ST ₂	-0.03	-23.67	0.00	1.76	-0.03	-0.02	-27.51	-19.82	14	-	-	-	-	

7.2 PUBLICATION II.



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Biogeosciences 

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

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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 (N₂O) emissions and organic fertilization is additionally known to increase N₂O emissions from managed grasslands. Our study addressed the questions (a) to what extent biogas digestate and cattle slurry application increase N₂O and methane (CH₄) fluxes as well as the mineral nitrogen use efficiency (NUE_{min}) and grass yield, and (b) how different soil organic matter contents (SOMs) and nitrogen contents promote the production of N₂O. In addition NH₃ 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_{org-medium} and C_{org-high}) 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 N₂O and CH₄ were measured on three replicates over 2 years using the closed chamber method. For NH₃ measurements we used the calibrated dynamic chamber method. On an annual basis, the application of biogas digestate significantly enhanced the N₂O fluxes compared to the application of cattle slurry and additionally increased the plant

N-uptake and NUE_{min}. Furthermore, N₂O fluxes from the C_{org-high} treatments significantly exceeded N₂O fluxes from the C_{org-medium} treatments. Annual cumulative emissions ranged from 0.91 ± 0.49 to 3.14 ± 0.91 kg N ha⁻¹ yr⁻¹. Significantly different CH₄ fluxes between the investigated treatments or the different soil types were not observed. Cumulative annual CH₄ exchange rates varied between -0.21 ± 0.19 and -1.06 ± 0.46 kg C ha⁻¹ yr⁻¹. Significantly higher NH₃ losses, NUE_{min} and grass yields from treatments fertilized with biogas digestate compared to those fertilized with cattle slurry were observed. The total NH₃ losses following the splash plate application were 18.17 kg N ha⁻¹ for the digestate treatments and 3.48 kg N ha⁻¹ for the slurry treatments (36 and 15 % of applied NH₄⁺-N). The observed linear increase of 16 days' cumulative N₂O-N exchange or annual N₂O 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_{org-rich} 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 (N_2O) 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 N_2O losses through denitrification (Clayton et al., 1997). Enhanced N_2O emissions are of major concern due to the fact that N_2O acts as a radiative forcing GHG (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). In Germany, about 78 % of N_2O 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 N_2O , due to the very high mineralization rates of degrading peat (Kasimir-Klemmedtsson et al., 1997; Freibauer et al., 2004; Klemmedtsson et al., 2005; Goldberg et al., 2010) and to soil moisture conditions that favor anaerobic microsites. According to Maljanen et al. (2010), N_2O 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 N_2O emissions from drained organic grassland soils revealed very high N_2O 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 N_2O 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 N_2O 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 N_2O 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 (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 N_2O 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 N_2O 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 N_2O 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 N_2O , slurry application leads to short-term methane (CH_4) and ammonia (NH_3) emissions. Methane acts as a strong GHG, whereas NH_3 is considered an indirect GHG through ammonia deposition which could promote the formation of N_2O (Moiser, 2001). Moreover, 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 NH_3 emissions (Haenel et al., 2010). Particularly high NH_4^+ contents and high pH values, which are typically for the biogas digestate, promote accelerated NH_3 volatilization (Quakernack et al., 2011). High 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 N_2O and 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

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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 ³ ha ⁻¹]
20 Aug 2010	mowing
25 Aug 2010	manuring [20 m ³ ha ⁻¹]
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 ³ ha ⁻¹]
1 Aug 2011	mowing
13 Sep 2011	mowing
22 Sep 2011	manuring [20 m ³ ha ⁻¹]
4 Nov 2011	manuring [25 m ³ ha ⁻¹]

be tested. Furthermore, NH₃ 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 N₂O is emitted after biogas digestate than after slurry application because of higher NH₄⁺-N concentrations in the substrate and, thus, higher NH₄⁺-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) N₂O emissions increase with increasing soil C_{org} 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⁻¹ yr⁻¹, with NH₄⁺-N : NO₃⁻-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_{org}-medium) and as sapric Histosol (named C_{org}-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 m²) 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 NH₃ 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 m³ ha⁻¹). This method is typical for farming practices, but produces diverging N application rates per event between slurry and digestate based on NH₄⁺ or N_{tot} applications. It is known that the splash plate application technique can result in very uneven

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Table 2. Soil properties of the study site.

	Sampling depth	C _{org} -medium	C _{org} -high	<i>n</i>
Soil type (WRB, 2006) ¹		mollic Gleysol	sapric Histosol	
Soil type (German classification KA5)		GMq	KV-KM	
Peat depth [cm] ¹		80	70	1
pH value ²		4.1	4.2	
Total nitrogen [%] ²		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 ⁻³]	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. ¹ World Reference Base for Soil Resources. ² Relative to the upper horizon (C_{org}-medium 0–20 cm; C_{org}-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 m² 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 N₂O and CH₄ flux measurements

As a background, we measured fluxes of N₂O and CH₄ 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 N₂O (ECD temperature 380 °C) and a flame ionization detector (FID) for CH₄ 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/-

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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 ³ ha ⁻¹]	20	20	25	20	20
Total carbon [kg ha ⁻¹]	579	676	798	797	1073
Organic carbon [kg ha ⁻¹]	410	573	655	706	960
Total nitrogen [kg ha ⁻¹]	47	64	70	85	97
NO ₃ ⁻ [kg N ha ⁻¹]	0	0	0	0	0
NH ₄ ⁺ [kg N ha ⁻¹]	20	28	23	33	38
NH ₄ ⁺ : N _{tot} ratio	0.42	0.44	0.33	0.38	0.39
C : N ratio	12	11	11	9	11
pH (CaCl ₂)	–	–	6.8	7.0	7.0
Dry matter content [%]	5	7	7	9	10
Biogas digestate					
Fertilizer quantity [m ³ ha ⁻¹]	20	20	25	20	20
Total carbon [kg ha ⁻¹]	384	373	167	184	178
Organic carbon [kg ha ⁻¹]	306	337	148	161	178
Total nitrogen [kg ha ⁻¹]	49	52	78	35	61
NO ₃ ⁻ [kg N ha ⁻¹]	0	0	0	0	0
NH ₄ ⁺ [kg N ha ⁻¹]	22	28	51	17	40
NH ₄ ⁺ : N _{tot} ratio	0.45	0.53	0.65	0.49	0.66
C : N ratio	8	7	2	5	3
pH (CaCl ₂)	–	–	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 N₂O or CH₄ fluxes, fluxes were also accepted if the coefficient of determination was ≥ 0.90 and the regression slope was between -1 and 1 ppb min⁻¹. The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

2.4 NH₃ 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 NH₃ 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 cm²) 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⁻¹) through four connected (via Teflon tubes) conical stainless

steel chambers to an ammonia indicator tube (Drägerwerk AG, Lübeck, Germany). The NH₃ volume concentration was corrected for air temperature and air pressure (Pacholski et al., 2006). To prevent overestimation of NH₃ volatilization through NH₃ enriched ambient air from surrounding area, ammonia concentration from the control treatments was subtracted from the fertilized treatments prior to NH₃ flux calculation. Different studies report a distinct underestimation of up to one order of magnitude of NH₃ 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 NH₃-N losses determined by the DTM, Pacholski et al. (2006) developed the following calibration formula to correct the NH₃ 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 NH₃ flux_{IHF} is NH₃ flux measured by the integrated horizontal flux method (kg N ha⁻¹ h⁻¹); NH₃ flux_{DTM} is NH₃ flux measured by the DTM (kg N ha⁻¹ h⁻¹); $v_{2\text{m}}$ is wind speed at 2 m height (m s⁻¹). Quakernack et al. (2011) compared the DTM method with the frequently used micrometeorological method, concluding that the corrected DTM method also allows quantitative NH₃-loss measurements. The total cumulative NH₃ 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 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 m²). 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 N_2O 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_{tot}) and total nitrogen (N_{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_{tot} or N_{min} use efficiency (NUE, NUE_{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_{tot} or N_{min} applied, corrected by NH_3 -N losses. Emission factors for 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⁻¹ related to applied 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_{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_{tot} applied, N min_{t_1} and N min_{t_2} are the amounts of N_{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, N_{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 N_2O -N losses, and NH_3_{cum} is the amount of the annual cumulative 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 CaCl_2 (0.0125 M) for 1 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. 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_{tot} and organic carbon (C_{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 cm³) 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 N_2O emissions and treatment 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 NO_3^- comparison in 2010) or the nonparametric Mann–Whitney *U* test (for soil type NO_3^- comparison in 2011). For time series data (N_2O , 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

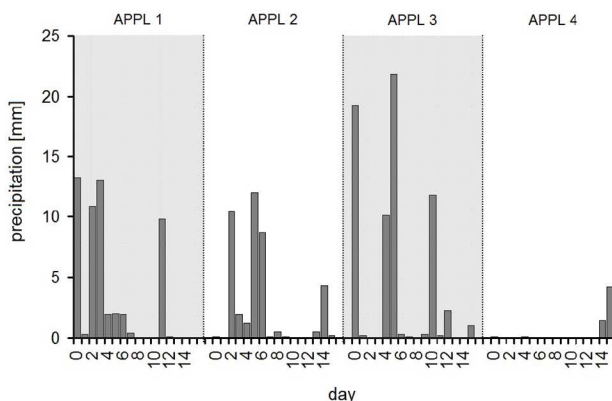


Figure 1. Daily sums of precipitation following the organic fertilizer application events (APPL).

(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 N_2O , CH_4 and NH_3 fluxes. We accepted significant differences if $P \leq 0.05$. Results in the text are given as means ± 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 C_{org} -medium site and was slightly higher with 10.5 °C at the C_{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 C_{org} -high treatments were significantly higher (all $P < 0.001$) compared to the C_{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 kg N ha^{-1} for slurry treatments and 101 and 174 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 N_{min} contents of the soils were dominated by NO_3^- whereas NH_4^+ was only of minor importance, especially at the C_{org} -medium treatments (Fig. 2b and c). The NO_3^- content was significantly higher ($P < 0.001$) at the C_{org} -high treatments than at the C_{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 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 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 C_{org} -medium site; Table 4).

3.3 N_2O emissions

N_2O fluxes were generally low for all treatments (Fig. 2d). Background emissions rarely exceeded $50 \mu\text{g N m}^{-2} \text{ h}^{-1}$. Highest N_2O 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 C_{org} -medium treatments N_2O fluxes returned to background emission level within 3 to 7 days, whereas the C_{org} -high treatments had longer lasting increased N_2O emissions, particularly for the digestate treatment.

Short-term (16 days) N_2O fluxes of fertilized treatments significantly ($P < 0.01$) exceeded N_2O fluxes of control treatments at all fertilization events. However, only in one out of four fertilization events were short-term N_2O fluxes significantly ($P < 0.001$) higher for the digestate treatments compared to the slurry treatments. Additionally, significantly ($P < 0.001$) higher short-term N_2O fluxes were observed at the C_{org} -high treatments compared to the C_{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)

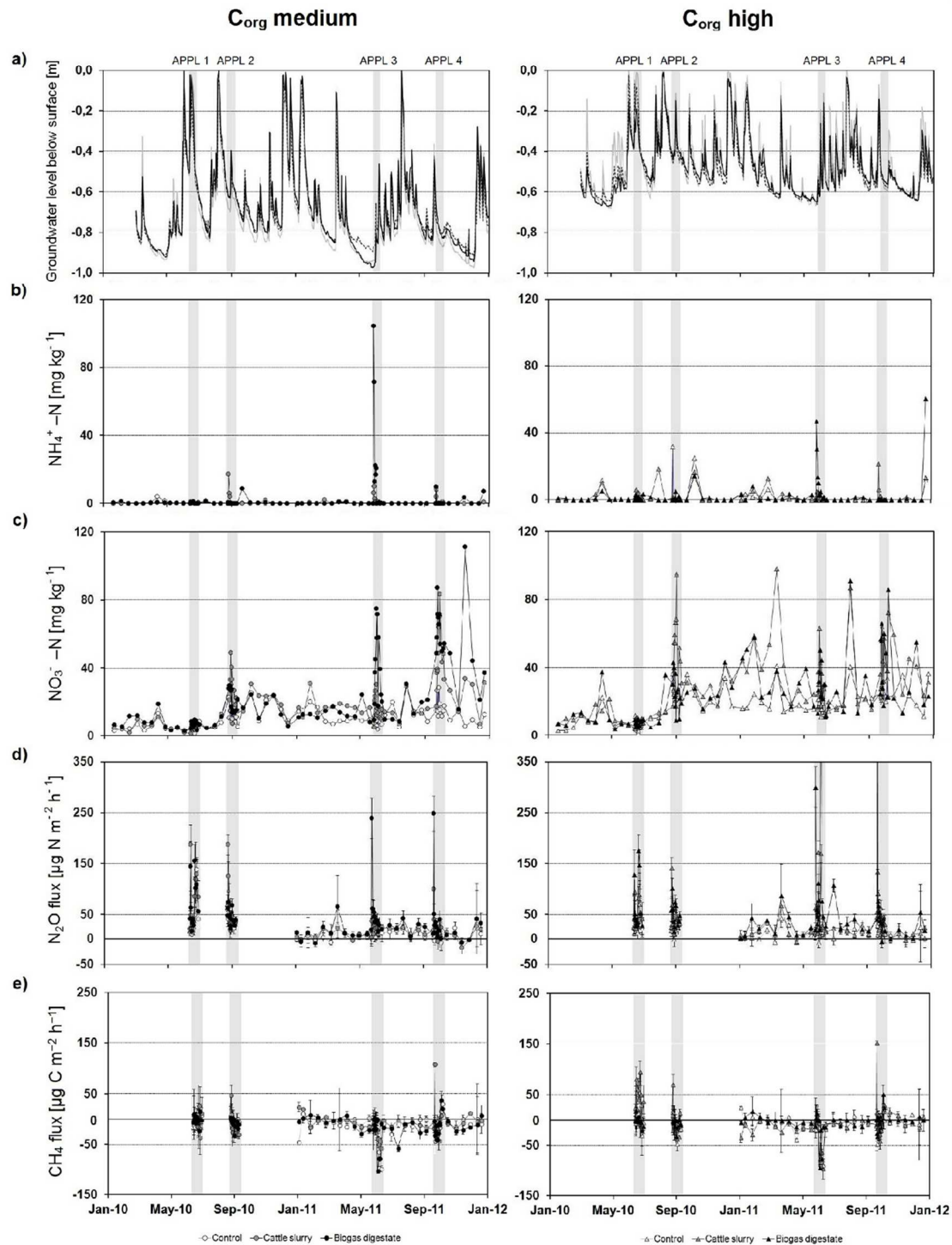


Figure 2. Variation in groundwater level (a), extractable NH_4^+ (b) and NO_3^- (c) contents for the soil depth 0–10 cm, N_2O (d) and CH_4 fluxes (e) (mean \pm SD, $n = 3$) of the C_{org} -medium and C_{org} -high sites from January 2010 to January 2012. Gray bars mark the 15 or 16 days period of intensive gas flux measurements following organic fertilizer application.

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Table 4. Mean (minimum/maximum) groundwater level (GW), NO₃⁻ and NH₄⁺ content in the soil following organic fertilizer application and for the investigated years 2010 and 2011.

Sampling depth [cm]	C _{org} -medium			C _{org} -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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 ₃ ⁻ [mg N kg ⁻¹]	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 ₄ ⁺ [mg N kg ⁻¹]	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 N₂O emissions were not significantly different from the control treatments in 2010 (Fig. 4), but for 2011 short-term cumulative N₂O 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 N₂O fluxes compared to unfertilized treatments. Additionally, the application of biogas digestate significantly ($P < 0.01$) enhanced the N₂O fluxes compared to the application of cattle slurry. Furthermore, N₂O fluxes from the C_{org}-high treatments significantly ($P < 0.001$) exceeded N₂O fluxes from the C_{org}-medium treat-

ments. Annual cumulative emissions ranged from $0.91 \pm 0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (control treatment, C_{org}-medium site) to $3.14 \pm 0.91 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (digestate treatment, C_{org}-high site; Table 5). Calculated EFs based on the amount of N_{tot} 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 N₂O 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 N₂O–N exchange rates, 53 % was explained by the amounts of applied NH₄⁺-N and the mean groundwater levels below surface during the same time

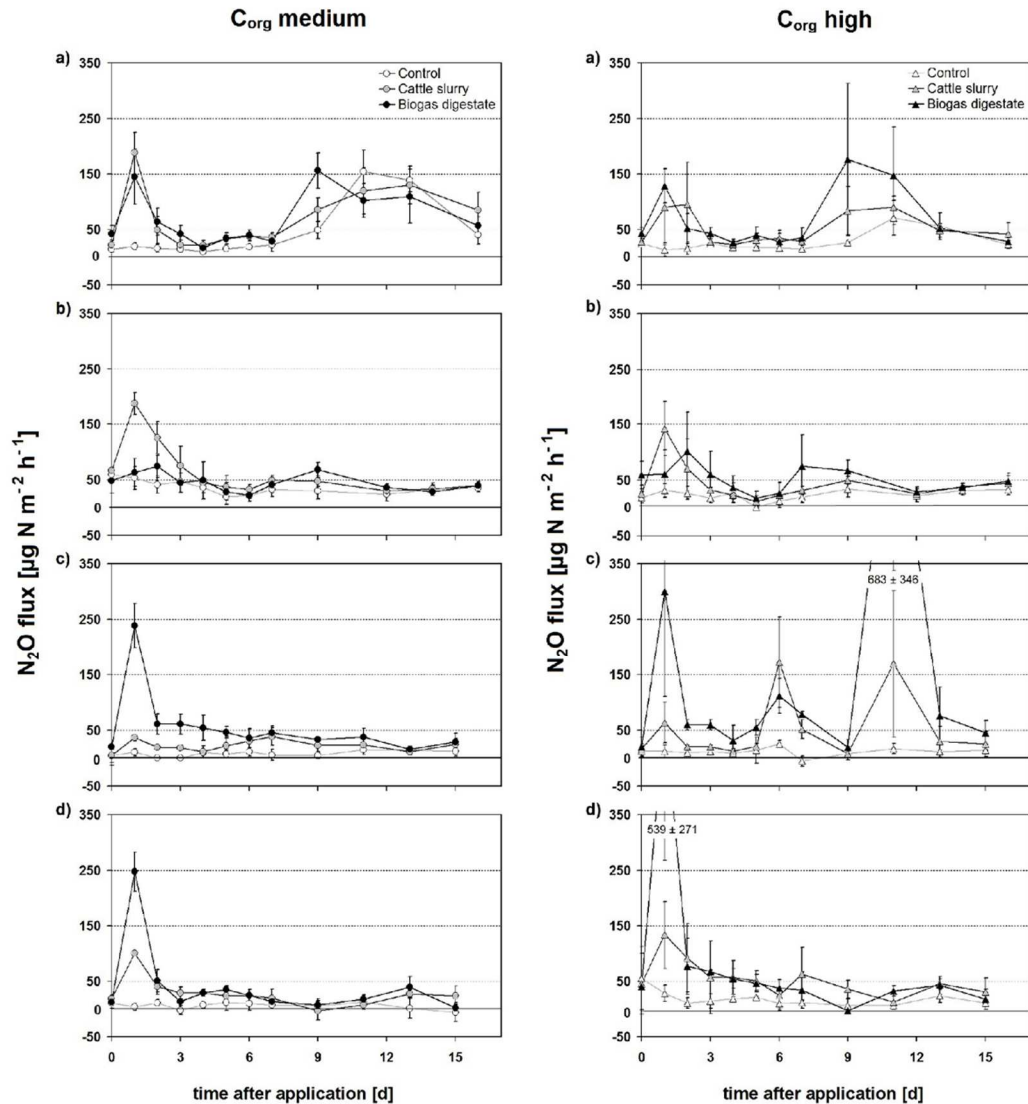


Figure 3. Mean (\pm SD, $n = 3$) N_2O fluxes following organic fertilizer application events (a) 14–30 June 2010; (b) 25 August–10 September 2010; (c) 27 May–11 June 2011 and (d) 22 September–7 October 2011.

(Fig. 6). A similar trend was observed for the annual cumulative N_2O emissions, but regression analysis was not possible due to the small sample size ($n = 6$).

3.4 CH_4 emissions

Most of the time, CH_4 emissions could not be detected (Fig. 2e). Occasionally CH_4 peaks were only found immediately after cattle slurry application. However, with the exception of the slurry treatment of the C_{org} -high site at the first application event, the organic fertilization did not result in significantly different short-term (15 or 16 days) CH_4 fluxes between the treatments or the investigated soil types. The observed weak CH_4 emissions or uptakes amounted to cumulative annual CH_4 exchange rates of -0.21 ± 0.19

to $-1.06 \pm 0.46 \text{ kg C ha}^{-1} \text{ yr}^{-1}$. Significantly different CH_4 fluxes between the investigated treatments or the different soil types could not be observed regarding the annual fluxes in 2011.

3.5 NH_3 volatilization

Highest NH_3 losses were observed immediately after fertilization (Fig. 7). During the first 24 h, 64 and 100 % of total NH_3 losses occurred at the digestate and slurry treatments, respectively. Since differences in the response of NH_3 volatilization were not significant, treatment data were pooled by soil type prior to regression analysis. The total 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

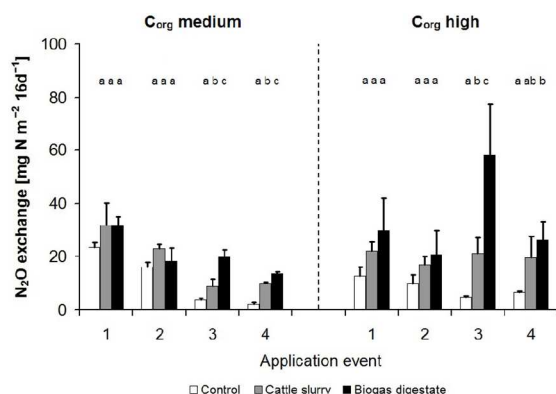


Figure 4. Cumulative N_2O exchange during 16 days following organic fertilizer application. Bars indicate mean values \pm SD ($n = 3$). Means with the same letter indicated no significant differences between treatments at a single application event for sites $\text{C}_{\text{Org-medium}}$ and $\text{C}_{\text{Org-high}}$ respectively (ANOVA, Tukey HSD test at $P \leq 0.05$).

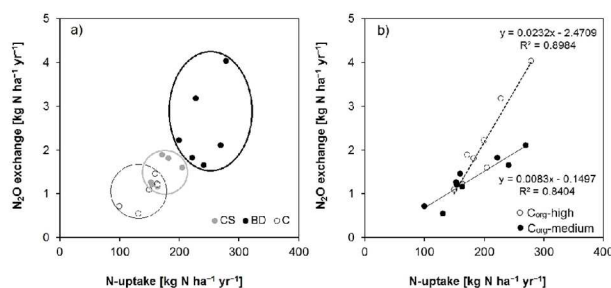


Figure 5. Relationship between cumulative annual N_2O emissions and annual plant N uptake for the treatments (a) and for the investigated soil types (b). Dots represent mean annual values of each PVC collar; CS, cattle slurry; BD, biogas digestate; C, control.

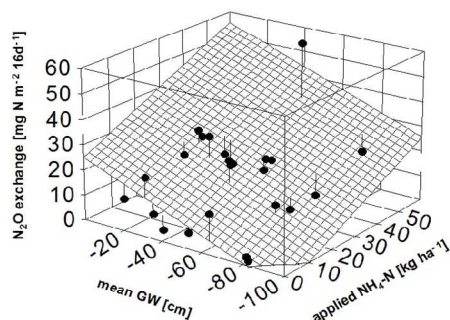


Figure 6. Relationship of plot-wise mean 16 days' cumulative N_2O -N emissions of the four application events (y) to mean groundwater level (x_1) and the amount of applied $\text{NH}_4\text{-N}$ (x_2). The regression equation is $y = 24.98 (\pm 4.98) + x_1 \cdot 0.30 (\pm 0.09) + x_2 \cdot 0.51 (\pm 0.11)$; $R^2 \text{ adj.} = 0.53$, $P < 0.001$, $df = 21$. 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 (N_{tot}) without consideration of $\text{NH}_3\text{-N}$ losses.

	Control	Cattle slurry	Biogas digestate
$\text{C}_{\text{Org-medium}}$			
N_2O exchange [$\text{kg N ha}^{-1} \text{ yr}^{-1}$]	0.91 ± 0.49	1.21 ± 0.05	1.86 ± 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
$\text{C}_{\text{Org-high}}$			
N_2O exchange [$\text{kg N ha}^{-1} \text{ yr}^{-1}$]	1.18 ± 0.07	1.77 ± 0.15	3.14 ± 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 NUE_{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. NUE_{min} values were always $> 100 \%$ for biogas digestate treatments, whereas for cattle slurry NUE_{min} values averaged $74 \pm 68 \%$ in 2011 but were $> 100 \%$ in 2010. Besides fertilizer type effects, higher NUE and NUE_{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

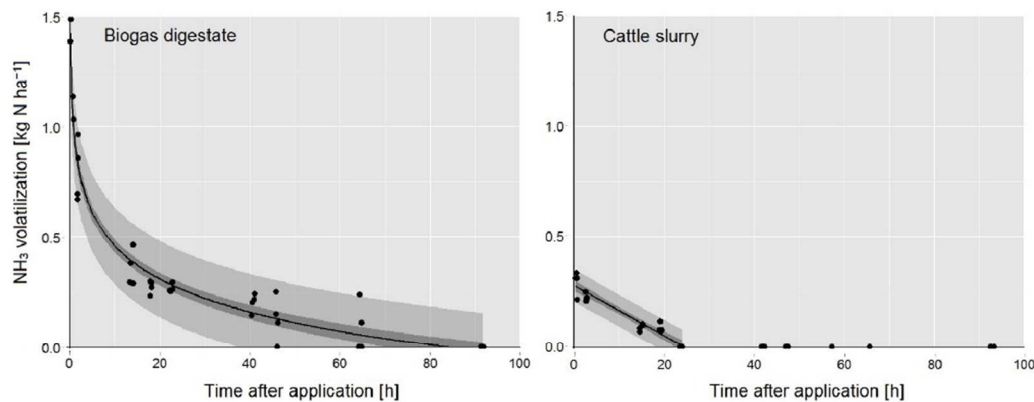


Figure 7. Ammonia (NH_3) volatilization following organic fertilizer application at event 3 (27 May 2011). Dots present single NH_3 measurements for a time period of 94 h. Black lines show the estimated NH_3 volatilization with 95 % confidence band (dark gray) and 95 % prediction band (light gray). The 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 [kg N ha^{-1}]	N applied [kg N ha^{-1}] ^b	N_{\min} applied [kg N ha^{-1}] ^b	N use efficiency [%]	N_{\min} use efficiency [%]
Control C_{org} -medium	24 May 2010	–	2.04 ^a	2.52	51	–	–	–	–
Control C_{org} -high	24 May 2010	–	2.14	2.93	63	–	–	–	–
Cattle slurry C_{org} -medium	24 May 2010	N.A.	2.37	3.19	76	–	–	–	–
Cattle slurry C_{org} -high	24 May 2010	N.A.	2.14	3.58	77	–	–	–	–
Biogas digestate C_{org} -medium	24 May 2010	N.A.	2.04	4.17	85	–	–	–	–
Biogas digestate C_{org} -high	24 May 2010	N.A.	2.27	4.39	100	–	–	–	–
Control C_{org} -medium	20 Aug 2010	–	2.03	2.02	41	–	–	–	–
Control C_{org} -high	20 Aug 2010	–	2.00	2.63	53	–	–	–	–
Cattle slurry C_{org} -medium	20 Aug 2010	14 Jun 2010	2.19	3.06	67	45	17	58	153
Cattle slurry C_{org} -high	20 Aug 2010	14 Jun 2010	1.93	3.23	62	45	17	22	57
Biogas digestate C_{org} -medium	20 Aug 2010	14 Jun 2010	2.03	2.99	61	38	14	52	140
Biogas digestate C_{org} -high	20 Aug 2010	14 Jun 2010	2.00	3.51	70	38	14	47	125
Control C_{org} -medium	23 May 2011	–	1.96	2.66	52	–	–	–	–
Control C_{org} -high	23 May 2011	–	1.70	3.82	65	–	–	–	–
Cattle slurry C_{org} -medium	23 May 2011	25 Aug 2010	2.01	2.58	52	61	24	0	0
Cattle slurry C_{org} -high	23 May 2011	25 Aug 2010	1.70	4.20	71	61	24	11	27
Biogas digestate C_{org} -medium	23 May 2011	25 Aug 2010	1.96	3.97	78	40	18	64	144
Biogas digestate C_{org} -high	23 May 2011	25 Aug 2010	1.83	4.54	83	40	18	45	101
Control C_{org} -medium	1 Aug 2011	–	1.71	2.06	35	–	–	–	–
Control C_{org} -high	1 Aug 2011	–	1.48	2.88	43	–	–	–	–
Cattle slurry C_{org} -medium	1 Aug 2011	27 May 2011	1.71	2.73	47	67	20	17	58
Cattle slurry C_{org} -high	1 Aug 2011	27 May 2011	1.51	3.19	48	67	20	8	28
Biogas digestate C_{org} -medium	1 Aug 2011	27 May 2011	1.78	4.88	87	60	33	86	158
Biogas digestate C_{org} -high	1 Aug 2011	27 May 2011	1.48	5.34	79	60	33	61	112
Control C_{org} -medium	13 Sep 2011	–	2.53	1.71	43	–	–	–	–
Control C_{org} -high	13 Sep 2011	–	2.26	2.27	51	–	–	–	–
Cattle slurry C_{org} -medium	13 Sep 2011	27 May 2011	2.57	2.28	59	(55) ^c	(8) ^c	28	189
Cattle slurry C_{org} -high	13 Sep 2011	27 May 2011	2.53	2.64	67	(61) ^c	(14) ^c	25	110
Biogas digestate C_{org} -medium	13 Sep 2011	27 May 2011	2.53	3.15	80	(8) ^c	(0) ^c	436	–
Biogas digestate C_{org} -high	13 Sep 2011	27 May 2011	2.26	3.25	74	(24) ^c	(0) ^c	94	–

^a N contents from control treatments were estimated from fertilized treatments. ^b Applied N_{tot} and N_{\min} were corrected by NH_3 -N losses (23 and 5 % from N_{tot} , or 36 and 15 % from N_{\min} for biogas digestate and cattle slurry, respectively). ^c Hypothetically remaining N_{tot} and N_{\min} from the application event 3 (27 May 2011). N.A. = not available.

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Table 7. Estimated nitrogen balance for the year 2011.

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

^a Reference date for t₁ is 6 April 2011 and for t₂ 18 October 2011. ^b NH₃-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 NH₄⁺; Haenel et al., 2014).

up to 108 kg N ha⁻¹ yr⁻¹ 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_{org}-high treatments than at the C_{org}-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⁻¹ yr⁻¹ (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 NH₄⁺:N_{tot} ratios and thus relatively higher NH₄⁺ contents than the cattle slurries (see also Möller and Stinner 2009). The amounts of NH₄⁺-N were not distinctly different between the applied organic fertilizers but in 2011 biogas treatments received 15 % more NH₄⁺-N compared to cattle slurry treatments.

We observed an unexpected small change in the NH₄⁺ 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 NH₄⁺ from the organic fertilizer was lost in a few hours after splash plate application via NH₃ volatilization. Thirdly,

and probably most importantly, in well aerated soils applied NH₄⁺ underwent rapid nitrification, as was indicated by the increasing soil NO₃⁻ contents in the upper soil layer after fertilizer application. In general, the continuously observed absent or low NH₄⁺ contents with simultaneously high extractable NO₃⁻ in the soil indicate that net nitrification entirely controlled net nitrogen mineralization at all treatments of the investigated study sites. Nitrification requires sufficient oxygen (O₂) 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_{min}. This becomes evident in the observed significantly higher NO₃⁻ 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_{min} 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_{tot} and NH₄⁺ 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., N₂O losses, NO₃⁻ 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⁻¹ yr⁻¹. However, the strong negative N balances of the control treatments reveal that large amounts of up to 148 kg N ha⁻¹ yr⁻¹ 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 NO₃⁻ in the soil, as observed especially at the fertilized treatments of the C_{org}-high sites, carry the

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_{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_{org} -high treatments compared to C_{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_{org} -high site significantly exceeded those from the C_{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_{org} -high treatments compared to the C_{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

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soil C_{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 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, N_2O 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 N_2O produced from applied N compared to cattle slurry, yet at a low level.

One reason of generally low N_2O 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 N_2O 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 NO_3^- content close to the groundwater level (van Beek et al., 2004). Given the high NO_3^- contents, in particular in the C_{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 N_2O emissions. Moreover, through the splash plate application technique high amounts of NH_4^+ were rapidly lost as NH_3 , and therefore reduced the proportion of immediately available N for nitrification and denitrification.

As expected from the literature, highest N_2O fluxes were found immediately after fertilizer application. The initial N_2O peak could mainly be attributed to the denitrification of available soil 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 N_2O could be ascribed to the rapid nitrification (Chadwick et al., 2000) or to nitrifier denitrification of slurry NH_4^+ . In contrast, the partially observed second N_2O 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 N_2O 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 N_2O emissions from the digestate treatments compared to the slurry treatments. Higher N_2O 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_{org} content compared to C_{org} rich soils. However, contrary to our hypothesis, the significantly higher N_2O 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 NH_4^+-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 N_2O 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 N_2O emissions, due to the stimulating effect of plant roots on denitrification activity (Klemmedtsen 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 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; Klemmedtsen et al., 1987). Furthermore, several authors have suggested that root exudates may increase bacterial metabolism (Klemmedtsen, 1987; Mounier et al., 2004; Henry et al., 2008), further lowering the oxygen concentration and thus increasing denitrification (Klemmedtsen 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 N_2O 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 N_2O emissions,

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due to a higher mean groundwater level and a higher application rate of NH_4^+-N , reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C_{org} -rich grasslands. The same was postulated for mineral soils by Ruser (2010).

4.4 Fertilizer- and site-induced CH_4 emissions

The observed consumption rates of CH_4 were in the range of CH_4 uptakes reported by Flessa et al. (1998) for two different meadows in a southern German fen peatland. Slightly higher 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 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 CH_4 increased with lowering of the groundwater level. Nevertheless, significant differences in the amount of the annual CH_4 uptake capacity between the two study sites C_{org} -medium and C_{org} -high could not be seen, although distinct differences in the groundwater table were observed.

The occasionally observed CH_4 peak emissions were only found immediately after cattle slurry application. This was in line with several other studies that reported short-term CH_4 emissions immediately after organic fertilizer application, due probably to volatilization of dissolved 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 CH_4 emissions observed after the first application event at the slurry treatment of the C_{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 CH_4 during this time period. However, we could not find any significant differences in the short term or annual CH_4 emissions between the two investigated fertilizers. According to Chadwick et al. (2000) more than 90 % of total 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 CH_4 emissions. However, all studies from literature confirm the minor importance of 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 NH_3 volatilization

The 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 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 NH_4^+-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 NH_3 loss rates were rather low (Haenel et al., 2014). It can be assumed that the higher concentration of 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 NH_3 losses (Sommer et al., 1996; Ni et al., 2011). There over a limited range (slurry DM of 2–5 %), 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 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 NH_3 exchange with the atmosphere and has been proposed as an NH_3 mitigation measure for slurry

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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 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 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 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 $\text{NH}_4^+ - \text{N}$ demonstrates that 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 NH_3 volatilization decreases N fertilizer use efficiency. One of the most effective measures to reduce NH_3 emissions from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several studies reported a considerable increase of GHGs, mainly N_2O , 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 N_2O , CH_4 , and NH_3 fluxes after splash plate application of biogas digestate and cattle slurry in a region known for its risk of high N_2O and NH_3 emissions and we were the first to study digestate application on high organic carbon soils with 10 to 17 % C_{org} content in the topsoil. To our surprise, N_2O emissions and EFs were lower than generally observed on mineral soils in the vicinity of the sites. We attributed the low N_2O 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 NUE_{min} . N_2O emissions increased with C_{org} content and fertilization. As hypothesized, N_2O 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, 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 N_2O

emissions with increasing 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 C_{org} -rich grasslands.

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7.3 PUBLICATION III.



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

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Abstract. Black alder (*Alnus glutinosa* (L.) Gaertn.) forests on peat soils have been reported to be hotspots for high nitrous oxide (N₂O) 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 (N₂)-fixation of alder trees. Our study addressed the question to what extent drainage enhances the emissions of N₂O from black alder forests and how N turnover processes and physical factors influence the production of N₂O 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 N₂O 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 N₂ 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 N₂O fluxes in the field but did in the laboratory experiment. N₂O fluxes measured were low for all sites, with total annual emissions of 0.51 ± 0.07 (U), 0.97 ± 0.13 (D-1) and 0.93 ± 0.08 kg N₂O–N ha⁻¹ yr⁻¹ (D-2). Only 37 % of the spatiotemporal variation in field N₂O fluxes could be explained by peat temperature and groundwater level, demonstrating the complex interlinking of the

controlling factors for N₂O emissions. However, temperature was one of the key variables of N₂O fluxes in the incubation experiment conducted. Increasing soil moisture content was found to enhance total denitrification losses during the incubation experiment, whereas N₂O fluxes remained constant. At the undrained site, permanently high groundwater level was found to prevent net nitrification, resulting in a limitation of available nitrate (NO₃⁻) and negligible gaseous N losses. N₂O flux rates that were up to four times higher were measured in the incubation experiment. They reveal the potential of high N₂O losses under changing soil physical conditions at the drained alder sites. The high net nitrification rates observed and high NO₃⁻ contents bear the risk of considerable NO₃⁻ 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 N₂-fixation of up to 85 kg N ha⁻¹ yr⁻¹ (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 N₂-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 N₂O emissions, in particular, are of great interest due to the fact that N₂O 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 N₂O emissions from *Alnus* forest ecosystems on drained or undrained peatlands range between 0.1 and 72.0 kg N ha⁻¹ yr⁻¹ (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 N₂O-N ha⁻¹ yr⁻¹ (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 N₂O 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 N₂O 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 N₂O fluxes are mainly related to incomplete denitrification. This requires the presence of efficient electron acceptors (e.g., NO₃⁻) to prevent the reduction of N₂O to N₂ (Bremner and Blackmer, 1981; Speir et al., 1995; Jungkunst et al., 2004). Due mainly to analytical difficulties in the determination of microbially produced N₂, 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 N₂ by Helium (He) in laboratory studies possibly represents the most reliable method for the direct and simultaneous determination of N₂O and N₂ 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) N₂O emissions and the factors regulating the N₂O emissions and N₂O/N₂ ratio from waterlogged and drained black alder forest on organic soil.

We hypothesize that (1) in drained black alder forests high N₂O emissions occur due to accelerated N turnover and N mineralization, and (2) N₂O is replaced by N₂ losses during periods of temporarily high water levels. In contrast, NO₃⁻ limitation in permanently waterlogged peat soils results in negligible N₂O and N₂ 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 Weihenstephan, 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⁻¹ yr⁻¹ with a NH₄⁺-N:NO₃⁻-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 N₂O 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

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Table 1. Groundwater level, water-filled pore space (WFPS), extractable nitrate (NO_3^-) and ammonium (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) ^a	−41 (−71/−3)	−47 (−77/−5)	
		3 (−20/22) ^b	−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
NO_3^- [mg N kg ^{−1}]	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
NH_4^+ [mg N kg ^{−1}]	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, NO_3^- and NH_4^+ at $P \leq 0.05$). ^a Values give the mean data from the water level loggers (15 min log interval). ^b 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 ^{−3}]	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.

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2.2 Field measurements

2.2.1 N₂O flux measurements

We measured fluxes of N₂O 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 N₂O (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 N₂O fluxes, fluxes were also accepted if the coefficient of determination was ≥ 0.90 and the regression slope was between -1 and 1 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_{tot}), organic carbon (C_{org}) and total nitrogen (N_{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 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 CaCl₂ (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°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 ± 2.2 % WFPS). For site U, however, WFPS had been adjusted to 83.0 ± 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 N₂, N₂O, CO₂ and CH₄ 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/O₂ gas mixture (20.58 % O₂, 347.8 ppm CO₂, 1.780 ppm CH₄, 0.290 ppm N₂O, 3.04 ppm N₂, rest He), were conducted to remove ambient N₂. Subsequently, the air temperature of the climate chamber was set to 0 °C and a continuous He/O₂ 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 N₂O, CO₂ and CH₄ headspace concentration once and the N₂ 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 ± 0.9 % and 2.7 ± 0.3 % of their initial water content at 100 % and 70/83 % WFPS during the incubation procedure of five days. Concentration of N₂ 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⁻¹). Concentrations of trace gases were analyzed by a GC (Shimadzu, Duisburg, Germany, GC-14B) equipped with a flame ionization detector (FID) for CH₄ and an ECD for N₂O and CO₂. GC settings were as follows: FID temperature 310 °C, ECD temperature 310 °C, column Porapack 80/100 mesh, oven temperature 60 °C, carrier gas N₂ 6.0 (13 mL min⁻¹). Background N₂ concentrations varied between 3.5 and 4.5 ppm (ca. 3 ppm originated from the artificial He/O₂ 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/O₂ gas mixture. The lowest detectable flux rates were 200 µg CO₂-C m⁻² h⁻¹, 0.2 µg CH₄-C m⁻² h⁻¹, 0.5 µg N₂O-N m⁻² h⁻¹, and 0.04 mg N₂-N m⁻² h⁻¹.

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 (CO₂, CH₄, N₂O, N₂) rates (mg C or N m⁻² h⁻¹; µg C or N m⁻² h⁻¹); and T_1 and T_2 are temperature (°C).

2.3.3 Estimation of available N_{min} and NO₃⁻ 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., NO₃⁻) supply and thereby falsify the results. The amount of N_{min} in the solution from soil cores was not ascertained in the present study. However, a rough estimation of available NH₄⁺ and NO₃⁻ was performed on the basis of t₀ 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 N₂ as the end product. Thus only samples incubated at 100 % WFPS were potentially affected by NO₃⁻ limitation. According to our estimation, samples from site U at 100 % WFPS were presumably permanently NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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 [$mg\ N\ kg^{-1}$] ^a		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 ^b	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

^aValues 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. ^bSamples 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 ± 1 standard error.

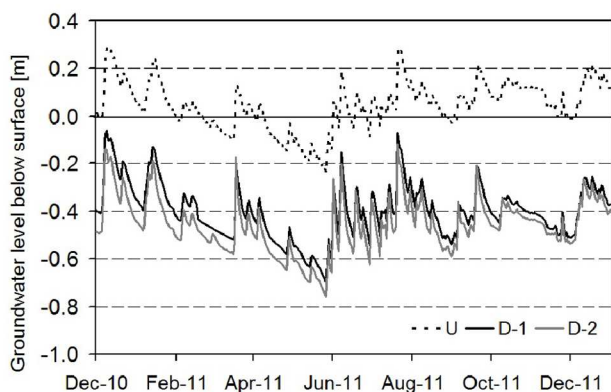


Figure 1. Annual variation in the groundwater level (U=undrained; D-1=drained site 1; D-2=drained site 2). Please note that the *x* axis starts on 1 December 2010.

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 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 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 NO_3^- , significantly higher NH_4^+ contents were measured at the undrained site than at the drained sites (Table 1). 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 ± 7 $\text{mg N m}^{-2} \text{d}^{-1}$ (U), 179 ± 35 $\text{mg N m}^{-2} \text{d}^{-1}$ (D-1) and 142 ± 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 ± 26 $\text{kg N ha}^{-1} \text{yr}^{-1}$ (U), 653 ± 128 $\text{kg N ha}^{-1} \text{yr}^{-1}$ (D-1) and 518 ± 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 (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 N_2O fluxes

Annual N_2O emissions were unexpectedly low at all three sites (Fig. 5) with 0.51 ± 0.07 $\text{kg N ha}^{-1} \text{yr}^{-1}$ (U), 0.97 ± 0.13 $\text{kg N ha}^{-1} \text{yr}^{-1}$ (D-1) and 0.93 ± 0.08 $\text{kg N ha}^{-1} \text{yr}^{-1}$ (D-2). The differences in N_2O fluxes between the sites were not statistically significant. At the drained sites the highest N_2O 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 N_2O fluxes; nevertheless only 37 % of the spatiotemporal variation could be explained ($P < 0.001$) (Fig. 6). Site-specific regression analyses explained 55 % of temporal N_2O variation at D-1 ($P < 0.001$), 32 % at D-2 ($P < 0.01$) and 20 % at U ($P < 0.04$).

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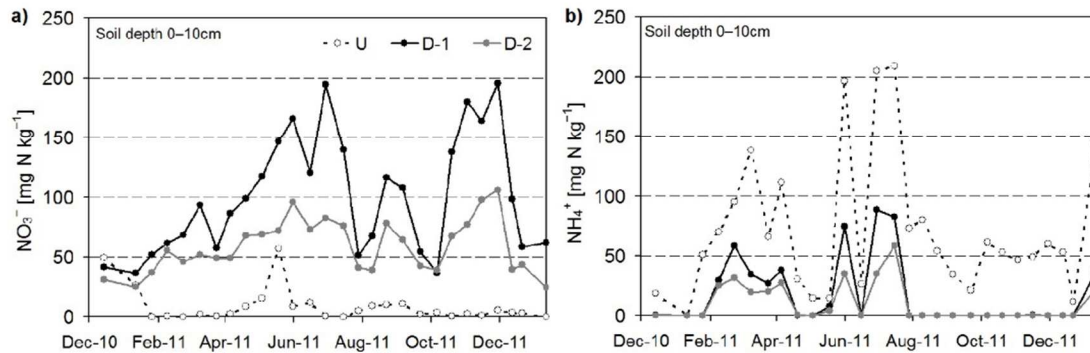


Figure 2. Annual variation in the extractable NO_3^- (a) and NH_4^+ (b) contents for the soil depth of 0–10 cm (U = undrained; D-1 = drained site 1; D-2 = drained site 2). Please note that the x axis starts on 1 December 2010.

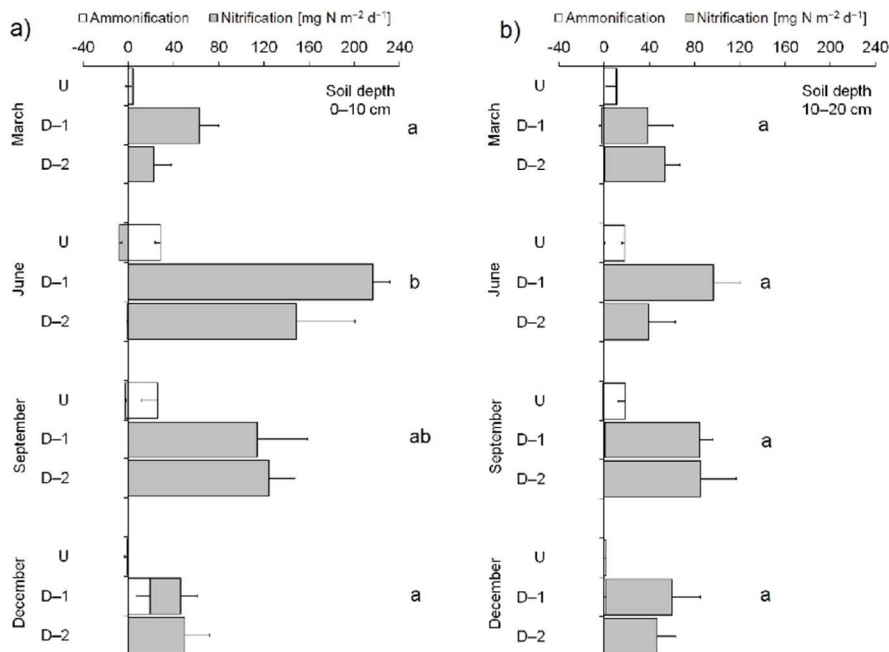


Figure 3. Net ammonification, net nitrification and net N mineralization rates (sum of net ammonification and net nitrification rate) for the soil depth of 0–10 cm (a) and 10–20 cm (b). Means (\pm SE; $n = 3$) followed by the same letter indicates no significant differences in the net N mineralization 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 CO_2 exchange

CO_2 exchange indicates heterotrophic soil respiration in the incubation. No significant effect of soil moisture and site type on 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 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 CH_4 exchange

No significant CH_4 emissions were observed in any treatment (Fig. 7b). Incubations at 100% WFPS showed consistent near zero CH_4 fluxes or slight CH_4 uptake without significant effects of site type and temperature. At 70/83% WFPS the uptake of CH_4 was significantly ($P < 0.0001$) higher at all temperature levels and for both sites compared

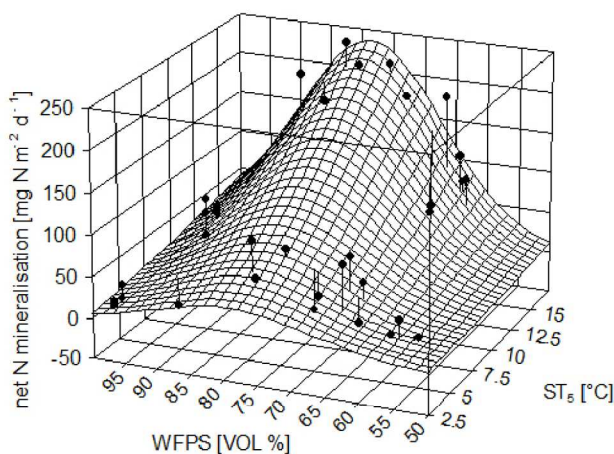


Figure 4. Relationship of net N mineralization in 0–10 cm soil depth (y) to mean water-filled pore space (x1) and mean soil temperature in 5 cm soil depth (x2) over 21 days of in situ incubation. Equation formula is $y = 304.28 (\pm 85.27) \cdot \exp(-0.5 \cdot (((WFPS - 25.72 (\pm 4.46)) / 11.47 (\pm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

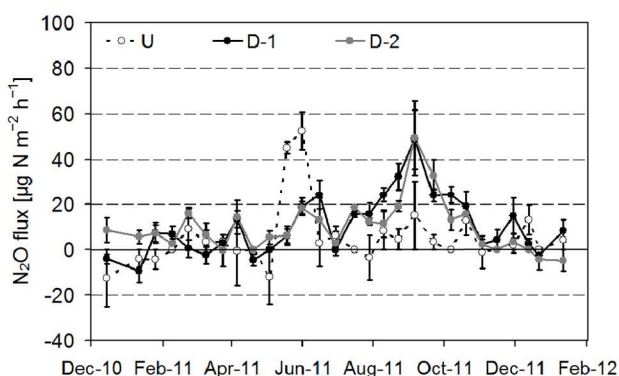


Figure 5. Mean (\pm SE, $n = 3$) N_2O fluxes of the undrained (U), drained 1 (D-1) and drained 2 (D-2) sites. Please note that the x axis starts on 1 December 2010.

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.

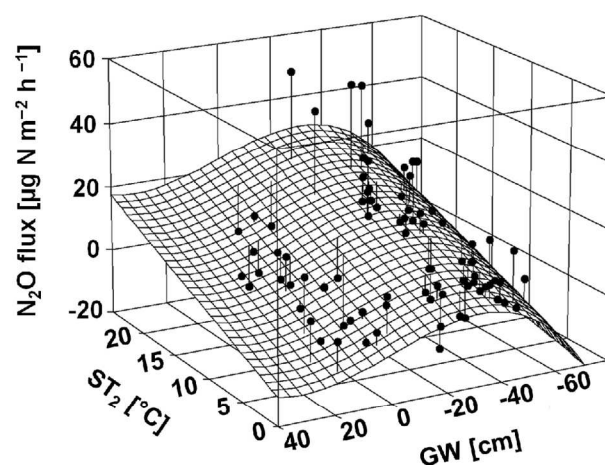


Figure 6. Relationship of mean N_2O flux (y) to mean soil temperature in 2 cm soil depth (x1) and to mean groundwater level (x2). Equation formula is $y = -4.884 (\pm 2.409) + 1.128 (\pm 0.179) \cdot ST_2 + (-0.322) (\pm 0.086) \cdot GW + 0.0004 (\pm 0.000) \cdot GW^3$ ($n = 80$; $adj-R^2 = 0.37$; $P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

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

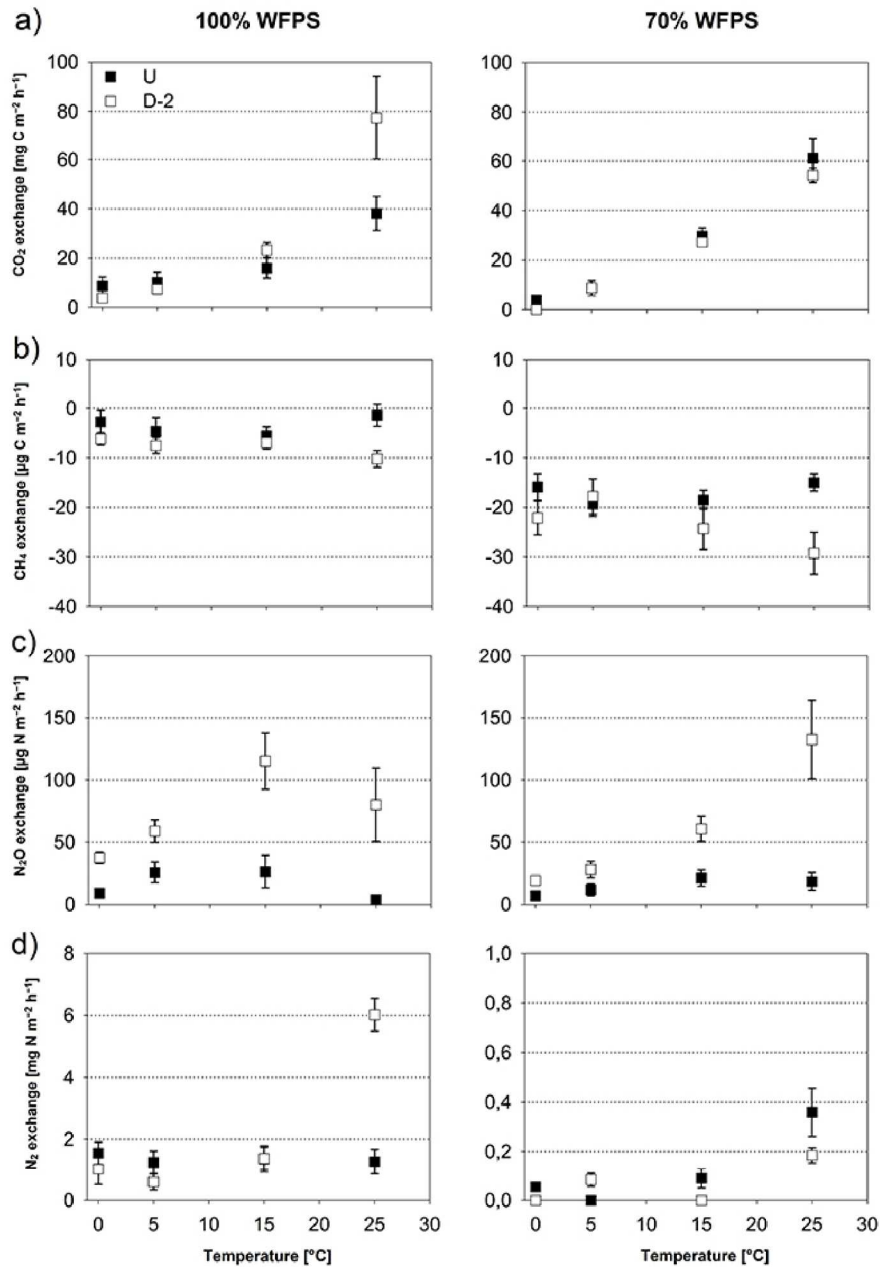


Figure 7. Mean (\pm SE, $n = 5$) of CO₂ (a), CH₄ (b), N₂O (c) and N₂ (d) exchange rates per water-filled pore space (vol. %; 70 % for D-2 and 83 % for U), temperature (°C) and site treatment. U = undrained; D-2 = drained 2. Please note the different scales for the N₂ exchange rates.

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

The high N₂ emissions observed at 100 % WFPS resulted in low N₂O/N₂ ratios, with mean values of 0.03 ± 0.01 (U) and 0.10 ± 0.02 (D-2). A similarly low N₂O/N₂ ratio (mean value of 0.12 ± 0.03) were found at 83 % WFPS for the samples from the U site, as a result of the low N₂O emissions. In contrast, the samples from the drained site D-2 showed a considerably higher N₂O/N₂ ratio, with a mean value of

0.62 ± 0.11 (note that in the case of zero N₂ fluxes no ratio was calculated). No relationship between temperature and N₂O/N₂ 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⁻¹ yr⁻¹) 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⁻¹ yr⁻¹ (0–15 cm soil depth) and of up to 321.2 kg ha⁻¹ yr⁻¹ (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⁻¹ yr⁻¹ (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 N₂ fixation by *Frankia* actinomycetes (Kätzel, 2003). Dittert (1992) estimated N₂ fixation rates of between 40 to 85 kg N ha⁻¹ yr⁻¹ 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 NO₃⁻ presence and NO₃⁻ 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 NH₄⁺ produced becomes immediately oxidized to NO₃⁻, 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 ¹⁵N 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 NO₃⁻ in the soil carry the risk of leaching or gaseous losses (Robertson, 1982). Several studies reported NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ into deeper soil layers. Analysis of groundwater samples from the sites investigated showed nitrate contents of up to 36.2 mg L⁻¹ and dissolved organic nitrogen (DON) contents of up to 2.8 mg L⁻¹ (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 N₂O/N₂ depends on the residence time of N₂O on its way from the production site in the anaerobic subsoil to the atmosphere (van Groenigen et al., 2005).

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4.2 Factors controlling temporal and site-specific variation in N₂O and N₂ fluxes

In the present study, field N₂O fluxes observed at the drained sites are very low. Different studies reported considerably higher values for N₂O emissions from drained black alder stands, varying from 5 to 75 kg N ha⁻¹ yr⁻¹ (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), NO₃⁻ availability is the main driver of N₂O emissions from drained histosols. However, despite distinct differences in the NO₃⁻ contents and NNM rates, significantly different N₂O 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 N₂O emissions. We cannot rule out, however, that we may have missed high N₂O events on the drained sites due to our regular measurement intervals. In addition many wetland adapted trees such as alder can mediate N₂O 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 N₂O emissions from the alder ecosystem.

In the alder forest investigated, temperature in -2 cm soil depth and the GW level best explained field N₂O flux rates, whereas no relationship was found between field N₂O fluxes and the amount of NO₃⁻ in the soil. It is well known that temperature is a key variable affecting the emission rates of N₂O 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 N₂O 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 N₂O flux rates. This demonstrates the complex interlinkage of the controlling factors for N₂O 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 N₂O emissions in fens; in contrast, Jungkunst et al. (2004) found highest annual N₂O 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 N₂O emissions. The observed cubic response to the GW level in our N₂O model reveals maximum N₂O 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 N₂O 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 N₂O 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 N₂O 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 N₂ increased more with increasing temperature than the production of N₂O, 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; Schindelbacher 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 N₂O 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 N₂O are only of minor importance compared to N₂ losses at water-saturated conditions. This agrees with findings that, with increasing anoxic conditions, the percentage of N₂ increases until it becomes the major gas evolved (Rolston et al., 1978; Davidson, 1991). Indeed several studies reported that high contents of available NO₃⁻ result in the inhibition of N₂O 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 NO₃⁻ availability inhibits the conversion of N₂O to N₂ at samples from site D-2. N₂O fluxes only declined in D-2 samples at water-saturated conditions and 25 °C with simultaneously exponentially increasing N₂ fluxes. While this mechanism supports our hypothesis that N₂O release is displaced by N₂ losses during periods of temporarily high water levels, the field observations never reached the point in which the decreasing N₂O : N₂ ratio overcompensated the increasing denitrification rate.

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In contrast to the field observations, significant differences in the N_2O 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 N_2O 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 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 CH_4 emissions were detected from water-saturated soil cores and aerobic and anaerobic CO_2 production was comparable and showed a distinct temperature response at both sites. However, at 100 % WFPS and 25 °C, the CO_2 to N gas emission ratio was 30 for site U and 13 for site D-2, indicating that anaerobic 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 N_2O and denitrification of the undrained site to NO_3^- limitation. The amount of 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, N_2O 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 NO_3^- limited at the undrained site, confirming our hypothesis that NO_3^- limitation in permanently waterlogged peat soils results in negligible N_2O and N_2 losses.

For N_2 fluxes no comparable values from the field are available in the literature, but 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 N_2O -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 N_2O 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 N_2O emissions from the drained alder sites under different soil physical conditions.

The low N_2O and 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 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, N_2O emissions in the field remained low at the drained sites, but we cannot rule out that we have missed N_2O emission peaks. The incubation experiment supported the potential for high N_2O emissions at the drained alder sites. Temporarily water-saturated conditions enhanced N_2 emissions, whereas N_2O emissions remained unchanged. In contrast, the permanently high groundwater level at the undrained site prevented net nitrification and resulted in negligible gaseous N losses.

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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 CO₂ fluxes from static chamber measurements, which were also determined simultaneously to N₂O 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 CO₂ exchange of ecosystems. However, despite of high uncertainty the site-specific mean CO₂ 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 CO₂ fluxes represent the sum of heterotrophic respiration (R_h), autotrophic respiration (R_a) from forest floor vegetation and autotrophic respiration from tree roots. Based on literature values, von Arnold (2005) assumed that 50% of the measured soil CO₂ 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 CO₂ release. There, R_h 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 CO₂ 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_a. 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. 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 GWP_{100} (reference period 100 years; IPCC, 2007) of the alder sites, net emissions of carbon equivalents of NECB and N_2O were summed, considering radiative forcing factors of 25 and 298 for the conversion of CH_4 and N_2O to 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 (CO₂, CH₄, N₂O) 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 _____

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9 CURRICULUM VITAE

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