Critical Factors of Post-Harvest Nitrous Oxide Emissions from Oilseed Rape – Cereal Rotations

- Evaluations Based on Field Studies and Stable Isotope Labeling -

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The sub-project of the project “Minderung von Treibhausgasemissionen im Rapsanbau unter besonderer Berücksichtigung der Stickstoffdüngung” of the division Plant Nutrition and Crop Physiology, Department of Crop Sciences of Georg-August University focused on steps in the nitrogen cycle that produce or interfere with N_2O emissions from soils. It addressed the question of how the N cycle is modified by a winter oilseed rape – winter wheat – winter barley crop rotation. The focus of the doctoral thesis was put on the post-harvest period and the production of N_2O emissions in winter oilseed rape. Several lab and field experiments were conducted:

(1) Incubation experiment using oilseed rape and ^{15}*N-labelled barley straw*

An incubation experiment carried out under controlled conditions aimed at comparing N addition and different straw qualities for their potential to provoke N_2O emissions from soil. Treatments consisted of non-treated control soil (CK), ^{15}N labelled barley straw (BST), oilseed rape straw (RST), ^{15}N labelled barley straw + mineral N (BST+N), or oilseed rape straw + mineral N (RST+N). N fertilizer was applied to the soil surface as calcium ammonium-nitrate at a rate of 67.5 mg N kg^{-1} soil equiv. to 100 kg N ha^{-1} and soil moisture was adjusted to 80% water-holding capacity. The experiment covered a measurement period of 43 days.

Cumulative N_2O emissions in this study summed up to 3, 19, 26, 439 and 387µg N_2O-N kg^{-1} soil 43 $days^{-1}$ for CK, BST, RST, BST+N and RST+N. Application of mineral N fertilizer to the straw amended soils enhanced N_2O emissions considerably in BST+N and RST+N treatments masking the effect of straw type. ^{15}N labeling showed that only about 0.72% and 0.46% of the emitted N_2O originated from straw-N in the BST and BST+N treatments after 22 days indicating a very low share of straw-borne N to the formation of N_2O emissions.

In agricultural practice, an N fertilization to soils amended with C-rich residues in the post-harvest period could lead to high N_2O emissions.

(2) Post-harvest N_2O *emissions as affected by N fertilizer and straw management – 2 year study at the site Reinshof*

Management options to mitigate N_2O emissions in oilseed rape cropping were tested in a 2-year field experiment at the field site Reinshof of the Faculty of Agricultural Sciences of Georg-August University of Goettingen. The treatments included a reduced spring N fertilization rate (1/2 of current recommendation), N fertilization of 180 kg N ha^{-1} and oilseed rape straw removal after harvest. N_2O sampling was done from oilseed rape harvest to the beginning of the following growth season. The COUP model (Coupled heat and mass transfer model for the soil-plant-atmosphere system) was employed to uncover possible mechanisms of N_2O emissions.

In 2013, cumulative August-March N_2O emissions ranged between 0.46±0.05 kg N_2O-N ha^{-1} (0 kg N ha^{-1}, with straw removal) and 1.05±0.1 kg N_2O-N ha^{-1} (180 kg N ha^{-1} with straw application) whereas in 2014 N_2O emissions were clearly higher accounting for 4.06±0.34 (90 kg N ha^{-1}, with straw application) und 7.33±0.24 kg N_2O-N ha^{-1} (unfertilized control soil with straw incorporation).

There was no statistically significant effect of fertilization ($p>0.05$), but straw removal compared to straw incorporation slightly increased N_2O emissions. In contrast to management measures, soil temperature and soil moisture showed a large influence on the rates of N_2O emissions. The modeling approach indicated the importance of decomposition activity. Decomposition accelerated N cycling and in particular denitrification rates with high N_2O emissions.

(3) Field studies in five regions of Germany in a winter oilseed rape – winter wheat – winter barley crop rotation

For a detailed evaluation of N_2O emissions in important oilseed rape cropping regions of Germany, 5 field experimental sites across Germany – Berge, Dedelow, Ihinger Hof, Hohenschulen and Merbitz – were chosen. To allow comparability, the crops were grown simultaneously from December 2012 to October 2015. Various parameters like soil temperature and water-filled pore space (WFPS) were recorded and N_2O emissions were measured in the crops oilseed rape, wheat and barley and yield-related N_2O emissions were calculated. To assess the impact of abiotic factors and crops, a generalized additive model was set up.

The generalized additive model revealed that the abiotic factors drove N_2O emissions. The impact of environmental drivers like temperature and WFPS on N_2O emissions varied depending on site, but not by crop type. Fertilizer-related N_2O emissions across all five sites were 0.76, 0.74 and 0.76% of the applied fertilizer N for oilseed rape, winter wheat and winter barley, respectively. N_2O emissions from non-fertilized soils were not considered in this approach.

Generally, the thesis demonstrated the dependence of N_2O emissions on a set of factors in the post-harvest period. The factor's level of importance changed as they were varying in magnitude. Management options have to be reevaluated and adopted to fit a changing climate.

1 Introduction

1.1 EU Renewable energies directive (2009/28/EC)

The EU members have agreed to cover 20 % of their final energy consumption by renewable energy sources by 2020. They also agreed to supply 10 % of the transport fuels by renewable sources. To reach these aims, the EU Renewable energies directive (EU RED 2009/28/EC, 2009) was implemented in 2009. As a consequence of the EU RED the availability of renewable energy has more than doubled in the years from 1990 to 2010 (European Commission, 2017). It should be noted that liquid biofuels like bioethanol or biodiesel, which were not present in the main body of renewable energy consumption in 1990, have increased to ca. 5 % in 2010 (Eurostat, 2014). Biodiesel is produced from plants that have high seed oil concentrations. Especially, the cultivation of oilseed rape has increased by 30 % to 1.3 million ha in Germany since 1995 (Statista, 2017, Statistisches Bundesamt, 2016).

1.2 N_2O emissions and their effect on the environment

N_2O is a product of several processes in the soil and, when released into the atmosphere, irretrievably lost for agricultural N management. Ultimately, N_2O photo-chemically reacts with O_2 in the troposphere and leads to the formation of ozone (O_3). O_3 is a compound harmful to humans, animals and vegetation and known to cause severe health problems (Amann et al., 2008).

Next to CO_2 and CH_4, N_2O is a very potent greenhouse gas with one of the highest warming potential. The IPCC (2014) defines the warming potential of one molecule of N_2O to be 265 times greater than one molecule of CO_2. This makes it vital to quantify, and if necessary, to mitigate its release from soil.

1.3 The production of oilseed rape and the soil N cycle

Oilseed rape is commonly integrated into cereal crop rotations with a share of 1/3. As a break crop it brings beneficial effects for the subsequent crop. For example, bulk density is decreased due to the penetration of soil by the tap root or the N-rich residues of oilseed rape promote to immobilize residual soil mineral N for the following cereal crop. Additionally, farmers grow oilseed rape as a break crop because it helps to prevent cereal specific diseases from spreading.

Oilseed rape cropping affects the N cycle in the soil in various ways. Winter oilseed rape is normally seeded from the middle of August to the beginning of September.

- Generally, The N demand of winter oilseed rape is assumed to amount to 200 kg N ha^{-1}. To calculate the amount of needed N fertilizer, the mineral N concentration in the first 90 cm of the soil must be subtracted (Landwirtschaftskammer Niedersachsen, 2015). N fertilization in the spring with two dressings is a common practice to meet the high demand of N for the built up of biomass during the early growth period. A study by Silvester-Bradley and Kindred (2009) described a low

N use efficiency (NUE) and a low N harvest index for winter oilseed rape compared to those of cereals. They defined NUE as the produced dry matter per unit N taken up by the crop. In the course of the growth period, the applied fertilizer N is taken up by oilseed rape. Even though the N uptake by the plant is high, it can be assumed that only a small share of N is removed by harvest which was evident in the data set by Gan et al (2011). The remaining N is contained in the aboveground biomass and enters the soil as N-rich residue. Gan et al. (2011) compared the C and N distribution in the root biomass of several oilseed crops. They found that the uppermost soil layer (0-40 cm), holding around ¾ of the entire root biomass contained 10 kg N ha^{-1}. Collectively, the input of N from oilseed rape straw and its roots accounted for ca. 50 kg N ha^{-1}. However, soil benefits from incorporation of straw remains. Straw can help to improve the soil quality with regulating soil moisture and supporting soil structure (Lal, 2005). It also supplies energy (C) for the heterotrophic microbes responsible for the N cycle in the soil. After the harvest, the remaining N in the soil can take several routes:

- The procedures during the oilseed rape harvest are usually accompanied by the loss of seeds due to side knife cutting, for instance, or the premature opening of pods caused by the machinery. The seed loss of a 2.2 t ha^{-1} harvest yield is approximated to 150 kg ha^{-1} (Hobson and Bruce, 2002). With the loss of seeds, the potential of emerging volunteer rape rises which can take up soil mineral N. Justes et al. (1999) summarized that the volunteer rape reached a density of 2600 plants m^{-2} and took up 28 kg N ha^{-1} of the residual N in the soil.

- After the harvest of oilseed rape, it is assumed that some part of the applied fertilizer N remains in the soil as NH_4 and NO_3. Especially a high load of NO_3 leaches into deeper soil layers and subsequently into the groundwater. It was found that N leaching during the cultivation of oilseed rape is comparatively higher than N leaching on winter barley fields (Sieling & Kage, 2006).

- NO_3 can also be reduced by the detrimental processes of denitrification.

1.4 N_2O-producing soil processes

N_2O is formed by various biochemical processes. In the following, their quantitative contributions and related experiments are outlined and disscussed:

Chemodenitrification defines the reduction of mineral N compounds (mainly nitrite NO_2) in the soil to NO or N_2O by iron or humic acids (Samarkin et al., 2010 , Kappelmeyer et al., 2003). However, chemodenitrification plays only a minor role in the production of N_2O in agricultural soils because it requires a low pH to take place (Hu et al., 2015). Other pathways which lead to the convertion of N into N_2O in the soil are described by the coupled biotic-abiotic production of N_2O, for instance, in which hydroxylamine (NH_2OH) is oxidized to N_2O by transition metals (Heil et al., 2015), or the reduction of dissimilatory NO_3 to NH_4 (Rütting et al., 2011, Schmidt et al., 2011). Ultimately, biological transformations of N compounds to N_2O include the processes of nitrification, denitrification and also nitrifier denitrification (Wrage et al., 2001).

Under aerobic conditions, nitrification is the oxidation of ammonia (NH_3) and ammonium (NH_4) in two steps with NH_2OH and NO_2 as intermediates and NO_3 as the oxidized product. Here, NH_3 and

NO_2 function as electron donators to obtain energy and O_2 is the final electron acceptor. N_2O is a side product and originates from the decomposition of NH_2OH. Under O2-limited conditions, the gradual reduction of NO_3 via NO_2, NO and N_2O to N_2 is defined as denitrification. Here, NO_x-molecules are electron acceptors and fulfil the same purpose as O2 does under aerobic conditions. Denitrification is also a central process in which N_2O can be reduced into the non-greenhouse gas (non-GHG) N_2. Nitrifier denitrification is mediated by ammonia-oxidizing bacteria and includes several steps: NH_3 is oxidized to NO_2 and further reduced to NO and N_2O.

N_2O production and release from the soil is caused by bacterial activity, but fungi and archaea also play important roles. Especially, the decomposition of large-sized particles is carried out by fungi and is a crucial process in cultivated soils.

1.5 Factors enhancing and reducing N_2O emissions from agricultural soils

Micro-organisms in the soil produce N_2O. However, the formation of N_2O is enhanced by specific soil conditions. García-Marco et al. (2014) propose a list of factors promoting N_2O production like, for example, the level of NO_3 availability, C sources and temperature. Particularly the source can vary in the degradability. Glucose is easily taken up and metabolized by soil microorganisms while C-rich straw particles require decomposition into smaller fragments before it can be utilized. Furthermore, Hu et al. (2015) name oxygen and water content as well as soil pH as important factors. These factors control the levels of nitrification, denitrification and nitrifier denitrification involved in the production of N_2O.

Cropped soils are subject to management modifications which influence a large part of the controlling factors. Before harvest, for example, the crop stands shade the surface of the soil and stabilize soil temperature and water content. Harvest causes the removal of the protective plant stand, so that the soil surface becomes exposed to radiation of the sun, on the one hand, and infiltration of water is increased as interception of plants is offset. Here, the input of N and C as straw into the soil can be high.

1.6 Structure and objectives

Farming in general, and oilseed rape cultivation in particular, produces N_2O emissions because of applied management practices and their interactions with biotic and abiotic factors. Common management practices include fertilization, e.g. the selection and dosage of suitable types of fertilizer. They also include the post-harvest management of a field like the clearing away of straw or working in of harvest residues into the soil by rototilling.

Biotic factors include the crop which require a specific management and its influence on the agroecosystem whereas the abiotic factors describe the physical and chemical conditions of the soil as well as the climatic factors affecting the stand like temperature and precipitation. In particular, the local seasonal climate pattern plays a major role in the formation of N_2O in agricultural systems.

To gain a systematic insight into the patterns and quantities of N_2O released from the soil and those controlling factors an incubation experiment and two field experiments were conducted in the course of oilseed rape cultivation. The 2nd and 3rd chapter of this study present new information about the post-harvest period in cropping systems. The 4th chapter gives a broader perspective on oilseed rape-based crop rotations and new information about post-harvest N_2O emissions in oilseed rape in contrast to N_2O emissions from cereal stands.

Chapter 2 addresses the incubation experiment which aims to elaborate on the importance of straw stoichiometry on N_2O emissions. The C/N ratio of straw shows a close connection to the N cycling and the release of N_2O from agricultural soils (see also meta-analysis by Chen et al., 2013). Numerous studies (e.g. Chen et al., 2013) discussed the addition of straw to soil and the triggering of N_2O emissions, but only a few connected it to the addition of ^{15}N labelled straw to estimate the straw-N released as N_2O (Ocio et al., 1991, Trinsoutrout et al., 2000). For this thesis the straw of oilseed rape and winter barley were incorporated into the soil and N_2O emissions and compared to a non-treated control soil. In general, straw provides an energy source to soil microorganisms, but also supplies substrate for other N processes. Mineralization and immobilization are key processes and were examined by measuring NH_4 and NO_3 concentrations in the soil. ^{15}N-N_2O emissions of barley straw were analyzed to investigate when straw-derived N_2O concentrations are highest and how much it contributes to the cumulative N_2O emissions. CO_2 emissions were also recorded as key indicators of soil microbial activity and straw decomposition.

Chapter 3 focusses on the 2-year field experiment conducted at the Reinshof research station near Goettingen. Oilseed rape is a crop with a high N demand during spring time. In the period approaching harvest, oilseed rape sheds its leaves which are partially broken down and enter the soil thereby increasing the mineral N concentration in the soil. During the post-harvest period, N and C-rich oilseed rape residues enter the soil providing substrate for decomposition which also fuels the N soil cycle. The aim of this study was to quantify the post-harvest N_2O emissions and investigate key processes controlling them in detail. To receive knowledge on N_2O emissions by straw, straw was either removed or added as treatments. Immediately after oilseed rape harvest, gas samples were taken until the following spring period in winter wheat. By means of the COUP model underlying processes leading to the contrasting N_2O emissions between the years 2013/2014 and 2014/2015 were analyzed. The Coup model was supplied with N_2O, NH_4, NO_3, CO_2, soil temperature, meteorological data like precipitation, air temperature, wind speed, relative humidity and global radiation and harvest parameters like yield and residue production.

Chapter 4 deals with a broader perspective of oilseed rape production and puts the focus on the level of a crop rotation. For biodiesel production, oilseed rape is mostly integrated into cereal crop rotations with wheat and barley. Oilseed rape prefers sandy to loamy soils which are found in. To evaluate the N_2O emissions for an oilseed rape based crop rotation with winter wheat and winter barley, a 3-year field experiment in the course of the crop rotation of winter oilseed rape, winter wheat and winter barley was conducted at five sites in Germany representing the typical production regions. With the help of climate datea and soil variables as well as mineral N concentrations of the soil it was possible to use a Generalized Additive Model to determine the factors triggering N_2O emissions for the respective crop and site. The simultaneous cropping of winter oilseed rape, winter wheat and winter barley enabled us to put a special focus on post-harvest N_2O emissions of each crop type in the respective years. To evaluate a crop rotation with respect to output units, N_2O emissions of oilseed rape, winter wheat and winter barley were associated to mass yield, nutritional yield and energy as reference values to evaluate their utility.

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2 Post-harvest N_2O emissions related to plant residue incorporation (oilseed rape and barley straw) depend on soil NO_3^- content

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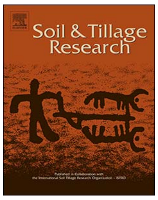

Post-harvest N_2O and CO_2 emissions related to plant residue incorporation of oilseed rape and barley straw depend on soil NO_3- content

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ABSTRACT

The sustainable production of bioenergy from crops like oilseed rape, barley, and maize presents a significant option to mitigate climate change by reducing fossil CO_2 emissions. Greenhouse gas emissions (specifically N_2O) during the energy crop production need to be quantified precisely for reliable life cycle analysis of bioenergy cropping systems. Energy crops (specifically oilseed rape) have a very high N demand, which results in a higher N-fertilizer application and thus higher risk of N_2O emissions not only during the vegetation period but also after crop harvest due to i) incorporation of N rich plant residue to soil and/or ii) residual N. An incubation experiment was conducted under conditions favoring denitrification (80% water-holding capacity), to study the drivers of N_2O emissions specifically during the post-harvest period. Here we compared two different plant residues varying in C/N ratio (oilseed rape (RST) and barley straw (BST)) with or without N supply and measured CO_2, and N_2O emissions. Stable isotope labeling (^{15}N) was used to quantify soil- and residue-born N_2O. Incorporation of both plant residues alone induced significant increases in CO_2 emissions compared to control soil without straw addition ($p < .05$). However, the increase in CO_2 emissions was less pronounced when straw was incorporated in conjunction with mineral N. There was a clear increase in cumulative N_2O emissions ($p < .05$) when soil amended with BST or RST (6- and 9-fold) was compared to control, however, the increase of cumulative N_2O emissions was drastic when mineral N was added (15- and 23-fold). No significant differences in N_2O emission were observed when comparing residue types ($p > .05$). Stable isotope labeling of barley straw clearly showed that the share of residue-born N_2O was very low (1.35 or 0.4%) in the overall N_2O fluxes in BST and BST + N.

The present study suggests that N fertilization in autumn should be avoided to minimize N_2O fluxes regardless of type of straw.

1. Introduction

Renewable energies have gained great attention in policy making and the EU Renewable Energies Directive has been released aiming to increase the share of renewable sources in the energy supply to 20% (EU RED 2009/28/EC, 2009). The latter aims to reduce the consumption of fossil fuels and the emission of climate relevant carbon dioxide (CO_2). However, there is great concern that in the course of producing energy crops, the formation and emission of other potent greenhouse gases such as nitrous oxide (N_2O) would negate climate benefits. In northwestern Europe, oilseed rape based crop rotations have moved into focus as this crop has reached a large share in biodiesel production. Additional crops in oilseed rape crop rotations are the cereals barley and wheat. So far, greenhouse gas (GHG) emissions in oilseed rape cropping systems seem to be greater than in others, e.g. cereal rotations (Walter et al., 2014).

After harvest, straw incorporation is a common and important agricultural practice to improve soil fertility. It improves soil physical conditions like aggregate stability and water infiltration and chemical properties like pH as well as macro- and micro-nutrient availability (Blanco-Canqui and Lal, 2009). Added straw provides a source of organic carbon and energy, but also a small share of nitrogen for decomposing soil microorganisms, which are essential for C and N mineralization (Chen et al., 2014a) as well as for vital soil microbial communities. Several studies show that the incorporation of plant residues into the soil increases both, biomass and activity of soil

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microorganisms (Blanco-Canqui and Lal, 2009; Potthoff et al., 2005; Rousk and Bååth, 2007), thus, contributing to CO_2 and also N_2O emissions from soil (e.g. Begum et al., 2014; Velthof et al., 2002). The velocity of CO_2 and N_2O emissions after straw incorporation depends on the mass and type of straw. Important characteristics are C and N concentrations of straw as well as the ratio of both (Huang et al., 2004). A low C/N ratio leads to the mobilization of straw C and N and its release into the soil mineral N pool which functions as substrates for microbial processes leading to CO_2 and N_2O emissions. Oilseed rape straw is ascribed a higher N concentration and a lower C/N ratio than barley straw which may accelerate its breakdown and its release of straw-N to the soil mineral N pool by soil microorganisms (Walter et al., 2014).

With respect to post-harvest processes in soil, there is another important post-harvest agricultural practice besides the incorporation of straw. Often N fertilizers are applied to foster straw mineralization and to warrant sufficient available N for the following crop. However, N addition to soil does not only promote residue mineralization and CO_2 production, but it may also favor nitrification and denitrification, potentially contributing to enhanced nitrate (NO_3^-) leaching and N_2O release from soil to atmosphere. This may pose economic and environmental risks (Crutzen, 1970; Kaiser and Brenninkmeijer, 2002; Prather and Hsu, 2010). Additionally, N_2O is one of the most potent greenhouse gases with a global warming potential being 265 times higher than that of CO_2 on a 100-year-basis (Myhre et al., 2013).

To prevent the release of large amounts of N_2O, it is crucial to distinguish the various chemical and biological pathways forming N_2O. The most dominant biological processes are nitrification, denitrification and also nitrifier denitrification (Wrage et al., 2001). The microbial formation of N_2O and N_2 is also enhanced by specific soil physiochemical properties. García-Marco et al. (2014) list various factors like high NO_3^- availability and a C source leading to favorable conditions for N_2O production by denitrification. The addition of a labile C source, e.g. straw or root exudates can increase microbial activities as well as greenhouse gas emissions. This effect is more pronounced if the added C-source has a low C/N ratio, as shown by Huang et al. 2004. Nevertheless, also the addition of straw with a high C/N ratio leads to increasing N_2O emissions, although they are lower than emissions from soils amended with low C/N straw (Huang et al. 2004).

A number of studies have highlighted the connection of organic amendments to agricultural soil and its importance on soil N cycling (e.g. Chen et al., 2013; Chen et al., 2014a; Knorr et al., 2005; Thangarajan et al., 2013). However, there is little information on the release of residue N in form of N_2O (Frimpong and Baggs, 2010; Gentile et al., 2008; Millar and Baggs, 2005). So far, there is evidence that the increase of released N_2O might not be directly triggered by N released from straw which entered the soil mineral N pool (Frimpong and Baggs, 2010; Millar and Baggs, 2005). In the course of agricultural management, plant residues are regularly incorporated into the soil after harvest where they influence nitrogen turnover processes.

In this context, we have following hypothesis:

(i) the annulment of N limitation will be followed by high soil CO_2 emissions and high soil mineral N content,
(ii) the low C/N ratio of the oilseed rape residue will lead to higher N_2O emissions compared to barley straw with high C/N, and
(iii) fertilizer N will promote the release of residue N as N_2O because of mineral N fluctuations that accelerate decomposition and soil N cycling.

For examining above mentioned hypothesis, we conducted an automated continuous flow incubation trial and monitored gas fluxes. In our incubation study, we focused on effects of incorporation of oilseed rape straw and barley straw on CO_2 emissions, soil N dynamics and N_2O emissions. In addition, N fertilizer application was considered to unravel potential nitrogen limitation of straw amended soils affecting the release of CO_2 and N_2O. Stable isotope labelling approach was used to study the share of straw-N emitted as N_2O. In addition, we quantified the genes encoding the subunit of the nitrous oxide reductase (*nosZ*), responsible for the reduction of N_2O to N_2.

2. Material and methods

2.1. Experimental incubation set-up

A soil incubation experiment was carried out in a fully automated continuous flow incubation system using 15 incubation vessels of 20 cm diameter and 22 cm height. Soil was repacked (5.8 kg FW, 4.8 kg DM) into each incubation vessel including control soils (non-treated soil) to a final soil density of 0.96 g soil DM cm^{-3}. The upper 15 cm of the mineral soil (Luvisol, clay 25%, silt 65.5%, sand 9.5%, pH $_{(CaCl2)}$ 6.6, C 1.02%, N 0.11%) had been collected in spring 2013 from an unfertilized farmer's field in Sattenhausen close to Goettingen (51.51° N, 10.13° E). It was carefully air dried to allow sieving with a 4 mm mesh sieve. Complete drying out was avoided to minimize mineralization after rewetting.

To simulate good agricultural practice, ^{15}N labeled barley (*Hordeum vulgare*, Total C: 41.17, Total N: 0.73, C/N: 56.45) or oilseed rape (*Brassica napus*, Total C: 43.97, Total N: 0.94, C/N: 46.61) straw was mixed with the upper 10 cm of soil prior to the experiment at a rate of 1.5 g straw DM kg^{-1} soil DM. The straw was cut with scissors to a length of 2 cm to avoid large straw particles.

Prior to the experiment, 0.325 g of N was applied to the soil surface in the form of calcium ammonium nitrate (CAN, solid commercial fertilizer, 100 kg N ha^{-1} equiv. to 67.5 mg N kg^{-1} soil) in the respective treatments following rewetting of soil to c. 80% water holding capacity (WHC) by carefully dripping distilled water on the soil surface including the control. WHC was determined by putting a soil column in a cylindrical tube with a water-permeable membrane fixed underneath. The tube with the soil column placed into a water bath to saturate the soil column with water. Subsequently, the tube with the soil column was removed from the water bath and left for 24 h so that excessive water could run off through the membrane by gravity. By weighing, water content left in the soil column can be calculated. The amount of water left after 24 h is equal to 100% WHC. To adjust to 80% WHC, the water contents of the fresh soil and that of 80% WHC were used for calculation. Moisture conditions normally vary from year to year. To simulate frequently occurring moist conditions in autumn and to favor denitrification, WHC has been set to 80%. N addition reflects a high soil N level as typical fertilizer rates range from 30 to 40 kg N ha^{-1} to agricultural fields in autumn.

All incubation vessels were sealed airtight and continuously flushed with synthetic air at a flow rate of 15 to 20 ml min^{-1} to ensure aerobic conditions. The experiment was carried out in a temperature controlled environment at 22 °C and lasted for 43 days. For additional soil sampling a parallel system was set up under the same conditions in the same laboratory. Soil sampling was done every other day and after day 10, the time between sampling of soil was increased. Soil samples for molecular analysis were collected at day 1, 7, 11 and 25 and stored at −80 °C until further use. Overall, there were five soil treatments including non-treated control soil (CK), barley straw incorporation only (BST), oilseed rape straw incorporation only (RST), barley straw + N (BST + N), or oilseed rape straw + N (RST + N), all carried out in three replications.

2.2. Soil analysis

For determination of soil mineral N content, 9 g of soil FW were sampled and immediately processed to minimize mineralization. Samples were extracted with a 0.0125 M $CaCl_2$ solution (1:5 w/v) for 45 min. on an overhead shaker (85 rpm). The extracts were filtered with 615 ¼ filter paper (Macherey – Nagel GmbH & Co. KG, Düren, Germany) and stored at 20 °C. The extracts were analyzed colorimetrically for the concentrations of NO_3^- and NH_4^+ using the San + + Continuous-Flow Analyzer (Skalar Analytical B.V., Breda, The Netherlands). Soil water content was determined with a parallel set of samples.

2.3. Trace gas measurements

For online analysis of N_2O and CO_2, gas samples from all vessel outlets were directed sequentially to a Bruker gas chromatograph (450-GC, Bruker, Billerica, USA) via two multi-position valves (9 and 16 ports) with a multi-position actuator control module (Valco Instruments Co. Inc., Huston, TX, USA) and an interface module (506C System Interface, Gilson, Inc., Middleton, WI, USA) controlled by Trilution Software (Gilson Inc., Middleton, WI, USA). The gas samples were analyzed by GC deploying a thermal conductivity detector (TCD) for CO_2, and an electron capture detector (ECD) for N_2O. Gas samples were taken at least every 7 h for 23 days. The resolution in time was decreased to one analysis per day for the remaining period.

2.4. Stable isotope analysis ^{15}N-N_2O

For the stable isotope study in the incubation experiment, barley straw was labelled with ^{15}N and had an enrichment of 33.07 at% ^{15}N. Serum flasks were evacuated and filled with gas sample via the outlet pipe of each incubation vessel. The gas sample was injected by a two-hole-needle by flushing the serum flask with He as carrier gas. Before stable nitrogen isotope analysis of N_2O was carried out with an isotope ratio mass spectrometer (MAT 253, Thermo Scientific, Waltham, MA, USA), the collected gas sample was cleaned from water with a Nafion Tube and to separate compounds, a molsieve (5A) GC column was installed.

In order to obtain the share of ^{15}N labelled N_2O in the emitted N_2O, gas samples were taken every day in the first week, then with a 10-day gap and a final sampling after 5 more days. ^{15}N labelled barley straw has been produced by growing summer barley plants (*Hordeum vulgare*) in 30 L plastic containers in a screenhouse with 95 at% ^{15}N-labelled urea at a level of 460 mg N kg^{-1} soil DM. To calculate straw-N-derived N_2O, an equation according to Gentile et al. (2008) was used:

$$Q_{Straw} = Q_{Sample}\left(\frac{^{15}N_{Sample} - {}^{15}N_{natural\ abundance}}{^{15}N_{Straw} - {}^{15}N_{natural\ abundance}}\right)$$

where Q_{Straw} is the quantity of N in the N_2O-N emissions derived from the straw, Q_{Sample} is the N measured in the N_2O, $^{15}N_{Sample}$ is the at % of N_2O, $^{15}N_{natural\ abundance}$ is the natural abundance of the control soil and the $^{15}N_{Straw}$ is the at % of the straw.

The ^{15}N natural abundance of the control soils (average 0.369 at% ^{15}N) was measured on every sampling day and the mean was subtracted from the ^{15}N enrichment of the gas sample, respectively.

2.5. Extraction of RNA and cDNA synthesis

To quantify the transcription of bacterial *nosZ* genes encoding nitrous oxide reductase, total RNA was isolated from 1 g of soil per sample using the RNA PowerSoil™ total RNA isolation kit, as indicated by the manufacturer (MO BIO Laboratories Inc., Carlsbad, CA, USA). The resulting RNA pellet was dissolved in 50 µl RNase-free water. To avoid degradation of the isolated RNA, 0.7 µl of the RiboLock RNase Inhibitor (Thermo Scientific, Inc., Waltham, MA, USA) were added to each sample. Residual DNA contaminations were removed using the TURBO DNA-*free*™ kit (Life Technologies, Carlsbad, CA, USA) as described by the manufacturer. The DNA-free RNA was further checked for remaining DNA contaminations using PCR. Additionally, DNase-treated RNA was purified and concentrated in a final volume of 14 µl using the RNeasy MinElute cleanup kit (Qiagen GmbH, Hilden, Germany). The concentration of the purified RNA extracts was determined using the Qubit RNA HS Assay Kit (Life Technologies) and a Qubit fluorometer (Life Technologies). Subsequently, 0.5 µl RiboLock RNase Inhibitor (Thermo Scientific, Inc) were added to each sample to avoid degradation of the purified RNA extracts during storage at −80 °C and the following procedures. The cDNA synthesis was performed using the SuperScript™ II reverse transcriptase (Invitrogen, Karlsruhe). Initial denaturation and primer annealing was conducted in a mixture (12 µl) containing 10 µl of isolated DNA-free RNA, as well as 2 µM random primer pd(N)6 (Roche, Mannheim, Germany) and 10 mM dNTP mix, which was incubated for 5 min at 65 °C and chilled on ice for at least 2 min. A mixture (6 µl) containing 4 µl 5-fold First Strand buffer and 2 µl of 0.1 M DTT, was added. The reaction mixture was incubated for 2 min at 25 °C before adding 200 U SuperScriptTM II reverse transcriptase. The cDNA synthesis mixture was incubated for 10 min at 25 °C and for additional 50 min at 42 °C. The reaction was terminated at 70 °C for 15 min and the resulting cDNA was stored at −80 °C.

2.6. Quantification of nosZ gene transcripts

The *nosZ* standard used was derived from (Bannert et al., 2011). As standard, serial plasmid dilutions of the *nosZ* gene derived from *Pseudomonas fluorescence* using the primer pair 5′-CGCRACGGCAASAAGG-TSMSSGT-3′ (nosZ2F) and 5′-CAKRTGCAKSGCRTGGCAGAA-3′ (nosZ2R), were used (Henry et al., 2006). The final concentration of the plasmid extract was determined using the Qubit dsDNA BR Assay Kit (Life Technologies) and a Qubit fluorometer (Life Technologies). The copy number per µl was calculated based on the concentration, weight and length of the respective plasmids. The serial plasmid dilution ranged from 10^1 to 10^8 gene copies per µl. Quantification of *nosZ* gene transcripts was performed on an iQ™5 real-time PCR detection system (Bio-Rad Laboratories, Inc., Hercules, CA, USA) using the SYBR® Green PCR Master Mix (Life Technologies) and the same primer pair (nosZ2F and nosZ2R) used for standard preparations. To quantify the gene transcript copy numbers we used 1 µl of 1:10 diluted cDNA, equivalent to 0.5% of the extracted RNA per g soil. The reaction mixture (25µL) contained 12.5 µL SYBR® Green PCR Master Mix, 2 µM of each of the primers and the template DNA. The following thermal cycling scheme was used: initial denaturation at 95 °C for 15 min, followed by 46 cycles of denaturation at 95 °C for 15 s, annealing at 62 °C for 30 s, extension at 72 °C for 30 s and data acquisition step at 80 °C for 15 s. Data were acquired at 80 °C to avoid signals from non-specific products or primer dimers. Standard curves were generated to depict the relationship between gene copy numbers and threshold cycle values. Furthermore, standard curves were conducted on every 96-well plate in every qPCR run. Copy numbers of the analyzed soil samples were determined using the standard curves. All measurements were conducted in triplicate.

2.7. Statistics

CO_2 and N_2O emissions were shown as arithmetic mean of the three replicates with one standard error. The cumulative CO_2 and N_2O emissions were calculated by linear interpolation between measurements. Cumulative CO_2 emissions were analyzed with an ANOVA followed by a Tukey test. For cumulative N_2O emissions, a One Way ANOVA was performed with the focus on straw addition and excluding the + treatments. To check for pairwise multiple differences among groups, Tukey's test with $p < .05$ as criterion for significant differences was used. Statistical analyses were done with SigmaPlot 13.0 (Systat Software GmbH, Erkrath, Germany).

3. Results

3.1. Soil GHG emissions

Emissions of CO_2 from non-treated control soils increased

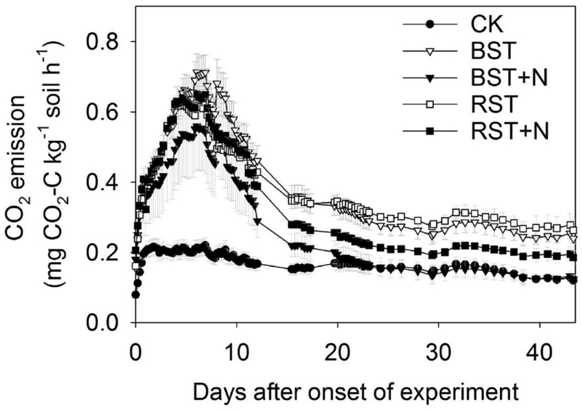

Fig. 1. Daily CO_2 emissions from soils after incorporation of oilseed rape straw (RST) and barley straw (BST) only and with N fertilizer (RST + N, BST + N) in the incubation experiment (CK: non-treated control soil). Error bars show the standard error of the mean of each treatment (n = 3). In some cases error bars are smaller than the symbols.

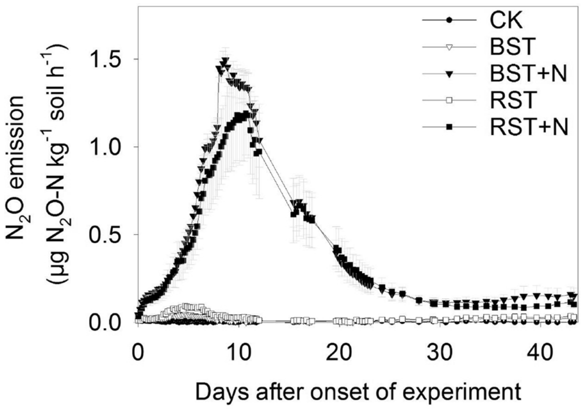

Fig. 2. Daily N_2O emissions from soils after incorporation of oilseed rape straw (RST) and barley straw (BST) without and with N fertilizer (RST + N, BST + N) in the incubation experiment (CK: non-treated control soil). Error bars show the standard error of the mean of each treatment (n = 3). In some cases error bars are smaller than the symbols.

significantly after onset of treatments for about 48 h and remained constant throughout the incubation period ($p < .05$, Fig. 1). Here, maximum rates were 0.2 mg CO_2-C kg^{-1} soil h^{-1} in the control treatment. Addition of straw (RST and BST) induced a significant increase ($p < .05$) in respiration, and maximum CO_2 emissions were reached within five days after onset of treatments (DAO). Afterwards, fluxes of CO_2 decreased steadily but were still significantly higher ($p < .05$) than those of non-amended control soil at 45 DAO (Fig. 1). In RST and BST, maximum CO_2 emissions were 0.6 and 0.5 mg CO_2-C kg^{-1} soil h^{-1}. Overall, daily CO_2 fluxes were almost similar (being slightly lower in RST than in BST) when comparing straw types.

Addition of mineral N to straw amended soils (BST + N and RST + N) decreased CO_2 emissions clearly and the effect was more pronounced in BST treatment. Soil CO_2 emissions in all treatments reached their minimum levels 25 DAO and remained almost constant afterwards.

Overall, cumulative CO_2 fluxes during the 43-day incubation were 402.4 ± 31.9, 402.6 ± 5.8 and 179.9 ± 18.1 mg CO_2-C kg^{-1} soil in BST, RST and control treatments (Table 1). Upon addition of mineral N, cumulative CO_2 emissions were clearly lower in both straw amended soils but the effect was significant only in the barley straw treatment ($p < .05$). Here, the decrease in CO_2 fluxes due to the N supply accounted for 33% in BST whereas in RST it was only 16%. Generally, straw incorporation triggered a release of CO_2 and cumulative CO_2 losses for the entire incubation period may be used to calculate the approximate amount of the added carbon substrate which is mineralized during the incubation. The mineralization of the substrate-C can be estimated as the difference between cumulative CO_2-C evolved in straw-amended soil minus that of the control soil. The calculated share of mineralized straw-derived C was 36%, 14%, 34% and 24% in BST, BST + N, RST, and RST + N treatments respectively.

Table 1
Cumulative CO_2-C and N_2O-N fluxes after 43 days of treatment.

	CO_2	N_2O[a]	Residue-derived ^{15}N-N_2O
	[mg C kg^{-1} soil DM 43 $days^{-1}$]	[µg N_2O-N kg^{-1} soil DM 43 $days^{-1}$]	[µg N_2O-N kg^{-1} soil DM 22 $days^{-1}$]
CK	179.85 (14.81) c	3.25 (0.94) a	n.d.
BST	402.37 (26.03) a	18.61 (1.61) b	0.12 (0.0)
RST	402.64 (4.78) a	26.34 (1.91) b	n.d.
BST + N	264.81 (33.78) bc	438.95 (40.93)	1.48 (0.18)
RST + N	337.36 (8.3) ab	386.71 (74.27)	n.d.

Values are means with ± 1 standard error (n = 3). Different letters within a column indicate significant differences between treatments (Tukey's HSD, $p < .05$).
n.d. = not determined.
[a] Significant differences were calculated for control soils and straw amended soils excluding + treatments.

N_2O emissions remained low until 3 DAO. Then, they increased slightly up to 0.09 and 0.05 µg N_2O-N kg^{-1} soil h^{-1} in RST, and BST treatments, respectively (Fig. 2). Daily N_2O fluxes showed a short-lived peak period from 4 DAO to 7 DAO and in this period they were significantly higher in RST than in BST and CK ($p < .05$). After day 6, N_2O fluxes decreased gradually to the background levels of the non-N fertilized treatments. Addition of N fertilizer led to an immediate and large increase in N_2O fluxes. Fluxes of N_2O in RST + N and BST + N treatments increased almost linearly (up to 1.2 ± 0.2 and 1.5 ± 0.1 µg N_2O-N kg^{-1} soil h^{-1} in RST + N and BST + N treatments) until 10 DAO. Thereafter they showed a continuous and quite rapid decrease and almost reached non-N fertilized background levels within 30 days.

Consequently, cumulative N_2O emissions were significantly lower ($p < .05$) in CK than in both non-N fertilized straw treatments (Table 1). Application of oilseed rape straw (RST) alone induced slightly higher cumulative N_2O emissions compared to CK and BST soils which might be attributed to the lower C/N ratio of the oilseed rape straw. Addition of mineral N (67.5 mg N kg^{-1} soil as CAN) however, led to a strong increase in cumulative N_2O emissions of up to 26-fold. Overall, there were no significant differences in cumulative N_2O emissions between oilseed rape and barley straw amended soils with fertilizer N addition ($p > .05$). Although not being significant ($p > .05$) in the + treatments, the cumulative N_2O emissions were lower in the soils amended with oilseed rape straw than the ones amended with barley straw.

Stable isotope labeling (^{15}N labeled barley straw) was used to study the contribution of the organically bound N in the straw to N_2O emission from straw and straw + N amended soils in BST and BST + N. Overall, the ^{15}N label of the emitted N_2O was very close to the natural ^{15}N abundance indicating dominance of non-straw derived N_2O (Table 1). Overall, the share of barley straw-N derived N_2O emissions was only 1.35% of 0.1 and 0.4% of 1.5 ± 0.18 µg N_2O-N kg^{-1} soil 22 $days^{-1}$ of the cumulative N_2O emissions in BST and BST + N treatments.

3.2. Soil NH_4^+ and NO_3^- dynamics

During the initial phase of the experiment, soil NH_4^+ concentrations were 0.9 ± 0.1, 1.4 ± 0.1, 31.7 ± 5.4, 2.4 ± 0.7 and 29.7 ± 1.0 mg NH_4^+-N kg^{-1} soil in the non-fertilized control soil (CK), BST, BST + N, RST and RST + N, respectively (Fig. 3a). In N fertilized soils, soil NH_4^+ concentrations decreased continuously to background levels within 25 days and remained low (being similar to

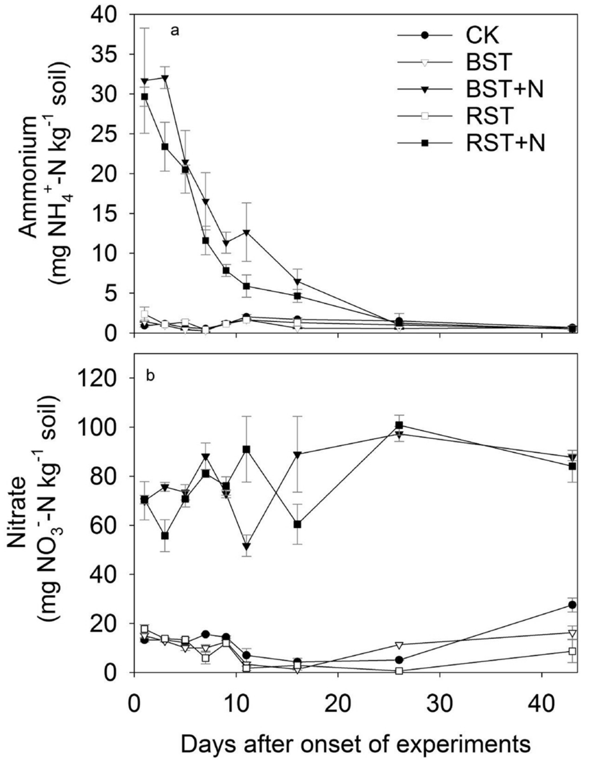

Fig. 3. **a** Soil NH_4^+ content and **b** soil NO_3^- content in soils after incorporation of oilseed rape straw (RST) and barley straw (BST) only and with N fertilizer (RST + N, BST + N) in the incubation experiment (CK: non-treated control soil). Error bars show the standard error of the mean of each treatment (n = 3). In some cases error bars are smaller than the symbols.

CK) afterwards.

Soil NO_3^- concentrations were 13.2 ± 0.8, 15 ± 0.9, 70 ± 7.8, 17.8 ± 1.7 and 70.5 ± 1.7 mg NO_3–N kg^{-1} soil in CK, BST, BST + N, RST and RST + N, respectively, 1 day after onset of treatments (Fig. 3b). In the period of 7–15 DAO, soil NO_3- concentrations in the RST treatments were similar to control soils (CK) and soils amended with barley straw (BST). In N-treated soils (BST + N, RST + N), NO_3- concentrations were always significantly higher than in soils without N supplementation ($p = .05$). In addition NO_3- concentrations showed a small but continuous increase throughout the experimental period.

3.3. Gene expression of nosZ

The overall average *nosZ* gene expression ranged from 2.1 × 10^4 to 6.8 × 10^5 copies per g soil. As shown in Fig. 4 highest *nosZ* copy numbers were observed at day 7 and day 11. Barley straw amended soils (BST) showed highest gene expression at day 11. The highest *nosZ* gene expression with 6.8 × 10^5 copies per g soil was observed for barley straw and N-fertilized soil (BST + N) at day 7 after onset of treatment, also variation within this treatment was high, ranging from 6.3 × 10^4 to 1.1 × 10^6 copies per g soil. Overall the barley straw amended soil (BST) showed the lowest *nosZ* gene expression peak with 1.1 × 10^5 copies per g soil. The *nosZ* copy numbers at the beginning (1 DAO) and towards the end of the experiment (25 DAO) were on a low and comparable expression level of 2.7 × 10^4 to 1.1 × 10^5 copies per g soil, for all treatments.

4. Discussion

4.1. Soil N transformations

The soil NH_4^+ concentrations in the two sole straw treatments remained on a low level and there were no differences among straw types as well as compared to the control soil. There was only a slight decrease until day 7 which might be due to a higher nitrification rate than mineralization of the straw-N in this phase of the experiment. Nitrification is one of the main processes leading to decreasing soil NH_4^+ values (Cai et al., 2001) which was particularly evident in treatments with added N (BST + N, RST + N) where NH_4^+ concentrations showed a very steep decline in the first ten days. Besides nitrification, abiotic immobilization and the preferential uptake of NH_4^+ by soil microorganisms may have contributed to depletion of the soil NH_4^+ concentration (Recous et al., 1990).

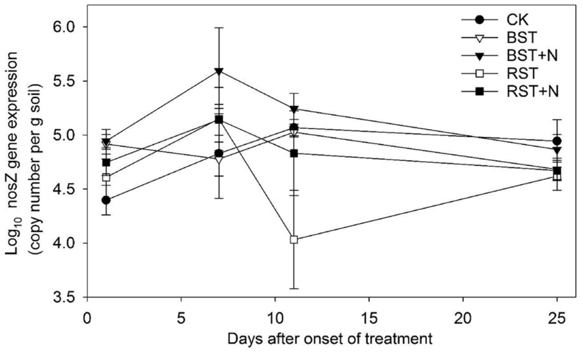

Fig. 4. *nosZ* gene expression at day 1, 7, 11 and 25 from soils after incorporation of oilseed rape straw (RST) and barley straw (BST) without and with N fertilizer (RST + N, BST + N) in the incubation experiment (CK: non-treated control soil). Error bars show the standard error of the median of each treatment (n = 3). In some cases error bars are smaller than the symbols.

The decrease of soil NO_3^- concentration in the sole straw treatments (BST, RST) until day 11 is most likely to be explained by microbial assimilation of N which is boosted by the decomposition activity by the microorganisms (Potthoff et al., 2005). Straw represents an additional carbon source for microorganisms favoring heterotrophic respiration as indicated by increased CO_2 emission rates.

NO_3^- concentrations in + treatments were higher than in non-N-fertilized treatments due to addition of nitrate as CAN. The additional increase until day 27 was probably due to nitrate production in the course of fertilizer ammonium nitrification which is in line with a matching decline in soil NH_4^+ concentrations during this period. As NO_3^- concentrations steadily remained on a high level in + treatments, denitrification obviously played a minor role with respect to soil N balances in the experimental period.

4.2. Effect of straw addition to CO_2 and N_2O emissions

Expectedly, the incorporation of straw into soil led to increased CO_2 emissions. Such rapid degradation of easily accessible C compounds in straw has been shown in earlier studies with similar CO_2 emission patterns and orders of magnitude (Chen et al., 2014c; Geisseler et al., 2009; Huang et al., 2004; Potthoff et al., 2005; Velthof et al., 2002). In our experiment, rather the addition of straw than the quality of straw (C/N) was an important factor for decomposition measured as soil CO_2 emissions. This is supported by Chapin et al. (2002) and Chen et al. (2015) who showed that the addition of a substrate has a much greater influence on the decomposition velocity than its C/N ratio.

N_2O emissions of soils amended with straw only (BST, RST) remained on the background levels during the first three days. It is likely that this lag phase was caused by heterotrophic respiration followed by O_2 consumption (Potthoff et al., 2005). The depletion of O_2 in microsites at the small scale is known to lead to the establishment of microaerophilic or even anaerobic microsites. Consequently, such hot spots provide favorable conditions for denitrification and N_2O production (Parkin, 1987). In BST and RST, N_2O emissions were higher from day 3 to day 7 as compared to control soils (CK) which might be attributed to the decomposition of incorporated straw-C which enhanced heterotrophic respiration. In a short period of day 3 to 7 emissions in RST were twice as high as in BST which may be attributed to the lower C/N ratio of the oilseed rape straw which was going along with higher availability of organic N. This enhances microbial decomposition/mineralization and the formation of NO_3^- which can lead to denitrification and hence higher N_2O emissions if O_2 is consumed and CO_2 released by mineralization.

These results are supported by several studies where a negative correlation of soil N_2O emissions to the C/N ratio of the soil-incorporated substrate was found (Chen et al., 2013; Frimpong and Baggs, 2010; Huang et al., 2004; Parkin, 1987; Velthof et al., 2002). Though, Chen et al. (2013) explain that an amendment with C-rich residues with a C/N ratio > 45 leads to a high demand of soil N for microbial growth. Here, it can be inferred that the N limitation is aggravated with increasing C/N ratios. In the treatments without mineral N addition, this relationship might have contributed to higher N_2O emissions in the oilseed rape straw amended soils compared to soils amended with the cereal straw of barley.

4.3. The effect of N addition to CO_2 and N_2O emissions

The addition of N and a straw source to soil changes the habitat conditions of soil microorganisms. The soil microorganisms can use the organic matter for energy production as well as metabolic utility of N and modify N cycling. Knorr et al. (2005) showed decreased soil CO_2 release for low-quality litters with high lignin content when in addition mineral N was supplied. In general, it is accepted that the addition of N affects soil C cycling (Knicker, 2011; Liu and Greaver, 2009; Treseder, 2008). Wang et al. (2004) observed that the addition of nitrate to straw and its influence on CO_2 emissions can be separated into two phases. In the early stage of straw degradation, they reported a generally higher rate of C mineralization and higher decomposition activity in the straw + N treatment compared to the sole straw treatment. In the later stages of their experiment, addition of N to straw amended soil reduced the decomposition rate. This was ascribed to a shift in the factors controlling decomposition. With progressing time, the factors moved from N content or C/N ratio in the initial phase to lignin/N and polyphenols/N ratios of the plant material in the treatments without N addition. Interestingly in the + treatments, other characteristics like N-alkyl or methoxyl C showed a correlation to cumulative C mineralization. N-alkyl C is a part of amino acids or sugars and methoxyl C is a substituent of lignin. While lignin/N and polyphenols/N ratios were not analyzed in the present study, the general CO_2 flux dynamics support the findings of Wang et al. (2004), i.e. initially, CO_2 emission rates did not show pronounced effects of N addition while after the first 5–7 days CO_2 fluxes were significantly lower in + treatments as compared to non-N amended equivalents ($p < .05$).

Treseder (2008) described that N addition negatively affects soil characteristics (e.g. a decrease in soil pH) and that microbial biomass may decline significantly with N addition. Thus, a possible reason for the decrease of soil CO_2 emissions in N applied soils may be ascribed to a reduction in microbial biomass and eventually activity like decomposition caused by N fertilization (Treseder, 2008). Nevertheless, the fate of carbon is a point of discussion; it can also be assumed that short-term microbial biomass production after residue addition and thus, uptake of C is enhanced due to the termination of C and N limitation by addition of C and N substrates which leads to the built up of fungal biomass (Bai et al., 2016; Henriksen and Breland, 1999; Rousk and Bååth, 2007).

In contrast to soil treated with straw alone, fertilizer N addition to straw amended soils (BST + N, RST + N) was followed by a steep increase in soil N_2O emissions due to seemingly unlimited NH_4^+ and NO_3^- availability in the first days of the experiment. Nevertheless, the soil NO_3^- pool remained on a stable and high level throughout the experimental period and – without any lag phase - the soil NH_4^+ concentration decreased steadily until day 26. Both, the high concentration of NO_3^- and the continuous decrease in the NH_4^+ pool are seen as evidence that a large share of the NH_4^+ was nitrified in aerobic microsites which probably made a certain contribution to the rapid increase in N_2O emissions. This view is supported by the subsequent period with decreasing N_2O emissions after day 10 since the NO_3^- pool at the subsequent sampling days remained on a high level. Thus, nitrification probably made a certain contribution to soil N_2O emissions; however nitrification has a lower share on N_2O emissions than denitrification (Vilain et al., 2014) as discussed in the following.

Cumulative N_2O emissions increased more than 15-fold when N was added to soils amended with barley or oilseed rape straw as compared to sole straw treatments. N addition to straw amended soils enhanced denitrification and oxidized N compounds such as NO_3^- were used as electron acceptors in heterotrophic respiration. When soil NO_3^- concentrations are high as observed in + treatments, nitrate reduction yields more energy than the reduction of N_2O (Saggar et al., 2013; Weier et al., 1993), thus when NO_3^- availability is high, N_2O reduction is likely to be low, leading to high N_2O emissions and comparatively low emissions of N_2. In addition, only a certain fraction of the soil microbial community is able to reduce N_2O to N_2 (Philippot et al., 2011; Saggar et al., 2013) which strengthens the view that rather N_2O than N_2 is produced in soils with ample N supply.

After approximately 12 days, a decrease in both, N_2O emissions and CO_2 emissions in the N fertilized soils (BST, RST) was observed which suggests that easily degradable carbon compounds were mostly consumed leading to a strong decrease in the activity of the N_2O producing microbial community with a subsequent adaptation to conditions with high N availability but less readily available C in relationship to slower decaying straw compounds.

Furthermore, with respect to the two types of crop residues examined in this study, it is noteworthy that similar to their influence on decomposition, i.e., CO_2 release from soil, the type of straw played a minor role in the formation of N_2O. It can be assumed that the oilseed rape straw, characterized by its slightly lower C/N ratio did not trigger higher N_2O emissions from soil than the straw of the cereal barley. Nevertheless, in agricultural practice the incorporated amount of oilseed rape straw (DM kg^{-1} soil) might be higher (Kaul et al., 1996) as oilseed rape and barley straw can differ in their residue production (Lal, 2005; Lickfett, 1993; Sieling and Kage, 2006).

4.4. *nosZ* expression and microbial metabolism

To examine the potential reduction of N_2O to N_2, we analyzed the transcription of *nosZ* genes using quantitative polymerase chain reaction (qPCR). The transcription of bacterial *nosZ* genes encoding nitrous oxide reductase, was low and ranged on an equal level for all treatments at day 1 and 25 after onset of treatment. This is in accordance with the observed CO_2 and N_2O emissions, which showed the lowest emission rates bevor day 3 and after day 20. At day 1, *nosZ* copy numbers in N fertilized soils (BST + N, RST + N) were low and exponentially increasing values for nitrification-derived N_2O emissions due to quickly decreasing soil NH_4^+ content suggest a low denitrification rate. Nevertheless, the *nosZ* copy number is lowest for control soils (CK) suggesting that the reduction of N_2O to N_2 is also occurring in treated soils (BST, BST + N, RST, RST + N). It could be argued that this minor increase of treated soils compared to control soils may be attributed to the reduction of NO_3^- since soil NO_3^- content is decreasing and NO_3^- reduction is less energy demanding for soil microorganisms than the reduction of N_2O (Saggar et al., 2013). In the sole straw treatments (BST, RST), C-rich substrate can be used as electron donor in the dissimilative metabolism for energy production (anaerobic/heterotrophic respiration). This explanation also supports the decrease in soil NO_3- in BST and RST which might have been used in dissimilative metabolism, i.e. NO_3- reduction. The N addition to barley straw and oilseed rape straw amended soils (BST + N, RST + N) changed habitat conditions in soil. However, the added N is an easily accessible substrate for soil microorganisms' metabolism and relieves the N limitation. It can be assumed that at a later stage, i.e. 10–14 days after onset of the experiment, a considerable share of the C-rich substrate was immobilized by soil microorganisms together with the N supplied by fertilization. Also no significant differences were observed, a clear peak of *nosZ* gene transcription at day 7 is visible for the barley straw and N-fertilized soil (BST + N), which showed the highest *nosZ* gene transcription. This is also in accordance with the observed CO_2 and N_2O emissions, which had the highest emission rates between day 6 and 10 after onset of treatments. There is a relation between *nosZ* gene expression and high availability of N_2O as a substrate. High production of N_2O reductase leads to decreasing N_2O emissions off soil due to a decreased N_2O/N_2 ratio. Following this argumentation pattern, for the RST + N treatment, we probably missed the highest gene expression of *nosZ*. Also changes in the mRNA transcript abundance should be analyzed cautiously, as they may not reflect protein production rates and activity, due to post transcriptional steps. Contrastingly, the oilseed rape straw treatment with N application (RST + N) showed only a peak of *nosZ* transcription at day 7, while the barley straw (BST) treatment, as well as the control (CK), showed a peak at day 11. The oilseed rape straw amended soils (RST) had the second highest *nosZ* transcription. Oilseed rape straw has compared to barley straw a lower and for microorganisms more favorable C/N than barley straw, as it is closer to the ideal diet (24:1). This leads to higher activity of microorganisms in the oilseed rape straw amended soils (RST) and thus contributes to higher N_2O emissions compared to barley straw. This is also supported by the depletion of the soil NO_3- pool, which in conclusion leads to a demand of other energy sources such as N_2O. The observed higher *nosZ* copy numbers at day 7 in RST treatments probably reflects the change of energy source used and increased demand of N_2O reduction (see Fig. 4).

Overall the variation in the determined transcription rates is high among replicates. The highest variation was observed for the BST + N, ranging from 6.3×10^4 to 1.1×10^6 copies per g soil among the three replicates. Several reasons may have led to the variation among treatments. Generally, there is a time lag between excess N_2O and the *nosZ* gene expression. Bacterial *nosZ* transcription may be enhanced by the N demand of denitrifiers and if the soil NO_3^- pool is depleted soil microorganisms have to seek for an alternative substrate such as the unfavorable N_2O. It is known that the reduction of N_2O is more energy demanding to bacteria (Saggar et al., 2013) and sudden high copy numbers in *nosZ* gene expression may be explained by accumulation of N_2O in microsites. Furthermore, soil heterogeneity may result in varying numbers of microsites causing high deviation in copy numbers within the treatments analyzed.

The high variability of copy numbers within treatments may also be explained by short turnover times of bacterial mRNAs due to RNases and other factors influencing the degradation (Deutscher, 2006).

4.5. *Barley straw-N-derived ^{15}N-N_2O*

Straw-N-derived N_2O emissions were investigated with barley straw amended soil. N_2O emissions and thus straw-N-N_2O emissions were low in soils amended with barley straw only. N fertilization led to an exponential increase in N_2O emissions and cumulative N_2O emissions were several times higher than in soils amended with barley straw only. Additionally, the share of straw N in N_2O release was even lower for soils amended with barley straw and N fertilizer. A generally low share of organic N-derived N_2O emissions was found in several studies (Frimpong and Baggs, 2010; Gentile et al., 2008; Ocio et al., 1991). In several studies, the fate of straw N was examined after its addition to soil. An alternate pathway of straw N was illustrated in the study of Ocio et al. (1991) which showed that up to $^2/_3$ of the increase in microbial biomass N was attributed to the supply of organic N by straw decomposition. Such direct incorporation of straw N implies that the straw-bound N did not enter the soil mineral N pool. Immobilization of straw N was also observed in an incubation study by Trinsoutrot et al. (2000). Here, the straw addition led to immobilization and in addition, with a higher C input immobilization of N was even higher. This decrease of the soil mineral N pool leaves unfavorable conditions for nitrification or denitrification. Hence as a rule, straw N entering the soil seems to be mostly unavailable for N_2O production. It can therefore be assumed that microorganisms in soils amended with barley straw alone typically undergo N limitation since soil mineral N pools are rapidly depleted. This underlines the possible explanation of direct uptake of organic N by soil microorganisms (Geisseler et al., 2009). Furthermore, the difference in straw-derived N_2O of BST and BST + N may reflect the dominance of different processes in the treatments. In + treatments, it can be assumed that soil N cycling, is accelerated which is clearly shown in the high N_2O emissions. As discussed, the addition of a carbon source and turnover of barley straw N in the + soils may have triggered a quick increase in microbial biomass N, but in parallel, the decline in easily available carbon due to decomposition could have led to remobilization of the biomass-bound N. In a study conducted by Shindo and Nishio (2005), ^{15}N labeled wheat straw was incorporated into soil and nitrate was applied. Here, straw and mineral N led to substantial increase in microbial biomass N after 7 days. At all sampling days, ^{15}N-labeled biomass N was about 10%. In the course of their experiment, there was no evidence, that a share of the straw N steadily increased the NO_3^- pool. Therefore plant residues should be primarily seen as an energy source and when in micro-sites the mineral N pool is exhausted, it will also serve as source of N for microbial biomass production (Chen et al., 2014b). Naturally, soil microorganisms die and the biomass N is released into the soil mineral N pool. Consequently, the formerly straw-bound N may enter the mineral N soil pools where it is available for nitrification, denitrification and eventually release as N_2O or through competitive processes like plant uptake, such as winter wheat following winter oilseed rape.

4.6. *Implications for bioenergy production*

The presented study was conducted to enlighten the role of post-harvest practices on N_2O emissions. The post-harvest period states a crucial part of the annual CO_2 and N_2O emissions. Here, we tested factors like straw addition which is a common agricultural practice and the effect of a high soil mineral N content. It should be mentioned that the conditions were set to favor denitrification. Firstly, the N rate was unusually high for autumn fertilization and secondly, the moisture level was set to very wet conditions being favorable for denitrifiation. With regard to biofuel crop production the increase of N_2O emissions with the incorporation of straw alone was significant, but nevertheless the magnitude was minor. Under field conditions, incorporation of straw leads to a short-timed peaks in N_2O emissions which may be overestimated on a whole year perspective. Additionally, it is difficult to scale our results to the whole process of biodiesel production as we only considered a short period, the post-harvest, of the total production process which is again divided into growing of crops, fuel production and transport. However, field emissions in the bioethanol/biodiesel production are assumed to have a fixed share (Majer and Oehmichen, 2010).

5. Conclusion

In agriculture, straw incorporation is a common practice in the post-harvest period and this may increase the risk of N_2O emission specifically in moist soils. Our study clearly showed that when soil mineral N content is low, incorporation of barley or oilseed rape straw cause only a slight increase in N_2O emission. However, when soil has high residual N and/or straw amended in conjunction with mineral N, soil N_2O emissions seem to increase drastically. In this context, the present study clearly suggests that straw type seems to have only minor effect on N_2O emission, but soil mineral N content plays a key role. Stable isotope labelling experiment was in line with that showing only a very small share of the nitrogen emitted as N_2O originates from incorporated organic matter.

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Appendix A. Supplementary data

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3 Climate overrides effects of fertilizer and straw management as controls of nitrous oxide emissions after oilseed rape harvest

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Abstract

Oilseed rape is an important bioenergy crop in the European Union and it contributes to the diversification of renewable energy supply and to the reduction of CO_2 emissions from fossil fuel consumption. Typical oil seed rape crop management systems include the use of significant rates of nitrogen (N) fertilizer and incorporation of oilseed rape straw into soil after harvest. While being economically meaningful, one of the downsides of both management options is that they contribute to an increased risk of N_2O emissions from soil. At this background we conducted a study focusing on the soil N dynamics with emphasis on N_2O emissions during the post-harvest period aiming at identification of regulating factors of N cycling. The post-harvest study was based on a two-year field experiment and process-based modeling. We measured N_2O emissions, soil ammonia (NH_4) and nitrate (NO_3) contents as well as crop residue and seed yield at Goettingen University research station Reinshof. Treatments included variation of fertilizer (non-fertilized (No fert), 90 kg N ha^{-1} (Fert-90) and 180 kg N ha^{-1} (Fert-180)) and residue management (straw remaining (+str), straw removal (-str)). Measured N_2O emission data showed large intra and inter-annual variations ranging from 0.5 ± 0.0 kg N_2O-N ha^{-1} (No fert +str) to 1.0 ± 0.1 kg N_2O-N ha^{-1} (Fert-180 +str) in 2013 and, from 4.1 ± 0.3 (Fert-90 +str) to 7.3 ± 0.2 kg N_2O-N ha^{-1} (No fert +str) in 2014. Cumulative N_2O emissions showed that straw incorporation into soil led to slightly reduced N_2O emissions compared to treatments with straw removal, while effects of different fertilizer levels applied in spring were insignificant. The study provides evidence that reduced post-harvest N_2O emissions were caused by reduced soil NO_3 concentrations following straw application. The process-based model Coup was employed to explain the large annual variation of N_2O after calibration with measured environmental data. Both, modelled and measured data suggest that soil water-filled pore space (WFPS) and temperature were the key factors controlling post-harvest N_2O emissions, even though the model seemed to show a higher N_2O response to the N fertilizer levels than our measured data. Overall, measured and modelled data showed that straw incorporation in oilseed rape cropping may be an environmentally beneficial measure to mitigate N losses by denitrification. This study also underlines the importance of multi-year measurements to assure capturing of climate variability.

3.1 Introduction

The European Renewable Energy Directive (Directive 2009/28/EC, European Union) provides the legal framework in the European Union (EU) to increase the share of renewable energy sources, secure the energy supply and reduce the greenhouse gas (GHG) emissions. To achieve this goal, oil crops are becoming increasingly important to shift from fossil fuel based energy supply to a more sustainable production chain. However to be economically viable, oil crop production requires higher N fertilizer use compared to cereals. High N demand of oilseed rape may increase the risk of soil N_2O emissions (a potent greenhouse gas (Crutzen et al., 2008; Don et al., 2012; Schmidt-Walter and Lamersdorf, 2012).

In general, oilseed rape N demand was reported to be c. 200 kg N ha^{-1} (Landwirtschaftskammer Niedersachsen, 2010), but it may also exceed 250 kg N ha^{-1} at sites with high potential productivity (Henke et al., 2009; Sieling and Kage, 2010). The average yield of winter oilseed rape in Germany is 3 t ha^{-1} in 2017 (Statistisches Bundesamt, 2019). The N harvest index for oilseed rape, defined as the portion of total N in the harvested crop component to the total N in the aboveground biomass, ranges between 0.6 and 0.7 (Sieling and Kage, 2010) and is about 15% lower compared to that of wheat (Schjoerring and Mattsson, 2001). Thus high N return to the soil can be expected from plant litterfall. Indeed, N litterfall as high as 45 kg N ha^{-1} (mainly from leaves) has previously been reported in the maturation period (Malagoli et al., (2005). Also, higher values, e.g. 53 kg N ha^{-1} (Engström and Lindén 2012) and up to 89 kg N ha^{-1} (Sieling and Kage 2006) have been reported after harvest. Thus N return by pre- and post-harvest residues is significant in particular since oilseed rape straw incorporation into soil as the standard management practice. This contributes to soil organic matter mineralization and to the soil mineral N pools (Hadas et al., 2004). Previous studies (Engström and Lindén, 2012, Sieling and Kage, 2006, Justes et al., 1999) stressed high soil mineral N concentrations after oilseed rape harvest and mostly, they discuss the risk of high NO_3 leaching.

N_2O in soil is produced by the microbial processes nitrification and denitrification processes, although other processes may also produce N_2O (Wrage-Mönnig et al., 2018). Nitrification is a microbial process that oxidizes NH_3 or NO_2 via NH_2OH to NO_3 and the nitrification products act as electron acceptors. Denitrification is also a microbial process where the stepwise reduction of NO_3 in the liquid phase via gaseous compounds to N_2 (Madigan et al., 2012). N_2O is also a very powerful greenhouse gas with a 265 times higher global warming potential than that of CO2 (IPCC, 2014). N_2O emission mitigation strategies mostly focus on the growing period of crops, but for complete evaluations of improved management options the post-harvest period has to be assessed as well. In incubation studies conducted under controlled conditions, oilseed rape straws with a C/N ratio of up to 65 showed a positive correlation with N_2O emissions, but this relation is hardly detectable under field conditions, maybe because straw particle size and spatial distribution are different (Chen et al., 2013). Therefore, understanding N_2O emissions and their interactions with environmental factors require a combined data-model approach that can distinguish the gas production processes and describe the multitude of controlling factors and their interactions (Butterbach-Bahl et al., 2013; Gundersen et al., 2012; Smith, 2010).

The aim of the study was to contribute to improved understanding of effects of straw removal as management option and its contribution to soil N dynamics. The post-harvest period varies in temperature and water. Both factors interfere with N_2O formation. To identify driving forces of post-harvest N cycling, a field experiment was conducted and followed by process-based modeling.

3.2 Materials and Methods

Site description

The field experiment was set up at the research farm Reinshof (51.49°N, 9.93°E, 150 m asl) of the Department of Crop Sciences of University of Goettingen in Germany. The climate is continental with a long-term (1961-1990) average precipitation of 645 mm and a mean temperature of 8.7 °C (DWD, 2019). The soil was classified as Luvisol according to the soil classification scheme suggested by IUSS Working Group WRB (2014) with a silt loam texture (sand: 12.2 %, silt: 72.7 %, clay: 15.1 %). It represents a typical agricultural soil used for oilseed rape cropping. The soil properties were characterized by a bulk density of 1.29 g/cm^3, pH 7.1, C 1.3 %, N 0.12 % and thus a measured C/N ratio of 10.5 in the top soil (0-10 cm).

Field experiment set-up

The field experiment was carried out in a fully randomized block design in the autumn and winters of 2013/2014 and 2014/2015. The plot size was 7.5m x 6m and all N fertilizer treatments were done with 3 replicates. The treatments of this first factor included three levels of calcium ammonium nitrate (CAN) mineral fertilizer (No fert: 0 kg N ha^{-1}, Fert-90: 90 kg N ha^{-1} and Fert-180: 180 kg N ha^{-1}). In spring, fertilizer application was done according to common farming practice with 67% of the total amount being applied as first dressing on 22nd April in 2013 and 19th March in 2014. The remaining 33% N were applied on 7th May in 2013 and 7th April in 2014 (Fert-90, Fert-180). Plant protection was done in line with local recommendations. Winter oilseed rape (Brassica napus L., cv. Visby) was harvested on 1st August 2013 and 23th July 2014. Following common agricultural practice the uppermost soil layer (0-10 cm) was rototilled one day later.

After harvest, all fertilizer plots were subdivided into 2 subplots with a size of 3 m x 2.5 m each. These were treated with residue incorporation (+str) by using the respective crop residues from the 0, 90 or 180 kg N ha^{-1} fertilizer treatments. The fourth subplot was kept without residues, i.e. all residues were removed (-str). For all subplots, the amounts of straw added were determined by residue biomass determinations in all treatments of the respective years and on average residue biomass was 7.17 t fresh matter ha^{-1}. Later-on in October, following typical regional crop rotations, winter wheat was sown in both years. N2O and other parameters were sampled from harvest until fertilizer application in winter wheat.

Soil mineral N (N_{MIN}) measurement

Soil mineral N contents (N_{MIN}) were measured on samples of the top 0-15 cm soil layer and for each analysis 50 g soil were taken. Samples were extracted with 0.0125 M $CaCl_2$ solution (1:5 w/v), then filtered with 615 ¼ filter paper (Macherey – Nagel GmbH & Co. KG, Düren, Germany) and stored frozen at -20°C (VDLUFA 2002). The extracts were analyzed colorimetrically for the concentrations of NO_3 and NH_4 using an automated continuous flow N analyzer (San++; Skalar Analytical B.V., Breda, The Netherlands).

Measurements of N_2O concentrations

N_2O gas fluxes were assessed using the manual chamber approach (Hutchinson and Mosier, 1981). In each of the 36 subplots, a round basal collar (PVC, diameter: 0.6 m, height 0.15 m) was driven into the soil to 5 cm depth and kept there permanently. For gas flux measurements these collars were covered by a closed chamber top of 0.3 m height. At their outside, both, collars and chambers were equipped with aluminum foil to reflect solar radiation. The joint of collar and chamber was sealed with a butyl rubber band of 10 cm width. Gas samples were taken 0 – 20 – 40 minutes after chamber closure using a 30 mL gastight syringe and filled into pre-evacuated 12 mL vials (Labco, Lampeter, UK). Gas sampling was conducted during the post-harvest period until the first fertilizer application for winter wheat was done in early spring. The gas measurements thus covered the periods from 8th August 2013 to 17th February 2014 and from 29th July 2014 to 3rd March 2015. Overall, the number of sampling days was 28 and 30, for 2013 and for 2014, respectively.

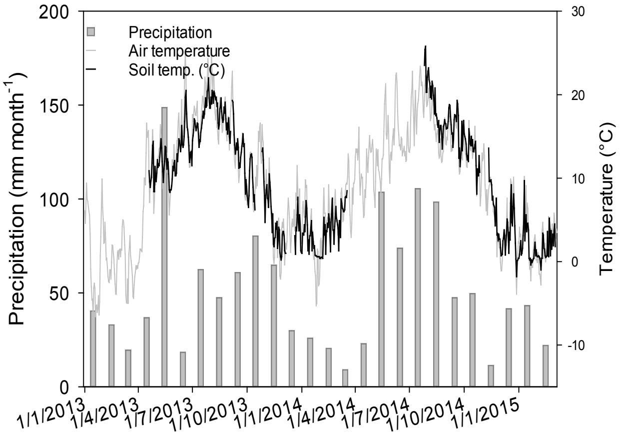

Figure 3.1 Air temperature (°C), mean soil temperature (°C) and precipitation (mm month-1) from January 2013 to March 2015 at the research site Reinshof.

Table 3.1 Oilseed rape seed yield and N and C removed by seeds at the experimental site Reinshof in 2013 and 2014 (n=3) as influenced by fertilizer treatments.Different letters indicate significant differences (p<0.05).

Treatment		Seed yield		Total N		Total C	
		t DM ha^{-1}		t N ha^{-1}		t C ha^{-1}	
		2013	2014	2013	2014	2013	2014
Measured	No fert	3.7±0.2a	3.6±0.2a	0.12±0.01a	0.11±0.01a	2.4±0.2a	2.1±0.2a
	Fert-90	4.1±0.3a	3.9±0.1a	0.15±0.02a	0.13±0.00a	2.6±0.2a	2.4±0.2a
	Fert-180	4.4±0.1a	4.1±0.1a	0.16±0.01a	0.13±0.00a	2.6±0.1a	2.4±0.1a
Simulated	No fert	5.7±0.7	5.0±0.7	0.14±0.01	0.13±0.01	2.9±0.3	2.5±0.3
	Fert-90	5.9±0.4	5.2±0.3	0.15±0.02	0.13±0.02	2.9±0.2	2.6±0.2
	Fert-180	6.4±0.4	5.5±0.5	0.16±0.03	0.14±0.03	3.2±0.2	2.9±0.3

Table 3.2 Amount of incorporated oilseed rape residue biomass, total N and total C in residues as well as residue C/N ratio at the experimental site Reinshof in 2013 and 2014 (n=3) as influenced by fertilizer treatments. Different letters indicate significant differences (p<0.05).

Treatment		Residue yield		Total N		Total C		C/N	
		t DM ha^{-1}		t N ha^{-1}		t C ha^{-1}			
		2013	2014	2013	2014	2013	2014	2013	2014
Measured	No fert	5.3±0.24a	5.1±0.1a	0.04±0.01a	0.03±0.00a	2.4±0.1a	2.4±0.0a	71	71
	Fert-90	5.9 ±0.3a	5.5±0.0a	0.04±0.00a	0.05±0.00ab	2.6±0.1a	2.2±0.1a	65	42
	Fert-180	6.1 ±0.2a	5.5±0.3a	0.05±0.01a	0.06±0.01b	2.6±0.0a	2.1±0.2a	57	38
Simulated	No fert	5.8 ±1.7	3.0±1.6	0.04±0.01	0.02±0.01	2.9±0.87	1.5±0.7	66	68
	Fert-90	7.0 ±1.0	5.6±1.0	0.06±0.02	0.06±0.02	3.5±0.5	2.8±0.5	57	51
	Fert-180	7.2 ±1.1	6.2±0.7	0.07±0.02	0.07±0.03	3.6±0.6	3.1±0.4	53	47

All analyses of N_2O concentrations were done on a Bruker gas chromatograph (456-GC, Bruker, Billerica, USA) equipped with an electron capture detector and controlled by CompassCDS Software. Sample introduction was done with a Gilson GX281 autosampler operated with Trilution Software (Gilson, Inc., Middleton, WI, USA). For calculation of N_2O fluxes, linear regression was performed for the three samplings after chamber closure and linear interpolation between measurement days was done to obtain cumulative gas fluxes.

CoupModel and modelling approach

The CoupModel (coupled heat and mass transfer model for soil-plant-atmosphere systems) is an updated version of the previous SOIL and SOILN model (Jansson and Moon, 2001). The main model structure is a one-dimensional, layered soil depth profile, in which water, heat, and C and N dynamics are simulated based on detailed descriptions of soil physical and biogeochemical processes. C and N dynamics are simulated both in the soil and in the plant, driven by canopy-intercepted radiation, regulated by multiplicative response functions of air temperature, and plant availability of water and N (He et al., 2016b; He et al., 2016a). The model is available at http://www.coupmodel.com/. A detailed description of the model, its model structure, parameterization and setup is given in He et al. (2016a), He et al. (2016b) and Jansson and Karlberg (2011).

The model simulates ecosystem variables in daily intervals and it is driven by measured meteorological variables from a nearby weather station including precipitation, air temperature, wind speed, relative humidity and global radiation. The general model parameterization was based on previous model applications on similar soil types (Johnsson et al., 1987; Nylinder et al., 2011). The soil physical characteristics i.e. water retention curve and hydraulic properties were estimated from the measured soil texture by using the pedo-functions of the model. When straw was applied, it was assumed to be added to both the soil litter C and N pools and assumed to be uniformly mixed into the soil to a depth of 0.05 m. The application of mineral fertilizer was assumed to directly add NH_4 and NO_3 to the soil surface N pool. The harvests in 2013 and 2014 were assumed to remove 100% of the grain and 10% of both leaf and stem. The initial conditions of the oil seed rape crop were defined by measured plant biomass data. Initial plant and soil conditions were set according to the measured data. The model was run for 5 years for initialization before the studied period with a duplicated climate.

Statistics

Soil NO_3, NH_4 and N_2O emissions are shown as arithmetic means ± 1 standard error. Cumulative N_2O emissions were obtained by linear interpolation between sampling dates and integration of area under the interpolated fluxes. Statistical analysis was done for the period of 7 months following harvest.

For statistical analysis of the split-plot design of the field experiment, a mixed model with repeated measurements with heterogeneous autoregressive structure was set up to test for significant differences for the factors fertilizer rate and residue application in each period (2013/2014 and 2014/2015). Significant differences among treatments were based on Tukey tests. For computing, the software SAS v. 9.3 (SAS Institute Inc., Cary, North Carolina, USA) was used. When necessary, Spearman correlations were calculated with * standing for $p<0.05$ and ** for $p<0.001$.

3.3 Results

Wheater conditions

The measured annual mean air temperature was 8.9 °C in 2013 and 10.6 °C in 2014. Annual precipitation in 2013 was 641 mm, higher than 609 mm in 2014 (Figure 3.1). In 2014, the period from June to August had high rainfall of 278 mm, whereas in 2013 it amounted to only 128 mm. In line with the rainfall data, WFPS values were lower in 2013 (dropping from 42% WFPS at the beginning of August to 26% WFPS in September) than in 2014 (remaining at c. 50% WFPS throughout the experimental period).

Oilseed rape seed and residue biomass

The oilseed rape in No Fert control subplots had a seed yield of 3.7 ± 0.2 and 3.6 ± 0.2 t DM ha^{-1} in 2013 and 2014. With N fertilizer input, seed yield showed consistent but insignificant increases in both years (Table 3.1). The measured residue biomasses in the No Fert control subplots were 5.3 ± 0.2 and 5.1 ± 0.1 t DM ha^{-1} in 2013 and 2014. The effect of N fertilization on residue biomass was also insignificant, but there was also a consistent positive trend. Similar to the seed C/N ratios, increasing applied N rates led to decreasing measured C/N ratios in both years (Table 3.2).

N_2O emissions

N_2O emission rates varied significantly ($p<0.001$) between years and the maximum N_2O peaks were significantly higher (c. 10-fold) in 2014 compared to 2013 (Figure 3.2). In both years, highest N_2O emission peaks were detected shortly after post-harvest tillage. In 2013, the highest measured daily N_2O emission rate was 0.04 ± 0.0 kg N_2O-N ha^{-1} day^{-1} (in the Fert-180 treatment with straw amendment), whereas it was 0.33 ± 0.08 kg N_2O-N ha^{-1} day^{-1} (in the straw amended Fert-180 treatment) in 2014, thus almost ten times higher. Winter N_2O emissions were generally low with measured emissions consistently being below 0.02 kg N_2O-N ha^{-1} day^{-1} from November to March in all treatments and years. The N doses applied in spring did not affect post-harvest N_2O emissions in both years despite higher residual N in treatment Fert-180. Similarly, straw amendment did not affect N_2O fluxes in 2014, but caused a slight ($p<0.05$) decrease in 2013 for the treatment Fert-90). Overall, cumulative post-harvest N_2O emissions were very substantially higher in 2014 than cumulative flux rates measured in 2013 (Figure 3.3).

Soil mineral N

Soil NH_4 concentrations in the uppermost 0.15 m soil layer were below 5 kg N ha^{-1} in both years and were not significantly affected by any treatments (Figure 3.4). In contrast, soil NO_3 concentrations measured shortly after harvest were 12.3±0.6 and 13.0±2.4 kg N ha^{-1} in the control treatment in August 2013 and August 2014. Fertilizer application in spring resulted in substantially higher residual NO_3 in the uppermost soil layer in August amounting to 28.2±3.6 and 28.3±1.6 kg N ha^{-1} in the Fert-180 treatment in 2013 and 2014. Soil NO_3 concentration remained more or less constant throughout the experiment in 2013 whereas in 2014, it decreased gradually over time to almost zero during winter. The data clearly

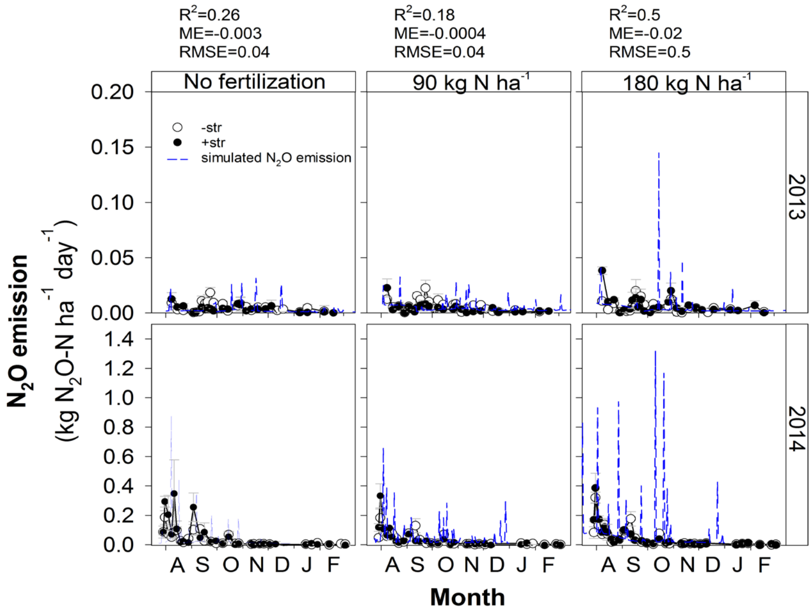

Figure 3.2 Measured and simulated daily N_2O emissions from non-fertilized soils (No fert) and soils fertilized with 90 kg N ha^{-1} (Fert-90) or 180 kg N ha^{-1} (Fert-180) in spring. In all soils straw was quantified and either removed (-str) or placed back in the respective fertilized soils (+str). Sampling period was from August 2013 to March 2014 and August 2014 to March 2015. Numbers above the panel describe the quality of the COUP model for the respective fertilizer treatment. Error bars show the standard error of mean of each treatment (n=3).

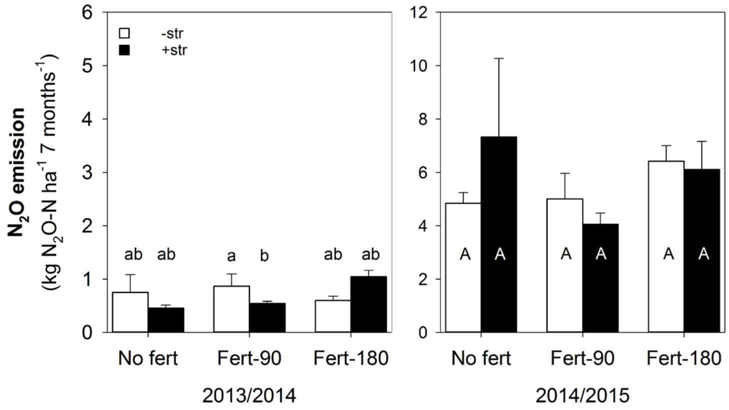

Figure 3.3 Cumulative N_2O emissions from non-fertilized soils (No fert) and soils in spring fertilized with 90 kg N ha^{-1} (Fert-90) or 180 kg N ha^{-1} (Fert-180) for the post-harvest period from August to March for the years 2013/2014 and 2014/2015, respectively. In all soils straw was quantified and either removed (-str) or quantified and placed back into the respective soils (+str). Error bars show the standard error of mean of each treatment (n=3). Different letters indicate significant differences ($p<0.05$) among treatments. Periods 2013/2014 and 2014/2015 were analyzed separately.

showed that straw amendment decreased soil NO_3 content significantly ($p<0.05$) in all treatments and years. The decrease in soil NO_3 concentration due to straw amendment was more pronounced in 2013.

Controls of N_2O emissions

In general, significant correlations were found between N_2O fluxes and environmental factors e.g. soil moisture WFPS and air temperature. Furthermore, soil NH_4 concentrations showed moderate but significant correlation with post-harvest N_2O fluxes (Table 3.3). In treatment Fert-180 air temperature showed the highest correlation with the post-harvest N_2O emissions, Spearma n R=0.91, $p<0.001$. Figure 3.5 clearly showed an exponential relationship between air temperature and N_2O emissions. High emissions occurred when air temperature was above 15 °C. It is also interesting to note that N_2O emissions show higher correlation with soil NH_4 than with NO_3 even though soil NH_4 contents were much lower than NO_3 contents.

The Coup model simulation was in good agreement with measured soil temperatures as indicated by an R2 of 0.93 but showed less accuracy in simulating the WFPS (Figure 3.6). The fit of modelled N_2O emission rate was highest in Fert-180 treatment ($R^2=0.5$, ME=0.02, RMSE=0.5). However overall data, the model seemed to underestimate the emissions in the No Fert treatment, but overestimated the emissions in 90 and 180 kg N ha^{-1} fertilization treatment as shown in Figure 2. The model also captured the measured emission peaks with some time shift. The model yielded higher denitrification rate estimates for soils fertilized with 180 kg N ha^{-1} compared to the No Fert treatment.

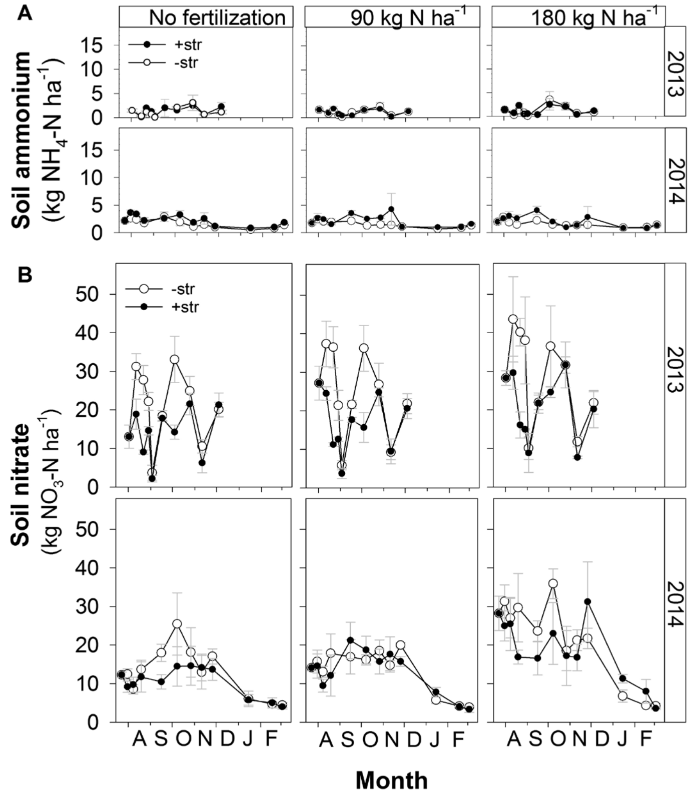

Figure 3.4 A: NH_4 and **B**: NO_3 concentration in the uppermost soil layer (0-0.15 m) from soils after oilseed rape harvest without straw incorporation (-str) and incorporation of oilseed rape straw (+str) from the non-fertilized treatment (No fert) and N fertilized treatments (Fert-90: 90 kg N ha^{-1}; Fert-180: 90 kg N ha^{-1}) in spring. Error bars show the standard error of mean of each treatment (n=3).

3.4 Discussion

Effects of residue return on soil N cycling

In our study, soil NO_3 concentrations at harvest were strongly governed by the N fertilizer level in spring and even at harvest they were higher with higher fertilizer rates. Similarly in a ^{15}N labelling study with oilseed rape, Malagoli et al. (2005) showed that about 45 kg N ha^{-1} entered the soil before harvest only by leaf loss. In the present study, the oilseed yield and their N concentration increased significantly with the increase in fertilizer N rates (Table 1). In the period from harvest to autumn (Sep/Oct), the incorporation of oilseed rape straw was accompanied by drops in soil NO_3 concentration (No straw (-str) vs. straw amendment of soil (+str)). In bare soils (-str), the net increase in NO_3 after harvest might leave the soil microorganisms with a shortage of electron acceptors and thus, a built-up of NO_3 in the top soil. A net mobilization of NO_3 in the soil in a period of ca. 6 weeks after harvest on bare soil was also found

Table 3.3 Spearman correlation R value for N_2O fluxes in 2014 differentiated by fertilizer treatment (No fert, Fert-90, Fert-180) and residue addition (-str, +str). Concentrations of NO_3-N, NH_4-N and WFPS refer to the uppermost soil layer (0-0.15 m).

N fertilization	Straw treatment	NO_3-N	NH_4-N	WFPS	Air temperature
No fert	-str	0.24	0.59**	-0.42*	0.78**
	+str	0.21	0.6**	-0.44*	0.82**
Fert-90	-str	0.12	0.45*	-0.48*	0.86**
	+str	0.3	0.57*	-0.31	0.77**
Fert-180	-str	0.49	0.56*	-0.56*	0.76**
	+str	0.45	0.61**	-0.48*	0.91**

* $p<0.05$
** $p<0.001$

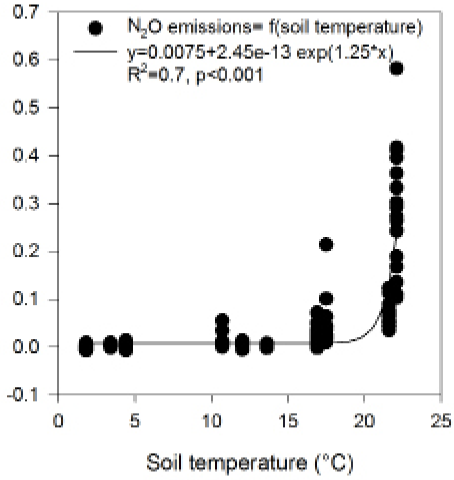

Figure 3.5 Air temperature and N_2O emissions from all plots from the uppermost soil layer (0-0.15 m) in the period from harvest to winter in the season 2014/2015.

in a study conducted by Engström and Lindén (2012). This could also explain the substantial drop in NO_3 concentration in all treatments in the first four weeks after harvest in 2013. However, a built-up of NO_3 could have also resulted from the stop of plant uptake with ongoing mineralization.

In the first weeks following harvest, and in particular in the first 30 days, the NO_3 concentration dropped substantially in 2013. There are several possible explanations. On one hand, Engström and Lindén (2012) observed a similar fluctuation in the soil mineral N pool. They conducted an in-situ incubation study in a field experiment. Treatments included the addition of oilseed rape straw after harvest and measurements of mineralization and immobilization of soil mineral N. The net N immobilization was 11 kg N ha^{-1} in a 6-week period right after harvest. Our field experiment confirmed a net immobilization of 19 kg N ha^{-1} in the 180 kg N ha^{-1} treatment with straw amendment (+str) from 2nd August to 3rd September 2013. On the other hand, the decline of the soil NO_3 could be ascribed to the uptake of N by volunteer rape. Volunteer rape results from grain loss during oilseed rape harvest and it has been reported to take up up to 28 kg N ha^{-1} (Justes et al., 1999). Moreover, high NO_3 concentrations in the soil N pool after harvest increase nitrate leaching loss rates into deeper soil layers (Engström and Lindén 2012). Such dynamics were also confirmed in our study by the process modeling where the highest simulated leaching losses were found in the 180 kg N ha^{-1} fertilizer treatment.

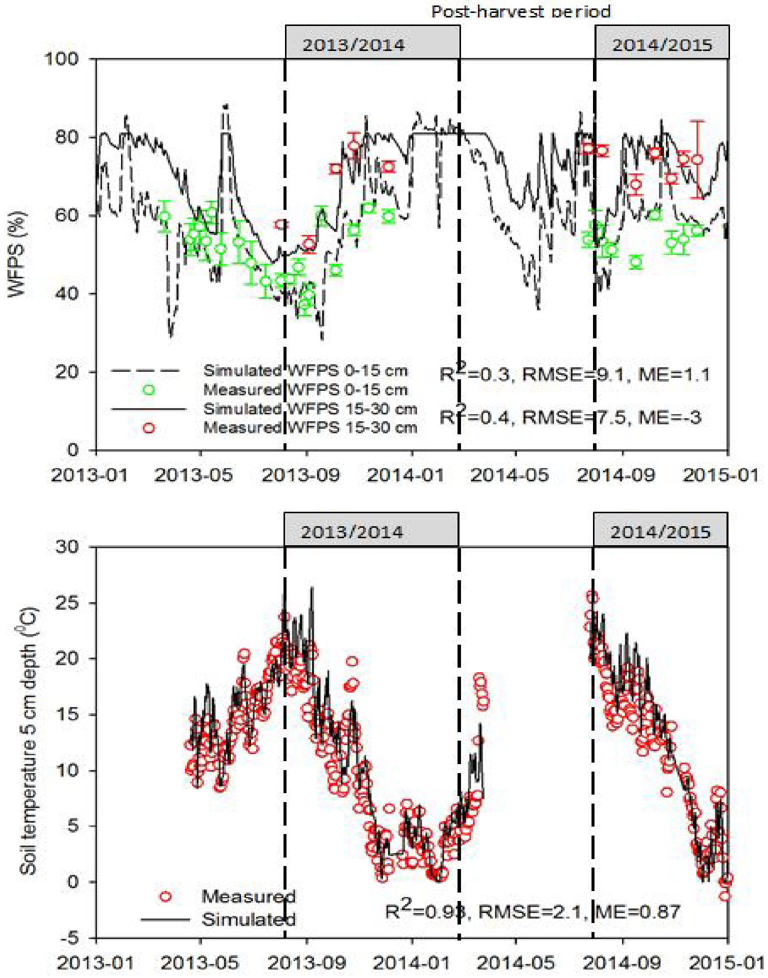

Figure 3.6 Measured and simulated water-filled pore space for the experiment period from spring 2013 to 2015.

N_2O emissions

After harvest and incorporation of oilseed rape straw, a short pulse in N_2O emission activity was found in both years. Though, the magnitude of fluctuation was considerably different for the two post-harvest periods. With progressing time towards winter, N_2O emissions declined to very low rates. In the two experimental years 2013/2014 and 2014/2015 the variation of residue incorporation into the soil and N fertilizer level revealed that both factors had only minor effects. N_2O emissions showed fluctuations, but most likely they were driven by other factors. For N_2O emissions in the post-harvest period, cumulative N_2O emissions of all treatments showed low variation within each year, but in 2014/2015, cumulative post-harvest N_2O emissions were 10-times greater than in 2013/2014.

It is a general finding (see review by Rees et al., 2013) that the N management is the dominating factor controlling the N_2O emissions from cropped soils. However for the post-harvest period, our results suggest that the climate effects (WFPS and more importantly temperature) seem to be more relevant in controlling N_2O emissions specifically after of oilseed rape cultivation. This is in agreement with the conclusions of Dobbie et al. (1999) who stressed the great relevance of the coincidence of nitrogen availability and moist soil conditions even though the main focus of their study was on the fertilizer application period.

The CoupModel can reproduce the measured high N_2O emissions in 2014, and according to the model, the emissions were primarily produced by denitrification since in 2014, temperature and also soil moisture were favorable for denitrification producing N_2O. However, it should be noted that for 2014, the model overestimated not only soil moisture (WFPS) but also residue biomass and seed yield. Therefore, the modeled high emissions might partly be due to a bias resulting from combined high residual mineral N and anaerobiosis in the model. Nevertheless, the modeled soil respiration agreed well with the measured data (not shown), therefore it is likely that organic matter decomposition and also mineralization were reasonably well described by the model. For the fertilized soil, model results indicate higher denitrification rates. Given that N_2O emissions for non-fertilized and fertilized soils were similar, this suggests that within the process of denitrification, there was a higher rate of reduction of N_2O to N_2 in soils fertilized with 180 kg N ha^{-1}. Therefore, our results suggest that possibly the $N_2O/(N_2O+N_2)$ ratio decreased as fertilization increased.

Surprisingly in 2013, the treatments with residues remaining in the soil only showed a significant reduction in N_2O emissions for soils fertilized with 90 kg N ha^{-1}. When rainfall increased the WFPS in the middle of September, conditions in soil changed from aerobic to anoxic. In soils amended with straw (+str), soil microorganisms immobilized NO_3. When the C/N ratio of the residue is high, N from the soil mineral N pool is taken up into the soil microbial biomass. Here, for example in a study by Potthoff et al. (2005) it has been shown that the soil mineral N concentrations decreased and the microbial biomass C and N increased after soil amendment with maize residue.

The comparison of N_2O fluxes of the post-harvest periods in both years shows marked differences. Here, rather than the fertilization or the removal of straw, the different climatic variations had a great influence with a 10-fold difference for the presented years. Ruser et al. (2001) conducted a field experiment covering several years and crops. NO_3 concentrations had a significant effect and also water-filled pore space showed quite high positive correlations with N_2O emissions. Both factors accounted for 52% of the variability of N_2O emissions. Repeated rewetting of soil showed highest cumulative

N_2O emissions compared to either continuously dry or wet soil in a study under controlled conditions (Harrison-Kirk et al., 2013). In our experiment, strong contrasts in rainfall distribution and the sums of precipitation occurred between years. Thus, this factor is seen as explanatory for a large share of the great differences in N_2O emissions in these two years. Several other agricultural soils also showed high N_2O emissions at 60% WFPS (Dobbie et al., 1999; Davidson and Firestone, 1989). Firstly, high WFPS led to anaerobic conditions. High N_2O emissions were found at WFPS of 60%. In our experiment, WFPS was just below 60% for some sampling days and above 50% for most of the days.

Secondly, another major factor for the substantial difference of N_2O emissions between 2 years was temperature which is a known strong control factor of soil microbial activity. Billings and Tiemann (2014) show in an incubation experiment that there is a high capability of warm June soils to produce N_2O displayed in the N_2O production which was underlined by the high amount of cnorB genes. In those soils, the nosZ genes were lower than cnorB genes which was in line with high rates N_2O production, but low N_2 production rates. We have not been able to measure this in our experimental approach. Nevertheless it underlines the potential of soils to produce N_2O by denitrification.

Thirdly, the share of N_2O released from the soil mineral N pool (NH_4 and NO_3) seems to draw a pattern. Since soil mineral N concentrations ranged on equal levels in both years, the ratio of released N_2O in relation to the soil mineral N concentration on a specific date was less than or equal to 0.12%, even for the dates shortly after harvest in 2013. In contrast, in 2014 the ratio of N_2O being released in relation to the soil mineral N pool was well above 1% right after harvest and it did not drop to the level of 2013 before beginning of October. This indicates that in 2014 there were greater rates of N_2O producing processes rather than greater pool sizes from which N_2O was produced. A possible explanation might be that in 2014 the high WFPS and low oxygen partial pressure and the high temperature induced anaerobic conditions more rapidly which then increased the ratio of N_2O emission to the pool size of soil mineral N which is indicative of a dominance of denitrification. Nevertheless, a large C source presented as root biomass may also lead to a production of N_2 as denitrification end product which could explain the same levels of N_2O emissions in treatment levels.

The IPCC (2014) totals the N_2O emission from agricultural soils to account for 1% of the fertilizer N input. So for the current study, this implies that for the 180 kg N ha^{-1} fertilizer level the share of emissions would be 1.8 kg N ha^{-1} for a complete year of oilseed rape cropping. It can be speculated that the N_2O emission for 2013 may reach the level of 1% since in the post-harvest period, N_2O emissions were lower. In 2014 however, cumulative N_2O emissions for a period of only 7 months amounted to 7.3 kg N ha^{-1} equivalent to 4.21%. Thus, considering both years, the IPCC default value of 1% is too low to fit our data. Our measured data are towards the higher end of the reported range of IPCC fertilizer-related emission factors. However, our results also give evidence that the rates of applied N fertilizer did not have the strong regulating effect on the rates of emissions that has often been stated. The IPCC default value is helpful to estimate N_2O emissions on a continental or country scale; however, at the field scale or for assessing new management measures, it is not a useful tool. Other regulating factors need to be additionally considered to give better estimations (Charles et al., 2017; Rochette et al., 2018); as one can see in the case for present example, consideration of the amount of N fertilizer alone may lead to an error of up to 300%. Besides effects of soil moisture and precipitation, this study also shows the high temperature sensitivity of N_2O production even under field conditions. At the background of predicted global temperature increases, this is another very important finding.

3.5 Conclusion

Straw removal is a common practice in cereal production and straw as a source of easily decomposable organic matter has been assumed to make major a contribution to N_2O emissions from agriculture in the post-harvest period. However for oilseed rape, the present study showed that leaving straw on the field after harvest seems to be equal to removal or even slightly beneficial with respect to reducing N_2O emissions.

This study underlines the importance of multi-year experiments to assure capturing of climate variability. Also, attempts to identify mitigation options should relate to the predicted changes in summer rainfall and temperature pattern in temperate regions.

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4 N_2O emissions from rapeseed - cereal crop rotations depend more on abiotic factors than on crop type

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Abstract

The intensification of cropping systems has raised the question of the sustainability of crop rotations. Diversification and widening of crop rotations is beneficial to crop health and yield stability. Knowledge of greenhouse gas emissions over several years and crops simultaneously grown on several sites is scarce. Our study aims to quantify N_2O emissions in an oilseed rape - cereal crop rotation and relate them to output values such as yield or the nutritional value of the harvest product. On five sites, a crop rotation including winter oilseed rape, winter wheat and winter barley was established and run simultaneously from 2012 to 2016 for three years. Winter oilseed rape was fertilised in a 50/50 split N application of 180 kg N ha^{-1}, while winter wheat and winter barley were fertilised according to site-specific recommendations. The gas was sampled weekly, at minimum, with additional sampling taken according to management or climate events. Average yield was 4.49, 8.16 and 8.22 t ha^{-1} for winter oilseed rape, winter wheat and winter barley. Daily N_2O emission increased after mineral N fertilisation, but also strongly responded to soil type, air temperature and water-filled pore space. Thus, overall N_2O emissions were strongly stimulated by abiotic factors and not, as expected, by crop. N_2O emissions as a share of fertiliser N input were 0.76, 0.74 and 0.76% for winter oilseed rape, winter wheat and winter barley. Since overall N_2O emissions did not depend on crop, related N_2O emissions for each crop depended on their reference value which were crop-specific and decided which crop performed best. In general, this study underlines the importance of a detailed evaluation of a complete crop rotation grown simultaneously. Here, all recorded drivers including crop were evaluated and give rise to a clear interaction between site or soil type and the climate drivers WFPS and air temperature when fertilisation met (winter wheat and winter barley) or was close by (oilseed rape) the requirements of the respective crops.

4.1 Introduction

Worldwide intensification of cropping systems has raised the need for the diversification of crop rotations to increase the resilience of agroecosystems and maintain yields in a changing climate. This is supported by several studies which demonstrate increasing yield stability with the integration of further crops to reduce monocultures or narrow rotations (Andrade et al., 2017; Congreves et al., 2017; Gaudin et al., 2015). Additionally, the EU member states agreed on an EU directive on integrated pest management with the aim of convincing farmers of the sustainable use of pesticides and to reduce the risk of tolerance in harmful organisms (EU 2009/128/EC, 2009). A major principle in the German National Action Plan on Sustainable Use of Plant Protection Products (Federal Ministry of Food and Agriculture, 2013) for reducing risks associated with pesticide application is to diversify crop rotations.

Generally, crop rotations consist of several crops. In Germany, a study conducted in the federal state of Lower Saxony revealed that the share of wheat was one of the largest (next to maize) on arable land. However, in crop rotations with more than two crops, wheat was complemented with oilseed rape and barley (Steinmann and Dobers, 2013).

Oilseed rape is a profitable and important crop with a share of 12% of the cropped area in Germany in 2016 (Statistisches Bundesamt, 2016). It provides considerable benefits for succeeding cereal crops. As a break crop, it interrupts the propagation of cereal pests and thus supports the maintenance of high yields (Henke et al., 2009; Lütke Entrup and Schäfer, 2011; Sieling and Christen, 2015; Sieling and Kage, 2010).

Winter wheat as a crop is preferred by farmers due to its high and stable crop yield (Statistisches Bundesamt, 2016). Barley is also acceptable as a further element in the rotation because, in contrast to wheat, some barley varieties can be harvested early which is advantageous for farming operating schedules. Additionally, the decomposition of barley straw is well advanced when oilseed rape is seeded resulting in favourable soil and nutrient conditions.

N_2O emissions from soil are mainly mediated by microbial processes. Among various processes of the soil nitrogen cycle (Butterbach-Bahl et al., 2013), nitrification, an aerobic process, and denitrification, occurring under anoxic conditions, constitute a varying share on N_2O emissions as soil conditions change. While nitrification produces NO_3 as an end product which can be taken up by plants, denitrification with its end product N_2 results in a loss of soil nitrogen thereby reducing N efficiency. Both processes produce N_2O, nitrification as a by-product and denitrification as an intermediate product, which can be emitted, in particular, if N_2O reduction to N_2 is inhibited by unfavourable soil conditions.

Thus, key drivers of N_2O emissions in agricultural ecosystems are influenced by a set of management and abiotic factors. The management system controls nutrient availability due to fertiliser and harvest residue inputs. Nutrient input can be supplied as organic or mineral fertilisers. Rate and timing of fertilisation vary considerably depending on crop type and development, and weather conditions. There is an extensive range of soil working operations: ploughing disturbs the soil structure, delivers O_2 into the soil and moves nutrients to soil microorganisms for growth and activity and thus impacts on mineralisation, nitrification, denitrification and other soil processes thereby changing N_2O emission patterns. Nevertheless, abiotic factors constrain the agricultural system. Climate and weather control soil temperature and, via rainfall, soil humidity. Several studies have shown how N fertilisation affects N_2O fluxes in different crops or even in crop rotations (e.g. Lehuger et al., 2011). Rees et al. (2013) report large variations in N_2O emissions and N_2O emission factors due to rainfall and N application.

Post-harvest periods are particularly vulnerable to producing N_2O emissions. Usually, the post-harvest period in central Europe is characterised by warm temperatures and rainfall events occur more often than in summer. Management interventions during this period include soil working such as ploughing and seed bed preparation. The root system of the harvested crop remains in the soil and plant residues are incorporated. Wheat and barley grain and straw are removed and only stubble remains on the field, but in oilseed rape cropping only the seeds are harvested and the straw and seed hulls remain on the field. The remaining C-rich rapeseed plant residues additionally have a higher N concentration than cereal residues (Gan et al., 2011). Furthermore, N uptake of winter oilseed rape slows down towards the maturation of seeds and stops earlier than in cereals, as a consequence leaving higher residual mineral N from fertilisation in soil after harvest. Therefore, it can be hypothesised that the post-harvest period of rapeseed cropping may be considered to be particularly vulnerable to producing increased N_2O emissions.

The complex interactions between processes of the soil nitrogen cycle make predicting N_2O emissions challenging. A field study by Engström and Lindén (2012) compares oilseed rape, oat and peas on two sandy loam soils and a clay soil. Results showed that mineral N concentration for the 0-0.9 m layer was highest in soils cropped with oilseed rape and almost double that in comparison to oats. A systematic field trial by Sieling and Kage (2006) reports mineral N concentrations up to 97 kg ha^{-1} (0 to 0.9 m) after harvest of oilseed rape which was higher under wheat or barley. The high mineral N concentrations enable NO_3 leaching after winter oilseed rape. On the other hand, straw incorporation results in N immobilisation which also decreases mineral N availability to N_2O producing processes.

The largest GHG emission share during cultivation, results from fertilisation such as fertiliser production emissions and direct and indirect emissions of N_2O after fertiliser application. N_2O is a potent greenhouse gas with a warming potential 265 times higher than CO_2 across a 100-year perspective (Myhre et al., 2013) and it also degrades the ozone layer (Ravishankara et al., 2009). GHG emissions from cultivation are estimated based on IPCC methodology for national inventories (IPCC, 2006), i.e., an emission factor of 1 % of fertiliser N is used to quantify direct N_2O field emissions. However, IPCC methodology does not consider the effects and benefits of crop rotation.

One approach to assess N_2O emissions and productivity of crops has been proposed by van Groenigen et al. (2010). They summarised information relating the difference of N fertilisation and N removal by grain to N_2O emissions per above ground biomass. In general, if the N surplus was negative, yield-related N_2O emissions were low, but with increasing N surplus towards positive values, yield-scaled N_2O emissions increased exponentially. This relationship corresponds to N fertilisation reaching and exceeding the N demand of the plant. From an agronomic perspective, the approach could be used to optimise yield with respect to N_2O emissions.

Previous studies investigating N_2O emissions from crop sequences, often measured the different crops at a later stage (Rees et al., 2013, Zhou et al., 2015). These studies do not permit separating crop specific effects from annual variation. Thus, five field trials were established to investigate crop specific effects on N_2O emissions in the crop sequence oilseed rape - winter wheat - winter barley.

The specific aims of the study were to:

- supply crop-specific N_2O emission data for the crop rotation oilseed rape, winter wheat and winter barley,
- capture site- or region-specific factors and the annual variability in N_2O emissions and
- evaluate and compare the yield-related N_2O emissions for oilseed rape, winter wheat and winter barley.

4.2 Materials and Methods

Sites and experimental design

The field experiments were set up at five sites in 2012. Field sites were Berge (52.62°N and 12.78°E, 40 m asl), Dedelow (53.37°N and 13.83°E, 34 m asl) , Hohenschulen (54.31°N and 9.99°E, 30 m asl), Ihinger Hof (48.74°N and 8.92°E, 579 m asl) and Merbitz (51.62°N and 11.91°E, 153 m asl). The sites represent regions favourable for oilseed rape cultivation in Germany. Rainfall, radiation and temperature were obtained from weather stations installed nearby the respective sites. The annual sum of precipitation, annual mean temperature and soil characteristics were presented by Ruser et al.

(2017). Soil temperature was recorded with temperature loggers (LogTag® TRIX-8, LogTag Recorders Limited, Auckland, New Zealand) in soil depths of 5 cm. The field experiments were established in autumn 2012 and were performed over three consecutive years from 08/2012 to 01/2016 including the three crops of the rotation, i.e., winter oilseed rape – winter wheat – winter barley in four replications in a randomised block design. All crops were present simultaneously. Plot size was 12 m x 3 m. For this study, the fertiliser rates for rapeseed was 180 kg N ha^{-1} in 50/50 split application at each site. Wheat and barley was N fertilised two to four times according to site-specific recommendation (Table 4.1). Mineral N fertiliser was applied as calcium ammonium nitrate (CAN). Plant protection was performed according to local management practices.

Soil mineral N

Soil from 0-30 cm was collected weekly using a soil probe. Soil mineral N was extracted by mixing 25 g soil with 100 ml of 0.0125 M $CaCl_2$ solution in an overhead shaker for one hour. The solution was filtered with 595 1/2 whatman filters (Macherey – Nagel GmbH & Co. KG, Düren, Germany) and analysed calorimetrically for NH_4 and NO_3 (San++ Continuous-Flow Analysator, Skalar Analytical B.V., Breda, The Netherlands). Analysis comparability was confirmed by an inter-laboratory test.

Gas flux measurements

To assess N_2O concentrations, rectangular polyvinyl chloride (PVC) collars (length = 0.71 m, width = 0.27 m) were driven 5 cm deep into the soil. Collars were placed between plant rows of winter oilseed rape while collars included cereal plants. To collect gas samples, white PVC chambers (PS-plastic, Eching, Germany; height: 0.11 m) were used with a rubber sealant according to the closed chamber method (Hutchinson and Mosier, 1981). A small vent was installed inside the chamber to ensure a homogenously mixed atmosphere in the headspace. Gas samples were taken at least once a week and more frequently at fertilisation, heavy rainfall events or soil management resulting in c. 10,000 gas samples. Collars were removed for soil work and harvest.

To analyse N_2O, gas chromatographs were equipped with an electron capture detector. Measurements for each site were conducted by the local lab and comparability was established by a ring test.

Table 4.1 Amount and splitting of N fertilizer for each site in winter wheat and winter barley for the years 2013, 2014 and 2015.

Experimental site	Winter wheat (kg N ha^{-1})			Winter barley (kg N ha^{-1})		
	2013	2014	2015	2013	2014	2015
Berge	60/60	60/60	60/60	60/60	60/60	60/60
Dedelow	81/70/54	46/80/50/60	80/80	81/70/54	46/80/50/60	80/80
Hohenschule	60/60/55	30/40/50	30/80/55	60/75/40	40/70/40	30/80/55
Ihinger Hof	80/80/60	80/80/60	80/80/60	80/60/60	60/60/60	80/60/60
Merbitz	40/120	40/93	40/97	40/80	40/70	40/67

Flux calculation was performed with software R v.3.2.2 and the package *gasfluxes*. The Akaike information criterion was obtained to select the appropriate model for flux calculation, i.e., the HMR model (Pedersen et al., 2010) or robust linear regression (Huber, 1981). The HMR model was used if the AIC value from linear regression was higher than the AIC from the HMR calculation and its kappa value was higher than 20 h^{-1}. Linear regression was used if only three gas samples were available for flux calculation due to sample loss. As a quality check, the Pearson correlation coefficient between CO_2 concentrations and chamber closure was computed and fluxes with an R^2 below 0.85 were removed. Due to our quality check, 7,047 fluxes remained, but only few dates lacked all data due to the quality check. We imputed missing N_2O fluxes according to Honaker et al. (2011). N_2O fluxes were log transformed to raise the quality of imputation. To account for data structure, imputation was done grouped by sites, treatments and years. Autocorrelations were considered by adding linear time effects. Imputed fluxes were transformed back and the median of imputations was chosen to obtain the flux estimate.

N_2O emissions are presented with mean±1 standard deviation. N_2O fluxes were aggregated by linear interpolation between two sampling days. Aggregation was done from seeding to seeding of the preceding crop. A mixed model (R packages *lme4* and *lmerTest*) with site and season (cropping period to differentiate between crops grown in different years) as fixed factors was set up to investigate the influence of crop on post-harvest N_2O emissions. To overcome the difference in length of bare soil periods after crop harvest, cumulative N_2O emissions were divided by the respective period to obtain mean daily N_2O emissions.

A generalised additive model was computed with R packages mgcv to analyse factors influencing daily N_2O emissions. To distinguish between sandy and loamy soils, the factor soil type was included into the generalised additive model. The sites Berge, Dedelow and Hohenschulen were classified as sandy while Merbitz and Ihinger Hof were characterised by loamy soils. Temperature was considered with one data point per day at each site. Factors like WFPS, NH_4 and NO_3 were considered per site and per crop in four replicates.

As no control treatment was considered in our study, fertiliser-related emissions (FRE) were calculated as the percentage of N_2O-N released from applied fertiliser referring to the IPCC reports with emission factors with the formula

$$Fertiliser - related\ emissions\ (FRE\ in\ \%) = \frac{annual\ N_2O\ emissions\ (kg\ N_2O{-}N\ ha^{-1}\ year^{-1})}{N\ fertiliser\ application\ (kg\ CAN{-}N\ ha^{-1}\ year^{-1})} * 100$$

N surplus and output – related N_2O emissions

N concentrations (%) in the seeds were obtained by grinding seeds and the powder was analysed using an elemental analyser (vario Max CN, Elementar Analysensysteme, Hanau, Germany). Oil in oilseed rape seeds was analysed with NIRS (NIRSystem 5000, Foss, Hamburg, Germany).

The N surplus ($N_{surplus}$) was calculated with the following formula:

$$N_{surplus} = N_{fert} - (Crop\ Yield * N_{conc})$$

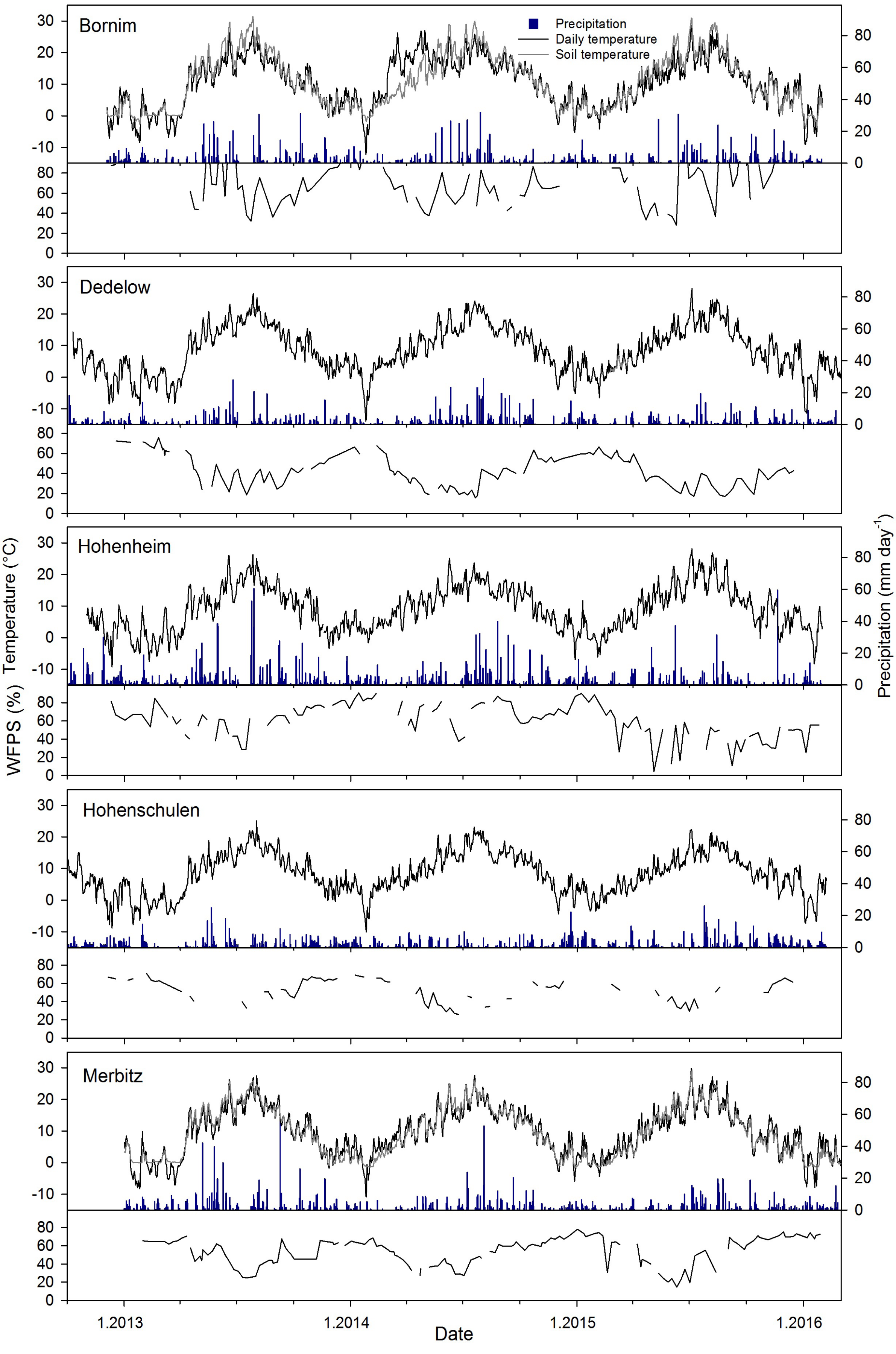

Figure 4.1 Daily mean temperature (°C), precipitation (mm d^{-1}) and soil WFPS (%) for the sites Bornim, Dedelow, Hohenheim, Hohenschulen and Merbitz from October 2012 to February 2016.

where N_{conc} was the N concentration in the seeds (%), N_{fert} was the respective N amount fertilised to the crop (kg N ha^{-1}) and crop yield was the dry matter seed yield (t ha^{-1}). Yield-related N_2O emissions for the respective fertiliser level and plot, were calculated by dividing the annual N_2O emissions by the amount of DM yield per hectare. To compute N_2O emissions referring to a nutritional unit for winter wheat and winter barley, N_2O emissions were divided by the sum of the nutritional value for the dried distillers grains with solubles as feed for cattle with 12.07 MJ kg^{-1} DM and the whole plant silage with 9.32 MJ kg^{-1} DM which was multiplied with the respective DM yield. For oilseed rape, the meal cake and nutritional value of oil accounted for 12.9 MJ kg^{-1} DM and 33.9 MJ L^{-1} for the oil yield of 1355 L ha^{-1}, respectively. Obtained numbers for oil yield were acquired from a database which is based on data from the Federal Office of Consumer Protection and Food Safety (Nährwertrechner, 2016) while feed numbers were obtained from a publication of the Bavarian State Research Centre for Agriculture (LfL, 2013).

Oil yield energy-related N_2O emissions were calculated with specific data for each crop. For winter wheat and winter barley, the DM grain yield was multiplied with 1.71 and added to the straw yield multiplied with 1.62. Oilseed rape energy yield was calculated with the factor 2.56 for the received oil content (Döhler, 2005).

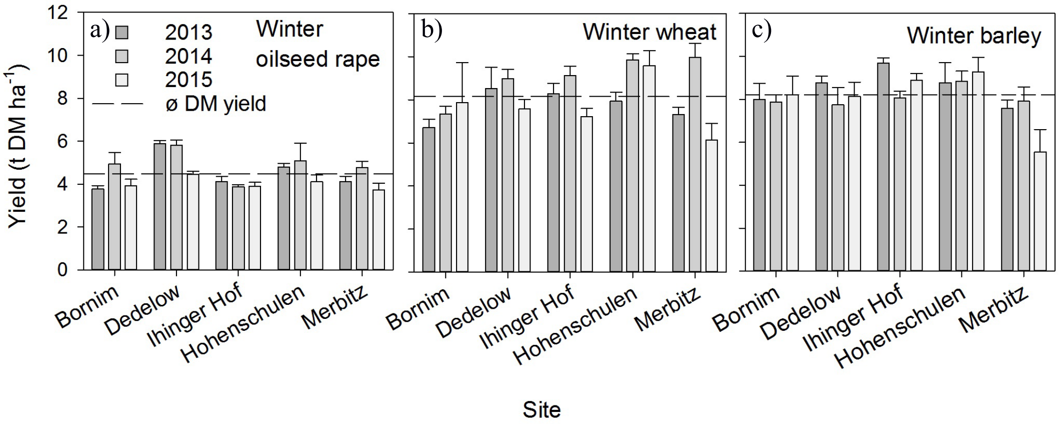

Figure 4.2 Yield (t DM ha^{-1}) of a) winter oilseed rape, b) winter wheat and c) winter barley for the years 2013, 2014 and 2015 (n=4). Lines for yield (dashed) represent the mean of all years and sites (n=60). Error bars show the standard deviation for each year and site (n=4).

Table 4.2 Annual mean temperature (°C) and precipitation (mm $year^{-1}$) for the years 2013, 2014 and 2015.

Experimental site	Temperature (°C)			Precipitation (mm $year^{-1}$)		
	2013	2014	2015	2013	2014	2015
Berge	9.4	13	10.6	615	482	570
Dedelow	8.7	9.9	9.7	446	561	414
Hohenschule	8.1	9.7	8.8	462	409	562
Ihinger Hof	8.7	10.5	10.1	923	763	544
Merbitz	9.1	10.7	10.4	700	456	429

4.3 Results

Climate conditions

Climate conditions varied between sites and years (Figure 4.1). For the studied period of the years 2013 to 2016, the mean temperature showed a variation of 1 to 2 °C between years for each site (Table 4.2). Berge had a minimum annual temperature of 9.4 °C in 2013 during the examined experimental years, while the year 2014 was 3.5 °C warmer. Here, long-term annual temperature was 8.7 °C. Generally, long-term mean annual temperatures were lower than the ones in the experimental years for all sites. The continental sites, Ihinger Hof and Merbitz, showed large differences in precipitation. In Ihinger Hof, precipitation ranged from 544.1 in 2015 to 922.7 mm year^{-1} in 2013. In Merbitz, on average, the precipitation in year 2013 was almost 60% higher than the following two experimental years but also well above the long-term mean annual precipitation of 520 mm year^{-1}. The recorded precipitation for the site Ihinger Hof, was a maximum 75% of the long-term mean annual precipitation in all experimental years.

Generally, the measured WFPS is closely connected to soil texture and rainfall which were site-specific. The sandy soils at the sites Berge, Dedelow and Hohenschulen were accompanied by rainfall events lower than 32 mm day^{-1} and a more even rainfall pattern. In particular, the site Dedelow had a WFPS lower than 50% for most of the time during crop growth. The continental soils of Ihinger Hof and Merbitz were more frequently exposed to heavy rainfall events with up to 60 mm day^{-1}. Notably, at the site Merbitz in spring 2013, WFPS was above 50 % for periods essential to plant growth along with the N fertiliser application. The following years 2014 and 2015 were characterised by low rainfall in winter and spring which was followed by sharply dropping WFPS in March.

Yield and N surplus

The yield was on average 4.49, 8.16 and 8.22 t ha^{-1} (n=240) for winter oilseed rape, winter wheat and winter barley for all sites and years. The annual variation in oilseed rape was more pronounced in winter oilseed rape than in winter wheat. High variations between years were especially found at the sites Hohenschulen and Merbitz (Figure 4.2). N concentrations were lowest for winter oilseed rape and winter barley with 0.14%, respectively, while winter wheat reached 0.16%.

The mean oil yield for winter oilseed rape was 1.89, 2.53, 1.88, 2.29 and 1.96 Mg ha^{-1} year^{-1} for the sites Berge, Dedelow, Ihinger Hof, Hohenschulen and Merbitz, respectively. Mean oil yield was closely related to yield.

The N surplus ranged around 0 kg N ha^{-1} for winter wheat and winter barley which leads to the assumption that the removal of harvest goods was as high as the N input from fertilisation. For winter oilseed rape the N surplus was significantly ($p<0.001$) higher with above 25 kg N ha^{-1} for all sites averaged over three years indicating an enrichment of N on the field from fertilisation to harvest.

N_{Min}

The course of N_{Min} concentrations during the year largely depended on management (Figure 4.3). In particular, the application of NH_4 and NO_3 as CAN-N led to high soil N concentrations at all sites shortly after fertiliser application. NH_4 concentrations were high after fertilisation in spring. With plant maturation, soil NO_3 concentrations decreased. A build-up of mineral N in the soils grown with winter oilseed rape due to leaf litter fall and its mineralisation was not observed. In December and January of the experimental years, NO_3 concentrations normally decreased.

N_2O emissions

N_2O emissions varied across sites. Only the sites Berge, Dedelow and Hohenschulen showed low fluxes with only sporadic N_2O emissions above 25 g N ha^{-1} day^{-1} in all crops during the years 2013 to the end of 2015 (Figure 4.4). The highest measured N_2O emissions were observed at the site Merbitz during 2013. Here, spring was characterised by high WFPS due to snow melt and NH_4 and NO_3 as CAN was added to plants at an early growth stage. The second N fertilisation was applied on warmer soils and N_2O emission peaked with 161, 226 and 166 g N ha^{-1} day^{-1} for winter oilseed rape, winter wheat and winter barley, respectively, most likely accelerated by increasing WFPS caused by a heavy rainfall event with 42 mm. This high N_2O emission period was found in all crops showing no difference in the respective year. In the years 2014 and 2015, neither fertilisation-triggered N_2O emission events were observed at this site, nor any specific crop effect on N_2O emissions. Fertilisation management at the site Ihinger Hof was varied due to the N demand of the cereals. In particular, the splitting and timing of N fertilisation in winter wheat and winter barley had an impact on N_2O emissions. At the site Ihinger Hof, soils grown with cereals showed high N_2O emissions where N was fertilised in three stages with the third in the beginning of June. Particularly, the third fertilisation and rainfall events in June and July triggered high N_2O emissions with peak N_2O emissions of 44 and 46 g N ha^{-1} day^{-1} in winter wheat and winter barley, while in the early growing season, the splitting into two events and even with high N dosages in soils grown with oilseed rape led to low N_2O emissions below 10 g N ha^{-1} day^{-1}.

To compare N_2O emissions from bare soil after harvest of the respective crop and to account for the length of the period from harvest to seeding, averaged daily N_2O fluxes for these periods were calculated. Generally, the bare soil period depended on crop. Winter wheat and winter barley were followed by a bare soil period of 35 and 36 days, respectively, while winter oilseed rape cropped soil was left bare for 55 days on average. Here, bare soils after winter oilseed rape showed significantly higher N_2O emissions with 6.22±1.57 g N ha^{-1} day^{-1} than from bare soils after harvest of winter barley with 2.25±1.58 g N ha^{-1} day^{-1} ($p<0.001$). Soils after winter wheat harvest emitted 4.08 g N_2O-N ha^{-1} day^{-1} ($p>0.05$ for bare soils after winter barley or winter oilseed rape). For example, in the postharvest period 2013 in Ihinger Hof, averaged N_2O emissions from soils after oilseed rape harvest averaged out at 7.78±1.85 g N ha^{-1} day^{-1} while soils after winter barley harvest emitted only 0.99±0.47. Here, the N_2O emissions amounted to 0.5 kg N ha^{-1} 63 days^{-1} and 0.02 kg N ha^{-1} 21 days^{-1} for bare soils after oilseed rape or winter barley harvest, respectively.

Impact of environmental drivers on N_2O emissions

The generalised additive model had an adjusted $R^2 = 0.226$ and explained 23.7 % of deviance. The coefficient ‘soil type’ affected log transformed N_2O emissions significantly ($p<0.001$) compared to sandy soils. Remaining (unexplained) site effects also resulted in significant differences of flux mean values between some sites. Notably, the crop did not affect N_2O emissions ($p>0.05$). Air temperature did

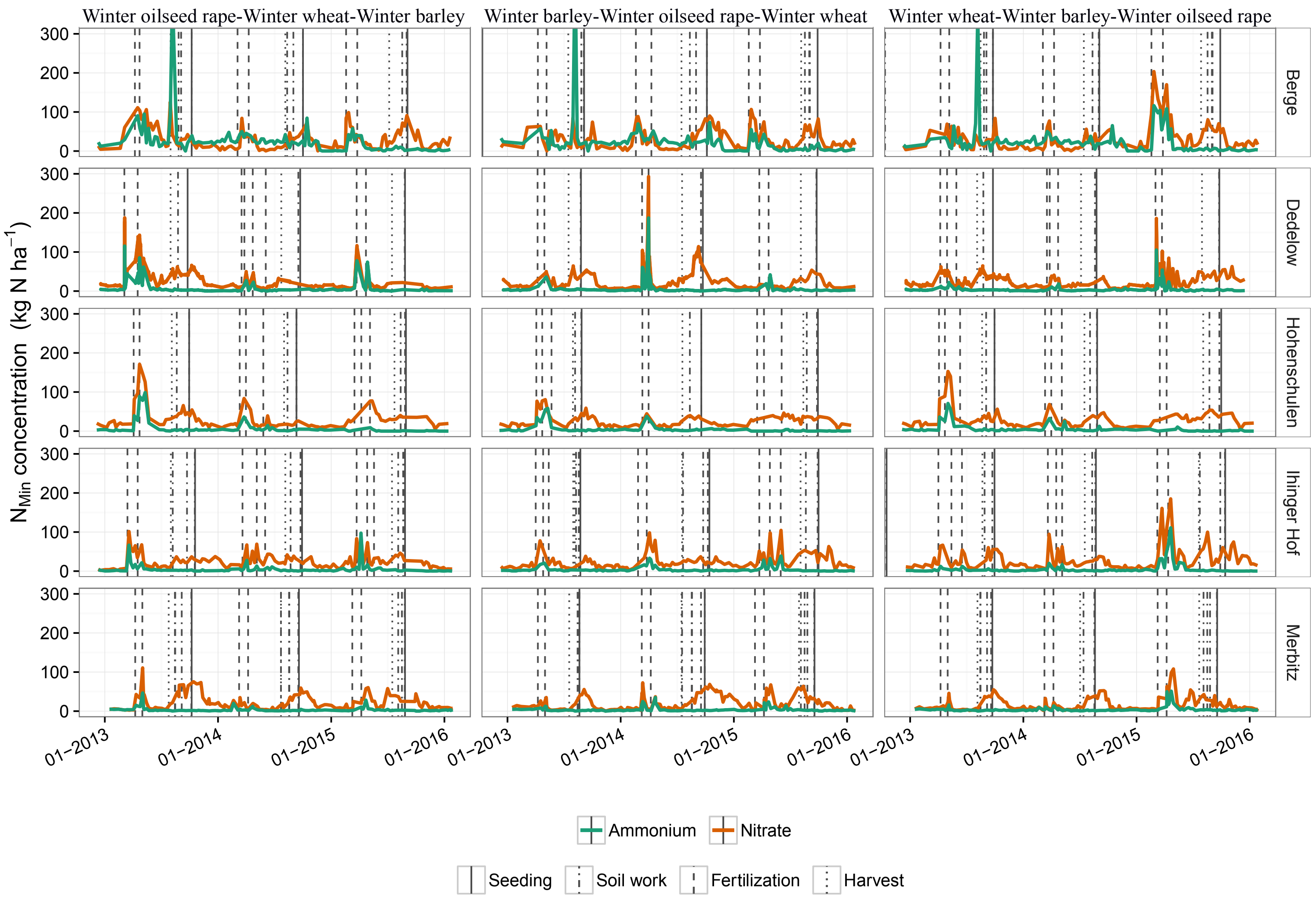

Figure 4.3 Mineral N (NH_4 and NO_3) concentration in the uppermost soil layer (0-0.3 m) for the sites Berge, Dedelow, Ihinger Hof, Hohenschulen und Merbitz from end of 2012 to January of 2016 for the respective crops in the crop rotations. N_{Min} analysis was pooled over the 4 field replicates. Dotted, dashed and solid lines represent CAN-N fertilization, harvest and seeding at the respective site and year.

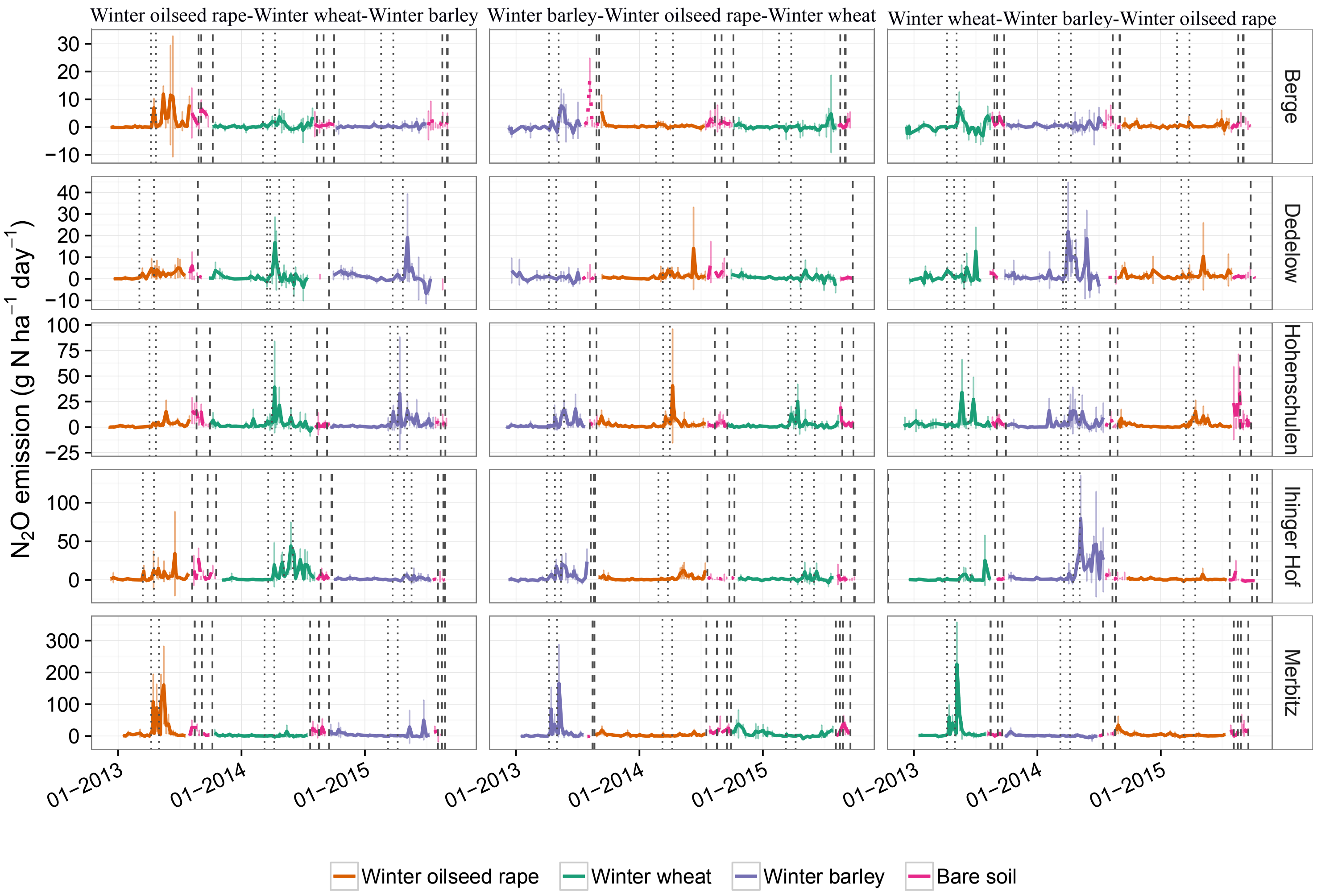

Figure 4.4 Daily N_2O emissions for the sites Berge, Dedelow, Ihinger Hof, Hohenschulen und Merbitz from end of 2012 to January of 2016 for the respective crops in the crop rotations. Bare soil is colored individually. Error bars show the standard deviation of mean of each treatment (n=4). Dotted lines represent CAN-N fertilization at the respective site and year. Note different y scale due to large variation of daily N_2O emissions.

not significantly impact N_2O emissions on the sandy sites Berge and Dedelow, but was highly significant ($p<0.001$) on the loamy soils of Merbitz (F=90.3) and Ihinger Hof (F=12.4) as well as in Hohenschulen (F=8.0).

In general, mineral N concentrations in soil shaped N_2O emissions at all sites. However, the magnitude varied and depended on site and its interaction with the crop. In particular, N_2O fluxes at the site Ihinger Hof exhibited dynamics depending on the specific crop. N_2O emissions in winter wheat and winter barley followed NH_4 ($p<0.05$, F=1.1; $p<0.001$, F=2.9) and NO_3 ($p<0.05$, F=1.6; $p<0.05$, F=2.2). It would appear evident that NH_4 and NO_3 showed the optimum concentrations for N_2O emissions while N_2O emissions from soils grown with winter oilseed rape did not respond to varying mineral N supply. On this site, for winter oilseed rape, N_2O emissions were significantly influenced by WFPS ($p<0.001$, F=0.5). However, WFPS as a driving force for N_2O emissions was smaller than soil mineral N concentrations. This is in contrast to results from the site Merbitz where in all crops, the dependence of N_2O emissions on WFPS was highly significant ($p<0.001$, F=21.2 for winter oilseed rape and F=30.2 for winter barley) and largest in winter wheat (F=38.1). The optimum WFPS for N_2O emissions was c. 62%.

Fertiliser-related N_2O emissions

Cumulative N_2O emissions from seeding to harvest appeared to be influenced by site characteristics. Soils with sand as the main grain fraction emitted less N_2O than silty soils (Figure 4.5). For the

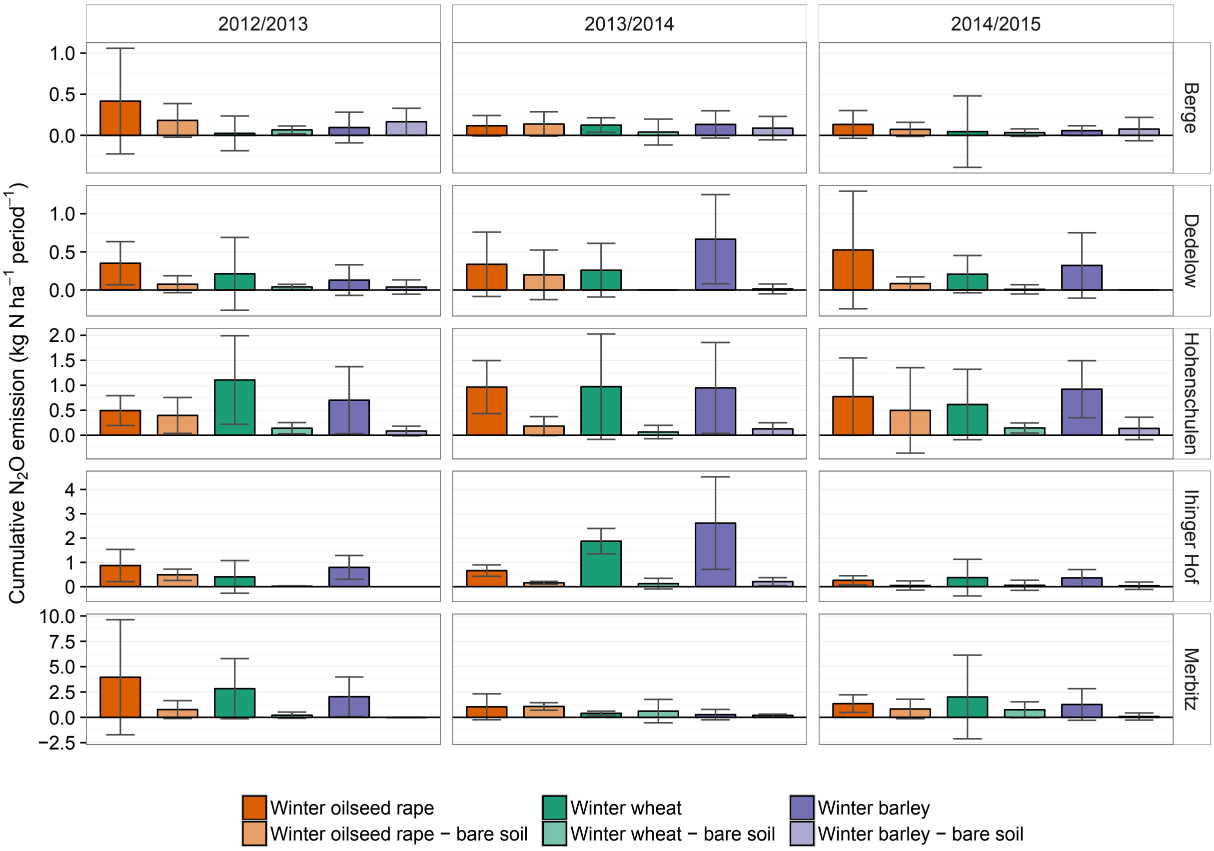

Figure 4.5 Crop-specific cumulative N_2O emissions for the sites Bornim, Dedelow, Hohenheim, Hohenschulen und Merbitz from seeding to harvest and in the periods with bare soil from harvest to seeding of the following crop. Error bars show the standard deviation of mean of each treatment (n=4). Note different y scale due to large variation of cumulative N_2O emissions.

sites Berge, Dedelow and Hohenschulen in all years, N_2O emissions ranged around 1.5 kg N ha^{-1} $year^{-1}$ or less. According to the daily N_2O emissions, at the sites Ihinger Hof and Merbitz higher cumulative N_2O emissions occurred and were most likely affected by climate drivers.

N_2O FREs summarised for all sites and years for oilseed rape, wheat and barley were close to 0.75%, but standard deviation was high due to large variation across sites and years. Overall, N_2O FREs were 0.76, 0.74 and 0.76 % for winter oilseed rape, winter wheat and winter barley. When following the subdivision of sites by their soil, N_2O FREs for all crops ranged closely around 0.34% for the sandy soils of Berge, Dedelow and Hohenschulen. For the heavier, loamy soils of Merbitz and Hohenschulen, the N_2O FREs were 1.3, 1.45 and 1.38% for winter oilseed rape, winter wheat and winter barley, respectively. No N_2O emissions from unfertilised soil were subtracted.

Output-scaled N_2O emissions

For comparing scaled N_2O emissions between oilseed rape and cereals, yield must be expressed as a comparable unit. Since dry mass yield is not comparable between an oil crop and cereals, nutritional as well as energy yield were also calculated (Table 4.3).

Scaled N_2O emissions for the respective crop reflect the site variability of the cumulative N_2O emissions. For example, yield-scaled N_2O emissions of winter wheat in Berge were only one sixth of the emissions from Hohenschulen. By scaling the dry matter yield, winter oilseed rape cropping produced around twice the N_2O emissions in comparison with cereals in accordance with the higher mass yield of winter wheat and winter barley. When scaling N_2O emissions to nutritional values winter oilseed rape and nutrition-scaled N_2O emissions equalled the cereals' N_2O emissions. The energy-scaled N_2O emissions revealed the same picture as the yield-scaled N_2O emissions with highest energy-scaled N_2O emissions for winter oilseed rape. However, usage of rape cake as a byproduct for livestock feed from oil production also largely contributes to the utilisation of oilseed rape and we did not allocate any emissions to it for these calculations.

4.4 Discussion

Nitrogen demand of crops

N surplus was significantly higher for winter oilseed rape. One indication may be given by the N harvest index which is defined as the proportion of total N in the harvested seeds to the total N in the above ground biomass. The N harvest indexes were surveyed in a study by Schjoerring and Mattsson (2001). Winter oilseed rape had a lower N harvest index of 0.33 and a higher N content in above ground biomass with 238 kg N ha^{-1} than winter wheat with an N harvest index of 0.73 and an above ground biomass 201 kg N ha^{-1}, respectively. With the mentioned values, the N surplus indicates a comparatively low N removal by harvested seeds while the demand of N by the plants is high. Sieling and Kage (2006) reported a positive N balance of 89 kg N ha^{-1} in oilseed rape. They also compared oilseed rape to cereals and confirmed that the soil mineral N concentration was generally lower in cereals (winter wheat 39 kg N ha^{-1} and winter barley 75 kg N ha^{-1}). Here, fertilisation was 120 kg N ha^{-1}. They also demonstrated that

Table 4.3 N_2O emissions scaled on dry matter seed yield, nutritional value for cattle feeding and bioenergy yield in Joule for winter oilseed rape, winter wheat and winter barley calculated for the years 2013 to 2015. Mean values are presented with 1 standard deviation.

Experimental site	Yield-scaled N_2O emission (g N Mg^{-1} DM yield)			Nutrition-scaled N_2O emission (g N GJ^{-1})			Energy-scaled N_2O emission (g N GJ^{-1})		
	Winter oil-seed rape	Winter wheat	Winter barley	Winter oil-seed rape[1]	Winter wheat	Winter barley	Winter oil-seed rape	Winter wheat	Winter barley
Berge	74.9±47.8	17.7±18.0	34.5±23.9	3.5±2	1.7±1.8	3.7±2.5	29.3±18.7	5.3±5.3	12.3±8.4
Dedelow	88.1±62.4	28.0±20.7	52.3±48.0	5.2±3.5	3.1±2.3	5.2±4.4	34.4±24.4	7.3±6.3	14.3±11.4
Hohenschule	190.7±110.5	136.1±106.5	259.6±208.8	8.3±5.2	15.0±12.5	30.1±24.7	74.5±43.2	45.6±35.6	94.6±78.8
Ihinger Hof	207.5±67.9	118.4±58.3	162.0±76.2	12.5±5.8	13.9±6.2	18.6±8.1	81.0±26.5	NA	NA
Merbitz	646.0±350.5	305.2±312.9	177.1±155.8	30.4±15.6	28.2±21.9	14.6±9.7	252.3±136.9	95.4±93.7	70.1±62.3
Mean	242.9±271.7	117.7±177.0	130.7±143.8	12.0±12.5	12.1±14.7	13.8±15.3	94.9±106.1	42.7±64.2	50.7±62.7

[1] Joule of oilseed oil for human nutrition was obtained from the Federal Food Key of the Federal Office of Consumer Protection and Food Safety

a positive N balance was also a good indicator of NO_3 leaching which is a major environmental concern. The field experiment included the combination of barley following winter oilseed rape and wheat following oilseed rape. They debated that an N surplus left by oilseed rape is more difficult to be taken up by the crop which follows. The date of seeding of winter wheat is later and the biomass uptake is lower than that of winter oilseed rape. Winter oilseed rape is sown at the beginning of September and thus, it has the ability to take up twice as much as wheat.

Temperature and water-dependency of N_2O losses by denitrification

The release of N_2O from soils is controlled by a large set of factors. N_2O emissions were dominated by the soil texture. Loamy soils at the sites Ihinger Hof and Merbitz in our field experiments potentially led to higher N_2O emissions which was also found in a field study by Jamali et al., (2016). In general, higher N_2O emissions were attributed to soils with a large share of medium-sized pores presenting favourable living conditions for soil microorganisms. When precipitation occurs the water retention is high, allowing the development of anaerobic and O_2 limited microsites due to water infiltration, easing the accommodation of denitrifying soil microorganisms.

Depending on site, several factors apparently had an increased effect on N_2O emissions. One of the most dominant factors was temperature. Denitrification is known to be temperature sensitive. The $N_2O/(N_2O+N_2)$ ratio increased along with increasing temperatures, showing that the last two steps in denitrification respond differently to variation in temperature (Phillips et al., 2015) and making high N_2O emissions more likely with high temperatures. Billings and Tiemann (2014) collected soils in January, March and June and incubated each soil at 5, 15, 25 and 35 °C. Firstly, only in soils collected in June, N_2O exceeded N_2 emissions and the cnorB:nosZ ratio was two-fold compared to soils from January and March, indicating a higher sensitivity of the nosZ genes to seasonal adaptation. Secondly, the gene copies for cnorB relative to microbial biomass increased over the progression of the year and generally with incubation temperature, while nosZ gene copies per unit of microbial biomass stayed at a lower level. This leads to greater potential by the microbial community to produce N_2O. Thirdly, the microbial biomass from June soils was unaffected by incubation temperature and one may assume great potential to keep N_2O production high. A further study by Molodovskaya et al. (2012) observed under field conditions that a temperature increase of 2 to 8 °C was followed by N_2O emission peak with a delay of one to two days. Roughly 80% of peak events were ascribed to hot moments with a rise in temperature. Observations in our field experiments follow these results since the highest N_2O emissions occurred at 20 °C at the sites Ihinger Hof and Merbitz.

Rainfall and soil physical properties like pore size and its distribution largely drive WFPS. Incubation experiments with varying water-filled pore space underlined the importance of WFPS to denitrification and N_2O emissions. Mostly, WFPS was fixed and higher water-filled pore space led to higher N_2O emissions (e.g. Bateman and Baggs, 2005, Pimentel et al., 2015), but also the magnitude of rewetting (Guo et al., 2014) and the number of wetting and drying cycles enhanced losses of N_2O-N (Harrison-Kirk et al., 2013). These studies demonstrated the importance of water under lab conditions, but here we present an experiment of its importance demonstrating it in field conditions. Nevertheless, it should be mentioned that the WFPS mostly influences the diffusivity with the O_2 and the substrate availability. O_2 and substrate concentration change when WFPS fluctuates.

The post-harvest period and N_2O triggers

In our experiment tillage was conducted in the post-harvest period which might have an effect on N_2O emissions from soil. Soil work included harvest, the incorporation of volunteer plants, seed bed preparation and the final seeding of the following crop. Chatskikh and Olesen (2007) showed that ploughing before sowing of barley significantly increased N_2O emissions. They deliberated that gas diffusion was lower for the directly drilled barley. Ploughing decreases soil density and the share of air-filled pores increases which eases gas exchange between soil and atmosphere and enables N_2O to diffuse into the atmosphere. On the other hand, Li et al. (2016) demonstrated that tillage had no influence on N_2O emissions, but in their study annual cumulative N_2O emissions ranged below 250 g N ha^{-1} and $year^{-1}$ even for soils fertilised with 100 kg N ha^{-1}. Our study included non-tilled grassland plots (data not shown) which allows for the supposition that additional tillage enhances N_2O emissions before winter.

In the post-harvest period, the number of rainfall events and the amount of precipitation increase and with dropping temperatures evaporation from soils declines and plant cover is sparse leaving bare soil. These coinciding dynamics eventually lead to a higher WFPS fostering good conditions for soil microorganisms and thus, also N_2O emissions to increase. Mean N_2O emissions after oilseed rape harvest were higher compared to emissions after the cereals winter wheat and winter barley.

In our experiments, the cereal straw was usually removed while the oilseed rape straw was incorporated into the soils. C-rich residues are known to be used in several ways by soil microorganisms. Next to the utilisation of residues to build up carbohydrates, proteins and lipids, they serve as an electron donor in heterotrophic respiration, but to obtain oxygen, NOx is reduced which can also lead to the intermediate product of N_2O. Increased N_2O emissions from soils after straw incorporation was found in a meta-analysis of Chen et al. (2013).

Percentage of released fertiliser-N as N_2O

The average N_2O FRE summarised to c. 0.75% for the considered sites for the crop rotation including winter oilseed rape, winter wheat and winter barley. The N_2O emission as a percentage of released fertiliser-N could also be reduced if the base N_2O emissions were subtracted, since in our experiment they would reduce the fertiliser-induced N_2O emissions. This point makes it even easier to fulfill the protocols where N_2O emissions were accounted for with 1% (IPCC, 2014). In other studies, the N_2O emission default values range around 1% on average. Lebender et al. (2014) reported that fertiliser-induced N_2O emissions in winter wheat summarised over all N treatments at three sites were 0.38%. Walter et al. (2014) calculated fertiliser-related N_2O emissions to be 1.35% for cereals and 1.53% for oilseed rape. They did not subtract background N_2O emissions from unfertilised control plots. They also found large annual variations and site effects. With regard to the mentioned studies and our own results, we summarise that the FREs give a good indication of expectations and variations, N_2O FREs will also be balanced over several cropping years. The uncertainty of future climate change should be born in mind.

Yield-scaled N_2O emissions

Generally, yield-scaled N_2O emissions are an indicator of the quantity of N_2O emitted per unit output, mostly used in studies with various fertiliser level inputs (e.g. Zhou et al., 2015) and can help to improve the balance between fertilisation and detrimental N losses from agricultural systems. We showed different approaches to compare our results in our crop rotation. Nevertheless, we encountered difficulty in creating comparability. Winter oilseed rape yield-scaled N_2O emissions were almost double in comparison to cereals mainly because of the lower gravimetric yield and energy-yield related N_2O emissions which depend on the utilisation of the plant, e.g. bioethanol from winter wheat vs. biofuel production based on rape seeds. One other major factor in oilseed rape cropping is the production of oilseed rape meal cake. In Germany, it is commonly used in feed and should be added to the value chain.

Even though none of the approaches displayed the advantages or side-effects of the crops grown in rotations and one may assume that relating N_2O emissions to yield is not suitable to examine the comparability of crops; nevertheless, we suggest comparing complete crop rotations on the basis of their purpose, e.g. energy crop rotations including maize or oilseed rape with complementary crops. Here, agricultural considerations such as beneficial effects from one crop to another, high residual mineral N concentration after winter oilseed harvest or adding break crops to rotations should also be indirectly accounted for. Additionally, a controversial debate about using cereals for energy production instead of human or animal consumption was revealed. Moreover, the approach neglects N losses from indirect N_2O emissions from ammonia volatilisation or N leaching.

4.5 Conclusion

The effect of the different crops on N_2O emissions was not pronounced in this crop rotation. Rather climate variabilities influenced N_2O emissions. On loam soils, N_2O emissions peaked higher in spring. At this point, N fertilisation should be carefully planned when soils are water-saturated. For example, a reduced dose and a later high rate of N fertiliser could be applied.

Oilseed rape cropping is followed by an N surplus in the autumn period. Our results underline the necessity to seek mitigation options to reduce N_2O emissions from soils under climate conditions with an increasing number of extreme events likely in the future. Sites with heavier soils tend to emit more N_2O which should be taken into consideration for the development of N_2O mitigation measures. Here, especially denitrification was assumed to be the driving process for high N_2O emissions and should be brought into focus.

FRE N_2O implies a lower value for our crop rotations than the assumed N_2O emission factor by the IPCC default values.

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5 Discussion

In recent years, sustainability has moved into the focus of food and energy production from crops. The mitigation of greenhouse gas emissions also needs to be put into the focus of life cycle analyses and resource-efficient systems (e.g. N fertilizer use) more likely meet sustainability criteria.

Diversifying rotations helps to maintain vital cropping systems and a handful of studies were conducted to estimate the value of wider crop rotations (Andrade et al., 2017; Congreves et al., 2017; Gaudin et al., 2015). Additionally, the use of fossil fuels has to be reduced and energy crops like oilseed rape have moved into the focus as possible substitutes for biodiesel production. Here, the thesis aimed to quantify N_2O emissions in oilseed rape production. Some mitigation options based on the results of the thesis will be discussed below.

5.1 Brief summary of the results of the experiments

The conducted experiments led to interesting results. In chapter 2, the major outcomes were that the application of straw significantly increased N_2O emissions. A limitation for N_2O emissions were the availability of soil NO_3. With addition of an N source to straw amended soils, N_2O emissions increased considerably and cumulative N_2O emissions were several times higher. In general, the type of straw seemed to play only a minor role. With ^{15}N labeling of barley straw, it was possible to quantify the share of straw-derived N_2O. Here, the share on cumulative N_2O emissions was low. Only in the first days, the share continuously rose coinciding with the maximum CO_2 emission rates. High CO_2 emissions are indicating decomposition activity.

The 2-year field experiment of the post-harvest period at the site Reinshof demonstrated the large variability of N_2O emissions between years (Chapter 3). In 2013/2014, a significant effect of straw amendment on N_2O emissions was found. Consequently, an adequate N fertilization for oilseed rape growth and subsequent straw application can reduce N_2O emissions under the climate conditions at that time. In the 2nd autumn period in 2014/2015, remarkably higher N_2O emissions than in the previous year were observed during the 2 1/2 months following harvest. However, the field experiment also illustrated the importance of climate drivers on emission rates. CO_2 emissions were closely related to soil temperature. Most likely, the decomposition was enhanced and the supply of labile C high which was responsible for the acceleration of soil N cycling as well. Here, N_2O emissions largely increased and led to a more than 10-fold increase in cumulative N_2O emissions for all treatments compared to the previous year 2013/2014.

N_2O emissions from the 3-year field experiment were evaluated on the scale of crop rotations including winter oilseed rape, winter wheat and winter barley at 5 sites for 3 complete years (Chapter 4). A complete crop rotation was studied with simultaneous cropping of oilseed rape, winter wheat and winter barley. Daily N_2O emissions were influenced by a set of interacting factors, such as temperature and WFPS. Interestingly, the crop only had a small effect compared to abiotic factors. Here, loamy soil increased the risk of high N_2O emissions. Post-harvest N_2O emissions from bare soil were highest in oilseed rape. Nevertheless, the fertilizer-related N_2O emissions were mostly well below 1%. Yield-scaled N_2O emissions were similar among oilseed rape, winter wheat and winter barley. The height of yield-scaled N_2O emissions depended on the respective yield unit. The approach neglected the types of products which logically depend on the respective crop. For example, the meal production of oilseed rape was ignored. The meal is usually used in animal feeding and states a high value to the farmer.

The share of straw-N on N_2O emissions

The incubation experiment revealed only a small share of straw-N was released as N_2O. To underline this result, a ^{15}N labeling experiment after oilseed rape harvest was conducted under field conditions.

5.2 Field experiment on ^{15}N labeled oilseed rape straw from varying fertilizer levels

The experiment was integrated into the main field experiment of chapter 3 (page 17). Here, the site Merbitz was chosen to conduct an experiment in the post-harvest period of oilseed rape. Aims of the experiment were

(i) to quantify the release of N_2O from unfertilized control plots and fertilized plots and

(ii) to measure the share of straw-N on N_2O emissions.

Material and Methods

Treatments for the experiment include 5 kg N ha^{-1} (RST-5) equivalent to a non-fertilized control oilseed rape straw, 150 kg N ha^{-1} (RST-150) and 180 kg N ha^{-1} (RST-180). For information on C and N concentration of the respective straw see Table 5.1. Sowing of oilseed rape was on the 29th August 2012 (*Brassica napus*, 'Visby'). To have homogenized plant material after harvest, fertilization was done in 8 m^{-2} plots. In line with the main field experiment, crops were fertilized on the 9th and 16th April 2013. The first dressing was 90 kg N ha^{-1} in the form of CAN and for the second dressing 60 and 90 kg NO_3NH_4-N ha^{-1} with 20 at% double-labelled N was applied in the RST-150 and RST-180, respectively. Fertilization of the control oilseed rape plants was applied with 5 kg NO_3NH_4-N ha^{-1} with 98 at% double-labeled N on the 25th April 2013. Plant protection measures were performed according to crop specific recommendation.

At the harvest date (26th July 2013), the aboveground biomass was collected, fractioned and quantified to calculate dry matter and N load of the harvest residues. In 4 subplots within the fertilizer treatment plots, the straw was removed and replaced by the ^{15}N labeled straw (n=4). The mass and fraction distribution of ^{15}N labeled straw matched the respective amount of straw harvested in the respective treatment. Based on agricultural practice, straw was distributed on to the soil surface before incorporation by ploughing on the 15th August 2013. Additional soil work was done at the 16th of August and 6th September 2013. Seed bed preparation and sowing of winter wheat (*Triticum aestivum*, 'Julius') took place on the 7th and 8th of October.

Results of N_2O and straw-derived N_2O emissions

At beginning of the field campaign, unfertilized soils with straw incorporation (RST-5) showed comparatively lower daily N_2O emissions than the other soils (RST-150, RST-180). N_2O emission pat-

Table 5.1 Characteristics of straw for the soils amended with straw fertilized with 5, 150 and 180 kg N ha^{-1}, respectively.

Treatment	C (%)	N (%)	C/N	δ‰^{15}N straw
RST-5	41.23	0.59	90	2463.9
RST-150	41.23	0.71	71	6299.9
RST-180	40.84	0.7	65	9038.2

terns in all treatments followed fluctuations in soil water status until Mid-October (Figure 5.1). Decreasing and later on constantly low soil temperature seemed to alleviate N_2O emissions in the later course of time, even though WFPS was high. After all, mean cumulative N_2O emissions in all treatments (RST-5, RST-120, RST-180) were 266, 299 and 267 g N_2O-N ha^{-1} from end of August to beginning of March (Figure 5.2). Mean straw-N-derived N_2O emissions remained under 5 g N ha^{-1} day^{-1} and only the treatment RST-150 showed a higher rate of straw-N-derived N_2O emission after the first sampling day until Mid-September. The higher share of straw-N-derived N_2O might be attributed to the degradation of labile N-containing organic compounds. Chiefly, the sampling at two days with higher daily N_2O emission rates enormously contributes to the significantly ($p<0.05$) higher cumulative mean straw-N-derived N_2O emissions in the medium fertilizer treatment (RST-150). However, the share of straw-N-derived N_2O with 16 % in the RST-150 treatment was significantly different ($p<0.05$) to the RST-5 and RST-180 treatment with 2 % and 6 % of cumulative N_2O emissions, respectively.

Discussion

Short-term N_2O emissions

Fertilization was assumed to leave high residual NO_3 concentrations after harvest. This was supported by results from NO_3 measurements in oilseed rape stands in chapter 3 and from the experiment which was described in chapter 4. In both experiments, NO_3 concentration in the top soil layer increased with N fertilizer level in oilseed rape. With the ^{15}N labeling of oilseed rape straw at the site Merbitz in 2013, NH_4 concentrations remained low after harvest. High NO_3 concentrations might be the cause of increased post-harvest N_2O emissions. When comparing NO_3 concentrations among treatments, it reveals that high N_2O emissions were found in the RST-150 and RST-180 treatment where NO_3 concentrations were high as well. High NO_3 concentrations also suggest denitrification as the main process leading to N_2O emissions. Denitrification may be the preferential pathway of N_2O release as rainfall events increased WFPS as well.

Generally, the addition of straw stimulates decomposition activity which leads to O_2 consumption and formation of CO_2. In the experimental period, heavy rainfall occurred after harvest. Both, the formation of CO_2 and increased soil water status led to anaerobic conditions in microsites favoring denitrification. When NO_3 as electron acceptor is available to denitrifiers, it is preferentially used over the other intermediate NOx compounds making denitrification inefficient (Benckiser et al., 2015, Madigan et al., 2012). This was reflected in higher N_2O emissions in the N fertilized soils than in the non-fertilized control soils shortly after harvest.

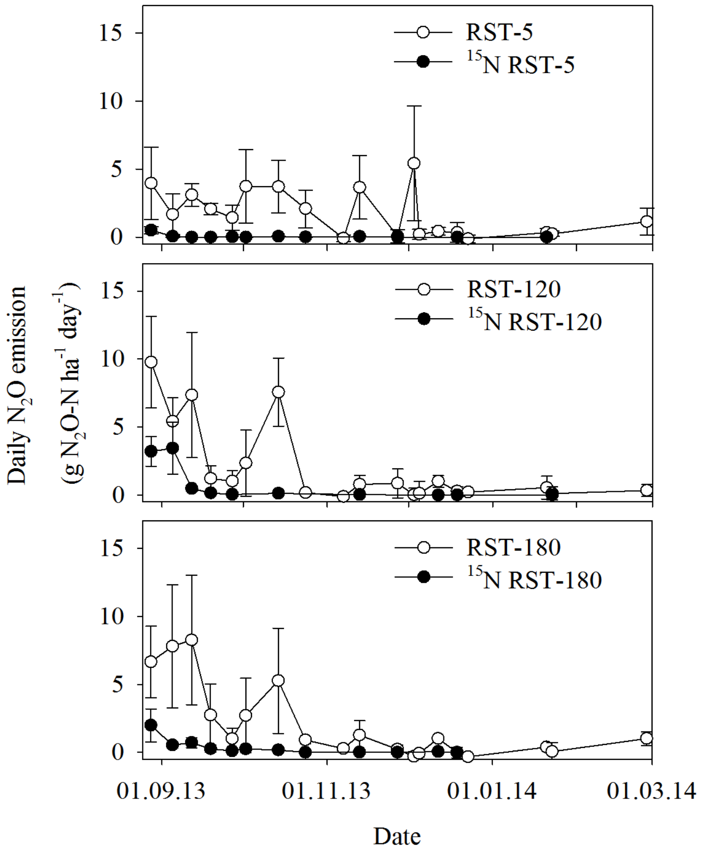

Figure 5.1 Daily N_2O fluxes and daily oilseed rape straw-N-derived N_2O emissions (^{15}N) from soils after incorporation of oilseed rape straw from 5 (RST-5), 120 (RST-120) and 180 (RST-180) kg N ha^{-1} fertilization measured at the experimental site Merbitz between August 2013 and February 2014. Error bars show the standard error of the mean of each treatment (n=4). In some cases error bars are smaller than the symbols.

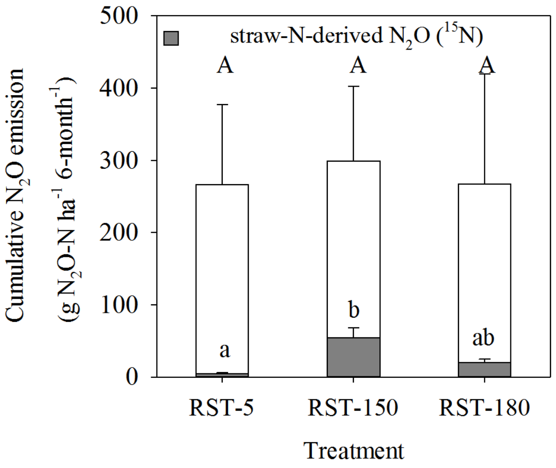

Figure 5.2 Cumulative N_2O fluxes and cumulative oilseed rape straw-N-derived N_2O emissions (^{15}N) from soils after incorporation of oilseed rape straw derived from 5 (RST-5), 120 (RST-120) and 180 (RST-180) kg N ha^{-1} fertilization measured between August 2013 and February 2014. Error bars show the standard error of the mean of each treatment (n=4). Different letters indicate significant differences (p<0.05).

Long-term N_2O emissions

Nevertheless, the cumulative N_2O emissions did not show significant differences. Here, other factors than management as a short-term event seemed to determined processes leading to N_2O emissions. Another important period is the period from autumn to winter. N_2O emissions remained low, yet the period autumn to winter was long and accounted for a high share on N_2O emissions masking the response of N_2O emissions shortly after harvest.

The effect of belowground biomass on N_2O emissions under field conditions

The presented field studies partially showed treatments with no straw incorporation. A neglected point so far was the contribution of the belowground biomass of plants namely roots on the soil nutrient status. During crop growths they have vital functions, but after harvest they remain in the soil and will be decomposed.

For oilseed rape cropping, it was be assumed that the biomass for the rooting system was 1.3 t ha^{-1} and C contained in straw was quantified with 534 kg ha^{-1} (Gan et al., 2011). With this information, it may be that the role of straw application is overestimated since the presence of a Carbon source was already given by the root-C. Especially, the field experiment presented in chapter 3 suggests when the N_2O emission level was low and N_2O emissions were constrained by temperature and water, other factors like straw management (application vs. removal) rank higher in priority. This may lead to differences in magnitude of N_2O emissions.

5.3 Linking the experiments

The field experiment showed that the straw-N was only a minor share on N_2O emissions. The field experiment matched the results of N_2O emission of the incubation experiment which showed a drastic increase of emissions with the application of CAN-N. In the field experiment, high NO_3 concentrations were found in the top soil in fertilizer treatments at harvest. This was accompanied with high N_2O emissions briefly after oilseed rape harvest.

5.4 Magnitude of N_2O release and ranking of factors

The presented experiments indicate an interaction of factors. The cancelation of a constraining factor leads to high N_2O emissions, but even then, other factors are capable of limiting emissions. Garcia-Marco et al. (2014) conducted an incubation experiment to determine the effect and their interaction between factors. They suggest a focus of this approach to be used in field experiments as well. With this thesis, it is possible to give a glimpse on the importance of factors and reveal interactions between them.

To sum up the insight into driving forces on N_2O emissions, it was essential to integrate the results of the experiments in a general concept which is presented in Figure 5.3. The incubation experiment demonstrated the relevance of soil NO_3. Yet, the experiment was conducted under controlled conditions with a set temperature and soil water. In field experiments, next to other factors, these abiotic factors

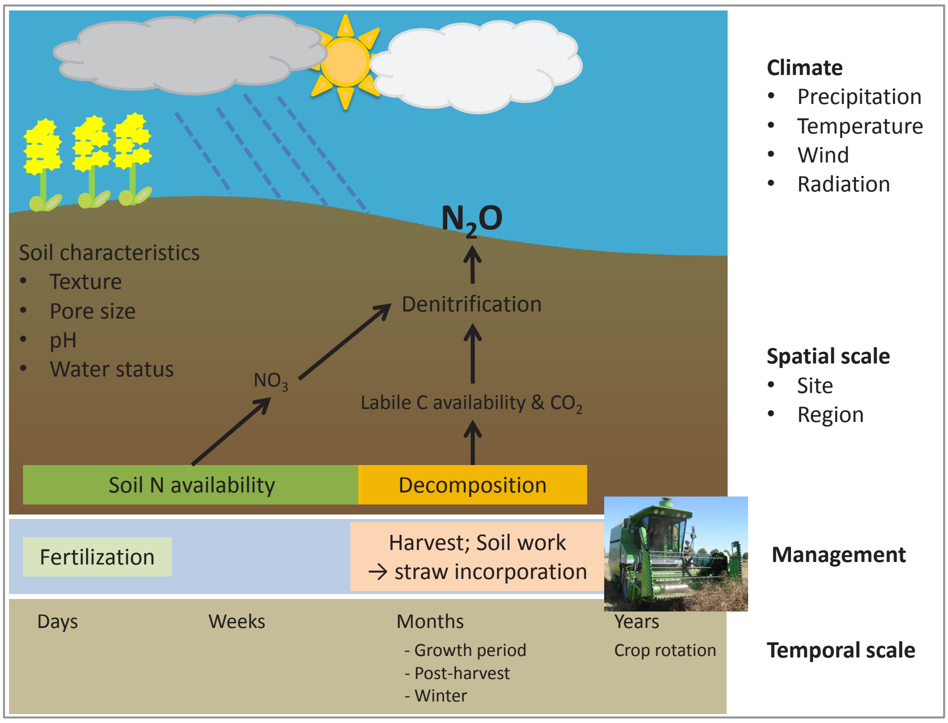

Figure 5.3 Schematic figure of the major factors and scales driving N_2O emissions from the incubation and field experiments.

can vary considerably. In sum for the two presented field experiments in chapter 3 and chapter 4, the abiotic factors (climate and soil) can be synthetized to have a higher impact on N_2O emissions than the management measures like N fertilization (Chapter 4). Neither N application to soil nor harvest with its high input of C-rich residues was automatically followed by high N_2O emissions.

In chapter 4, the potential effect of the site on N_2O emissions with a suitable set of climatic factors became evident.

On the temporal scale, days with high N_2O emissions occurred and can shape annual N_2O emissions. However, cumulative N_2O emissions depended on the duration and magnitude of those high emission events. Even though, short-term N_2O emissions can be high, their effect may be insignificant if the studied period is long and N_2O emissions are low.

Mostly, when NO_3 concentration was high and C was available, N_2O emissions were high. It can be hypothesized that denitrification is the dominant process. Here, verification could be proven by ^{15}N labeling of the NO_3 pool and subsequent ^{15}N-N_2O analysis.

5.5 The IPCC and Climate Change

The climate data especially in chapter 4 showed the variability of temperature and precipitation between years. The collected data demonstrated how N_2O emissions respond to different climate settings. The experimental period from 2012 to beginning of 2016 included an interesting bandwidth of climates. For example, spring 2013 was characterized by cool temperatures with snow fall and a snow cover at the site Merbitz. This resulted in a high WFPS until May. In 2014, the vegetation period started early and the spring was dry (Figure 5.4).

Figure 5.4 Climate conditions at the site Merbitz in the years a 2013 and 2014. Pictures were taken in the beginning of April in the respective years (2013: April 8th, 2014: April 10th).

The IPCC (2013) described a temperature increase for the last decades. Additionally, yield data was also analyzed with regard to changing temperature. Reports pointed out that yield declined for 1% with increasing temperatures per decade in temperate climate. In Northern and Central Europe, a temperature increase of 2 °C is predicted for the years 2081 to 2100, if compared to the 20-year period from 1986 to 2005. However, precipitation will only increase by 10% (van Oldenborgh et al., 2013).

The risk of high N_2O emissions is increased in the post-harvest period for example if the predictions are precise. Decomposition is temperature-dependent (Fierer et al., 2005) and the C which is added as harvest residues enhances soil N cycling in general and specifically denitrification. Thus, the development of mitigation options should focus on measures to reduce NO_3 concentrations after harvest. This can be achieved by N fertilization closely following the N demand of the respective crop (chapter discussion mitigation options).

5.6 Mitigation options

Management options to lower N_2O emissions can be derived from the presented experiments. For example, the incubation experiment suggests avoiding N fertilizer application to post-harvest soils with a high availability of residue-C.

Mitigation options from the presented experiments can be derived from high N_2O emissions events. The amount of N fertilizer should be closely related to the N demand of the respective crop to reduce soil mineral N concentrations. Several studies (Kim et al., 2013, Shcherbak et al., 2014) demonstrated a linear relation of N fertilizer rate and N_2O emissions as long as plant demand was satisfied whereas an N surplus led to non-linear and over proportionally high N_2O emissions. Especially, N fertilizer rates above plant demand led to an exponential response of N_2O emissions. This highlights the importance for a precise calculation of N application.

To maintain a supply of mineral N forms to plants nitrification inhibitors (NI) are discussed recently. NIs are chemical substances, like 3,4-dimethylpyrazole phosphate (DMPP) and dicyandiamide (DCD), also several others are commercially produced. As NIs differ in their chemical structure, the biochemical processes diverge. NIs modify the soil N cycling by blocking the first enzymatic step of nitrification, the ammonia monooxygenase. Dominantly, NH_4 oxidation is inhibited which results in less NOx species. Especially NO_3 is mobile in the soil and prone to leaching. NO_3 is also a substrate for denitrification. Wu et al. (2017) showed that a high NH_4 concentration with the addition of a C source (wheat straw) to soil led to high N_2O emissions. The NO_3 concentration was lower in the treatment with a NI. The N_2O emissions were decreased by 40% when adding a NI to straw amended soil. Although, the long-term effect of NIs is not clear yet, studies should focus on NIs and their effect on post-harvest NO_3 concentrations under field conditions. Here, data sets of a full year with measurements are needed to be able to evaluate the effectiveness under specific conditions (Ruser and Schulz, 2015).

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Publications and Conference Contributions

Peer-reviewed Publications

Köbke S, Senbayram M, Pfeiffer B, Dittert K (2018): Post-harvest N_2O emissions related to plant residue incorporation (oilseed rape and barley straw) depends on soil NO_3^- content. *Soil & Tillage Research* Soil and Tillage Research 179, pp. 105-113.

Ruser R, Fuß R, Andres M, Hegewald H, Kesenheimer K, **Köbke S**, Räbiger T, Suarez Quinones T, Augustin J, Christen O, Dittert K, Kage H, Lewandowski I, Prochnow A, Stichnothe H, Flessa H: Nitrous oxide emissions from winter oilseed rape cultivation. Submitted to *Agriculture, Ecosystems and Environment*.

Pietzner B, Rücknagel J, Koblenz B, Bednorz D, Tauchnitz N, Bischoff J, **Köbke S**, Meurer K, Meißner R, Christen O (2017): Impact of slurry strip-till and full-surface slurry incorporation on NH_3 and N_2O emissions on different plot trials in Central Germany. *Soil & Tillage Research 169*.

Senbayram M, Wenthe C, Lingner A, Isselstein J, Steinmann H-H, **Köbke S** (2016): Legume-based mixed intercropping systems may lower agricultural born N_2O emissions. *Energy, Sustainability and Society 6(2)*.

Conference Contributions

Oral Presentations

Köbke S, Kesenheimer K, Räbiger T, Andres M, Hegewald H, Suarez T, Fuß R (2015): Yield-scaled N_2O emissions of oilseed rape bioenergy crop rotations in Germany; International Workshop "Greenhouse gas emission from oilseed rape cropping and mitigation options" in Braunschweig, Germany.

Köbke S, Senbayram M, Hegewald H., Christen O, Dittert K (2015): Post-harvest N_2O emissions in soils planted with oilseed rape were not affected by the quality of incorporated straw; European Geosciences Union General Assembly 2015 in Vienna, Austria. Application for funding and conference grant received from Göttingen International.

Poster Presentations

Köbke S, Senbayram M, Dittert K (2014): Biochemical variations in plant residues (oilseed rape and barley straw) affect N_2O emissions and organic matter decomposition rate; 18th Nitrogen Workshop in Lisboa, Portugal.

Köbke S, Senbayram M, Hegewald H, Christen O, Dittert K (2014): Post-harvest N_2O emissions from oilseed rape fields do not differ from cereals; International Conference of the German Society of Plant Nutrition in Halle (Saale), Germany.

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Anlage 3: Erklärungen

1. Hiermit erkläre ich, dass diese Arbeit weder in gleicher noch in ähnlicher Form bereits anderen Prüfungsbehörden vorgelegen hat.

   Weiter erkläre ich, dass ich mich an keiner anderen Hochschule um einen Doktorgrad beworben habe.

   Göttingen, den ....

   ....
   (Unterschrift)

2. Hiermit erkläre ich eidesstattlich, dass diese Dissertation selbständig und ohne unerlaubte Hilfe angefertigt wurde.

   Göttingen, den ....

   ....
   (Unterschrift)