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Effects of Different Long-term Fertilization Strategies on Soil Organic Matter Stocks and N_2O Emissions from Arable Soils

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Preface and Outline

This thesis was composed at the University of Göttingen (Soil Science of Temperate Ecosystems) within the research training group 1397, “Regulation of soil organic matter and nutrient turnover in organic agriculture”, at the University of Kassel/Witzenhausen and funded by the German Research Foundation (DFG). Research activities in the field took place at the long-term fertilization experiment at the Institute of Biodynamic Research (IDBF), in Darmstadt. Cooperating partners were Dr. Joachim Raupp and Meike Oltmanns.

The cumulative dissertation is based on three manuscripts to which the PhD candidate predominantly contributed as the first author and one article to which she contributed as co-author. The studies are or will be published in international refereed journals:

Jäger, N., Duffner, A., Ludwig, B., Flessa, H.: Long-term and short-term effects of the application of mineral and organic fertilizer on N_2O and CO_2 emissions from a sandy soil – a laboratory incubation

Jäger, N., Stange, C.F., Ludwig, B., Flessa, H.: Emission rates of N_2O and CO_2 from soils with different organic matter content from three long-term fertilization experiments – a laboratory study

Jäger, N., Dechow, R., Oltmanns, M., Raupp, J., Flessa, H.: Effects of different long-term fertilization treatments on soil organic matter stocks, N_2O emissions and CH_4 uptake of a sandy soil

Ludwig, B., Jäger, N., Priesack E., Flessa, H.: Application of the DNDC model to predict N_2O emissions from sandy arable soils with differing fertilization in a long-term experiment, Journal of Plant Nutrition and Soil Science, accepted

This thesis starts with a general introduction that imparts knowledge about the climate-relevant trace gases CO_2 and N_2O. The processes of production and consumption in soils are explained and the reasons, how carbon sequestration influences the climate change and agriculture, are given. Then, the supposed mechanism of carbon sequestration leading to higher N_2O emissions will be introduced. Furthermore, the overall objectives of the thesis are given. In chapter two, a laboratory study is presented focusing on the impact of different fertilization strategies on N_2O emission under different soil moisture contents and after the short-term application of different fertilizer types. A second laboratory study is described in the third chapter. Here, the focus was on the long-term fertilization history with different soil texture and soil structure leading to different N_2O emissions, again following short-term fertilizer application and high soil water saturation. The fourth chapter presents the two-year field study at the IBDF in Darmstadt. The field study was conducted in order to explain whether the results of the two laboratory experiments can be underlined by field measurements. The fourth study is a modelling approach to test a calibration and validation scheme for DNDC model applications to describe the field experiment during the year 2007.

In the following, a general discussion of the influences of fertilization and increased soil C stocks on N_2O emissions is given, linking the results of the four studies. Finally, a conclusion with an outlook is drawn.

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Abstract

Agricultural soils represent a source of N_2O and CO_2 which are the major greenhouse gases and should be reduced to diminish global warming. The increase of organic matter in soils, which can be reached by the long-term application of organic fertilizer, is an important factor to improve soil quality and to bind atmospheric CO_2. However, the influence of long-term organic fertilization on trace gas emissions is not well understood. Therefore, the aim of the present study was to compare the emissions of N_2O and CO_2 in different long-term field experiments with addition of organic and mineral or no fertilizer.

The key question of this thesis is whether N_2O emissions, which are produced during the microbial processes of nitrification and denitrification, increase due to higher organic C stocks. On the one hand higher C stocks can increase microbial activity which in turn depletes the oxygen in the soil. This leads to optimal conditions for denitrification. On the other hand C is used as a substrate for heterotrophic nitrification and denitrification.

During this thesis the following four studies were performed to investigate the influence of organic fertilization on N_2O emissions. The first experiment was a laboratory incubation with the sandy soil from a long-term fertilization experiment at Darmstadt. The effects of long-term fertilization (organic vs. mineral) on N_2O emissions were determined at different soil moisture levels. Further, these long-term effects were compared with the short-term emissions following the application of different fertilizers (KNO_3, farmyard manure and biogas waste).

The second study was another incubation experiment, which was performed with soils from three different long-term experiments with similar fertilization history, but different texture and C stocks. The question underlying this study was whether different soil types lead to different C stocks and whether they have a different impact on N_2O emissions. For this experiment, emission rates of N_2O and CO_2 were measured at a constant soil moisture content of 60% water-holding capacity, following the application of different fertilizers (KNO_3 vs. farmyard manure from cattle) and after simulation of a heavy rainfall event, which increased soil moisture to field capacity.

The third experiment was a two-year field study, which was conducted to determine the effect of increased organic C stocks on N_2O emissions under field conditions. Gas fluxes were measured weekly with closed chambers on the sandy soil at the Darmstadt long-term fertilization experiment.

In the fourth study, a validation and calibration approach was tested to describe the field experiment at Darmstadt using the DNDC model.

The results showed that increased C stocks only play a minor role in terms of N_2O emissions. Two of the three soils investigated in the second study showed slightly increased N_2O emissions when incubated at 60% water-holding capacity. However, the effect of fertilization history and increased organic carbon contents on N_2O emissions was small. Moreover, these effects were not detectable anymore following the application of fertilizers, which resulted in large emissions independent of the fertilization history.

On the sandy soil from the Darmstadt site, the higher organic C stocks did not affect N_2O emissions, neither during the laboratory incubation (first study) nor during the field experiment (third study). This was attributed to the sandy soil texture and low soil moisture content during the incubation and during the field experiment. During the laboratory study, short-term emissions after fertilization were much more pronounced. Especially the application of biogas waste was followed by very high N_2O emissions. Tillage combined with fertilization led to the highest emissions in the field. The second laboratory incubation showed much higher emissions from a soil which was depleted of organic matter due to the lack of fertilization for 25 years. This indicates that a sustainable soil humus management is necessary to regulate N_2O emissions. Modelling C and N dynamics using the DNDC model indicated that the model was useful for a prediction of N_2O emissions after site-specific calibration when the same fertilizer type was used at a different rate. However, the model failed when a different fertilizer type was used.

Summing up, organic C stocks can influence N_2O emissions but only to a small extent and under certain conditions. On sandy soils, where soil moisture tends to be low, the risk of increased N_2O emissions at higher organic C stocks is probably low. Further, short-term effects like fertilization events influence emission dynamics to a much higher extent. Finally, it appeared that a balanced nutrient and humus management can even avoid N_2O emissions by it positive effects on soil structure. Our results indicate that feedback mechanisms of soil carbon sequestration on N_2O emissions have to be considered when discussing options to increase soil carbon stocks.

Kurzfassung

Das atmosphärische Spurengas Distickstoffoxid (N_2O) zählt neben Kohlendioxid (CO_2) zu den bedeutendsten klimarelevanten Gasen, deren Reduzierung mit der Zielsetzung einer Begrenzung der globalen Erwärmung von besonderer Bedeutung ist. Eine Quelle für beide Gase sind landwirtschaftlich genutzte Böden. Die Erhöhung der Vorräte an organischer Substanz im Boden ist ein wichtiger Faktor, um die Bodenqualität langfristig zu erhalten und um atmosphärisches CO_2 zu binden. Eine Möglichkeit, die Vorräte zu steigern, stellt die langfristige Applikation von organischen Düngern dar. Jedoch sind die Auswirkungen auf die Emissionen des Klimagases N_2O noch weitgehend unbekannt. Ein Anstieg der Vorräte an organischer Substanz im Boden könnte zu erhöhten N_2O-Emissionen führen, weil diese einerseits ein Substrat für Denitrifikation und heterotrophe Nitrifikation darstellen. Andererseits steigert ein höherer Gehalt an organischer Substanz die mikrobielle Aktivität, die den Sauerstoffgehalt reduziert und optimale Bedingungen für die Denitrifikation schafft.

Der Einfluss der organischen Düngung auf die N_2O-Emission wurde in der vorliegenden Arbeit anhand von vier Experimenten untersucht. Das erste Laborexperiment (erste Studie) wurde mit dem sandigen Boden eines Darmstädter Langzeit-Düngungsversuches durchgeführt. Die Auswirkungen der unterschiedlichen Düngungshistorie auf die N_2O-Emissionen wurden bei unterschiedlichem Wassergehalt und nach der Anwendung verschiedener Dünger (KNO_3, Rindermist, Gärsubstrat) in einem Laborinkubationsversuch untersucht. In einem weiteren Laborversuch (zweite Studie) wurden Böden aus drei verschiedenen Langzeit-Düngungsexperimenten mit unterschiedlichen Texturen und unterschiedlich hohen Vorräten an organischer Substanz herangezogen. Im Rahmen dieses Versuches wurde der Einfluss eines Wassergehalts von 60% wassergefülltem Porenraum, einer Düngerapplikation und der Simulation eines Starkregenereignisses auf die N_2O-Emissionen der unterschiedlich gedüngten Varianten untersucht. Darüber hinaus wurde durch Freilandmessungen (dritte Studie) der Einfluss der Düngung auf die N_2O-Emission in situ im Rahmen eines zweijährigen Feldversuches auf dem Darmstädter Düngungsversuch untersucht. Ziel der abschließenden vierten Studie war es, nach einem Kalibrationstest für eine DNDC-Modellanwendung das Darmstädter Feldexperiment zu beschreiben.

Die Ergebnisse zeigen, dass die Erhöhung der Kohlenstoffvorräte nur eine untergeordnete Rolle für die N_2O-Emissionen spielt. Zwei von drei während der zweiten Laborstudie

untersuchten Böden zeigten leicht erhöhte N_2O-Emissionen bei 60% wassergefülltem Porenraum. Der Effekt war jedoch sehr gering und nicht mehr nachweisbar, sobald eine Düngerapplikation höhere Emissionen nach sich zog.

Der Boden des Darmstädter Experiments (erste und dritte Studie) zeigte generell sehr niedrige Emissionen im Feld- wie im Laborversuch, was auf die sandige Textur und den geringen Wassergehalt zurückgeführt wurde. Eine wesentlich größere Rolle spielten kurzfristige Emissionen nach der Düngung. Besonders das Gärsubstrat zog extrem hohe N_2O-Emissionen nach sich. Im Feld waren kurzfristige Düngerereignisse in Kombination mit Bodenbearbeitung weit einflussreichere Steuerungsfaktoren als die Kohlenstoffgehalte des Bodens. Während der zweiten Laborstudie zeigten sich die höchsten Emissionen aus dem Boden, der an organischer Substanz durch langfristig unterlassene Düngung stark abgereichert war. Das zeigt, dass ein nachhaltiges Humus- und Nährstoffmanagement wichtig ist, um N_2O-Emissionen zu regulieren.

Mithilfe des DNDC-Modells war es nicht möglich, N_2O-Emissionen der Varianten mit unterschiedlicher Düngerart vorherzusagen. Die Kalibrierungs- und Validierungsergebnisse zeigen, dass die Vorhersagequalität zwar ausreichend für ähnliche Varianten mit ansteigender Düngerrate ist, jedoch nicht für unterschiedliche Düngerarten. Zusammenfassend kann festgestellt werden, dass erhöhte organische Substanz nur unter bestimmten Bedingungen und dann auch nur zu geringfügig höheren N_2O-Emissionen führen kann. Auf sandigen Böden, welche wenig organische Substanz anreichern und deren Wassergehalt zudem niedrig ist, ist das Risiko erhöhter N_2O-Emissionen durch höhere Vorräte an organischer Substanz als eher gering einzuschätzen. Kurzfristige Effekte wie Düngung spielen dann eine viel größere Rolle. Die vorliegenden Untersuchungsergebnisse zeigen, dass die Rückkopplung der erhöhten organischen Substanz auf die N_2O-Emissionen zu berücksichtigen ist, wenn über die Vorteile einer Erhöhung der organischen Substanz diskutiert wird.

1. General Introduction

1.1 Contribution of Agriculture to Greenhouse Gas Emissions

Climate change is one of the major environmental issues of current times. Since the climate summit of 2009 in Copenhagen, the importance of climate change and the necessity to prevent it has become known worldwide. Radiative forcing, determined by the balance of incoming and outgoing energy fluxes between the earth's surface and the atmosphere is the driver for global warming. An increase in the concentration of Greenhouse gases (GHG) is considered to cause a positive radiative forcing of the climate system, which results in a warming of the atmosphere. Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) as the major anthropogenic GHG are supposed to be key drivers for climate change, because they absorb and re-emit long-wave radiation (IPCC, 2007).

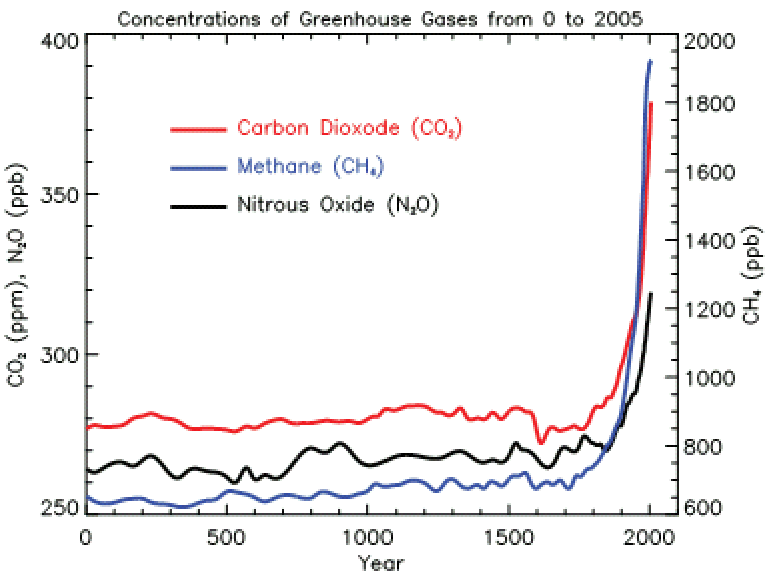

Figure 1: Atmospheric concentrations of the three major anthropogenic greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era (from IPCC, 2007).

Although N_2O and CH_4 are less abundant than CO_2, they are also important climate gases because their global warming potential is 298 times (N_2O) and 21 times (CH_4) higher than the global warming potential of CO_2 (IPCC, 2007).

Since the industrial era, global atmospheric concentrations of CO_2, CH_4 and N_2O have increased markedly as a result of human activities and at present far exceed pre-industrial values (Figure1), mainly induced by anthropogenic interference into the natural cycle of GHG (IPCC, 2001). The global increase of CO_2 concentration is primarily due to the combustion of fossil fuel and land use change, while those of CH_4 and N_2O are predominantly attributed to agricultural activities (IPCC, 2007). Over the last decades population pressure, economic growth and technological change led to an intensification of agriculture and especially the increased fertilizer use raised the N_2O emissions. CH_4 emissions from agriculture are mainly attributed to the wet rice cultivation and animal husbandry (Snyder et al., 2009). In general, agricultural activities account for about 60% of global anthropogenic N_2O emissions and about 50% of global anthropogenic CH_4 emission in 2005 (IPCC, 2007).

1.2 The Mechanisms Regulating CO_2 and N_2O Emissions

Organic matter (OM) in the world's soils contains about three times as much Carbon (C) as is found in the Earth's vegetation (IPCC, 2001). Hence, soil organic matter (SOM) plays an important role in the global C balance (Brady and Weil, 1997).

Plants use atmospheric CO_2 by photosynthesis to produce biomass (Figure 2), which can be separated into above ground net primary production (e.g. leaves) and below ground net primary production (e.g. roots) (Liu and Greaver, 2009). Plant residues, rhizodeposition and fertilizer can be converted via humification. In agricultural ecosystems, organic fertilization is an additional C source.

In the C cycle of the soils, most of the C is bound in soil organic matter (SOM), which is divided into pools of different stability. Von Lützow et al. (2007) describe an active pool with turnover times lower than 10 years, an intermediate pool with turnover times between 10 and 100 years and a passive pool with turnover times higher than 100 years. Easily available C in the soil often serves as heterotrophic energy source for microbial processes such as denitrification. Organic matter, like dissolved organic carbon (DOC) or particulate organic matter (POM) can act as electron donors. C may be lost from soil as CO_2 by heterotrophic or autotrophic respiration. Under anaerobic conditions in rice fields or wetlands, CH_4 is formed, whereas, under aerobic conditions, atmospheric CH_4 is usually oxidized in the soil to CO_2 by microorganisms (Liu and Greaver, 2009).

Nitrogen (N) is essential to life because it is part of the amino acids. Due to its relative scarcity, the lacking availability of N often limits biological activity (Brady and Weil, 1997). The atmosphere contains 78 Vol.% N_2 which can be transformed in the soil by symbiotic fixation (Figure 2). Legume and other rhizobium containing plants are able to transform N_2 to NH_4^+ (ammonium). In agricultural ecosystems additional N is applied as organic or mineral fertilizer or as plant residue to balance plant removal by harvest.

The great bulk of soil N is bound to organic compounds (Brady and Weil, 1997). Organic nitrogen in soil organic matter can be mineralized to NH_4^+ and further to nitrate (NO_3^-). It is widely accepted that N becomes plant available in the mineral forms (Brady and Weil, 1997). However, recent research has shown that also organic compounds can contribute to plant nutrition (Schimel and Bennett, 2004; Xu et al., 2007). Under alkaline conditions (i.e. pH > 7.5) NH_4^+ becomes volatile as ammonia (NH_3).

Nitrification to the plant available NO_3^- is the oxidation of NH_4^+ into nitrite (NO_2^-) followed by an oxidation of these nitrites into nitrates.

1. $NH_3 + CO_2 + 1.5\ O_2 \rightarrow NO_2^- + H_2O + H^+$
2. $NO_2^- + CO_2 + 0.5\ O_2 \rightarrow NO_3^-$

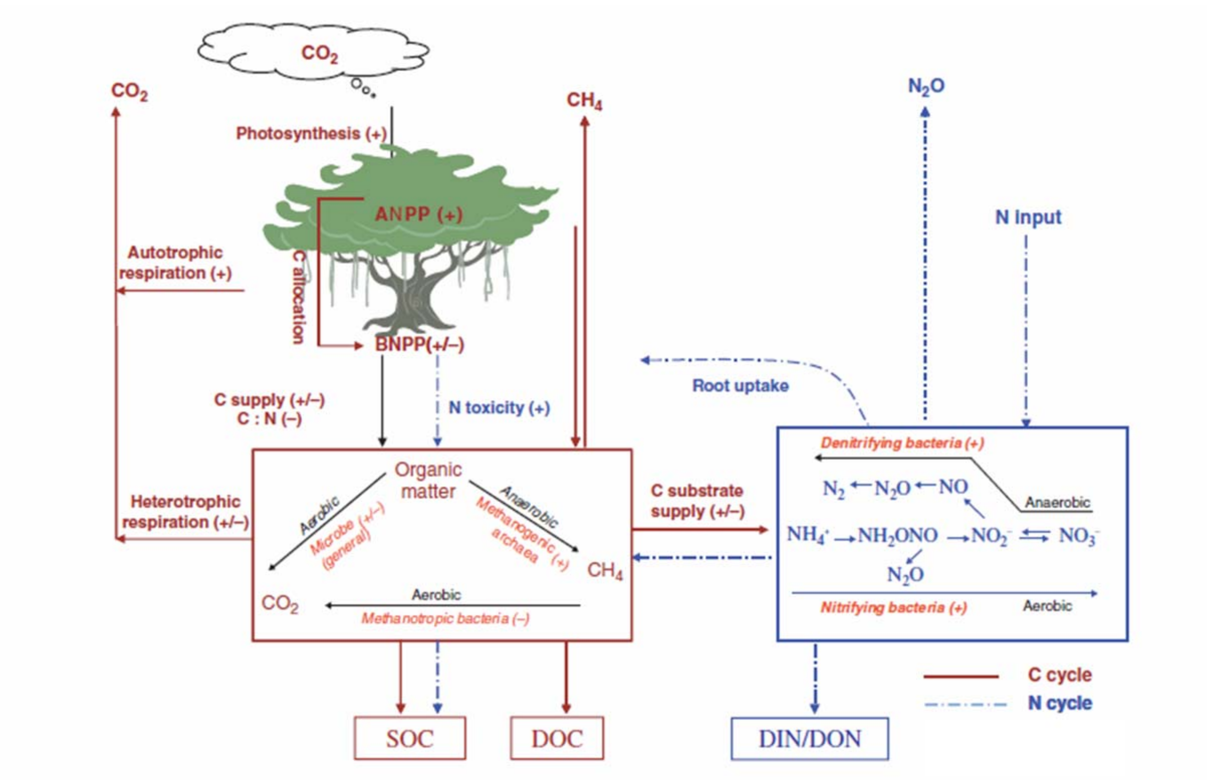

Figure 2: The potential mechanisms that regulate the responses of CO_2, N_2O and CH_4 production and consumption adapted from Liu and Greaver (2009) (ANPP/BNPP: Aboveground/Belowground net primary production)

Both sub-processes of nitrification are catalyzed by microorganisms. For the first step the nitrifiers with the prefix “nitroso“ (e.g. Nitrosomas) are responsible. During the second step the bacteria with the prefix “nitro“ (e.g. Nitrobacter) oxidize the nitrite. The nitrifying bacteria are mostly autotrophs and aerobic (Brady and Weil, 1997). They require O_2 and, thus, are favored in aerated soils. The highest nitrification activity typically occurs in soils at water filled pore space (WFPS) of 40% to 60%. Nitrifiers produce N_2O in two ways, by nitrification and nitrifier denitrification. During nitrification, N_2O is produced as a by-product of NH_3 oxidation. In nitrifier denitrification, N_2O is an intermediate of the reduction of NO_2 to N_2 (Wrage et al., 2001). Chemodenitrification and heterotrophic nitrification play only an important role under certain environmental conditions and are thus only briefly mentioned here (Stange and Doehling, 2005; Islam et al., 2007).
During denitrification NO_3^- ions are converted to gaseous forms of nitrogen by a series of reduction reactions (Brady and Weil, 1997; Firestone, 1982) with the end product N_2:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

N_2O is an intermediate of the reaction and is reduced by N_2O reductase to N_2 as a further step during the denitrification (Knowles, 2000). This step can be hampered under certain conditions that are unfavourable for N_2O reductase, such as higher O_2 levels or acid conditions (Brady and Weil, 1997). Denitrification takes place in soils under anaerobic conditions and in microsites and is favored at WFPS > 60% (Dobbie et al., 1999). In case the oxygen levels are low, the end product of denitrification is predominantly N_2. Denitrifiers are primarily heterotrophic, such as Paracoccus.
Both, nitrification and denitrification, depend on soil temperature as they are microbial processes. The temperature optimum of denitrification is between 30 °C and 50 °C (Granli and Bøckman, 1994). Nitrification shows its optimum temperature between 25 °C and 35 °C (Stark and Firestone, 1996; Stange, 2007). Both processes can occur simultaneously under the heterogeneous conditions of soils. Therefore, the contribution of the respective process to N_2O emission is difficult to determine experimentally (Baggs, 2008).
In the soil N_2O production is mainly governed by nitrification and denitrification. Davidson (1991) developed a simplified model of N_2O turnover; the so-called “Hole-in-the-pipe“ model (Figure 3), which shows that both processes can occur simultaneously

and, hence, N_2O is constantly produced and consumed depending on the environmental conditions in the soil.

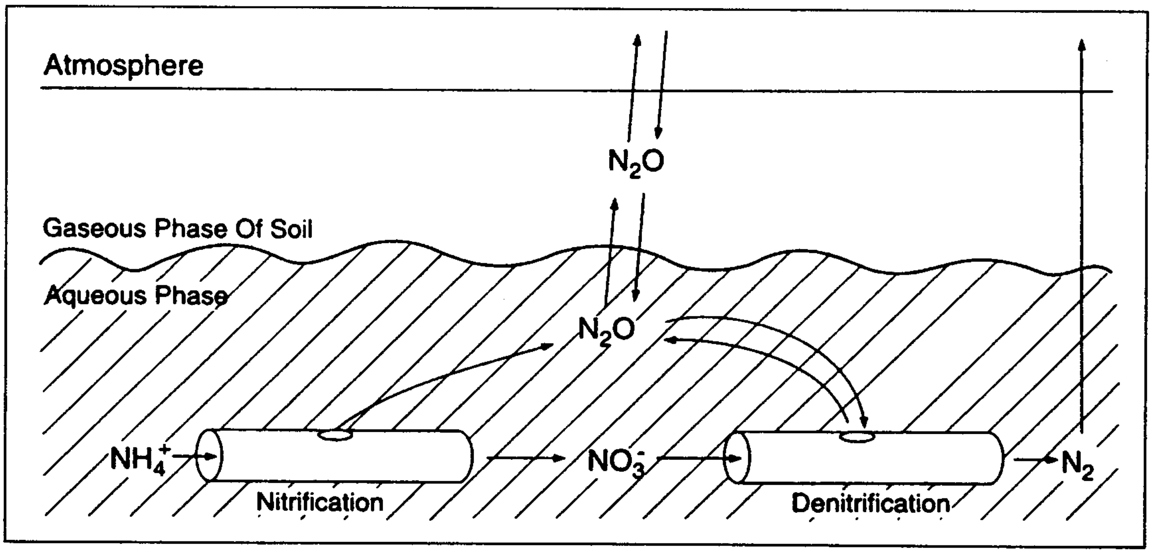

Figure 3: The "Hole-in-the-pipe" model adapted from Davidson (1991)

N_2O emissions from arable soils largely depend on site-specific characteristics (e.g. soil texture or climate) and on soil management (e.g. tillage or fertilization) (Bouwman et al., 2002).

1.3 C Sequestration in Agricultural Soils

Soils are the largest terrestrial pool of organic C (Batjes, 1996). The increase in SOM in agricultural soils has become a major issue in the past years because more than 70% of the terrestrial C stocks involved in the active C cycle are stored in the soil whereas only roundabout 30% are bound in the vegetation (IPCC, 2007).

On the one hand a high SOM content is a means to preserve soil quality (Manlay et al, 2007). Only some selected improvements of soil quality induced by OM increase will be mentioned. OM can provide organic substances like vitamins and auxins to stimulate plant growth and microbial activity (Weigel et al., 1997; Brady and Weil, 1997). An increase in soil C stocks results in a higher storage of nutrients as well as higher water holding capacity and pH buffering capacity.

Furthermore, physical soil properties become affected – higher aggregate stability and macro porosity lead to better aeration and oxygen supply to roots (Golchin et al., 1997;

Edmeades, 2003). Moreover, the increase in food supply for microorganisms leads to a higher microbial activity. Accordingly, fewer nutrients are leached and less irrigation is necessary. These factors can lead to a better environmental protection, that is, by inhibition of leaching or runoff, lower erodibility and higher plant production (Haynes et al., 1991; Edmeades, 2003; Manlay et al., 2007).

On the other hand increasing C stocks due to C sequestration offer a way to counteract global warming as soils can act as source or sink of CO_2. As soils represent a very large terrestrial stock of organic C, their depletion by intensive management has markedly contributed to the increased CO_2 concentration in the atmosphere (Lal, 2004; Snyder et al., 2009). However, the increase of soil C stocks by enhancing C sequestration can relieve the atmospheric CO_2 concentration (Janzen et al., 2006; Lal, 2004). Higher C stocks in agricultural soils can be achieved by preserving the C balance, e.g. by returning the C which is withdrawn by harvest or mineralized by tillage in the form of plant residues or fertilizers.

An important determining factor for C accumulation is soil texture: the higher the sand contents in the soil the lower the C accumulation because quartz particles exhibit only weak bonding affinities to SOM (von Lützow et al., 2007). Besides clay and silt particles protect C from microbial degradation (Hassink, 1997). Therefore, fine-textured soils are more likely to accumulate larger C stocks than coarse-textured soils.

There are several mechanisms to increase OM stocks like conservation tillage or no tillage, the return of plant residues, cultivation of catch crop, reduction in intensity of farming practices and fertilization. The addition of C to soils by residues or fertilizers tends to increase the soil C stocks directly. Catch crops increase the plant input and, especially legumes, increase the soil N status.

Cultivation of soils like ploughing and other tillage methods enhances mineralization. Tillage brings crop residues closer to microbes, decreases soil moisture and physically disrupts aggregates (Lal, 2004). Therefore, omitted ploughing or conservation tillage avoids decomposition of SOM and can lead to higher C stocks.

Fertilization, mineral as well as organic, can also contribute to the accumulation of OM. Fertilization stimulates plant growth and promotes the growth of aboveground and belowground biomass (Paustian et al., 1997). Accordingly, more plant residues are supplied to the soil (Liu and Greaver, 2009). N supply by fertilization is also chemically stabilizing C in the soil (Snyder et al., 2009).

Organic agriculture aims at closed nutrient cycles and the preservation of soil quality (Manlay et al., 2007). Nutrients are not supplied as mineral fertilizer, which has to be produced and transported externally, but as organic fertilizer like manure (Fließbach et al., 2007). Organic fertilizers directly supply C to the soil and contribute to the building of OM to a higher extent than mineral fertilizers (Christopher and Lal, 2007). Organic fertilization does not only provide nutrients but also OM and, especially in the long-term, it contributes to higher OM levels in the soil (Loveland and Webb, 2003; Blair et al., 2006 a and b). Gregorich et al. (2005) reported that C levels often increase linearly related to the quantity of manure added. Organic fertilization leads to a higher stabilization of SOM than C added by mineral fertilizer combined with straw (Heitkamp et al., 2009).

1.4 Fertilization and N_2O Emissions

Fertilization in agriculture is supposed to increase crop yields and compensate nutrient loss by biomass removal during harvest. Nitrogen lost by gaseous emissions reduces the efficiency of the fertilizer applied (Bouwman, 1996; Mosier et al., 1998). Mineral fertilization provides the nutrients which mainly restrict plant growth like N, phosphorus and potassium. Eichner (1990) summarized information which shows the relation between type and quantity of fertilizer application and N_2O emissions.

It was reviewed that the supply of N by fertilization induces N_2O emissions because the availability of mineral N is the most important factor controlling nitrification and denitrification (Davidson et al., 1986). Furthermore, it has been shown that the type and rate of fertilizer have an important impact on N_2O emissions (Bouwman et al., 2002; Granli and Bøckman, 1994; Eichner, 1990).

Organic fertilization can directly affect N_2O emissions due to the additional supply of immediately available organic matter into the soils as compared to mineral fertilizer. There are several authors who reported higher emissions from organic fertilized fields than from mineral fertilized fields (Velthof et al., 2003; Rochette et al., 2000; Van Groenigen et al., 2004). Chirinda et al. (2010) compared a conventional with an organic cropping system and found that N_2O emissions from both systems were in the same range although the N input was lower in the organic system. Application of organic fertilizer provides OM which increases microbial activity and provides substrate for denitrification (Chang et al., 1998, Mogge et al., 1999). Additionally, the largest part of N supplied as organic fertilizer has to be mineralised to become plant available. Thus, organic fertilizers like manure can provide a steady but low supply of N by the transformation of the organic N (Chang et al., 1998).

1.5 Feedback Mechanisms of Carbon Sequestration by Organic Long-term Fertilization on N_2O Emissions

Many agricultural management practices that increase soil C stocks, e.g. no till, conservation tillage, crop residue incorporation, organic fertilization, result in higher N_2O emissions (Gregorich et al., 2005). Two studies modelled the impact of C sequestration on N_2O emissions (Li et al. 2005; Qiu et al 2009). Both studies suggest that the increased GHG emissions may offset the benefit achieved by C sequestration due to CO_2 reduction.
Repeated manure application is supposed to have long-term effects on soils. The direct emissions of N_2O following the organic fertilizer application may lead to higher annual losses. Thus, the repeated application contributes to higher short-term N_2O losses compared to a single application (Raun et al., 1998; Chang et al., 1998).
Long-term application of organic fertilizer can also influence N_2O emissions because N in its mineral forms is the substrate for the microbial processes producing N_2O. Nitrate can accumulate by the repeated application of fertilizer (Kilian et al., 1998). The applied C provides energy for the heterotrophic nitrification and also serves as electron donor for denitrification (see also chapter 1.2). Higher C input, especially as DOC, could lead to higher N_2O emissions (Qiu et al., 2009). Repeated application of manure with high amount of organic but stable C and a slow mineralization could lead to a steady release of C.
Moreover, SOM is supposed to increase N_2O emissions because higher C stocks can lead to higher microbial activity and to higher respiration. CO_2 is respired which could lead to locally O_2 depleted zones in the soil, the so-called anoxic microsites (Flessa and Beese, 1995). Then the conditions are optimal for denitrification (Raun et al., 1998; Chang et al. 1998; Flessa and Beese, 1995).
Beyond, long-term application of organic fertilizers can improve the physical soil properties. Contrary to the hypothesis that increased C stocks lead to higher N_2O emissions, SOM can reduce N_2O emissions by improving the soil structure. Aggregation is

mediated by SOC, biota, ionic bridging, clay, and carbonates (Bronick and Lal, 2005). Soil organic C acts as a binding agent and as a nucleus in the formation of aggregates (Tisdall and Oades, 1982; Golchin et al., 1997) and macroaggregates lead to a better gas diffusion (Edmeades, 2003; Golchin et al. 1997). In this case higher C stocks could lower N_2O emissions.

The soils higher in SOM can also influence the short-term dynamics of N_2O. Velthof et al. (2005) concluded that specific soil properties like higher SOM contents induced higher short-term N_2O emissions right following the manure application. Hence, there would not only be effects in the long-term but also in the short-term.

1.6 Objectives

The overall objective of this thesis was to analyse if C accumulation in soil leads to increased N_2O emission. For this purpose, a set of two laboratory studies, one field study and a modelling approach were conducted, focusing on different combinations of soil parameters and agricultural management practices and the resulting effect on N_2O emissions.

The aim of the first incubation study was to elucidate the relation between N_2O emission and C accumulation under different soil water contents. Another aim was to analyse if long-term organically fertilized soils emit more N_2O after the short-term application of different fertilizers (farmyard manure, KNO_3, biogas waste from fermented maize silage). Here, the focus was also on the N_2O and CO_2 emissions in relation to different fertilizer types and how their constituents impact on the emission.

The objective of the second incubation study was to evaluate the impact of different soil textures on soil C stocks and on N_2O emissions. For this purpose, soils from three different long-term fertilization experiments were incubated and the effects of long-term fertilization on the emission rates of N_2O were studied at constant soil moisture of 60% water-holding capacity. Furthermore, the short-term fluxes of N_2O following the application of different fertilizers (KNO_3 vs. farmyard manure from cattle) and the response to a simulated heavy rainfall event which increased soil moisture to field capacity, were investigated.

Within the context of the 3rd study the research questions underlying the two laboratory studies were transferred to the field. The effects of different C stocks on N_2O emissions were examined under field conditions of a long-term fertilization experiment. Two different fertilization strategies (mineral vs. organic) were tested in combination with three different fertilization rates. A two-year field study on a sandy soil in Darmstadt with closed-chamber measurements was established to study the influence of different C stocks on N_2O emissions under natural climate and management factors. Additionally, the impact of the rate determining factors on N_2O emissions like mineral N content in soil, climate or management should be assessed.

The fourth study was a modelling approach to test a calibration and validation scheme. The DNDC model was used to describe and predict crop growth and N_2O emissions of the field experiment.

2. Long-term and Short-term Effects of the Application of Mineral and Organic Fertilizer on N_2O and CO_2 Emissions from a Sandy Soil – a Laboratory Incubation

Abstract

Increasing organic C stocks in soils reduce atmospheric carbon dioxide (CO_2) but it may cause enhanced emissions of N_2O by providing substrate for nitrification and denitrification and by increasing microbial O_2 consumption in soils. The objectives of this study were to determine the effects of the long-term application of farmyard manure (S-FYM) and mineral fertilizer (S-MIN) to a sandy arable soil, which has resulted in different soil organic C and N stocks, on the emissions of N_2O and CO_2 at different soil moisture and to compare this long-term fertilization effect with the short-term emissions following the application of different fertilizers (KNO_3, farmyard manure, and biogas waste). A laboratory incubation experiment was performed to test the effect of soil moisture (water-filled pore space of 40%, 60%, 70% and 78%) on N_2O and CO_2 emissions for S-FYM and S-MIN. Furthermore, we tested the differences in emissions between the S-FYM and S-MIN soils following fertilization with three different N sources: farmyard manure, KNO_3 and biogas waste from fermented maize silage. The long-term application of farmyard manure for 27 years increased organic matter in the topsoil (10.0 g C_{org} kg^{-1} in S-FYM compared to 7.9 g C_{org} kg^{-1} in S-MIN). N_2O emissions increased with increasing soil moisture, but there was no evidence that the higher organic matter content of S-FYM increased the risk of N_2O emissions in this sandy soil. Increased N_2O emissions were observed following fertilizer application. Emissions of N_2O during the first 53 days following fertilizer application amounted to 0.01% (mineral fertilizer), 0.21% (composted manure) and more than 24% (biogas waste) of the total amount of N applied. The high emissions induced by biogas waste were attributed to the high availability of both organic C and NH_4^+ in the fermented waste. Again, the fertilization history did not influence N_2O emissions. These results suggest that the characterization of C and N pools in organic fertilizers is required to assess their impact on soil N_2O emissions. Overall, there was no feedback of increased C and N stocks on N_2O emissions from this sandy soil. However, the application of organic fertilizers which promote organic C sequestration in soils resulted in short periods of increased N_2O emissions.

2.1 Introduction of the First Study

Soils can act as a source but also as a sink of the greenhouse gases (GHG) such as carbon dioxide (CO_2) and nitrous oxide (N_2O) (Mosier et al., 1998; Smith et al., 2003). Worldwide, organic C stocks in soils at 0 – 200 cm depth are approximately three times greater than the quantity of CO_2-C in the atmosphere (Batjes, 1996; Jobbágy and Jackson, 2000) and N_2O emissions from agricultural soils account for approximately 60% of the current increase of atmospheric N_2O (IPCC, 2007). Results from fertilization experiments show that organic C and total N stocks in cultivated soils can be increased by the long-term application of organic fertilizers (Raun et al., 1998; Powlson et al., 1998; Blair et al., 2006a). Thus, the implementation of fertilization strategies which are based on organic fertilizers and the associated transient increase in soil C sequestration might result in a reduction of the net GHG emission from crop production. However, increased contents of organic C and total N in arable upland soils may also promote emissions of N_2O (Lal, 2004) which is approximately 298 times more effective in terms of radiative forcing than CO_2 (based on a time horizon of 100 years; IPCC, 2007). Therefore, from the perspective of global warming it is crucial to assess the impacts of C sequestration strategies not only for CO_2 but also for other greenhouse gases (Qiu et al., 2009).
Little is known about the long-term effects of different fertilization strategies and the associated changes in SOC and total nitrogen (N_t) contents on the emissions of N_2O. Model results suggest that N_2O emissions probably increase with increasing stocks of organic C in soils (Li et al., 2005; Qiu et al., 2009). In particular, easily available organic matter fractions were found to trigger N_2O emissions because they can promote the formation of anoxic microsites in soils (Parkin, 1987; Flessa and Beese, 1995) and because they can provide substrates for nitrification and denitrification (Velthof et al. 2003; Chang et al., 1998). Several authors reported increased N_2O emissions directly after the application of organic fertilizers (Chang et al., 1998; Petersen, 1999; Flessa and Beese, 2000; Van Groenigen et al., 2004). However, the long-term effects of C accumulation in agricultural soils on N_2O emissions are less clear. Kilian et al. (1998) reported a promoting effect of C and N enrichment in arable soils on N_2O release, whereas Meng et al. (2005) found that long-term application of manure did not result in greater N_2O emissions than the mineral fertilized treatment, despite higher C and N contents in the manured soil. Chang et al. (1998) determined N_2O emissions from soils with the annual application of solid

manure for 21 years. They found increasing N_2O emissions with increasing manuring rates and suggested that repeated manure application may promote N_2O losses by the accumulation of organic C and nitrate in soil. Theoretically, increased SOC stocks may result in increased microbial activity and microbial O_2 consumption in soils. As a consequence, the availability of O_2 in soil air at a given soil moisture may decrease with increasing SOC stocks. This might affect the relationship between N_2O emissions and soil moisture and it might also influence the size of N_2O emissions factors (N_2O emissions related to the N input). However, SOC accumulation may also influence N_2O emissions by changing soil physical properties like pore size distribution, aggregate stability and soil structure (Golchin et al., 1997; Edmeades, 2003).

We hypothesized that the long-term application of farmyard manure and the associated increase of SOC and N_t stocks leads to N_2O emissions and that increased organic matter stocks affect the quantity of N_2O emitted at different soil moisture or following the application of different N fertilizers. In addition, we hypothesized that the long-term impact of different fertilization strategies (application of mineral N or organic fertilizer) on N_2O emissions is low compared with the short-term effect induced by the direct application of different fertilizers. The objective of this study was to determine the effects of two long-term fertilization strategies with either mineral fertilizer or farmyard manure which had resulted in different soil C_{org} and N_t stocks, on (i) the emissions of N_2O and CO_2 at different soil moisture levels and (ii) the short-term emissions of N_2O and CO_2 following the application of fertilizers with different availability of organic C and mineral N (farmyard manure, KNO_3, biogas waste from fermented maize silage).

2.2 Materials and Methods of the First Study

2.2.1 Study Site and Soil Sampling

The long-term fertilization experiment at the IBDF (Institute for Biodynamic Research) is situated in Darmstadt, Germany (49°5’ latitude, 8°34’ longitude, 100 m above sea level). The crop rotation consisted of red clover (*Trifolium pratense* L.), spring wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum* L.) and winter rye (*Secale cereale* L.).

Since 1980, composted dairy cattle manure (S-FYM) and calcium ammonium nitrate (S-MIN) have been applied in a split block design with four replicates. The fertilization rates in both fertilization treatments (mineral fertilizer and composted farmyard manure) were 140 kg N ha^{-1} for wheat and rye and 150 kg N ha^{-1} for potato. There was no fertilizer application when clover was cultivated. The farmyard manure from cattle was composted in piles for about nine months before application. After harvest, straw remained on the mineral fertilized field. On the S-FYM field straw was removed and recycled as composted farmyard manure. The mean annual C input by straw incorporation in the S-MIN treatment was 0.93 t C ha^{-1} yr^{-1} whereas the input by manure in the S-FYM treatment was 1.3 t C ha^{-1} yr^{-1} (Heinze et al., 2009). The soil type is a sandy Cambisol with 86% sand, 9% silt und 5% clay in the Ap horizon. The water holding capacity was at 11.3% of the soil dry weight. The main chemical properties of the soil are summarized in Table 1.

In February 2007, soil samples were taken from the topsoil (0 – 10 cm) of both fertilization treatments (n = 4). The last farmyard manure application took place 29 months before the soil samples were taken (no fertilizer application to clover in 2006). The field moist soil samples were sieved (< 2 mm). After drying at 40 °C and grinding the samples, organic C and N contents were determined by an automated C and N analyser (Heraeus Vario EL, Hanau, Germany). Soil pH was measured in a 10^{-2} M $CaCl_2$ solution with a soil/solution ratio of 1:2.5 (König and Fortmann, 1996). To determine the effective cation exchange capacity (CEC) the soil samples were leached with 100 ml of a 1 M ammonium chloride (NH_4Cl) solution for four hours as described by König and Fortmann (1996). Cations in the extract were measured by ICP-AES (Spectro, Kleve), and exchangeable protons were calculated from the pH of the NH_4Cl solution before and after percolation (Table 1).

2.2.2 Experimental Design and Analyses

Effect of fertilization history on CO_2 and N_2O emissions at different soil moisture levels

In an incubation experiment, we determined the effect of soil moisture on the emissions of N_2O and CO_2 from the soils with the two different fertilization histories (S-MIN and S-FYM). 120 g of field-moist, sieved (< 2 mm) soil were filled into incubation vessels with a volume of 0.36 l (Sartorius, Göttingen) and compacted to a soil density of 1.4 g cm^{-3}. All samples were adjusted to a soil moisture content of 40% of the water-holding capacity and pre-incubated for 12 days. After this period, four replicates of S-MIN and S-FYM were adjusted to a water filled pore space (WFPS) of 40%, 60%, 70% and 78% by adding distilled water. The samples were incubated at 20 °C in the dark for 19 days. Soil moisture was determined gravimetrically and readjusted if necessary. Emissions of CO_2 and N_2O were determined at intervals of two days by closing the lid of the incubation vessel for 1 – 1.5 hours (the longer accumulation time was used for treatments with low N_2O emission rates). Gas samples (8 ml) were taken with a gas-tight syringe via a sampling port in the lid of the incubation vessels directly before the lid was closed and at the end of the gas accumulation period. Air in the incubation vessels was mixed before sampling. CO_2 and N_2O analyses were performed by manual injection of these gas samples into a gas chromatographic system with an electron capture detector (described by Loftfield et al. (1997)). Emission rates were calculated from the concentration increase with time under consideration of the headspace (0.273 l) volume of the incubation vessel. Concentrations of ammonium and nitrate in soils were determined after extraction with 0.01 M $CaCl_2$ (soil:solution 1:2) at the beginning and at the end of the incubation period using parallel incubated soil samples. The photometric analysis of mineral N in soil extracts was carried out using a continuous flow analyser (S/A 20/40 Skalar Analytical, Erkelenz).

Effect of fertilization history on short-term emissions of CO_2 and N_2O following the application of different N fertilizers

In this incubation experiment, we determined the short-term effect of the application of different fertilizer types on the emission dynamics of N_2O and CO_2 at constant soil moisture of 60% WFPS (maximum soil water content under field conditions, data not shown). Again, the response of the two soils with a long-term fertilization history of either exclusively mineral fertilizer or exclusively manure (S-MIN, S-FYM) was tested. We used the same incubation system and conditions as described above (except soil moisture) and established the following fertilization treatments: (1) control without fertilizer application (control), (2) application of farmyard manure (FYM), (3) application of KNO_3 (MIN), and (4) application of the fermentation effluent of a biogas plant (biogas waste, BW). The combination of the treatments (fertilization history and fertilizer application during the incubation experiment, n = 4) resulted in the following abbreviations for the long-term mineral fertilized treatments: S-MIN control, S-MIN MIN, S-MIN FYM, S-MIN BW. The corresponding abbreviations for the long-term organic fertilized treatments were S-FYM control, S-FYM MIN, S-FYM FYM, S-FYM BW.

All fertilizers were applied at a rate of 31 mg N_t per incubation vessel which corresponds to a N input of 60 kg ha^{-1}. The composition of the fertilizers applied is summarized in

Table 2. The farmyard manure from cattle was stored for two months in piles before application. The biogas waste originated from a biogas plant in Obernjesa, Germany (www.bioenergiehof.de). Maize silage was fermented for about 90 days at 39 °C followed by a cold secondary fermentation for 70 to 90 days. The biogas waste was then anaerobically stored for few weeks at 5 °C. The organic fertilizers (FYM, BW) were mixed with the soil; the KNO_3 (MIN) was dissolved before application. The volume of water (24 ml) added with the dissolved fertilizer was taken into consideration when adjusting the soil moisture to 60% WFPS. The emission rates of N_2O and CO_2 were determined at intervals of two to three days during the incubation period of 53 days using the sampling and measurement procedures described above, with the exception that the closing period of the incubation vessels was reduced when flux rates were high: in this case the incubation vessels were put into larger gas accumulation jars (volume of 2.16 l) for the determination of very high flux rates (necessary only for the treatment with biogas waste). This procedure ensured that the CO_2 concentration during the accumulation period did not exceed 0.5%. The concentrations of soil nitrate and ammonium were determined at the beginning of incubation and after 26, 41 and 53 days. Total nitrogen of the organic fertilizers was determined by the DUMAS-combustion method (FP 2000, Fa. Leco Instruments, Mönchengladbach). The ammonium and nitrate contents were analyzed by the extraction-distillation method described by Bremner et al. (1966) and the C_{org} content was determined with an elemental analyser (Elementar Vario Max, Hanau).

2.2.3 Statistical Analyses

Differences in the content of soil organic carbon (C_{org}), N_t, pH, cation exchange capacity (CEC), CO_2 and N_2O emissions and NO_3^- contents between the two soils with different fertilization history were tested with Student's t-tests ($p \leq 0.05$). The same procedure was used to test the differences between the two soils with respect to the cumulative CO_2 and N_2O emissions following the addition of different fertilizers. Differences between the analyzed soil moisture levels (WFPS of 40, 60, 70 and 78%) and between the different fertilization treatments (control, MIN, FYM, BW) were tested with a one-way ANOVA followed by the Tukey HSD test. The distribution of residuals was tested using the Shapiro-Wilk test. Emission rates of N_2O were transformed to pass the test for normality (transformation: (emission rate)$^{0.2}$ for the experiment at different soil moisture, (emission rate)$^{-1}$ for the experiment with application of different fertilizers). Statistical analyses were carried out using the R 2.81 software package.

Table 1: Chemical properties (means, n = 4) of the soils (0 − 10 cm) with different fertilization history. Soils were fertilized with composted farmyard manure (S-FYM) or calcium ammonium nitrate (S-MIN) for 27 years.

Treatment	C_{org} g kg^{-1}	N_t g kg^{-1}	pH ($CaCl_2$)	CEC mmol$_c$ kg^{-1}
S-FYM	9.95^a	0.95^a	6.1	44.64^a
S-MIN	7.88^b	0.72^b	5.6	45.69^a

Different small letters indicate significant differences between the differently fertilized soils (Student's t-test).

2.3 Results of the First Study

2.3.1 Emissions of N_2O and CO_2 from Soils with Different Fertilization History at Different Soil Moisture Levels

After almost 30 years of different fertilization history C_{org} and N_t contents were significantly higher in the organic fertilized treatment than in the mineral fertilized treatment (Table 1). After setting a constant WFPS, fluxes of N_2O and CO_2 were nearly constant. Therefore we present average values over 19 days for emission rates of CO_2 and N_2O (Table 3). In the soil with organic fertilization history, mean CO_2 emission rates were higher at 60% WFPS than at 40% or 78% WFPS. For the S-MIN treatment mean CO_2 emissions were higher at 60% and 70% WFPS than at lower (40% WFPS) or higher (78% WFPS) soil moisture (Table 3). There were no differences in CO_2 emissions between the soils with different fertilization history, despite a higher SOC stock in the soil fertilized with farmyard manure (Tables 1 and 3).

The N_2O emission rates were generally low at a soil moisture content of 40% WFPS with mean flux rates ranging between 0.01 and 0.11 µg N_2O-N kg^{-1} h^{-1} (Table 3). The highest fluxes of 0.99 (S-FYM) and 1.29 µg N_2O-N kg^{-1} h^{-1} (S-MIN) occurred at 78% and 70% WFPS, respectively (Table 3). Differences between the two soils were not significant, except for N_2O emissions at 60% WFPS, which were higher for S-MIN than S-FYM ($p \leq$

0.05). Soil nitrate contents at the beginning of the incubation period were higher for S-FYM (35 mg NO_3^--N kg^{-1}) than for S-MIN (25 mg NO_3^--N kg^{-1}).

Table 2: Composition of the fertilizers (MIN: KNO_3; FYM: farmyard manure from cattle; BW: biogas waste) used in the incubation study and application rates of total N and organic C.

Fertilizer	Dry matter	C_{org}	N_t	NO_3^--N	NH_4^+-N	C/N	Applied C_{org}	Applied N
	%	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}		mg kg^{-1}	mg kg^{-1}
FYM	21.94	91.38	5.55	0	0.06	16.5	4249.2	258
MIN			14.00	14.00	0			258
BW	7.56	34.68	1.65	0	1.22	21.5	5427.4	258

No changes of soil nitrate content occurred during the incubation period, except for the highest soil moisture content (78% WFPS) where soil nitrate contents decreased in both treatments (Table 3). Total N_2O-N emissions from these treatments (78% WFPS) accounted for 3.3% (S-FYM) and 4.8% (S-MIN) of the observed decrease of NO_3^--N. The extractable NH_4^+ content was below the detection limit of 0.01 mg NH_4^+-N kg^{-1} on both sampling dates.

2.3.2 Short-term Emissions of N_2O and CO_2 from Soils with Different Fertilization History after Application of Three Different Fertilizers

Emission rates of CO_2 from the unfertilized controls and the KNO_3 application treatments were nearly constant with a mean flux rate of approximately 160 µg CO_2-C kg^{-1} h^{-1} (Figure 4). Cumulative CO_2 fluxes of the control treatments (without fertilizer application) (Table 4) indicated that 2.1% (S-MIN) and 2.0% (S-FYM) of the total SOC (Table 1) was mineralized during the incubation period of 53 days (CO_2-C emissions related to the SOC content). CO_2 emission rates were higher after the application of farmyard manure (FYM), and much higher after the application of biogas waste (BW) throughout the entire incubation period (53 days) (Figures 4 and 5). Maximum CO_2 release rates of approximately 1000 µg CO_2-C kg^{-1} h^{-1} (FYM) and almost 5000 µg CO_2-C kg^{-1} h^{-1} (BW) were measured during the second week after fertilization. In our experiment, fertilizer application was standardized with respect to the total quantity of N applied (addition of 31 mg N_t to 120 g of dry soil). Thus, the amount of OC added was 21.7% greater for biogas waste (BW) than for farmyard manure (FYM) (Table 2). Total CO_2 emissions were approximately 2.7 times higher for the treatment with application of biogas waste than farmyard manure (Table 4). The cumulative CO_2 flux indicated that 38% (in S-FYM) and 28% (in S-MIN) of the BW-carbon and 13% (both treatments) of the FYM-carbon were mineralized during the experiment if we assume that there were no priming effects (Table 4).

Table 3: Emission rates of CO_2 and N_2O (means over 19 days, n = 4) from two soils with different fertilization history (S-FYM and S-MIN) which were adjusted to different soil moisture (water-filled pore space (WFPS) of 40%, 60%, 70%, and 78%). The soil nitrate content (means and standard deviation, n = 4) was measured at the beginning (day 0) and at the end (day 19) of the incubation experiment.

Soil	WFPS %	Emission rate µg kg^{-1} h^{-1}		Nitrate contents (NO_3^--N) mg N kg^{-1}	
		CO_2-C	N_2O-N	Start (day 0)	End (day 19)
S-FYM	40	79.3^{Aac}	0.01^{Aa}	35.0^{Aa}	38.5^{Aa}
S-MIN	40	68.3^{Aa}	0.11^{Aa}	24.5^{Ba}	23.4^{Ba}
S-FYM	60	120.7^{Ab}	0.03^{Aa}	35.0^{Aa}	30.8^{Aa}
S-MIN	60	102.1^{Ab}	0.29^{Ba}	24.5^{Ba}	27.1^{Aa}
S-FYM	70	104.0^{Abc}	0.46^{Ab}	35.0^{Aa}	33.8^{Aa}
S-MIN	70	108.6^{Ab}	1.29^{Ab}	24.6^{Ba}	12.7^{Aa}
S-FYM	78	72.5^{Aa}	0.99^{Ab}	35.0^{Aa}	21.2^{Ab}
S-MIN	78	68.8^{Aa}	0.95^{Ab}	24.5^{Ba}	15.5^{Bb}

Flux rates followed by different capital letters indicate significant differences among the two soils (S-MIN, S-FYM) at the same soil moisture (Student's t-test, $p \leq 0.05$). Different small letters indicate significant differences between soil moisture levels for the same soil (ANOVA with Tukey HSD test, $p \leq 0.05$). For the nitrate contents, small letters indicate significant differences between start and end contents and capitals indicate differences between the two soils (Student's t-test, $p \leq 0.05$).

There was no clear effect of fertilization history (S-MIN, S-FYM) on CO_2 emission dynamics following the application of different fertilizers (Figure 4 and 5). However, the cumulative CO_2 emissions following BW application were higher for S-FYM than S-MIN, indicating a slightly more rapid mineralization of BW carbon in the soil with a long-term history of organic fertilizer application.

The application of organic fertilizers (FYM and BW) resulted in increased N_2O emission rates throughout the entire incubation period (Figure 4 and 5) relative to the control and MIN treatments. The highest N_2O emission rates by far occurred after the application of BW to S-MIN and S-FYM and similar N_2O emission dynamics were observed in both soils: low emissions during the first week after application followed by a strong increase to more than 180 µg N_2O-N $kg^{-1}h^{-1}$, followed by a decline to 2 − 5 µg N_2O-N $kg^{-1}h^{-1}$ on day 53 (Figure 5). These relatively low final N_2O flux rates were still larger than the maximum N_2O emission rates observed for the soils fertilized with farmyard manure (max. emissions 1.4 and 1.1 µg N_2O-N $kg^{-1}h^{-1}$ for S-FYM and S-MIN, respectively).

Table 4: Cumulative N_2O and CO_2 emission (means, n = 4) during a period of 53 days following the application of different fertilizers (control = without fertilizer application, MIN = KNO_3, FYM = farmyard manure, BW = biogas waste) to soils with different fertilization history (S-FYM and S-MIN).

Soil	Fertilizer	CO_2-C		N_2O-N	
		Total emission	Related to the C input*	Total emission	Related to the N input*
		mg kg^{-1}	%	mg kg^{-1}	%
S-FYM	control	201.6^{Aa}		0.00^{Aa}	
S-MIN	control	164.3^{Ba}		0.03^{Aa}	
S-FYM	MIN	136.1^{Aa}		0.02^{Aa}	0.01
S-MIN	MIN	146.5^{Aa}		0.05^{Aa}	0.01
S-FYM	FYM	738.8^{Ab}	12.6	0.50^{Ab}	0.20
S-MIN	FYM	700.5^{Ab}	12.6	0.71^{Ab}	0.27
S-FYM	BW	2259.3^{Ac}	37.9	63.87^{Ac}	24.74
S-MIN	BW	1692.2^{Bc}	28.2	61.43^{Ac}	23.78

The proportion of the added fertilizer C and N that was emitted was calculated from the amount of C_{org} and N_t added in relation to the difference of the total emission from the fertilized soil and the control. Flux rates with different capital letters indicate significant differences between the two soils (Student's t-test, $p \leq 0.05$). Flux rates with different small letters indicate significant differences among the fertilizer types and the control (ANOVA with Tukey test, $p \leq 0.05$).

The cumulative N_2O emissions for the entire incubation period of 53 days increased in the following order: Control = MIN < FYM < BW (Table 4). The total N_2O emissions represented 24% of the applied N for BW treated soil, 0.21% for FYM treated soil and 0.01% for MIN treated soil. The estimated emissions of 24% of applied N for BW are actually a conservative estimate: we failed to record the maximum emission rate during the third week after BW application because our system was not configured to register such unexpectedly high emission rates (Figure 5).

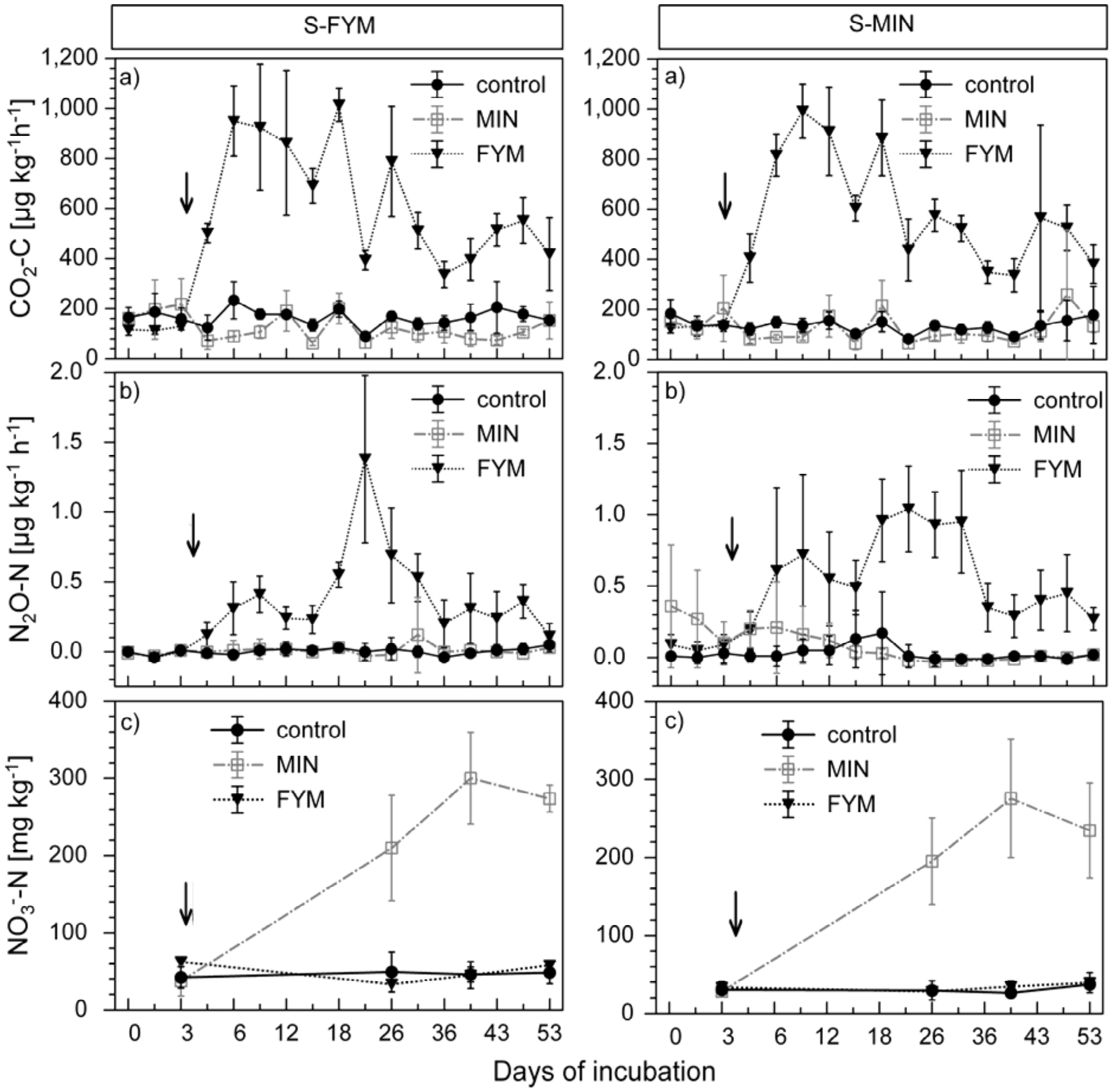

Figure 4: Emission rates of (a) CO_2 and (b) N_2O, and (c) soil nitrate concentration (means ± standard deviation, n = 4) of two soils with different fertilization history (S-FYM: soil with long-term application of farmyard manure; S-MIN: soil with long-term application of mineral fertilizers) after the application of KNO_3 (MIN) and farmyard manure (FYM) at day 3 (black arrows) and without fertilizer application (control).

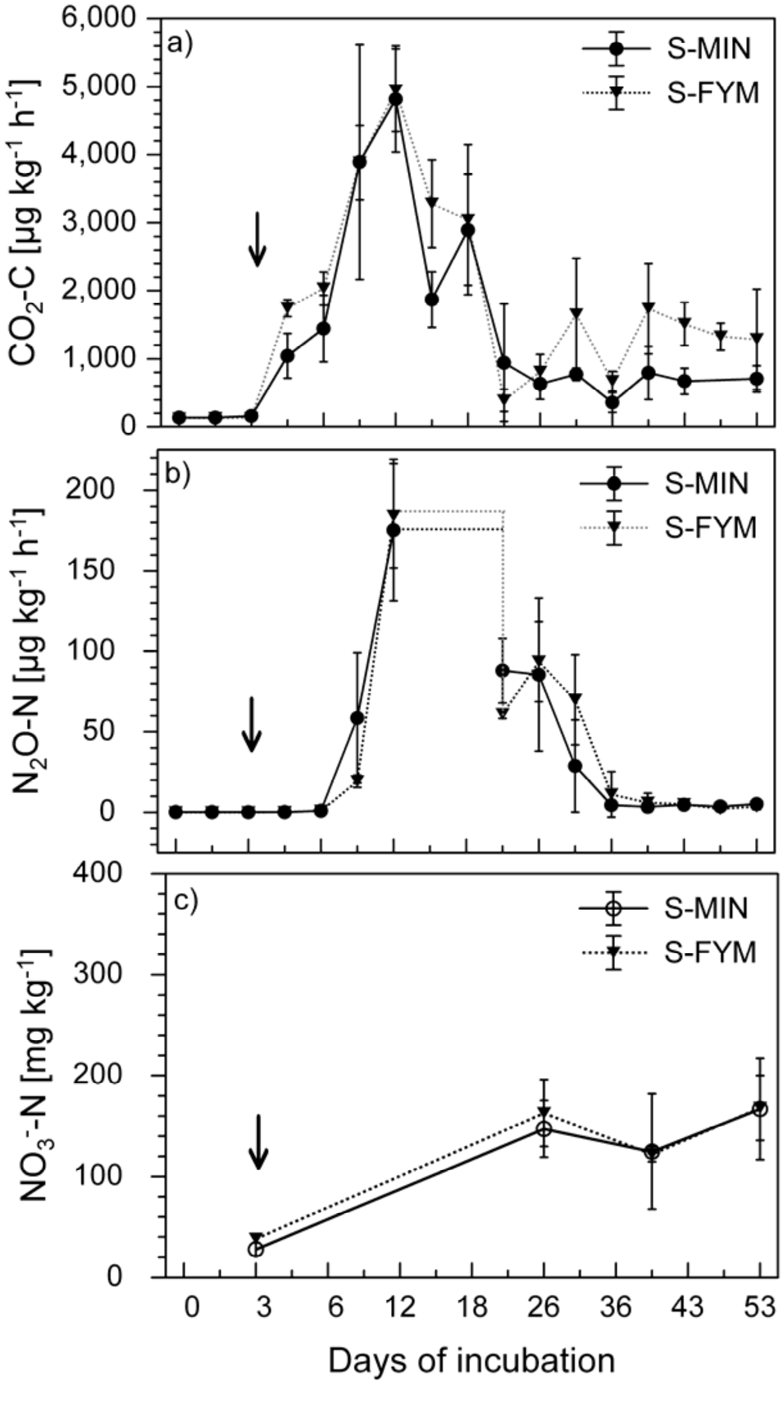

Figure 5: Emission rates of (a) CO_2 and (b) N_2O, and (c) soil nitrate concentration (means ± standard deviation, n = 4) of two soils with different fertilization history (FYM: soil with long-term application of farmyard manure; S-MIN: soil with long-term application of mineral fertilizers) after the application biogas waste (BW) at day 3 (black arrows). The maximum emission rates of N_2O during the third week after BW application were not recorded by our analytical system.

2.4 Discussion of the First Study

2.4.1 Emissions of N_2O and CO_2 from Soils with Different Long-term Fertilization History at Different Soil Moisture Levels

Mean CO_2 emission rates were slightly higher for S-FYM than S-MIN at three of the four different soil moisture levels analysed, but the differences observed were not significant ($p \leq 0.05$) (Table 3). Our results indicate that microbial respiration and the associated microbial O_2 consumption in the analyzed sandy soil were not affected by the long-term application of composted farmyard manure and the associated increase in SOC content. Furthermore, there was no effect of the last manure application at S-FYM 29 months ago on the emissions of CO_2 emissions. The specific mineralization rate (cumulative CO_2-C emissions listed in Table 3 related to the SOC content listed in Table 1) was higher for the soil with long-term application of mineral fertilizer (S-MIN) than for the soil fertilized with farmyard manure (S-FYM). This observation indicates a relatively high stabilization or recalcitrance of the additional SOC in S-FYM, which originates from the long-term input of composted farmyard manure. The results are in line with the observation that long-term application of farmyard manure favours the accumulation of aliphatic compounds in soil organic matter (Sîmon, 2005), which are considered to represent a particularly recalcitrant form of soil C (Baldock et al., 1997). Our results are in agreement with model results published by Heitkamp et al. (2009) who suggested that the labile SOC fractions of the analyzed soils were not influenced by the type of fertilizer applied. The higher SOC content of the soil fertilized with FYM was explained by an increase of the SOC pool with intermediate stability.

The N_2O emissions without fertilizer application were generally low (< 1.3 µg N_2O-N kg^{-1} h^{-1}) even if soil moisture and soil nitrate contents were considerably higher than the threshold values reported for high N_2O emission rates (> 5 mg NO_3-N kg^{-1}, WFPS > 65%; Dobbie and Smith, 2001). These results suggest that the low N_2O emission rates were mainly due to a low denitrification potential of this sandy soil. Emissions of N_2O were lower at a soil moisture of ≤ 60% WFPS than at higher soil moisture contents (≥ 70% WFPS). A similar relationship between soil moisture and N_2O emissions was found in several studies and was explained by increasing denitrification activity, especially at WFPS > 60% (Granli and Bøckman, 1994; Dobbie et al., 1999; Khalil and Baggs, 2005; Bateman and Baggs, 2005). The net decrease of the soil nitrate content observed at 78% WFPS,

especially in the S-FYM treatment, supports the assumption that denitrification was the main cause of the increased N_2O emission rates at this high soil moisture level. Our study indicated that the increase in SOC (by 26%) and N_t content (by 32%) induced by long-term application of farmyard manure did not lead to a significant change in N_2O emissions. This might be attributed to the sandy soil texture. Moreover, there was no effect of fertilization history on N_2O emissions at constant soil moisture. The only exception were the N_2O emissions at 60% WFPS which were higher for S-MIN than for S-FYM.
Overall, our results indicate that the hypothesis that OM accumulation in soils promotes N_2O emissions is not valid for the sandy soils at the Darmstadt long-term experiment site. Our results should not be applied to soils with finer textures where organic matter accumulation may have a stronger effect on O_2 availability and soil physical properties. In agreement with our results, Meng et al. (2005) reported that organic C and N contents were higher in a sandy loam soils with long-term application of manure than with application of mineral fertilizer but there were no significant differences of N_2O emissions. Kilian et al. (1998) measured N_2O emission rates from field plots established on loess-derived soils with different fertilization histories in Southern Germany. They concluded that the C and N enrichment of these arable soils by long-term organic fertilization resulted in a detectable increase in N_2O emissions. However, this effect was small compared to the direct effects of the quantity and timing of fertilizer application. In summary, it can be concluded that our measurements did not reflected the model results which suggest that increased C sequestration in soils results in increased N_2O emissions (Qiu et al., 2009). The model assumptions are probably applicable to sites where the additional organic C and N are part of rather labile SOM pools.

2.4.2 Emissions of N_2O and CO_2 from Soils with Different Fertilization History after the Application of Different Fertilizers

The emission dynamics of CO_2 following the application of organic fertilizers reflect the mineralization of the added organic matter. Our results show that mineralization rates were considerably higher for the treatments fertilized with BW than those treated with FYM. This difference could not be explained by the addition of 1.3 times more organic matter to the BW-treatments since the increase of the cumulative CO_2 emissions induced by the addition of biogas waste was 3.8 times (S-FYM) and 2.8 times (S-MIN) higher than for the respective FYM-treatments. Thus, the results indicate that the specific mineralization rate was higher in the BW than in the FYM treatment. The different substrates of these fertilizers, i.e. cattle excrement with straw for FYM and maize silage for BW, probably contributed to these differences. Both processes, composting and anaerobic digestion, reduce the amount of easily available OC and result in a biological stabilization process which is reflected by decreasing C mineralization rates (FYM) and decreasing CH_4 production rates (BW), respectively (Bernal et al., 1998; Gómez et al., 2007; Li et al., 2009). However, the composition of the organic remains and their stability in aerated soils are different. The composting of cattle manure results in a more advanced stage of OM oxidation and a greater enrichment in aromatic compounds than the digestion process (Gómez et al., 2007). The latter allows the accumulation of short-chain fatty acids, which can be rapidly mineralized under aerated conditions (Kirchmann and Lundvall, 1993). Kirchmann (1991) analyzed the mineralization of aerobically and anaerobically treated animal manures in soil. He found a consistent pattern for all manures tested with higher CO_2 emissions following application of anaerobic manures than aerobic manures. As a result of the digestion in the rumen, the residues of cattle waste are more stable and depleted in easily mineralizable organic compounds compared to the forage (Kirchmann and Lundvall, 1993). Thus, the different substrates of the organic fertilizers analyzed in this study might have contributed to the differences observed in C stability. Senbayram et al. (2009) also determined CO_2 emissions from an arable soil after the application of biogas waste from fermented maize plants. Their results agree with our observation that the biogas waste contains an easily available organic C pool which is mineralized within the first weeks after application.

N_2O emissions following nitrate application were at the same low level as emissions from the unfertilized soils, even if soil nitrate availability was highest in these treatments. This indicates that denitrification was restricted by adequate aeration of the sandy soil at 60% WFPS, which is in line with the results from our first incubation experiment.

The application of organic fertilizers induced significantly increased N_2O emission rates even if soil nitrate availability was lower. This suggests that the increase in OC availability was the rate-determining factor for N_2O emissions from the soils analyzed. Available C can trigger denitrification and N_2O emissions by different processes: it is a substrate for denitrifying bacteria (Dendooven et al., 1996) and it increases metabolic activity and O_2 consumption, which can result in the formation of anaerobic microenvironments (Flessa and Beese, 1995; Clemens and Huschka, 2001). In addition to these direct effects of available C, mineralization of organic compounds with high N contents can also stimulate nitrogen release and provide mineral N for nitrification and denitrification (Dendooven et al., 1996). Our results are in line with several other studies which provided evidence for higher N_2O emissions from arable soils receiving organic fertilizers than synthetic mineral N (Petersen, 1999; van Groenigen et al., 2004; Rochette et al., 2008a). Furthermore, our results show that N_2O emissions were 86 to 127 times larger following the application of BW produced by the anaerobic digestion of maize silage than after the addition of FYM. This clear difference can be explained by the content of available OC and mineral nitrogen contained in each organic fertilizer. The anaerobic (BW) and aerobic (FYM) treatment resulted in contrasting chemical characteristics. Both procedures reduced the initial content of readily available OC. However, composting results in C and N stabilization, whereas anaerobic digestion results in the accumulation of considerable quantities of NH_4^+ and available organic compounds. The large amount of NH_4^+-N is typical for biogas waste.

Ammonium is the main form of nitrogen accounting for about 57% to 67% of the total nitrogen in biogas slurries (KTBL, 2009). The combination of increased availability of organic C and mineral N results in a much greater potential for BW than for FYM to stimulate nitrification, denitrification and N_2O emissions. The high net nitrification rates induced by BW application are reflected in the increasing nitrate concentrations in these treatments. Several studies have shown that anaerobic digestion reduced N_2O field emissions induced by slurry application (Petersen, 1999; Clemens and Huschka, 2001; Amon et al., 2006). This was explained by a reduction of readily available OC during fermentation. However, our results suggest that C availability is still considerably greater than in composted farmyard manure. Recently, Senbayram et al. (2009) found in a grassland experiment that N_2O emissions were higher following application of cattle slurry or biogas waste from maize plants than after applying calcium ammonium nitrate. There was no difference between cattle slurry and biogas waste. However, more studies are needed on the effects of biogas waste from different substrates on gaseous N emissions because their composition and physical properties can be different from animal slurries. Compared with cattle slurry, biogas waste from cofermentation of cattle slurry with maize has higher contents of NH_4^+-N, a lower C/N ratio, a higher pH, and it also differs in viscosity (KTBL, 2009; Gehricke, 2009). The delayed increase in N_2O emissions in the second week after the application of biogas waste was also found by Senbayram et al. (2009). They explained this time pattern of N_2O emissions with the absence of nitrate and

the high availability of OC in biogas waste. The low availability of soil nitrate limits denitrification during the first week and in combination with high OC availability it favours the reduction of N_2O to N_2. The effect of organic fertilizers on N_2O emissions may change with soil moisture because the decreasing soil aeration with increasing soil moisture affects total denitrification and the reduction of N_2O to N_2 (Dambreville et al., 2006). In summary, the present results indicate that the characterization of C and N pools in organic fertilizers is required to assess their impact on soil N_2O emissions.
We found no effect of fertilization history and soil organic matter content on the emissions of N_2O induced by fertilizer application. These results are in line with the observations from the first incubation experiment that long-term accumulation of OC and N in the analyzed sandy soil did not result in an increased potential for N_2O emissions.

2.5 Conclusions of the First Study

There was no evidence that the long-term application of composted farmyard manure to a sandy soil, which had resulted in increased SOC and total N stocks, promoted emissions of N_2O. The effects of soil moisture or fertilizer application on N_2O emissions did not depend on fertilization history and the related soil C_{org} and N_t stocks. The results indicate that there was no long-term feedback of increased C and N stocks on N_2O emissions from this sandy soil. This was probably due to the stability of the accumulated C and N and the good aeration of the sandy soil.
However, increased N_2O emissions occurred directly following the application of organic N fertilizers, with the highest emissions being induced by the application of biogas waste. Anaerobic and aerobic treatment of plant residues and animal waste resulted in different availabilities of OC and mineral N in the fertilizer produced. This, in turn, affected the potential for N_2O emissions. The results indicate that N_2O emissions from the application of biogas waste can be large and, thus, they have to be considered when determining the net effect of biogas production on mitigating greenhouse gas emissions.

3. Emission Rates of N_2O and CO_2 from Soils with Different Organic Matter Content from Three Long-term Fertilization Experiments – a Laboratory Study

Abstract

Increasing organic matter stocks in soils reduce atmospheric carbon dioxide (CO_2), but they may also promote emissions of nitrous oxide (N_2O) by providing substrate for nitrification and denitrification and by increasing microbial O_2 consumption. The objectives of this study were to determine the effects of fertilization history, which had resulted in different soil organic matter stocks on (i) the emission rates of N_2O and CO_2 at a constant soil moisture content of 60% water-holding capacity, (ii) the short-term fluxes of N_2O and CO_2 following the application of different fertilizers (KNO_3 vs. farmyard manure from cattle) and (iii) the response to a simulated heavy rainfall event, which increased soil moisture to field capacity. Soil samples from different treatments of three long-term fertilization experiments in Germany (Methau, Spröda and Bad Lauchstädt) were incubated in a laboratory experiment with continuous determination of N_2O and CO_2 emissions and a monitoring of soil mineral N. The long-term fertilization treatments included application of mineral N (Methau and Spröda), farmyard manure + mineral N (Methau and Spröda), farmyard manure deposition in excess (Bad Lauchstädt), and nil fertilization (Bad Lauchstädt). Long-term addition of farmyard manure increased the soil organic carbon (SOC) content by 55% at Methau (silt loam), by 17% at Spröda (sandy loam) and by 88% at Bad Lauchstädt (silt loam; extreme treatments which do not represent common agricultural management). Increased soil organic matter stocks induced by long-term application of farmyard manure at Methau and Spröda resulted in slightly increased N_2O emissions at a soil moisture content of 60% water-holding capacity. However, the effect of fertilization history and SOC content on N_2O emissions was small compared to the short-term effects induced by the current fertilizer application. At Bad Lauchstädt, high N_2O emissions from the treatment without fertilization for 25 years indicate the importance of a sustainable soil humus management to maintain soil structure and soil aeration. Emissions of N_2O following the application of nitrate and farmyard manure differed because of their specific effects on soil nitrate availability and microbial oxygen consumption. At a soil moisture content of 60% water-holding capacity, fertilizer-induced

emissions were higher for farmyard manure than for nitrate. At field capacity, nitrate application induced the highest emissions. Our results indicate that feedback mechanisms of soil carbon sequestration on N_2O emissions have to be considered when discussing options to increase soil carbon stocks.

3.1 Introduction of the Second Study

The long-term application of organic fertilizers improves soil quality and can contribute to climate protection by increasing C sequestration in soils (Powlson et al. 1998; Lal 2004; Blair et al. 2006a; Janzen et al. 2006). However, increased contents of organic carbon and total nitrogen (N_t) in arable soils by regular application of organic fertilizers may also promote emissions of N_2O. Thus, from the view of global warming it is crucial to assess the impacts of C sequestration strategies not only for CO_2 but also for the greenhouse gas N_2O (Qiu et al. 2009).

Several authors have reported increased N_2O emissions directly after the application of organic fertilizers (Chang et al. 1998; Petersen 1999; Flessa and Beese 2000; Van Groenigen et al. 2004). In particular, easily available organic matter fractions were found to trigger N_2O emissions since they promote the formation of anoxic microsites in soils (Parkin 1987; Flessa and Beese 1995) and because they provide an easily available substrate for nitrification and denitrification (Velthof et al. 2003; Chang et al. 1998). However, the significance of long-term effects of SOC accumulation in agricultural soils on N_2O emissions is less well understood. The few experimental results on long-term effects of increased organic matter stocks do not provide a consistent picture (Chang et al. 1998; Kilian et al. 1998; De Wever et al. 2002; Meng et al. 2005) even though it is often assumed that increased C sequestration results in increased N_2O emissions. Kilian et al. (1998) reported a promoting effect of C and N enrichment in arable soils on N_2O release, whereas Meng et al. (2005) found that long-term application of manure on a sandy loam did not result in greater N_2O emissions than those observed for the application of mineral fertilizer, despite higher C and N contents in the manured soil. Model results suggest that N_2O emissions probably increase with increasing C sequestration in soils (Li et al. 2005; Qiu et al. 2009). The inconsistent picture with regard to the long-term effects of C

sequestration on N_2O emissions might be partly due to the different experimental conditions and site dependent differences in the extent of organic matter accumulation.
We hypothesize that the long-term application of farmyard manure and the associated increase in SOC and N_t stocks may result in increased N_2O emissions. The objectives of this study were to determine the effects of long-term fertilization of differently textured soils with either mineral fertilizer or farmyard manure, which result in different soil SOC and N_t stocks, on (i) the emission rates of N_2O and CO_2 at a constant soil moisture content of 60% water-holding capacity, (ii) the short-term fluxes of N_2O and CO_2 following the application of different fertilizers (KNO_3 vs. farmyard manure from cattle) and (iii) the response to a simulated heavy rainfall event, which increased soil moisture to field capacity.

3.2 Materials and Methods of the Second Study

3.2.1 Study Site and Soil Sampling

In October 2008, soil samples from the Ap horizon (0 – 25 cm) were collected from three German long-term fertilization experiments in Spröda, Methau and Bad Lauchstädt. Samples were taken twelve months (Bad Lauchstädt) and seven months (Spröda and Methau) after the last fertilizer application at all sites (except for the unfertilized treatment at Bad Lauchstädt).

Spröda long-term experiment

The field experiment at Spröda (51°32` latitude, 12°26` longitude), Saxony, was established in 1966. The annual rainfall is 540 mm and the mean annual temperature is 8.3 °C. The soil is an albic Luvisol (WRB), and the soil texture consists of mainly sand and silt, whereas the clay content in the soil was only small (6%, Table 1). The crop rotation consisted of winter wheat (2005), sugar beet (2006), spring barley (2007) and potato (2008). Straw was removed from the field. Long-term fertilization consisted of 150 kg N ha^{-1} yr^{-1} as calcium ammonium nitrate (Mineral N treatment) and additionally 2100 kg C ha^{-1} and 102 kg N ha^{-1} as cattle farmyard manure every second year (Mineral N & manure treatment, total annual N input: 201 kg N ha^{-1}, Albert and Lippold, 2002).

Methau long-term experiment

The field experiment at Methau (51°04` latitude, 12°51` longitude), Saxony, was also established in 1966. The annual rainfall is 600 mm and the mean annual temperature is 8.0 °C. The soil is gleyic Luvisol (WRB) with silt and clay contents of 80% and 15%, respectively. Crop rotation and long-term fertilization treatments were the same as at Spröda (Albert and Lippold, 2002).

Bad Lauchstädt long-term experiment

The experiment in Bad Lauchstädt (51°24` latitude, 11°53` longitude), Saxony-Anhalt, started in 1983. The annual rainfall is 484 mm and the mean annual temperature is 8.7 °C. The soil is a haplic Chernozem (WRB) with silt and clay contents of 68% and 24%, respectively. The crop rotation consisted of sugar beet (2006), silage maize (2007), potato (2008). The organic fertilized field plots in Bad Lauchstädt were treated with cattle manure in excess (excess manure treatment). The application rate of 100 t manure ha^{-1} yr^{-1} (dry matter content 24.4% with 424 g C_{org} kg^{-1} dry matter, 28.5 g N_t kg^{-1} dry matter calculated as mean over the last four years) greatly exceeded a common fertilization rate. It represents an extreme example of manure deposition. The second treatment at Bad Lauchstädt was not fertilized (control treatment) (Körschens et al., 1998).

3.2.2 Incubation Experiments

Field-moist, sieved (< 6 mm) soil was filled in cylindrical incubation vessels with a height of 10 cm and a diameter of 14.4 cm (volume of 1.65 l). The filling height was 7 cm for all samples. The soils were compacted to bulk densities which were typically observed in the surface horizons of these soils (1.1 g cm^{-3} for the silty samples from Methau and Bad Lauchstädt and 1.4 g cm^{-3} for the sandy soil from Spröda). The corresponding soil dry weight in each incubation vessel was 1.2 kg for the treatments from Methau and Bad Lauchstädt and 1.6 kg for the treatments from Spröda. Soil samples were adjusted to a soil moisture content of 60% water-holding capacity and incubated for 105 days at 12 °C in darkness. The set soil moisture content was controlled gravimetrically and readjusted if necessary. The incubation experiment consisted of thee consecutive periods:

During the first 23 days (period 1) soil samples (8 replicates per treatment) were incubated at a soil moisture content of 60% water-holding capacity to determine N_2O and CO_2 fluxes under well aerated conditions.
After this period, four replicates each were fertilized with KNO_3 (Mineral N treatment) and cattle farmyard manure (Manure treatment), respectively, to determine short-term effects of fertilizer addition. In the mineral N treatment, KNO_3 was applied superficially at a rate of 100 kg N ha^{-1} (165 mg N per vessel) with 15 ml distilled water. The change in mean soil moisture due to fertilizer addition was small (< + 2% gravimetric soil moisture). In the manure treatment, cattle manure was mixed with the upper 2 cm of the soil at the same rate (100 kg N ha^{-1}, 165 mg N and 2440 mg C per vessel). Incubation period 2 started with the application of fertilizer at day 24 and lasted for 28 days until day 51.
The third period (period 3) started at day 52 with the addition of water to determine the effect of a simulated rainfall and the associated increase of soil moisture to field capacity on emission rates of N_2O and CO_2. At day 52, we added water to each soil sample until 100% water-holding capacity was reached. Water was injected into the samples to ensure a homogeneous increase of soil moisture within the samples. The water-holding capacity of the treatments differed as a result of different soil texture and humus content. The adjusted soil moisture during period 3 equalled 75% water-filled pore space (WFPS) at Methau, 50% WFPS in Spröda and 90% WFPS at Bad Lauchstädt.
Overall, twelve different treatments were performed which differed with respect to the sites, the fertilization history and the fertilization in period 2 of the incubation experiment (Tables 6 and 7).

3.2.3 Automated CO_2 and N_2O Flux Measurements

The incubation vessels were sealed with a lid, which had an air inlet port and an air outlet port. The headspace of each incubation vessel was continuously flushed with 10 ml min^{-1} of fresh air. Concentrations of CO_2 and N_2O in the fresh air input, in the exhaust air of each incubation vessel, and in calibration gases were measured automatically every 4 hours during the entire incubation period using an automated gas chromatographic system as described by Flessa and Beese (1995) and Loftfield et al. (1997). Gas flux rates were calculated from the air flow rate through the incubation vessels and the difference in the gas concentration between the input air and the exhaust air.

3.2.4 Soil Analyses

The organic C and the total N contents of all soil samples were determined after drying and grinding by an automated C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany). Soil pH was measured in a 10^{-2} M $CaCl_2$ solution with a soil/solution ratio 1:2.5. The concentrations of extractable NH_4^+ and NO_3^- were measured after extraction with 10^{-2} M $CaCl_2$ solution. The soil/solution ratio during extraction was 1:2. The photometric analysis of mineral N was performed using a continuous flow analyzer (S/A 20/40 Skalar Analytical, Erkelenz, Germany). Soil samples for the extraction of mineral nitrogen were taken four times during the incubation period: on day 0, on day 24 (before fertilizer application), on day 68 (16 days after increasing soil moisture to field capacity) and at day 105 (at the end of the incubation).

The fractionation of water-stable soil aggregates was conducted after the incubation experiment with the four treatments from the site Bad Lauchstädt in order to obtain further insights into the causes for the unexpected emission patterns of these soils (discussed below). The fractionation scheme was modified from the method described by Elliott (1986) in accordance with Helfrich et al. (2008). Briefly, 100 g of dried soil were soaked in distilled water for 10 minutes to allow slaking. The mixture was poured into a 250 µm sieve, which was moved up and down in water by approximately 3 cm 50 times. Aggregates > 250 µm (macroaggregate fraction) were collected and sieving was repeated using a 53 µm sieve. Aggregates (53 – 250 µm; microaggregate fraction) were collected and particles <53 µm were precipitated with 0.5 M $AlCl_3$. All size fractions (macroaggregates: 250 – 2000 µm, microaggregates: 53 – 250 µm, fraction < 53 µm) were oven-dried at 40 °C and weighed.

3.2.5 Statistical Analyses

The Student t-test ($p < 0.05$) was used to test for the differences between the two soils of the same site with different fertilization history with regard to the content of SOC and total nitrogen (N_t). The Mann-Whitney U-test ($p < 0.05$) was employed to test for the differences between mean emission rates of CO_2, N_2O and contents of NO_3^- measured in treatments with different long-term fertilization history and the differences between emissions following the fertilizer application in incubation period 2 because data were not normally distributed.

3.3 Results of the Second Study

3.3.1 Soil Organic Matter and Total Nitrogen

At all sites the different fertilization history resulted in significantly higher SOC and N_t contents in the organic fertilized treatment than in the treatments with long-term mineral N application. This was especially important for the Bad Lauchstädt soil with the excessive manure fertilization (Table 5). Besides the annual quantity of added manure, the soil texture also affected the organic C stocks. The contents of SOC and N_t increased with increasing soil clay content in the order Spröda < Methau < Bad Lauchstädt. The increase in the SOC stocks induced by long-term application of farmyard manure (calculated as difference of the SOC contents of manure and mineral N (Spröda, Methau) or nil fertilization treatments (Bad Lauchstädt)) increased with increasing clay content (Spröda: 1.2 mg kg^{-1}, Methau: 5.4 mg kg^{-1}, Bad Lauchstädt: 18.9 mg kg^{-1}). The same order was found for the effect of fertilization history on total soil nitrogen content (Table 5).

Table 5: Description of soil characteristics (0 – 25 cm) at the three sites with different long-term fertilization histories. For the contents of soil organic carbon (SOC) and N_t, means and standard deviations are shown (n = 4). Values followed by different letters indicate significant differences between two fertilization treatments of the same site (Student t-test: $p < 0.05$).

Site	Long-term fertilization history	SOC mg g^{-1}		SOC g $vessel^{-1}$	N_t mg g^{-1}		pH	Sand %	Silt %	Clay %
Methau	Mineral N	9.9	$(0.7)^a$	11.9	1.02	$(0.1)^a$	6.4	5	80	15
	Mineral N & manure	15.3	$(0.9)^b$	18.4	1.48	$(0.1)^b$	6.4			
Spröda	Mineral N	7.1	$(0.3)^a$	11.4	0.65	$(0.0)^a$	5.6	63	31	6
	Mineral N & manure	8.3	$(0.6)^b$	13.3	0.75	$(0.0)^b$	5.3			
Lauch-städt	Control	21.6	$(1.9)^a$	25.9	1.79	$(0.2)^a$	7.2	8	68	24
	Excess manure	40.5	$(6.4)^b$	48.6	3.52	$(0.1)^b$	7.1			

3.3.2 Emissions of CO_2

The emissions of CO_2 during period 1 (at constant soil moisture of 60% water-holding capacity) were 1.2 to 2.0 times higher for the treatments with long-term application of farmyard manure than those with mineral N or nil fertilization (Table 6, Figure 6). As expected, the excess manure treatment at Bad Lauchstädt exhibited much higher soil respiration rates than all the other treatments. The specific SOC mineralization (CO_2-C emission related to the SOC content) during period 1 decreased with increasing SOC content in the order Spröda > Methau > Bad Lauchstädt. The application of farmyard manure for many years had no clear effect on the calculated specific mineralization rates of SOC (data not shown).

Application of farmyard manure at the beginning of period 2 induced a rapid increase in CO_2 emissions from all soils and emissions remained on a higher level than the soil fertilized with mineral N until the end of the incubation experiment (Fig 6).

We estimated the quantity of the added farmyard manure, which was mineralised during period 2 (29 days), from the difference of the cumulative CO_2 emissions calculated for the treatments with and without farmyard manure addition. This approach assumes that manure application does not change mineralization of SOC (no priming effects). Using this simplified approach, estimated mineralization of the manure (added at the beginning of period 2) during incubation period 2 decreased in the order (site and fertilization history in parentheses) 13.5% (Bad Lauchstädt, excess manure) > 12.6% (Methau, mineral N) > 12.3% (Methau, mineral N & manure) > 11.4% (Spröda, mineral N) > 8.2% (Bad Lauchstädt, control) > 5.6% (Spröda, mineral N & manure). Thus, a long-term history of organic fertilization had no clear effect on the mineralization of farmyard manure in these soils. CO_2 emissions of the treatments which received no manure during the experiment were generally lowest during period 3 when soil moisture was increased to field capacity (Table 6).

In addition to the general dynamics of CO_2 emission rates during period 1 to 3, there were distinct short-term fluctuations of CO_2 emissions in each period. These fluctuations were due to the addition of small quantity of water to readjust soil moisture.

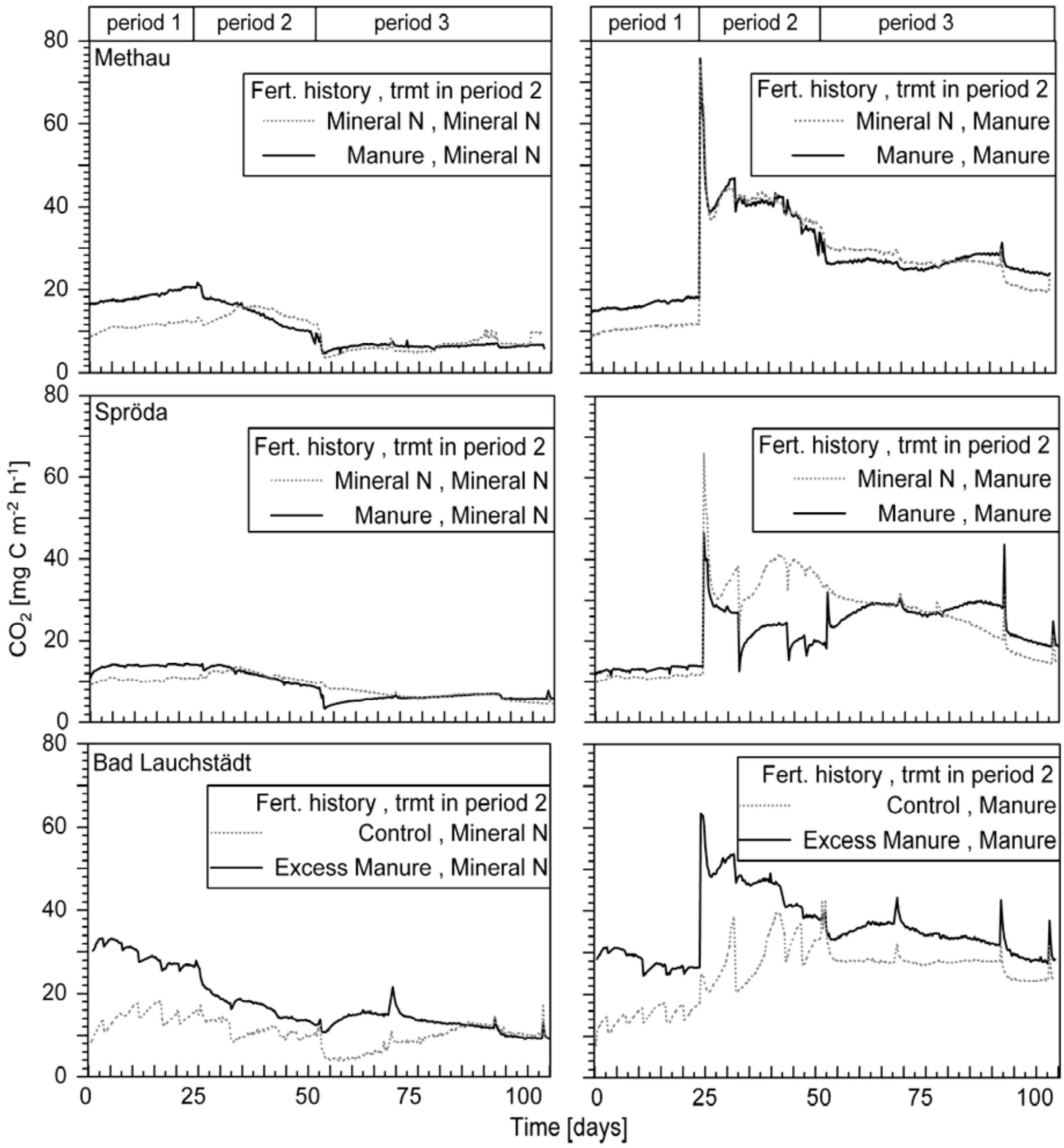

Figure 6: Mean emission rates of CO_2 from the three soils (Methau, Spröda, Bad Lauchstädt) each with different fertilization history (Fert. history: Manure/Excess Manure or mineral fertilizers/no fertilizer (Control)) at constant soil moisture of 60% water holding capacity (period1), following the application of KNO_3 (Mineral N) and farmyard manure (Manure) (treatment in period 2), and after increasing soil moisture to field capacity (period 3).

Table 6: Emissions of CO_2 (means and standard deviation in parentheses, n = 8 for period 1 and n = 4 for the other periods) from soils with different fertilization history during the incubation in the three consecutive periods*. Different lowercase letters indicate significant differences between the long-term fertilization treatments and different capital letters indicate significant differences between the fertilization treatments at the beginning of period 2 (Man-Whitney U-test, $p < 0.05$).

Site	Long-term fertilization history	Period 1 CO_2 emission rate mg C $m^{-2}h^{-1}$		Treatment in incubation period 2	Period 2 CO_2 emission rate mg C $m^{-2}h^{-1}$		Period 3 CO_2 emission rate mg C $m^{-2}h^{-1}$		Cumulative CO_2 emission g C m^{-2}	
Methau	Mineral N	11.1	$(1.0)^{a}$	Mineral N	14.0	$(1.9)^{aA}$	6.3	$(2.3)^{aA}$	23.4	$(3.8)^{aA}$
				Manure	41.2	$(4.2)^{aB}$	26.5	$(1.9)^{aB}$	66.3	$(4.8)^{aB}$
	Mineral N & manure	17.5	$(2.4)^{b}$	Mineral N	14.3	$(4.1)^{aA}$	6.4	$(2.8)^{aA}$	27.7	$(7.8)^{aA}$
				Manure	40.8	$(3.6)^{aA}$	26.6	$(1.5)^{aB}$	69.2	$(4.2)^{aB}$
Spröda	Mineral N	10.8	$(0.8)^{a}$	Mineral N	11.6	$(1.6)^{aA}$	6.8	$(1.0)^{aA}$	21.9	$(1.6)^{aA}$
				Manure	36.2	$(1.7)^{aB}$	25.0	$(1.1)^{aB}$	61.2	$(4.3)^{aB}$
	Mineral N & manure	13.4	$(1.1)^{b}$	Mineral N	11.4	$(1.0)^{aA}$	6.0	$(1.1)^{aA}$	22.7	$(2.2)^{aA}$
				Manure	23.5	$(4.7)^{bB}$	26.3	$(1.5)^{bB}$	55.3	$(5.2)^{aB}$
Bad Lauch-städt	Control	14.3	$(1.6)^{a}$	Mineral N	11.5	$(1.1)^{aA}$	9.0	$(1.2)^{aA}$	26.3	$(2.1)^{aA}$
				Manure	29.2	$(2.6)^{aB}$	27.3	$(3.2)^{aB}$	61.2	$(4.3)^{aB}$
	Excess manure	28.5	$(2.6)^{b}$	Mineral N	17.3	$(3.1)^{bA}$	13.0	$(1.5)^{bA}$	43.8	$(5.5)^{bA}$
				Manure	46.3	$(4.3)^{bB}$	33.8	$(1.0)^{bB}$	88.2	$(2.7)^{bB}$

*Period 1 (constant soil moisture content of 60% water-holding capacity) lasted for 23 days, period 2 (application of mineral N or farmyard manure) for 29 days and period 3 (simulated heavy rainfall) for 53 days.

3.3.3 Emissions of N_2O and Soil Mineral Nitrogen

N_2O emissions during period 1 (at constant soil moisture content of 60% water-holding capacity) were higher for treatments with long-term application of farmyard manure than mineral fertilizer at the sites Methau and Spröda (Table 7). At Methau, a 1.5 times higher SOC content in the mineral N & manure treatment was associated with a 2.5 times higher N_2O emission rate compared to the mineral N treatment. At Spröda, N_2O emission rates during period 1 were 9.0 times higher for mineral N & manure treatment than the mineral N treatment. However, the results from Bad Lauchstädt did not agree with the hypothesis that N_2O emissions increase with increasing content of SOC and N_t in soil. Surprisingly, the excess manure treatment showed a 2.3 times lower emission rate of N_2O during period 1 than the unfertilized treatment, which contained much less SOC and total N (Tables 5 and 7). The soil without fertilizer application for 25 years showed higher N_2O emission rates during period 1 than all the other soils, which were analyzed in our experiment.

The application of farmyard manure at the beginning of period 2 resulted in increased N_2O emission rates from all three soils (Figure 7). The emissions which were induced by manure application were considerably higher than those occurring after the application of mineral fertilizer for three of the four treatments of the sites Methau and Spröda (Table 7, Figure 7). At Spröda, emissions from soil with the fertilization history of mineral N & manure were higher than from the soil with the mineral N fertilization history when mineral N was applied in period 2 (Table 7).

The Bad Lauchstädt soils showed results which were very different from the Spröda and Methau soils: the unfertilized treatment had the highest N_2O emission rates after application of mineral N in period 2 (Figure 7) and these emissions were much higher than those measured from all other soils and treatments. The extreme treatments at the Bad Lauchstädt site (nil fertilization and excess manure treatments) showed differences following application of KNO_3. Emission rates of N_2O from the nil fertilization treatment in period 2 were 7 times higher than from the treatment with the excess manure history (Table 7, Figure 7).

Table 7: Emissions of N_2O (means and standard deviation in parentheses, n = 8 for period 1 and n = 4 for the other periods) from soils with different fertilization history during the incubation in the three consecutive periods*. Different lowercase letters indicate significant differences between the long-term fertilization treatments and different capital letters indicate significant differences between the fertilization treatments at the beginning of period 2 (Man-Whitney U-test, $p < 0.05$).

Site	Long-term fertilization history	Period 1 N_2O emission rate $\mu g\ N\ m^{-2}h^{-1}$		Treatment in incubation period 2	Period 2 N_2O emission rate $\mu g\ N\ m^{-2}h^{-1}$		Period 3 N_2O emission rate $\mu g\ N\ m^{-2}h^{-1}$		Cumulative N_2O emission $mg\ N\ m^{-2}$	
Methau	Mineral N	0.6	$(0.4)^{a}$	Mineral N	1.8	$(0.8)^{aA}$	90.1	$(25.9)^{aA}$	114.7	$(33.9)^{aA}$
				Manure	9.6	$(3.6)^{aB}$	6.0	$(5.0)^{aB}$	13.8	$(3.8)^{aB}$
	Mineral N & manure	1.5	$(0.9)^{b}$	Mineral N	1.6	$(1.0)^{aA}$	41.2	$(9.4)^{bA}$	51.6	$(12.0)^{bA}$
				Manure	8.5	$(0.2)^{aB}$	14.7	$(7.5)^{aB}$	22.5	$(6.3)^{aB}$
Spröda	Mineral N	0.3	$(0.2)^{a}$	Mineral N	1.0	$(1.0)^{aA}$	29.2	$(29.3)^{aA}$	36.5	$(35.9)^{aA}$
				Manure	15.3	$(1.6)^{aB}$	0.5	$(0.2)^{aB}$	10.6	$(0.7)^{aA}$
	Mineral N & manure	2.7	$(1.3)^{b}$	Mineral N	16.0	$(12.1)^{bA}$	83.5	$(25.5)^{aA}$	115.7	$(41.0)^{aA}$
				Manure	16.2	$(8.0)^{aA}$	6.4	$(6.5)^{bB}$	19.5	$(12.4)^{bA}$
Bad Lauch-städt	Control	34.6	$(17.3)^{a}$	Mineral N	211.2	$(49.1)^{aA}$	65.1	$(25.5)^{aA}$	240.4	$(63.5)^{aA}$
				Manure	30.5	$(23.4)^{aB}$	0.8	$(0.4)^{aB}$	34.3	$(23.2)^{aB}$
	Excess manure	15.0	$(7.8)^{b}$	Mineral N	8.2	$(3.6)^{bA}$	25.3	$(10.3)^{bA}$	43.7	$(17.7)^{bA}$
				Manure	15.9	$(1.3)^{aB}$	13.5	$(2.5)^{bA}$	30.8	$(2.2)^{aA}$

*Period 1 (constant soil moisture content of 60% water-holding capacity) lasted for 23 days,
period 2 (application of mineral N or farmyard manure) for 29 days and
period 3 (simulated heavy rainfall) for 53 days

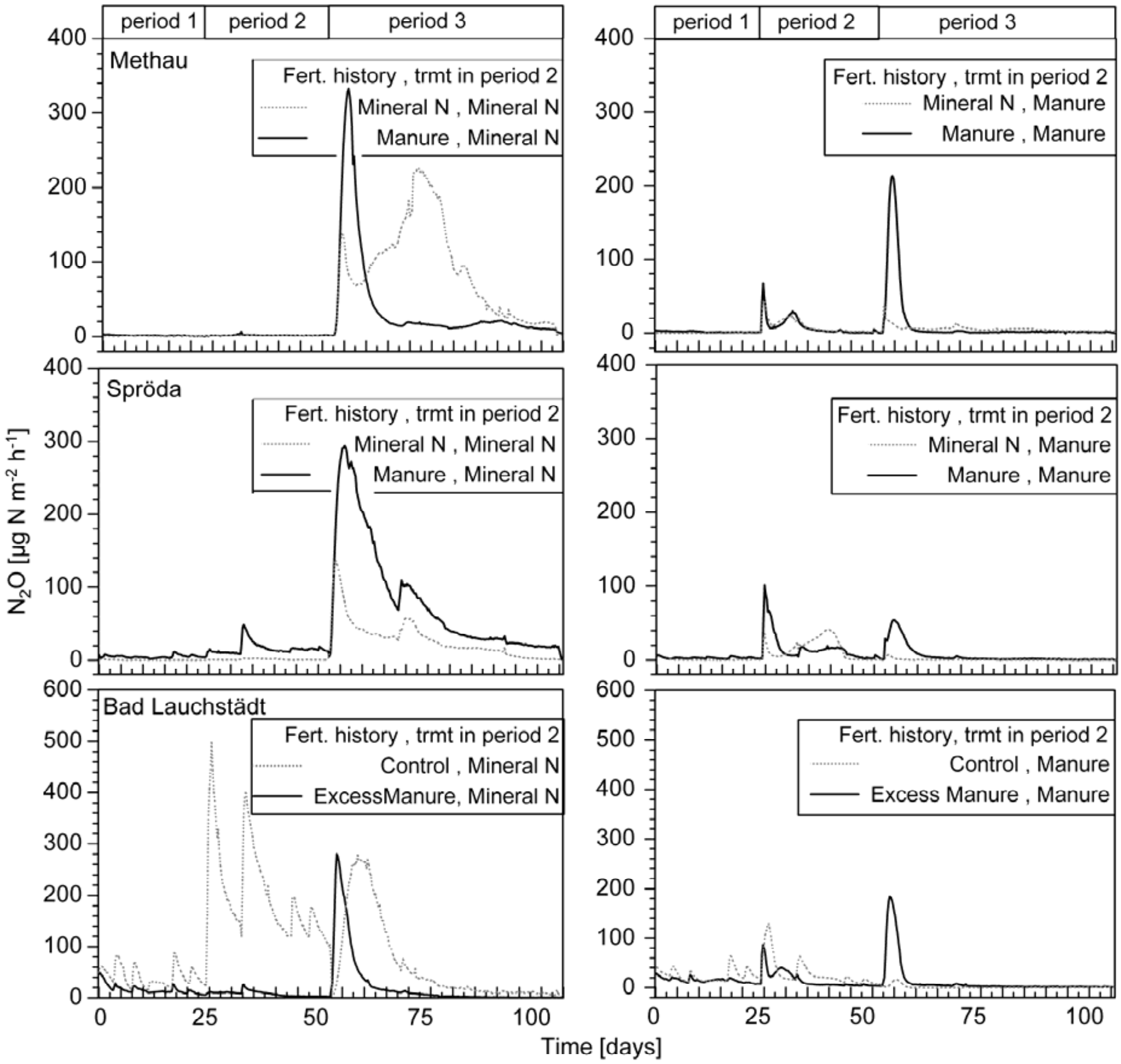

Figure 7: Mean emission rates of N_2O from the three soils (Methau, Spröda, Bad Lauchstädt) each with different fertilization history (Fert. history: Manure/Excess Manure or mineral fertilizers/no fertilizer (Control)) at constant soil moisture of 60% water holding capacity (period1), following the application of KNO_3 (Mineral N) and farmyard manure (Manure) (treatment in period 2), and after increasing soil moisture to field capacity (period 3).

The increase in soil moisture to field capacity at the beginning of period 3 stimulated N_2O emissions at all treatments (Figure 7), and the increase in N_2O emissions after the simulated heavy rainfall event was higher and prolonged for those treatments which were fertilized with mineral N at the beginning of period 2 than for those amended with farmyard manure: N_2O emissions rates (µg N m^{-2} h^{-1}) in period 3 decreased in the order (site, fertilization history and fertilization at the beginning of incubation period 2 in parentheses) 90.1 (Methau, mineral N, mineral N) > 83.5 (Spröda, manure, mineral N) >

65.1 (Bad Lauchstädt, control, mineral N) > 41.2 (Methau, manure, mineral N) > 29.2 (Spröda, mineral N, mineral N) > 25.3 (Bad Lauchstädt, excess manure, mineral N, Table 7). In contrast, the other treatments with manure application at the beginning of incubation period 2 exhibited N_2O emission rates in a range of 0.5 to 14.7 µg N m^{-2} h^{-1} in period 3 (Table 7).

The initial contents of nitrate in the studied soils were similar with the exception of the Bad Lauchstädt soil with long-term application of excess manure (Figure 8). In all soils, ammonium contents were always lower than 0.01 mg NH_4^+-N kg^{-1} (data not shown). Nitrate contents in the incubation periods 2 and 3 depended largely on the fertilization performed at the beginning of period 2. The availability of soil nitrate was increased in treatments with KNO_3 addition, whereas it slightly decreased after application of farmyard manure (Figure 8).

Table 8: Water-stable aggregate size fractions of differently fertilized soils from the site Bad Lauchstädt (n = 4 ± standard deviation). Different letters indicate significant differences between the long-term fertilizer treatments Control and Excess Manure (Man-Whitney U-test, $p < 0.05$).

Long-term fertilization history	Treatment in incubation period 2	Aggregate size							
		> 2000 µm		> 250 µm		> 53 µm		< 53 µm	
		%		%		%		%	
Control	Mineral N	0.25	$(0.20)^a$	5.88	$(1.93)^a$	64.62	$(2.47)^a$	26.95	$(4.05)^a$
	Manure	0.67	$(0.27)^a$	9.24	$(0.69)^a$	62.89	$(1.72)^a$	26.50	$(1.93)^a$
Excess manure	Mineral N	0.55	$(0.18)^b$	10.68	$(1.54)^b$	61.27	$(3.02)^a$	24.95	$(2.67)^a$
	Manure	1.52	$(0.38)^b$	13.07	$(2.48)^b$	61.17	$(2.21)^a$	21.01	$(3.26)^a$

3.3.4 Soil Aggregate Stability of the Treatments from Bad Lauchstädt

The two treatments at the Bad Lauchstädt site largely differed in soil structure. This difference was obvious by visual observation because the long-term deposition of manure (excess manure) led to a friable soil structure, whereas the treatments without any fertilization exhibited a sticky structure. To detect these differences and to elucidate the unexpected observation that long-term deposition of manure (excess manure) resulted in lower emissions of N_2O than the unfertilized soil, the distribution of water-stable aggregate fractions (Table 8) was determined for the treatments of the Bad Lauchstädt site. The proportion of megaaggregates (> 2000 µm) and macroaggregates (2000 – 250 µm) were significantly lower in the unfertilized soil than in the treatment that received excess manure. No significant differences between the treatments were found for the fractions < 250 µm, which made up 82% to 90% of the total soil mass.

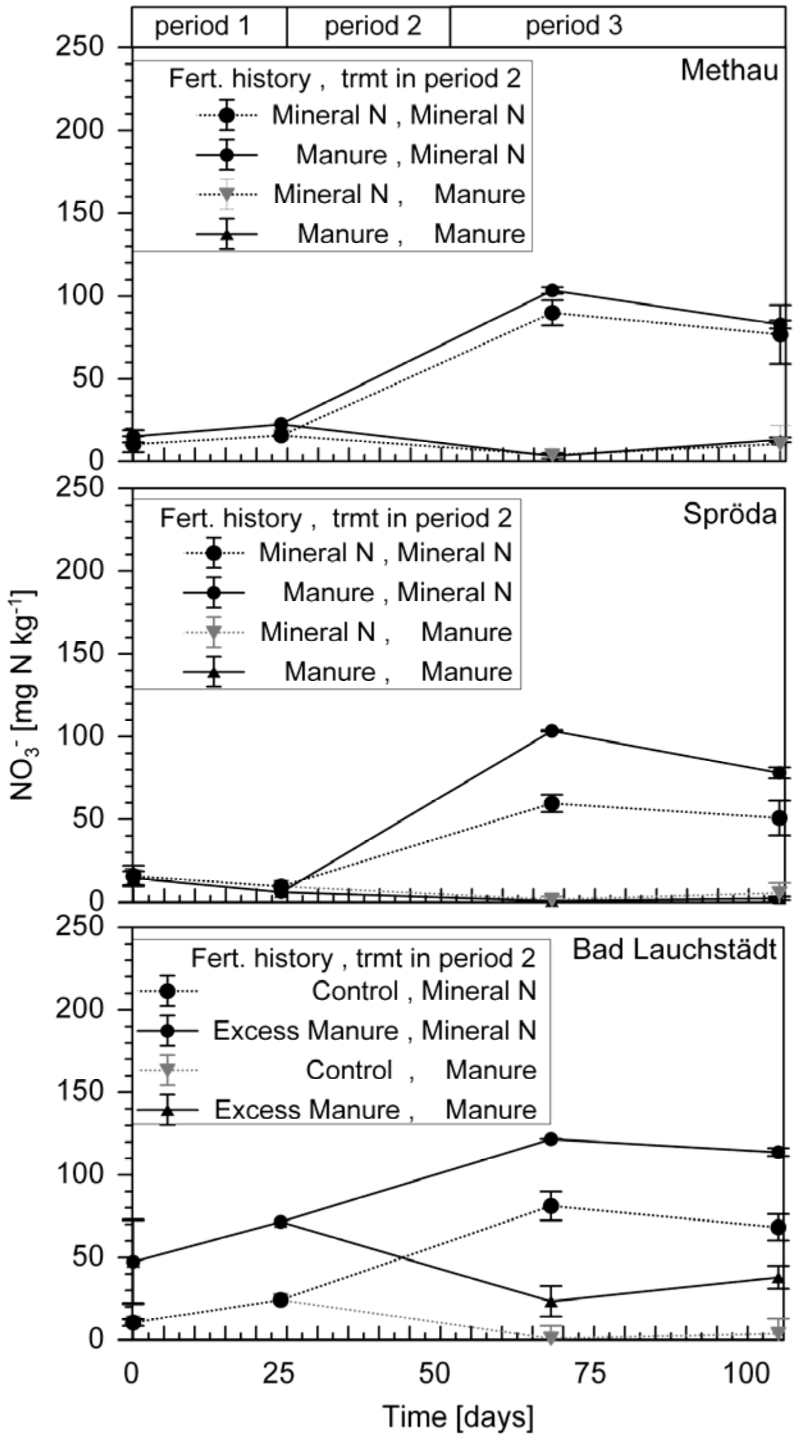

Figure 8: Nitrate contents (means ± standard deviation) measured in the three soils (Methau, Spröda, Bad Lauchstädt) each with different fertilization history (Fert. history: Manure/Excess Manure or mineral fertilizers/no fertilizer (Control)) at constant soil moisture of 60% water holding capacity (period 1), following the application of KNO_3 (Mineral N) and farmyard manure (Manure) (treatment in period 2), and after increasing soil moisture to field capacity (period 3).

3.4 Discussion of the Second Study

3.4.1 Soil Organic Matter and Total Nitrogen

Our data indicate that annual carbon inputs as manure as well as the clay contents of the soils are important determinants for C sequestration. For all three sites studied, the last fertilization had been performed a year (Bad Lauchstädt) and seven months (Methau, Spröda) before sampling. Thus, observed differences are not due to short-term management effects, but are the result of the fertilization history. The increase in the SOC stocks in the treatments with application of farmyard manure reflects the potential of regular manure application for C sequestration and confirms the results of other long-term fertilization experiments (Edmeades, 2003; Freibauer et al., 2004; Powlson et al., 1998).

The comparison of the increase in SOC stocks as a result of long-term manure application between Spröda (1.2 mg kg^{-1}, clay content: 6%) and Methau (5.4 mg kg^{-1}, clay content: 15%) shows the importance of the fine soil particles for the increased C stabilization, as emphasized by Hassink (1997), Weigel et al. (1997) and Albert and Lippold (2002). Our finding is also in line with the conceptional model proposed by von Lützow et al. (2007), which considers organo-mineral associations as an important pool for C stabilization and also with the Rothamsted Carbon Model, which calculates a decreasing fraction of CO_2 produced to C sequestered in the pools microbial biomass and humified organic matter with increasing clay contents (Coleman and Jenkinson, 1999). However, the site conditions in our study do not allow a detailed quantitative analysis because the two long-term experiments (which had the same crop rotations and manure applications) differed not only in the textures of the soils, but also slightly in the annual precipitation (540 mm at Spröda, 600 mm at Methau) and soil types (albic and gleyic Luvisols).

3.4.2 Emissions of CO_2

In our study, long-term fertilization with manure resulted in a 1.6 to 2.0-fold increase of CO_2 emission rates during period 1 of the incubation (soil moisture content at 60% of the water-holding capacity). Increased emission rates of the manure-amended soils were expected because of the added organic materials. For instance, for long-term trials at Bad Lauchstädt and Darmstadt Ludwig et al. (2010) reported that the manure carbon was mainly sequestered in the soils in an intermediate (turnover time estimated to be in the range of 10 to 100 years) pool and to a smaller extent in a labile pool (turnover time estimated as < 10 years), which are responsible for the increased CO_2 emissions. However, besides the manure additions, mineral fertilizations (due to increased plant growth) or straw applications also contribute to the soil respiration as demonstrated by Vanotti et al. (1997) and Jacinthe et al. (2002) in field experiments with different rates of mineral fertilizer or straw applications.

The specific mineralization (CO_2-C emission related to the SOC content) reflects the mean bioavailability of the soil organic matter. We observed a decrease in the specific mineralization with increasing clay content and SOC stock (Spröda > Methau > Bad Lauchstädt), which can be explained by the high capacity of the clay fraction for the stabilization of organic carbon (Baldock et al., 1997; Christensen, 2001; von Lützow et al., 2007). Clay-sized particles provide a large surface area where soil organic matter can be sorbed by strong ligand exchange and polyvalent cation bridges (Sposito et al., 1999).

The long-term application of different fertilizers (mineral fertilizer versus farmyard manure) affected the mineralization rate as discussed above, but had no definite effect on the specific mineralization rate. This absence of this effect suggests that the long-term partitioning of C inputs to labile SOC pools was similar in both fertilization treatments. However, since the last fertilization was performed a year (Bad Lauchstädt) or seven months (Spröda, Methau) before the sampling, the turnover of any very labile compounds in the manure was probably no longer detectable.

In our study the application of manure at the beginning of incubation period 2 resulted in a pronounced increase of CO_2 emission rates for all soils treated with manure, whereas mineral N fertilization did not affect CO_2 emissions markedly. Similar dynamics of CO_2 emissions following application of farmyard manure and other organic fertilizers (e.g. slurry) have been described in several studies (e.g. Merino et al., 2004; Sänger et al., 2010). Moreover, it was shown that the high respiratory O_2 consumption during mineralization of the added substrate favours the formation of anoxic microsites and promotes the emissions of N_2O if nitrate is available (Flessa and Beese, 1995, 2000).

In incubation period 3, in which a heavy rainfall was simulated, CO_2 emission rates decreased in all treatments. Similarly, for incubation experiments with different irrigation patterns Sänger et al. (2010) reported that CO_2 emissions were negatively correlated with WFPS. Linn and Doran (1984) explained decreasing mineralization rates at high water saturation as limitation of O_2 diffusion through pore spaces and consequently limited microbial respiration.

3.4.3 Emissions of N_2O and Soil Mineral Nitrogen

The results from the Methau and Spröda sites support our hypothesis that long-term application of farmyard manure and the associated increase in SOC and N_t stocks promote emissions of N_2O. The results are in agreement with observations by Kilian et al. (1998) and by Chang et al. (1998) that repeated application of organic fertilizers resulted in increased SOC contents and increased losses of N_2O. Several factors can contribute to enhanced emissions from arable soils with increased SOC stocks. The higher availability of organic carbon and nitrogen and the greater microbial biomass promote the processes of N_2O formation (Granli and Bøckman, 1994; Chang et al., 1998; Lal, 2004). Furthermore, an increased microbial respiration, as was found in our study, can favour N_2O production due to its effect on soil aeration (Flessa and Beese, 1995; Clemens and Huschka, 2001; Smith et al., 2003; Russow et al., 2008). However, these findings should not be generalized because there are other studies which did not detect significant changes of N_2O emission as a result of organic matter accumulation in arable soils. For a sandy loam soil Meng et al. (2005) found that long-term application of manure did not result in greater N_2O emissions than the mineral fertilized treatment, despite higher C and N contents in the manured soil. Recently, Jäger et al. (2010) analyzed N_2O emissions from a sandy soil which had been fertilized with composted farmyard manure or mineral N for 27 years. The increase of the SOC content by 26% induced by the long-term application of farmyard manure did not lead to a significant change of N_2O emissions under laboratory conditions. The lack of an unambiguous effect of SOC and N_t accumulation on N_2O emissions was explained by the generally well aerated conditions in the sandy soil and by the stability of the accumulated soil organic matter. In addition, the net effect of long-term application of organic fertilizers on N_2O emissions may also be influenced by changes in soil physical properties. An increase of soil porosity and aggregate stability, which is often observed in treatments with application farmyard manure (Blair et al., 2006a, Schjønning et al., 2007, Bronick and Lal, 2005), can improve soil structure and soil aeration. This might even result in a decrease in N_2O emissions.

Such a positive effect of organic matter input on soil structure may have contributed to the surprising results of the two extreme treatments of the long-term experiment at Bad Lauchstädt, which do not represent usual agricultural management (without fertilization for 25 years and farmyard manure deposition in excess). Twenty-five years without fertilizer application resulted in a lower yield of water-stable macroaggreagtes compared with the intensely manured soil. The poor soil structure may have decreased soil aeration and increased N_2O losses from the long-term unfertilized soil. Russow et al. (2008) determined N_2O emissions from nearby field plots with common fertilization rates but slightly different SOC contents (18 and 22 mg kg^{-1} soil) which were a result of liquid manure fertilization at the site with enriched SOC. Emission rates in this field experiment reported by Russow et al. (2008) were much lower than those observed for the nil treatment of Bad Lauchstädt in our study but the results agree with our findings for the treatments from Spröda and Methau where N_2O emissions were higher from soils with increased SOC contents. Furthermore, the results reported by Russow et al. (2008) suggest that increased SOC contents may also affect N_2O emissions following fertilizer application. They reported that emissions following nitrate application were higher for the treatment with higher SOC content and they identified denitrification as the main N_2O producing process. The results suggest that the unexpected high N_2O emissions from our control treatment of Bad Lauchstädt are exceptional for this site and that these emissions are probably a result of changes in soil structure, which were caused by strong nutrient depletion and changes in SOC pools caused by 25 years without fertilization.

Nitrate application at the beginning of period 2 did not induce high N_2O emissions. This indicates that N_2O production was not restricted by nitrate availability, and it suggests that denitrification was restricted because of an adequate aeration of the soils at a soil moisture content of 60% water-holding capacity. However, there was one exception. Adding nitrate to the nil treatment of the Bad Lauchstädt site induced large and persistent N_2O emissions. This supports our assumption that soil structure and soil aeration were affected by the management without fertilization for 25 years. The emissions from the excess manure treatment at Bad Lauchstädt after nitrate application were much lower, even though the higher SOC content and the high nitrate availability provided more favourable conditions for N_2O production via denitrification. A nearly complete reduction of N_2O to N_2 in this treatment, which could explain the low N_2O emissions, seems to be unlikely because of the persistent high nitrate availability and the relatively low soil moisture content of 60%

water-holding capacity (Weier et al. 1993; Swerts et al., 1996; Ruser et al., 2006). The results suggest that soil structure may be an underestimated control of N_2O emissions.

Overall, our results on N_2O emissions following the application of different fertilizer types (KNO_3 versus farmyard manure application at Spröda and Methau) show that the response of fertilizer-induced N_2O emissions to changes of soil moisture depends on the fertilizer type. Emissions were higher following application of farmyard manure than KNO_3 at a soil moisture content of 60% water-holding capacity whereas increasing soil moisture to field capacity led to highest emissions from the treatments with nitrate application. The results can be explained by fertilizer-induced differences in nitrate availability and microbial oxygen consumption. At high soil moisture, N_2O emissions were strongly restricted by nitrate availability, and thus nitrate application resulted in highest emissions. At 60% water-holding capacity, oxygen availability appeared to be the most important factor limiting N_2O emissions. The local increase in carbon availability by the addition of farmyard manure triggered denitrification primarily because of the microbial O_2 consumption, which can result in the formation of anaerobic microenvironments (Flessa and Beese, 1995; Clemens and Huschka, 2001).

The simulation of heavy rain (increasing soil moisture to field capacity) increased N_2O emissions for all treatments indicating that rainfall distribution after N fertilization influences fertilizer-related N_2O emissions. The importance of soil moisture in fertilizer-induced N_2O emissions was also stressed by Dobbie et al. (1999), who found a strong positive correlation between the amount of rainfall during the first 4 weeks after N application and the cumulative N_2O emission in field measurements. Our results suggest that such rainfall-driven emissions following fertilization are probably higher for nitrate than farmyard manure addition.

3.5 Conclusions of the Second Study

We found significantly increased N_2O emissions from arable soils with increased SOC and N_t stocks which were a result of the regular application of farmyard manure for many years. However, the effect of fertilization history and SOC content was small if compared to the short-term effects induced by the current fertilizer application. High N_2O emissions from the treatment without fertilization for 25 years indicate the importance of a sustainable humus and nutrient management for soil structure and N_2O emissions. Thus, increasing SOC stocks in arable soils can probably promote or lower N_2O emission, depending on the initial soil conditions and SOC stocks. Increasing SOC stocks by organic fertilizers involves the addition of nitrogen, which can induce high N_2O emissions. Application rates beyond the crop N demand have to be avoided even if they increase SOC stocks.

Emissions of N_2O following the application of nitrate and farmyard manure differed. At a soil moisture content of 60% water-holding capacity, fertilizer-induced emissions were higher for farmyard manure than nitrate. At field capacity, nitrate application induced the highest emissions. Our results are based on a laboratory incubation study under controlled conditions and without plants, which makes it easier to identify significant effects of different fertilization (fertilization history and current fertilizer application) on N_2O emissions. It is still a challenge to determine whether these effects are significant under field condition where spatial and temporal variability of N_2O emissions are much higher.

4. Effects of Different Long-term Fertilization Treatments on Soil Organic Matter Stocks, N_2O Emissions and CH_4 Uptake of a Sandy Soil

Abstract

Only limited information is available for sandy soils on the combined long-term effect of fertilizer type and rate on soil organic matter stocks, N_2O emissions and CH_4 uptake. Objectives were to study the effects of long-term fertilization at different rates on N_2O emissions and CH_4 uptake and to relate the N_2O emissions to other observations of N_2O emissions from European croplands using a fuzzy logic model. A long-term experiment near Darmstadt, Germany, with organic versus mineral fertilization, was established in 1980 incorporationg six treatments: straw incorporation plus application of mineral fertilizer (MIN) and application of farmyard manure (FYM) each at high (140 – 150 kg N ha^{-1} $year^{-1}$), medium (100 kg N ha^{-1} $year^{-1}$) and low (50 – 60 kg N ha^{-1} $year^{-1}$) rates. SOM stocks and N_2O emissions and CH_4 uptake were measured weekly between 2007 and 2009. After 27 years, organic carbon and total nitrogen stocks were higher on the organic fertilized treatments than on the mineral fertilized treatments. However, N_2O emissions and CH_4 uptake rates were not higher in the organic fertilized treatment than in the mineral fertilized treatment. Additionally, increased SOC stocks did not interact with management practices or climatic factors in relation to N_2O emission and CH_4 uptake. The N_2O emissions were generally very low on this sandy and well aerated soil. Short-term events like fertilization or tillage were the main controlling factors for the increased N_2O emissions. The straw incorporation combined with tillage, which only took place on the mineral fertilized treatments, increased the risk of N_2O emissions. Increasing fertilization rates did not result in consistent changes of N_2O emissions or CH_4 uptake. In a fuzzy-logic modelling approach, N_2O measurements were related to other observations of N_2O emissions on European croplands.

4.1 Introduction of the Third Study

Agricultural land use strongly affects the net-emissions of the greenhouse gases carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) from soils (IPCC, 2007; Bouwman et al., 2002; Le Mer and Roger, 2001; Snyder et al., 2009). The cultivation of upland soils is generally associated with a loss of soil organic carbon (Lal, 2004; Manlay et al., 2006), the increase of N_2O emissions (Stehfest and Bouwman, 2006; Mosier et al., 1998) and a decrease in the soil uptake of atmospheric CH_4 (Smith et al., 2000; Powlson et al., 1997). Different fertilization strategies can have a pronounced effect on the net-exchange of CO_2, N_2O and CH_4 between arable soils and the atmosphere. Thus, from the point of global warming, it is crucial to assess the impact of fertilization on the exchange of all three greenhouse gases.

Fertilizer application can affect soil organic carbon stocks (SOC) through its influence on the amount and quality of organic matter inputs (e.g. biomass production and related inputs of crop residues, addition of different organic fertilizers) as well as by its influence on mineralization processes (e.g. by changing nutrient availability and soil physical and chemical properties). Long-term experiments indicate that a sustainable fertilization management not only enables high crop yields but also contributes to soil carbon storage by its effect on the amount of crop residues (Körschens et al., 1998; Albert, 2001; Edmeades, 2003; Powlson et al., 1998). In addition, long-term application of organic fertilizers improves soil quality and can contribute to climate protection by increasing carbon sequestration in soils (Powlson et al., 1998; Lal, 2004; Blair et al., 2006a; Janzen et al., 2006).

However, increased contents of organic carbon and total nitrogen in arable soils by regular application of organic fertilizers may also promote the emissions of nitrous oxide. In particular, the increase of readily available organic matter fractions were found to trigger N_2O emissions because they can promote the formation of anoxic microsites in soils through higher microbial activity (Parkin, 1987; Flessa and Beese, 1995) and because they can provide substrates for nitrification and denitrification (Velthof et al., 2003; Chang et al., 1998). It is well-established that the N fertilization rate is a main control of the annual N_2O emission at most sites (Stehfest and Bowman, 2006; Snyder et al., 2009; IPCC, 2007). However, it is not clear how long-term fertilization strategies (e.g. fertilization rate and fertilizer type), which may change stocks and availability of organic matter in soils, affect

N_2O emissions. Model results suggest that N_2O emissions increase with increasing C sequestration in soils (Li et al., 2005; Qiu et al., 2009). However, the few experimental results on long-term effects of increased SOC stocks do not provide a consistent picture. Chang et al. (1998) and Kilian et al. (1998) reported higher N_2O emissions from sites where long-term organic fertilizer application had resulted in increased SOC stocks. This is in contrast to Meng et al. (2005), who found that long-term application of manure on a sandy loam soil did not result in greater N_2O emissions as compared to the application of mineral fertilizer, despite higher C and N contents in the manured soil.

The uptake of atmospheric CH_4 is considerably lower in cultivated soils than in forest soils (Smith et al., 2000) because soil management and fertilization can affect atmospheric CH_4 uptake by several factors. Soil CH_4 uptake can be restricted by reduced gas diffusivity, e.g. through soil compaction, in the upper soil layers (Hansen et al., 1993; Ruser et al., 1998) which controls diffusion of atmospheric CH_4 to the methanotrophic bacteria. Then, it can be inhibited by increased availability and turnover of ammonium (NH_4^+) due to competition of CH_4 with NH_4^+ for methane oxidizing enzymes (Schnell and King, 1994, Powlson et al., 1997). Furthermore, it can be reduced by changing soil microbial population structures (Priemé et al., 1997). Results from long-term fertilization experiments in England and Germany indicated that soil uptake of atmospheric CH_4 was greater for the unfertilized treatments than for treatments receiving mineral N fertilizer (Hütsch et al., 1993; Hütsch, 1996; Powlson et al., 1997). In addition, it was reported that atmospheric CH_4 uptake activity by soils can be reduced not only by application of mineral N fertilizer, but also by organic fertilizers (Hütsch, 1996; Bodelier et al., 2004). The results suggest that the fertilization strategy (e.g. amount and type of N fertilizer applied) may influence soil CH_4 uptake in particular by its effects on N availability and soil structure.

In this study we present results from a two-years field experiment on net-exchange of N_2O and CH_4 on soils of six different long-term fertilization treatments (2 fertilizer types (farmyard manure and calcium ammonium nitrate), 3 fertilization rates), which had been established 30 years ago on a sandy soil. We hypothesize that N_2O emissions increase with fertilization rate for both fertilizer types and that treatments with higher SOC stocks show higher N_2O emissions (comparing the same N application rate). In addition, we expect that soil uptake of atmospheric CH_4 decreases with increasing fertilization rate and that it is not affected by the fertilizer type. The objectives of our study were to determine the effects of different long-term fertilization with either farmyard manure or mineral N applied at three different rates on; a) stocks of SOC and N_t in the Ap horizon, b) emissions of N_2O and on

c) uptake rates of atmospheric CH_4. In addition, we aimed to model and relate N_2O emissions from all treatments to emissions observed from other European croplands using a fuzzy logic model.

4.2 Materials and Methods of the Third Study

4.2.1 Study Site

A field study was conducted on the long-term fertilization experiment of the IBDF (Institute for Biodynamic Research) in Darmstadt (49° 50’ N, 8° 34’ E), Germany. The mean annual temperature was 11.1 °C in 2007 and 10.6 °C in 2008 and the annual precipitation was 713 mm in 2007 and 558 mm in 2008. The soil was a sandy Cambisol (WRB) composed of 86% sand, 9% silt and 5% clay in the Ap horizon (Table 2).

In 1985, the following long-term fertilization treatments were started:

(i) MIN-140: high application rate of mineral fertilizer (150 kg N ha^{-1} to root crops or 100 kg N ha^{-1} plus 40 kg N ha^{-1} as second application to cereals) plus straw incorporation.

(ii) MIN-100: medium application rate of mineral fertilizer (100 kg N ha^{-1} to root crops or 80 kg N ha^{-1} plus 20 kg N ha^{-1} as second application to cereals) plus straw incorporation.

(iii) MIN-60: low application rate of mineral fertilizer (50 kg N ha^{-1} to root crops or 60 kg N ha^{-1} to cereals) plus straw incorporation.

(iv) FYM-140: high application rate of rotted farmyard manure: 27 t fresh weight ha^{-1} as manure (≈ 150 kg N_t ha^{-1}) to root crops or 16 t fresh weight ha^{-1} (≈ 100 kg N_t ha^{-1}) plus 40 kg N_t ha^{-1} with urine (second application) to cereals. The total N input corresponded to the N input by mineral fertilization in treatment MIN-140.

(v) FYM-100: medium application rate of rotted farmyard manure: 18 t fresh weight ha^{-1} as manure (≈ 100 kg N_t ha^{-1}) to root crops or 12 t fresh weight ha^{-1} (≈ 80 kg N_t ha^{-1}) plus 20 kg N_t ha^{-1} with urine (second application) to cereals. The total N input corresponded to the N input by mineral fertilization in treatment MIN-100.

(vi) FYM-60: low application rate of rotted farmyard manure: 9 t fresh weight ha^{-1} as manure (≈ 50 kg N_t ha^{-1}) to root crops or cereals. The total N input corresponded to the N input by mineral fertilization in treatment MIN-60.

Mineral fertilization was carried out with calcium ammonium nitrate. After harvest, straw remained on the field at all MIN-treatments. The mean annual C input by straw incorporation in the MIN treatments was 0.80 t C ha^{-1} for MIN-60, 0.88 t C ha^{-1} for MIN-100, and it was 0.93 t C ha^{-1} for MIN-140. All FYM-treatments were fertilized with cattle farmyard manure which was stored in piles for approximately nine months before application. The addition of organic carbon with farmyard manure increased from 0.63 t C ha^{-1} at the treatment FYM-60 to 0.95 t C ha^{-1} at the treatment FYM-100 and further to 1.3 t C ha^{-1} at the treatment FYM-140 (Heinze et al., 2009). Liquid manure was applied as second donation on the FYM treatments with medium and high fertilizer application. When legumes were planted no fertilizer was applied. The crop rotation for all treatments consisted of legumes, mainly red clover (*Trifolium pratense* L.), spring wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum* L.) and winter rye (*Secale cereale* L.). The main crops during our experimental period (March 2007 to March 2009) were spring wheat in 2007 and amaranth (*Amaranthus hypochondriacus*) in 2008 (as exception from the crop rotation). Catch crop was rye grass (*Lolium multiflorum* Fabio) in 2007/2008 and radish in 2008/2009 (*Raphanus sativus spp. oleiformis* L.) (Table 9). Tillage and fertilization during our experimental period of two years is summarized in Table 9. During the cropping season in 2007 the treatments were irrigated two times with a maximum of 13 mm per day. In 2008 the treatments were irrigated in May (2 times) and in June (one time), and weekly in July. The amount of irrigated water generally ranged between 9 and 13 mm, with an exceptional large amount of 19 mm at the 16th of July 2008.

4.2.2 General Soil Analyses

In February 2007, before the gas measurements started, undisturbed and mixed soil samples were taken fro the Ap horizons (0 − 25 cm) of all treatments. Soil pH was measured in a 10^{-2} M $CaCl_2$ solution with a soil/solution ratio 1:2.5. The effective cation exchange capacity (CEC) was determined by leaching soil samples with 100 ml of a 1 M ammonium chloride (NH_4Cl) solution for four hours (König and Fortmann, 1996). Cations in the extract were measured by ICP-AES (Spectro, Kleve) and exchangeable protons were calculated from the pH of the NH_4Cl solution before and after percolation. Soil bulk density was determined gravimetrically on undisturbed soil cores (250 cm^3) taken in different depths (0 − 10 cm, 10 − 25 cm). For the calculation of the WFPS the bulk density in 0 − 10 cm depth was applied and for the calculation of the SOC and N_t stocks the mean value of 0 − 25 cm depth was calculated. Organic carbon and total nitrogen contents were determined with an elemental analyzer (Heraeus Vario EL, Hanau, Germany).

4.2.3 Measurement of N_2O and CH_4 Flux Rates, Mineral Nitrogen and Soil Moisture

N_2O and CH_4 fluxes were measured weekly and additionally after special events like fertilization with circular, dark PVC chambers (diameter: 29.5 cm, height: variable from 28.5 to 78.5 cm). For gas flux determination these closed chambers were placed on permanently installed PVC-collars with the same diameter and sealed with an elastic lid. Using extensions rings of the same material, the height of the chamber could be adjusted to plant growth. We installed one collar on each replicate (n = 4) of the six fertilization treatments (MIN-60, MIN-100, MIN-140, FYM-60, FYM-100, FYM-140) described above.

Four air samples were taken at equal sampling intervals after closing the chambers for 60 minutes using evacuated glass vials as decribed by Flessa et al. (1995) and Ruser et al. (1998). The closing time was extended up to 90 minutes during the growing period when the chamber volume was enlarged by extension rings. Air samples were analyzed for N_2O and CH_4 with an automated gas chromatographic system with a ^{63}Ni electron capture detector (ECD, for N_2O) and a flame ionisation detector (FID, for CH_4). The gas fluxes were calculated from the linear regression of the temporal concentration changes in N_2O and CH_4 within the closed chamber. The R^2 of the regression was used as a measure to identify significant fluxes. Fluxes with correlation coefficients of the slope of $R^2 \geq 0.85$ were accepted for further analysis. Fluxes with a $R^2 < 0.85$, which were observed when changes in gas concentrations were very small, were rated to be insignificant and were assumed to be equal to zero. Cumulative N_2O and CH_4 fluxes were calculated assuming constant flux rates between two consecutive measurement dates.

At the time of each gas flux determination, soil samples were taken to a depth of 0 – 10 cm. Soil moisture content was determined gravimetrically after drying at 105 °C for 24 h. The water-filled pore space (WFPS) was calculated using the mean bulk density measured at the experimental sites as follows: WFPS = [(gravimetric water content × soil bulk density)/total soil porosity], where the soil porosity = [1 – soil bulk density/2.65],

2.65 being the assumed particle density of the soil. Mineral nitrogen (NO_3^- and NH_4^+) was determined after extraction with 10^{-2} M $CaCl_2$ (soil/solution ratio of 1:2) by photometric analysis using a continuous flow analyzer (S/A 20/40 Skalar Analytical, Erkelenz).
Air temperature and daily precipitation were measured continuously. We present the WFPS as the mean of the three fertilization rates (for MIN and FYM, respectively) because there were no differences of WFPS between the fertilization rates the different fertilizer rates.

4.2.4 Modeling

We used a fuzzy logic inference scheme of Takagi Sugeno type to simulate the influence of the factors weather, soil conditions and management on the time series of daily N_2O emissions. A detailed model description can be found in Dechow et al. (in preparation). They calibrated and validated this model on a data set comprising 49 data sets of N_2O emissions and controlling factors from 12 cropland sites in Europe. Cross validation of modeled and measured annual N_2O fluxes indicate that the model was able to explain 61% of the variability of annual N_2O flux rates which ranged from about 1 to 15 kg N_2O-N ha^{-1} yr^{-1}.
The model was applied to the data in this study by using the site-specific time series of the considered factors as input but without any site-specific calibration of the N_2O response.
The general scheme of the model is illustrated in Figure 1. Factors considered in the model were 1) soil temperature, 2) WFPS in 10 cm depth, 3) SOC content in 30 cm depth, 4) available nitrogen in 30 cm depth, and 5) freeze-thaw cycles (Dechow et al. submitted). The factors were divided into classes and normalized to the range [0; 1]. The classes were defined by fuzzy sets A_1, A_2,… A_n. Here a factor value can be a member of several classes to a certain degree (DOM: degree of membership). The model consists of several if – then rules. Each rule links a set of factor values a_1, a_2,… a_n to a N_2O emission b.
Every possible combination of fuzzy sets is realized as a rule:

If $a_1 \in A_{1i}$ and $a_2 \in A_{2i}$ and … and $a_n \in A_{ni}$ then b_i

Where a_1, a_2,… a_n are factor values in the fuzzy sets A_1, A_2,… A_n and b is the emission value described by rule i (see figure 9 [rule tree from Dechow et al., in preparation]). As demonstrated in Figure 9 each rule of the rule system can be fulfilled with a certain degree (degree of fulfillment: DOF) given a set of input factors. Rule responses (rule specific N_2O emissions) are aggregated by using the DOF as weighting factors.

$$y = \frac{\sum_{i=1}^{r} DOF_i b_i}{\sum_{i=1}^{r} DOF_i}$$

Soil temperature in the top soil was calculated by a submodel of the EPIC model (Williams, 1995). Water-filled pore space in the top soil was calculated by a combination of the Darcy equation and a capacity approach. The influence of snow melt and soil frost on water flow in the soil was accounted for (details in Dechow et al., in preparation).
Available nitrogen was represented by the “emission forcing potential by nitrogen availability” E_N (Dechow et al., submitted). E_N was calculated on daily time steps by balancing readily available nitrogen sources and sinks. Sources included N input from fertilizer application, atmospheric N deposition and nitrogen mineralized from soil organic matter. The degradation of the slow and fast organic matter pools of the RothC model (Coleman et al., 1997) was used to calculate mineralized N whereby a threshold of C/N = 25 was used to distinguish between N was released in readily available form (C/N < 25) or stored in biomass or soil organic matter (C/N > 25). Sinks of available N by leaching and plant uptake were estimated by simple assumptions (Dechow et al., in preparation).

4.2.5 Statistical Analyses

The field trial was divided into main rows and main columns. To account for the structure of the strip design we applied a mixed model (Piepho et al. 2003) in order to test for significant effects between the treatments MIN and FYM at the three different rates. The model applied is described in detail by Heitkamp et al. (2009). Briefly, effects listed like main row, main column, their interaction, fertilizer type, and rate and their interaction were assumed to be fixed whereas the error of the fertilizer rate, main row and main column

interaction and the error of the subplot were random. We tested the differences between means using least significance difference (LSD) at $p \leq 0.05$.
Additionally, the relationship between nitrate contents, water filled pore space, temperature, precipitation and N_2O and CH_4 fluxes were assessed by linear regression on the means of the four plots on the six treatments. Analyses were conducted using R version 2.8.1.

4.3 Results of the Third Study

4.3.1 Soil C and N Contents, pH and Yields

After thirty years of different fertilization, the SOC and N_t contents were significantly higher in the FYM treatment than in the MIN treatment (Table 10). In addition, the SOC and N_t contents increased with increasing N application rate for both fertilizer types but only for the FYM treatments (Heitkamp et al., 2009). The C/N ratio ranged from 10.1 to 10.9 and was slightly higher for the MIN treatments than the FYM treatments. The mean soil pH was slightly higher for the treatments which received farmyard manure (pH = 6.3 – 6.4) than for those fertilized with calcium ammonium nitrate (pH = 6.0 – 6.1). However, no significant differences between the fertilization rates could be observed for pH (Heinze et al., 2009).
Table 10 shows that the grain yields of spring wheat (2007) ranged between 24.7 and 31.1 dt dm ha^{-1} for the MIN treatment and between 30.8 and 24.8 dt dm ha^{-1} for the FYM treatments. The yields of the amaranth harvest (2008) were determined between 24.6 and 25.4 dt dm ha^{-1} for the MIN treatments and between 20.6 and 28.1 dt dm ha^{-1} for the FYM treatments. There were no significant differences between the long-term fertilization treatments. An effect was only visible for the MIN-140 treatment in 2007, which was higher than the MIN treatments with lower annual N input, and for the FYM-60 treatment, which was lower than the FYM-100 and FYM-140 treatments.

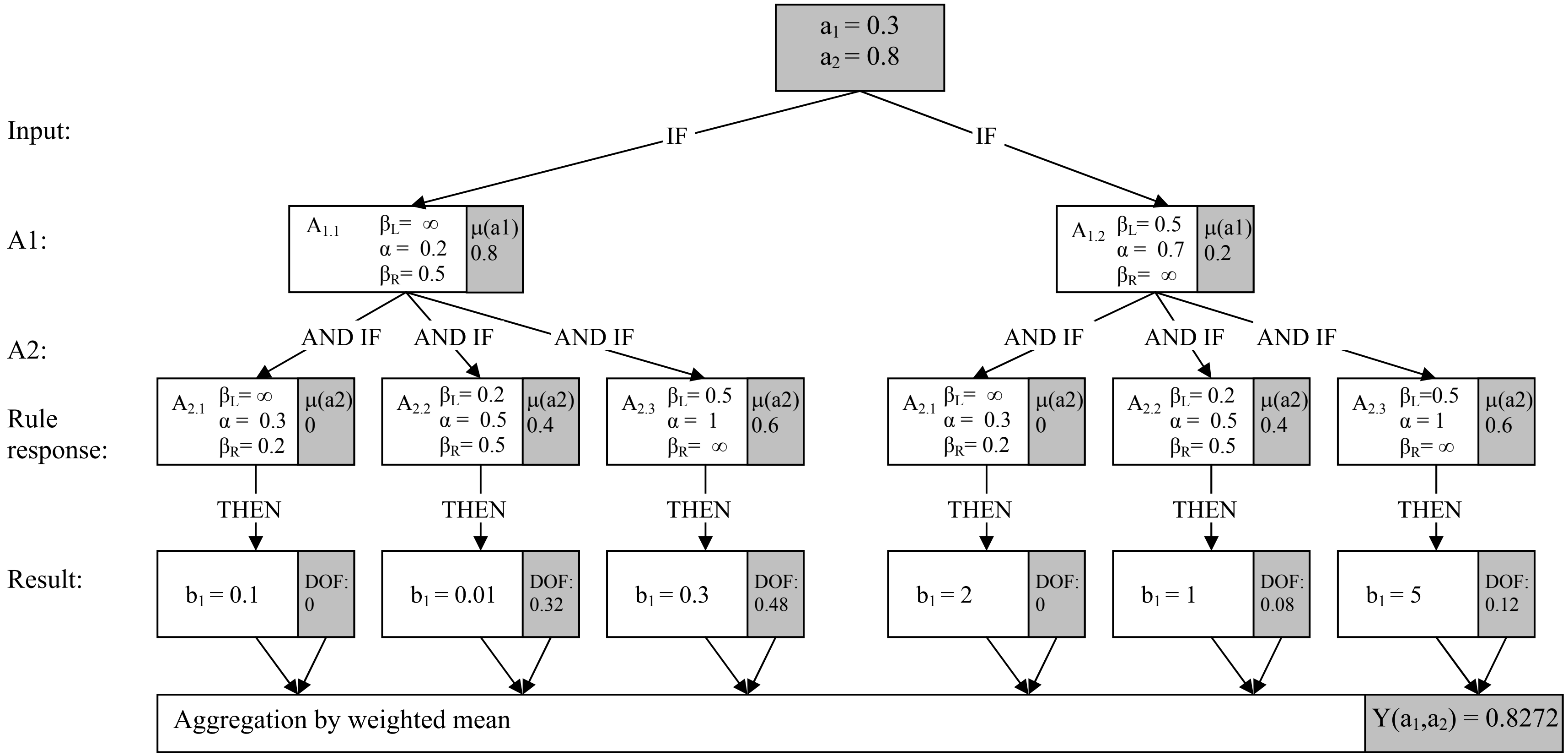

Figure 9: Model chart of a fuzzy logic inference scheme with only two normalized input parameters (a_1 and a_2) two factors A_1 (2 fuzzy sets) and A_2 (3 fuzzy sets) and 6 rules equivalent to the model structures developed by Dechow et al. (in preparation). The shaded fields show a calculation example. For a more detailed description see section 2.3.

Table 9: Management of the fertilization treatments of the long-term field experiment in Darmstadt during the experimental period from March 2007 to March 2009

Management	Fertilization treatments					
	MIN-60	MIN-100	MIN-140	FYM-60	FYM-100	FYM-140
Year 2007						
Tillage (spring)	Ploughing (depth: 25 cm, date: 09/03/2007)					
Main crop	*Triticum aestivum* L. (date of sowing: 21/03/2007)					
1. N application (kg N ha^{-1})*	60	80	100	60	80	100
1. N application, date	21/03/2007			07/03/2007		
2. N application (kg N ha^{-1})**	-	20	40	-	20	40
2. N application, date	21/05/2007					
Harvest	Date of harvest: 01/08/2007					
Straw incorporation	14/08/2007					
Tillage (autumn)	Ploughing (depth: 25 cm, date: 13/09/2007)					
Intercrop	*Lolium multiflorum* L. (date of sowing: 9/10/2007)					
Year 2008						
Tillage (spring)	Ploughing (depth: 25 cm, date: 18/04/2008)					
Main crop	*Amaranthus hypochondriacus L.* (date of sowing: 23/05/2008)					
1. N application (kg N ha^{-1})*	60	80	100	60	80	100
1. N application, date	23/05/2008			17/04/2008		
2. N application (kg N ha^{-1})**	-	20	40	-	20	40
2. N application, date	30/06/2008			04/07/2008		
Harvest	Date of harvest: 11/09/2008					
Intercrop	*Raphanus sativus ssp. Oleiformes* (date of sowing: 20/10/2008)					
Year 2009						
Tillage (spring)	Ploughing (depth: 25 cm, date: 15/03/2009)					
1. N application (kg N ha^{-1})*				60	80	100
1. N application, date	after the experimental period			14/03/2009		

* Applied fertilizer type: calcium ammonium nitrate for MIN treatments, composted farmyard manure from cattle for FYM treatments
**Applied fertilizer type: calcium ammonium nitrate for MIN treatments, liquid manure for FYM treatments

4.3.2 N_2O fluxes, Soil Organic Matter and Total Nitrogen

During the 2-years study period, N_2O emissions from the sandy soil were generally low for all fertilization treatments. Between 94% and 98% of the measured flux rates were below 30 µg N_2O-N m^{-2} h^{-1} (Figure 10). Even peak emissions which occurred during the cropping period after tillage, fertilizer application or heavy rainfall did not exceed 80 µg N_2O-N m^{-2} h^{-1}. In autumn 2007 after harvest, ploughing induced N_2O emissions on both treatments and the additional straw incorporation on the MIN treatments seems to intensify emissions: 39% (low), 42% (medium) and 31% (high) of the annual N_2O emissions in 2007 were emitted within eight weeks after ploughing in autumn and straw incorporation on the MIN treatments. In contrast, 33% (low), 35% (medium) and 23% (high) of the annual N_2O emissions were emitted from the FYM treatments within the same period. Emissions during winter were constantly low (< 10 µg N_2O-N m^{-2} h^{-1}) and we found no evidence for enhanced emissions induced by frost-thaw events.

Soil nitrate contents were increased during short periods following fertilization and tillage (Figure 11) (up to 110 mg NO_3^--N kg^{-1}) but they did not exceed 2 mg NO_3^--N kg^{-1} during the rest of the year. Nitrate availability was considerably higher following application of calcium ammonium nitrate (MIN) than farmyard manure (FYM). Ammonium contents (data not shown) followed a similar pattern with high values (up to 35 mg NH_4^+-N kg^{-1}) after tillage and fertilization but during the rest of the experimental period, the ammonium contents did not exceed 2 mg NH_4^+-N kg^{-1}. Neither the soil nitrate nor the ammonium contents were correlated with the N_2O emissions. We found a weak but significant positive relationship between air temperature and N_2O emissions with $R^2 = 0.35$ to 0.39 ($p \leq 0.001$) and an even higher correlation between soil temperature in 5 cm depth with $R^2 = 0.37$ to 0.46 ($p \leq 0.001$).

Cumulative N_2O emissions were 1.5 to 2 times higher in 2007 than in 2008. They ranged between 0.74 – 0.83 kg N_2O-N ha^{-1} yr^{-1} for the first year and from 0.39 – 0.83 kg N_2O-N ha^{-1} yr^{-1} for the second year. An exception was the MIN-140 treatment which emitted more N_2O in the first year with a cumulative emission of 1.1 kg N_2O-N ha^{-1} yr^{-1}. The higher N_2O emission rates in the first year coincided with elevated precipitation, WFPS and higher temperature values in comparison to the second year. Additionally, the nitrate contents, especially the peak values after fertilization and tillage, were lower in 2008 than in 2007. The annual N_2O emissions did not increase with N application rate. Moreover, no significant differences were apparent, between the long-term fertilization treatments MIN and FYM (Table 11).

Yield related N_2O emissions were calculated from the yields of the main crop which were related to the N_2O emissions during the cropping season in 2007 and 2008, respectively (Table 11). The results show that the yield related emissions did not decrease linearly for all treatments and the fertilizer type did not influence the yield related emissions with one exception, again, the MIN-140 emitted more N_2O as related to the yields on this treatment.

4.3.3 Modeling of N_2O Emissions

Annual N_2O emission rates calculated by the model ranged from 0.96 to 1.06 kg ha^{-1} yr^{-1} the first year and from 0.73 to 0.83 kg ha^{-1} yr^{-1} the second year, respectively (Table 11). Overall, the model results agreed fairly well with the measured results (Table 11). It was able to capture the generally low emission level of the experimental site, it displayed the observed interannual variation of the emission with slightly higher N_2O losses during the first experimental year, and it agrees with our observation that the fertilizer rate and type had no clear effect on N_2O emission from this site.

The seasonal dynamics of N_2O emissions – characterized by low emissions during winter time and higher emissions during the growing season – was matched by the model (data not shown). However, the model calculated a frost induced emission peak at the end of 2008, which was not affirmed by the measurements. This peak was a major source of the systematic overestimation of N_2O fluxes in the second year.

Table 10: Contents and stocks of C_{org}, N_t, pH and texture of soils (0 – 25 cm) with different fertilization history of the long-term field experiment at Darmstadt (samples from spring 2007, mean values and standard deviation in parentheses (n = 4)). Different letters indicate significant differences between means of long-term fertilization treatments with different fertilizer types (MIN vs. FYM) but the same N application rate ($p \leq 0.05$).

Treatment	C_{org} (g kg^{-1})	C_{org}* (t ha^{-1})	N_t (g kg^{-1})	N_t* (t ha^{-1})	pH	Clay (%)	Silt (%)	Sand (%)
MIN-140	7.43 (0.1)^a	24.2 (0.5)^a	0.68 (0.1)^a	2.3 (0.1)^a	6.0^a	4.6 (0.3)^a	9.0 (0.5)^a	86.5 (0.3)^a
MIN-100	6.93 (0.1)^a	23.7 (0.9)^a	0.65 (0.1)^a	2.2 (0.1)^a	6.1^a	4.9 (0.5)^a	9.2 (0.9)^a	85.9 (0.9)^a
MIN-60	6.71 (0.1)^a	23.6 (0.8)^a	0.63 (0.1)^a	2.2 (0.1)^a	6.0^a	4.7 (0.4)^a	10.5 (1.8)^a	84.8 (1.8)^a
FYM-140	8.59 (1.0)^b	28.1 (0.9)^b	0.82 (0.1)^b	2.8 (0.1)^a	6.3^b	4.9 (0.4)^a	8.9 (0.3)^a	86.2 (0.3)^a
FYM-100	8.17 (0.7)^b	28.1 (1.0)^b	0.79 (0.1)^b	2.7 (0.1)^a	6.3^b	5.8 (0.2)^a	8.5 (0.5)^a	85.7 (0.7)^a
FYM-60	7.47 (0.7)^b	25.3 (1.2)^b	0.74 (0.1)^b	2.5 (0.1)^a	6.4^b	5.6 (0.3)^a	9.0 (0.8)^a	85.4 (1.0)^a

*data adapted from Heitkamp et al. (2009)

Table 11: Grain yields, measured and modelled annual N_2O emissions, yield related N_2O emissions and measured annual uptakes of atmospheric CH_4 (means ± standard deviation) for the first and the second experimental year;

Treat-ment	Grain yields (dt dry matter ha^{-1})		Measured N_2O emissions (kg N_2O-N ha^{-1} yr^{-1})		Modelled N_2O emissions (kg N_2O-N ha^{-1} yr^{-1})		Yield related emissions[$$$] (kg N_2O-N dt^{-1})		Measured CH_4 uptake (kg CH_4-C ha^{-1} yr^{-1})	
	1. year[$]	2. year[$$]	1. year[$]	2. year[$$]	1. year[$]	2. year[$$]	1. year[$]	2. year[$$]	1. year[$]	2. year[$$]
MIN-140	24.7 (0.9)[A]	24.6 (4.3)	1.07 (0.4)[aA]	0.55 (0.3)	0.96	0.75	21.2 (10.0)[aA]	7.3 (6.5)	−1.44 (0.2)	−1.08 (0.2)
MIN-100	30.0 (2.0)[B]	25.4 (3.8)	0.74 (0.2)[B]	0.50 (0.1)	0.96	0.75	10.5 (1.6)[B]	8.2 (4.1)	−1.52 (0.3)	−1.26 (0.4)
MIN-60	31.1 (1.8)[B]	25.1 (2.2)	0.83 (0.4)[B]	0.42 (0.5)	0.97	0.73	12.5 (2.4)[B]	5.5 (8.3)	−1.42 (0.3)	−1.21(0.5)
FYM-140	34.3 (0.8)	28.1 (2.1)[B]	0.70 (0.2)[b]	0.48 (0.2)	1.02	0.83	8.8 (2.9)[b]	4.2 (4.5)	−1.54 (0.2)	−1.25 (0.2)
FYM-100	34.8 (0.8)	25.4 (2.4)[B]	0.75 (0.1)	0.39 (0.0)	1.04	0.78	10.4 (2.4)	5.0 (4.0)	−1.57 (0.2)	−1.32 (0.2)
FYM-60	30.8 (3.1)	20.6 (3.3)[A]	0.81 (0.1)	0.41 (0.1)	1.06	0.77	12.1 (3.4)	5.1 (2.9)	−1.46 (0.3)	−1.30 (0.3)

[$] from March 2007 until February 2008 (main crop: spring wheat),
[$$] from March 2008 until February 2009 (main crop: amaranth)
[$$$]cumulative emissions were calculated for the vegetation period of the crop.

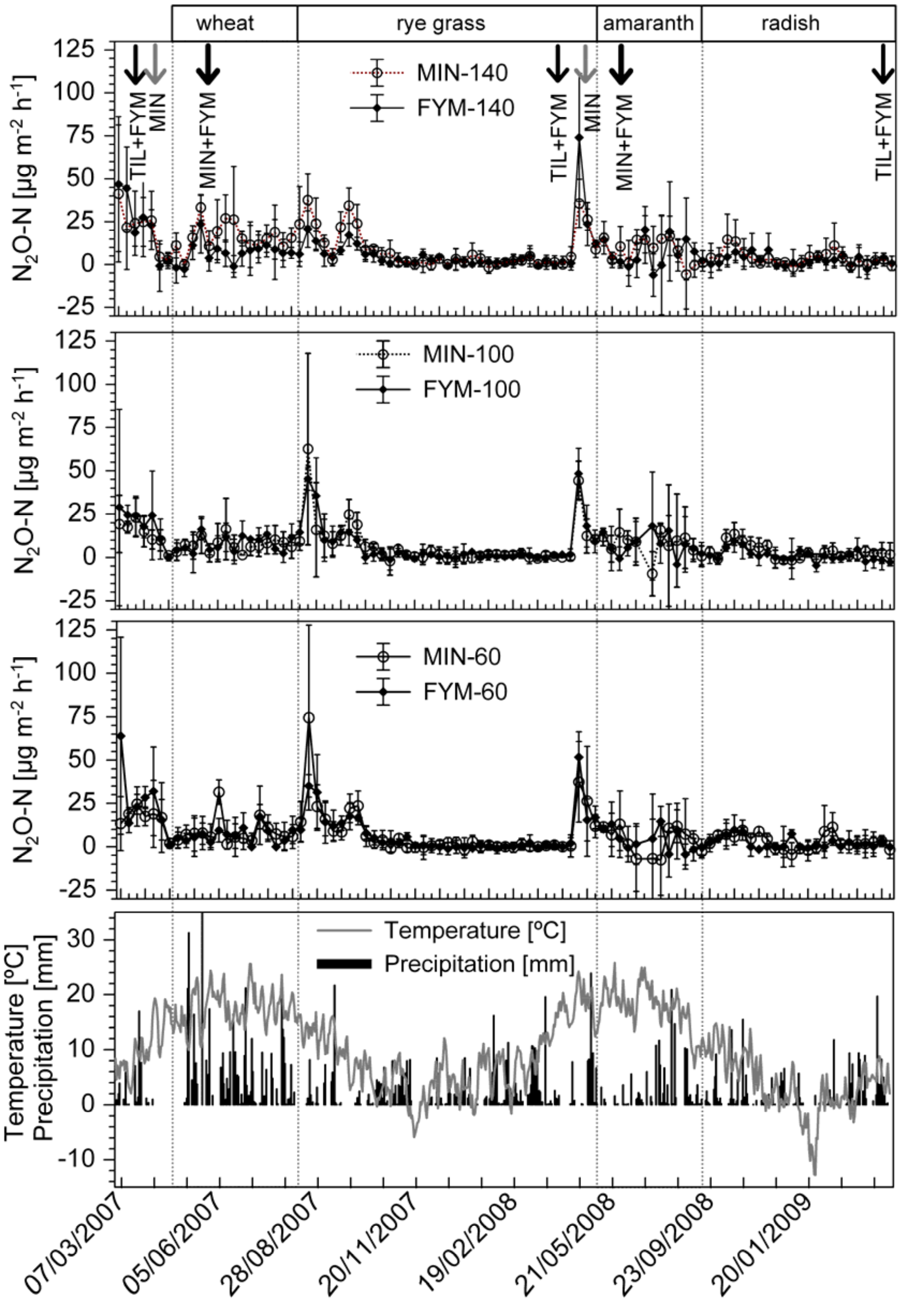

Figure 10: N_2O emission rates (means ± standard error, n = 4) from the treatments with long-term application of composted farmyard manure (FYM) and mineral fertilizer (MIN) at the fertilization rates (60, 100, 140 kg N ha^{-1}) and average daily air temperature and daily precipitation from March 2007 to March 2009. Arrows indicate the dates of fertilization (MIN or FYM) and tillage (TIL). The grey lines mark the cropping season (2007: wheat, 2008: amaranth).

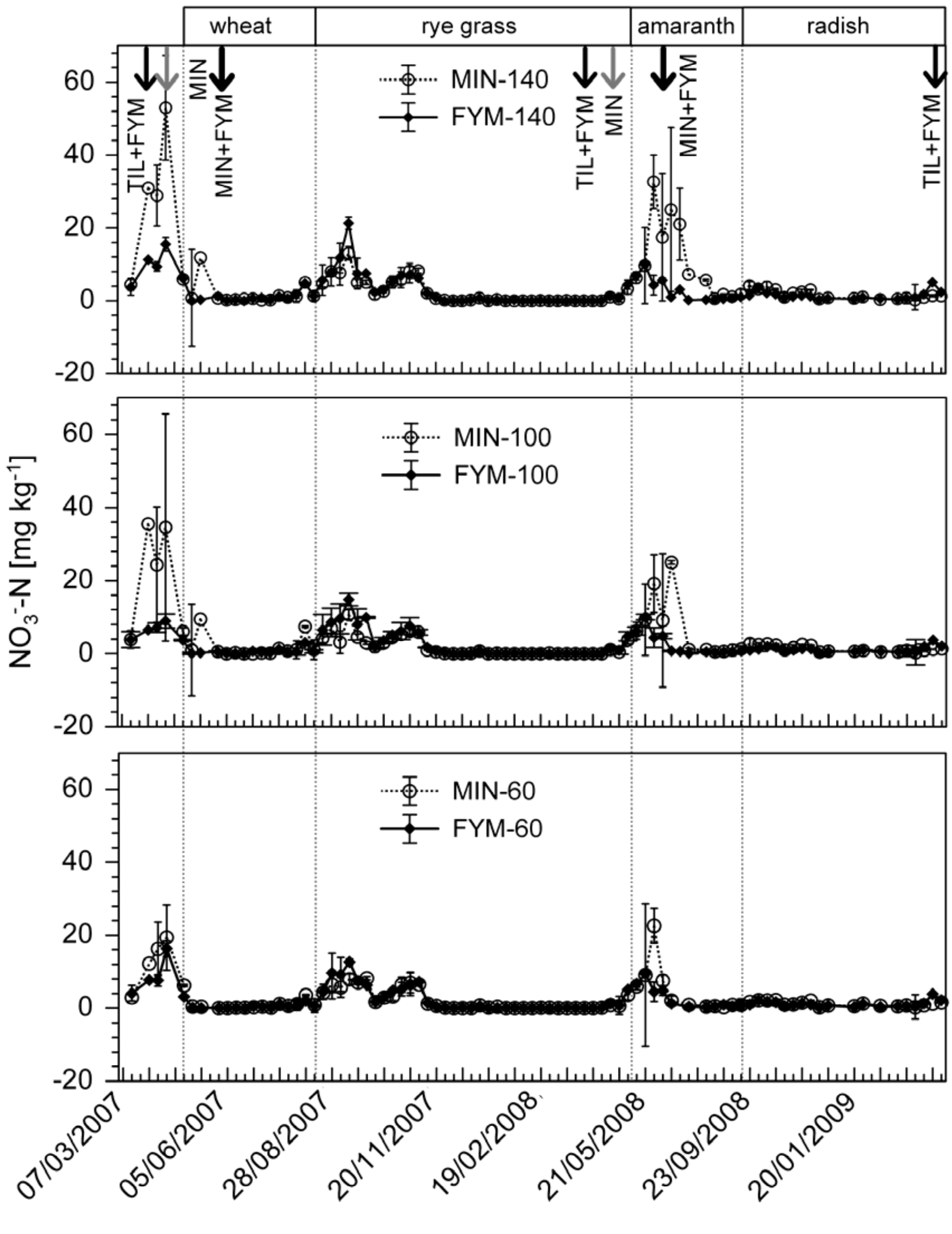

Figure 11: Soil nitrate contents (means ± standard error, n = 4) of the treatments with long-term application of farmyard manure (FYM) and mineral fertilizer (MIN) at the fertilization rates (60, 100, 140 kg N ha^{-1}) from March 2007 to March 2009. The grey lines mark the cropping season (2007: wheat, 2008: amaranth). Arrows indicate fertilization (MIN or FYM) and tillage (TIL).

4.3.4 CH_4 Fluxes

The soils of all treatments were net sinks for atmospheric CH_4 throughout the study period (Figure 12). The CH_4 uptake rates varied between 2 and 30 µg CH_4-C m^{-2} h^{-1} and showed a seasonal trend of lower uptake during winter and higher uptake during summer, especially in the dry summer 2008.

The time course of CH_4 uptake rates was similar for both fertilizer types (MIN and FYM) and also for the different fertilization rates. There was no clear effect of tillage or fertilizer application on the uptake rate of atmospheric CH_4.

We found a positive correlation between soil temperature in 5 cm depth and CH_4 uptake (R^2 = 0.39 to 0.50 for MIN and 0.51 to 0.61 for FYM, $p \leq 0.001$) and also between air temperature and CH_4 uptake (R^2 = 0.44 to 0.56 for MIN, R^2 = 0.34 to 0.49 for FYM, $p \leq 0.001$). WFPS was negatively correlated with CH_4 uptake (R^2 = −0.19 to −0.39 for MIN and −0.24 to −0.39 for FYM, $p \leq 0.001$) and precipitation had an even higher correlation with CH_4 uptake, namely R^2 = −0.44 to −0.56 for MIN and, R^2 = −0.34 to −0.49 for FYM, $p \leq 0.001$.

For the first experimental year, the cumulative annual CH_4 uptake amounted to 1.4 – 1.6 kg CH_4-C ha^{-1} for both fertilizer types and there was no effect of the fertilization rate on the uptake. In the second year, annual CH_4 uptake rates were slightly lower with 1.1 (MIN) and 1.3 kg CH_4-C ha^{-1} (FYM). Again, differences between the fertilizer types were not significant (Table 11). The cumulative uptake between both years was not significantly different.

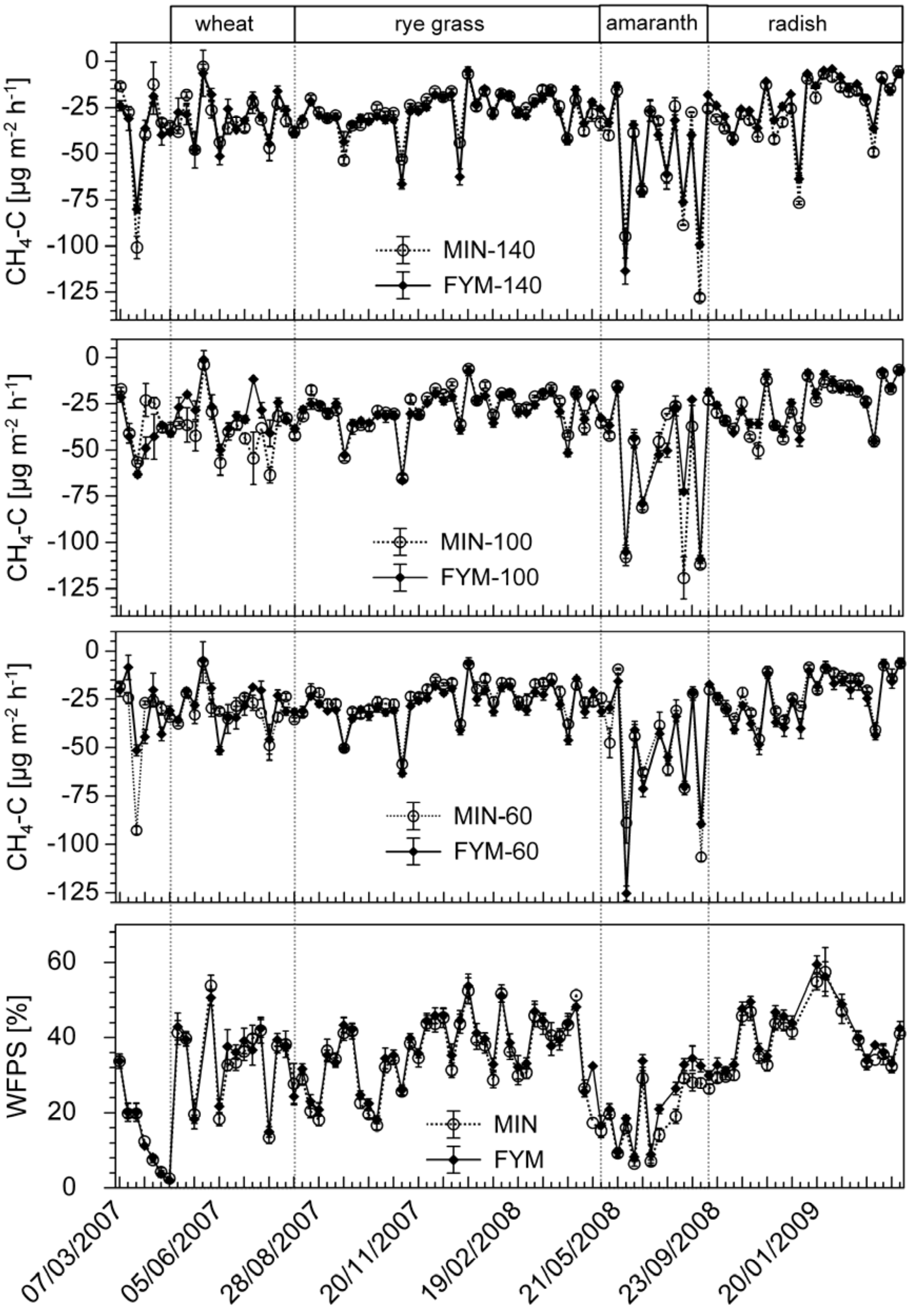

Figure 12: CH_4 uptake rates (means ± standard error, n = 4) from the treatments with long-term application of composted farmyard manure (FYM) and mineral fertilizer (MIN) at the fertilization rates (60, 100, 140 kg N ha^{-1}) and mean WFPS (water-filled pore space) (means ± standard error for all FYM and MIN treatments) from March 2007 to March 2009. The grey lines mark the cropping seasons (2007: wheat, 2008: amaranth).

4.4 Discussion of the Third Study

4.4.1 N_2O Fluxes, Soil Organic Matter and Total Nitrogen

Our data shows that long-term organic fertilization led to increased C_{org} and N_t stocks. This is in line with the results from other long-term experiments as reported by Edmeades (2003) and Powlson et al. (1998). The increase was significant even though the sandy soil texture provides a lower capacity to stabilize organic carbon than clayey soils (Christensen, 2001; Sposito et al., 1999). Furthermore, we found increasing SOC and N_t stocks with increasing fertilization rate and crop yield for the FYM treatments. This can be explained by an increasing input of manure with fertilization rates and crop residues estimated by Heitkamp et al. (2009).

In our study, however, these differences in C_{org} and N_t stocks did not result in increased annual N_2O emissions. This is contrary to our hypothesis that the treatments with higher SOC and nitrogen content are prone to higher N_2O emission. Rochette et al. (2000) also found no long-term effect of SOC accumulation induced by 18 years of different fertilization management because increased N_2O emissions were restricted to a relatively short period of about 30 days after organic fertilizer application. Similar to our hypothesis, Chang et al. (1998) concluded for American long-term fertilization experiments that repeated application of manure results in higher N_2O emissions. This was explained by the higher SOC and N content in the organic fertilized treatments, which was assumed to result in increased microbial activity and O_2 consumption. In agreement with the assumptions by Chang et al. (1998) for their sites, Heinze et al. (2009) reported for our study site that the microbial biomass in the MIN treatments was lower than in the FYM treatments. The missing effect of fertilization history and SOC accumulation on N_2O emission in our study is probably a result of the sandy soil texture. The high sand content (86%) ensures a generally good soil aeration, which restricts N_2O production by denitrification (Rochette et al., 2008a; Weier et al., 1993) and it also restricts SOC content and SOC accumulation by different fertilization (von Lützow et al., 2007). Thus, the denitrification potential of the sandy soil was probably generally low and it was not influenced by a moderate increase of soil organic matter stocks, which were generally low (SOC: < 9 mg kg^{-1}) in all treatments. A laboratory incubation carried out with the same soil at the highest fertilization rate confirmed the finding that there was no long-term fertilization effect on N_2O emissions and this was also explained with the sandy soil texture (Jäger et al, in preparation).

The generally low potential for N_2O emissions is also evident from the missing effect of N fertilization rate on the annual emission which indicates that other factors than the input of nitrogen and the availability of mineral N restricted N_2O emissions. The main reason for the low emissions was probably that the WFPS never exceeded 60%, which was reported to be the critical value for increasing N_2O emissions produced by denitrification (Dobbie et al., 1999; Khalil and Baggs, 2005). Soil texture is an important factor which determines N_2O emissions from cultivated soils (Bouwman et al, 2002; Skiba and Ball, 2002) and soils with high sand contents often exhibit relatively low emission rates (Hellebrand et al., 2003, Jungkunst et al., 2006; Bouwman, 1996). Our annual emissions are in the range of other studies for sandy soils. Stehfest and Bouwman (2006) reported a wide range of −0.6 to 46.4 kg N_2O-N ha^{-1} from coarse textured soils. However, our cumulative emissions are below the mean of 3.21 kg N_2O-N ha^{-1} as calculated from 509 observations.

The N_2O emissions in 2007 were higher than in 2008, which was probably a combined effect of the higher precipitation, temperature and availability of soil nitrate in the first experimental year. All treatments showed a similar seasonal pattern of N_2O emissions with higher emissions during summer and lower emissions during winter. Overall, winter emissions only played a minor role for this site and we found no evidence that freezing-thawing events caused high emission rates as reported for many other sites (Christensen and Tiedje, 1990; Röver et al., 1998; Kaiser and Heinemeyer, 1996; Flessa et al., 1995). As shown by Öquist et al. (2004) N_2O emissions induced by freezing-thawing cycles depend on soil moisture before freezing and high emissions occurred when high soil moisture resulted in the formation of a compact ice layer. Thus, the low water holding capacity of the sandy soil and the resulting low soil moisture content, even during wintertime, probably restricted the formation of a compact ice layer which can act as is a barrier for gas exchange.

Grain yields were low on this sandy soil which was attributed to the low soil fertility (Heitkamp et al., 2009), however, the cumulative emissions were also very low. Therefore, the yield related emissions were small as compared to Sehy et al. (2003) but they were higher for the spring wheat cropping than for the amaranth cropping.

At several dates, increased N_2O emissions appeared to be affected by specific management factors. In spring 2007 the N_2O emissions started at a relatively high level because clover from 2006 as N fixing plant was incorporated and higher soil nitrate content was the consequence. N_2O peaks followed ploughing and residue incorporation of the catch crop and of the main crop residues on both treatments. In agreement with this, Ruser et al. (2001), Baggs et al. (2003) and Garcia-Ruiz and Baggs (2007) reported that tillage and mineralization of plant residues triggered N_2O emission. This period of higher emissions after straw incorporation on the MIN treatments was the main reason why the cumulative annual losses from the MIN-140 treatments were higher than from the FYM-140 treatments. In our study, ploughing and a heavy rain event coincided in April 2008 and induced emissions on both treatments. The manure application, which took place in spring, played a subordinate role because the MIN treatments were not fertilized at that time but emitted in the same range. Overall, ploughing and catch crop incorporation were the main controlling factors in the spring periods. The second fertilization in 2007 induced shallow peaks at both treatments. These peaks can be explained by the coincidence of the second fertilization and the heavy rain which took place in the evening between fertilization and measurement. In contrast, the second fertilization in 2008 was not followed by higher emissions, presumably because of an extended dry period in June 2008. We found no evidence that long-term fertilization influenced N_2O emissions following short-term events like fertilization or tillage.

Our observation, that N_2O emission rates following fertilizer application were strongly affected by precipitation rates, agree with the results of Dobbie et al. (1999), who found a significant positive relation between N_2O emissions from grassland soils and the precipitation within the first four weeks following fertilizer application.

4.4.2 Modeling of N_2O Emissions

The application of the fuzzy logic model to our site exhibited no differences between N_2O emissions from FYM and MIN treatments. Moreover, the model was able to capture the missing effect of the fertilization rate on N_2O emission. The soil organic C content was of minor importance for the modelled N_2O fluxes because the model sensitivity to changes of SOC below a threshold of 1% is low. The WFPS, which were modelled and observed during the growing period, were most of the time markedly beneath the threshold of 60% for all treatments. The response functions of the applied model assume significant increases of N_2O emissions above this value. The reason for the similarity of the emission behaviour of all treatments was therefore the generally low soil moisture. The low sensitivity of model results against fertilization rates for conditions not suitable for N_2O production was supported by the measured N_2O fluxes of this data set. These model results are contrary to recent national inventory methods, which assume a linear relationship between readily available nitrogen sources and the annual N_2O emission amount independent from environmental conditions. Even though those approaches are valid on a national to global scale the N_2O emission / N input ratio on a regional scale is strongly controlled by meteorological conditions and soil properties. Therefore, these factors have to be taken into account for assessing the influence of management options on N_2O budgets of agricultural soils.

Soil temperature, WFPS and SOC are factors controlling soil anaerobiosis via soil diffusivity and microbial O_2 consumption. At elevated SOC levels, model applications suggested an increase of N_2O fluxes with increasing SOC. However, the training data set used to calibrate the model exhibited correlations between soil texture and SOC, and the influence of soil texture on gas diffusivity (Moldrup et al., 2001) could be masked by this correlation.

Ludwig et al. (2010) modelled N_2O emissions for the treatments MIN-60, MIN-100, FYM-60 and FYM-100. They used the treatment MIN-60 for a site-specific calibration of the model. In contrast to the fuzzy model, the DNDC model showed a distinct sensitivity of modelled N_2O emissions towards the initial SOC content. In the calibration, slight changes (0.12 mg g^{-1}) of initial SOC resulted in an improved description of annual N_2O emissions of the treatment MIN-60. The validation, however, indicated that the model was useful for a prediction of N dynamics for the treatment MIN-100, but not for the treatments where farmyard manure was used.

4.4.3 CH_4 Fluxes

Neither fertilizer type, fertilization rates nor the SOC content influenced the uptake of atmospheric CH_4 in our study. In contrast to this, previous studies indicated that long-term application of FYM may improve gas diffusivity by its positive effect on soil aggregation (Abiven et al. 2009), however, the positive effects of FYM application on soil structure were probably negligible for the sandy soil in our study.

The range of CH_4 uptake during our two-year field study was within the expected range of 1.23 ± 1.22 kg CH_4 ha^{-1} yr^{-1} for agricultural ecosystems with coarse soil texture (Dutaur and Verchot, 2007). Soil texture is one of the most important factors determining the uptake rate of atmospheric CH_4 in soils (Dörr et al., 1993; Del Grosso et al., 2000) because it is a key factor which determines diffusion of atmospheric CH_4 into the soil. Thus, sandy soils often exhibit a higher uptake rate of atmospheric CH_4 than fine grained soils (Bodelier and Laanbroeck, 2004; Le Mer and Roger, 2001).

In our study, soil moisture was negatively correlated with the CH_4 uptake and determined the time course of the CH_4 uptake during the year from 19% to 30%. This negative correlation is well established (Ridgwell et al., 1999; Omonode et al. 2007; Chu et al. 2007, Goulding et al. 1996), since gas diffusion is restricted in wet soils and reduces the supply of atmospheric CH_4 (Striegl, 1993; Guckland et al., 2008). We found a significant relationship between temperature and the CH_4 uptake. Several processes may have contributed to this relation. Microbial activity increases with increasing temperature. Additionally, evaporation and transpiration increased with higher temperature and led to lower soil water content (Dobbie and Smith, 1999). Therefore, highest uptake rates occurred during summer when temperature was high and soil moisture was low.

Organic fertilization might introduce methanogenic activity at least during the time following manure application (Dittert et al., 2005; Chadwick et al., 2000), however, we found no evidence for a period with significant methanogenic activity. Any increase in methanogenic activity after organic fertilization was probably short-lived and was therefore, not detected in our study. Dittert et al. (2005) reported that CH_4 emissions after slurry application lasted only a few hours and assumed that this CH_4 was directly released from the slurry. In contrast to Hütsch (1996) we found no evidence that CH_4 uptake rates were lowered in periods with increased mineral N contents, such as the period following fertilization or tillage.

Cumulative uptake of atmospheric CH_4 in 2007 was higher than in 2008 although the precipitation in 2008 was lower and the air filled pore space might have been lower. In spite of this, the sandy soil never exceeded 60% WFPS throughout the experimental period and the WFPS was probably too low to impact on CH_4 uptake. A reason for the slightly lower uptake in 2008 could have been the lower temperature, which may have affected methanotrophic activity (Dobbie and Smith, 1996).

4.5 Conclusions of the Third Study

We found no evidence that increased SOC and N_t stocks by long-term application of composted farmyard manure increased N_2O emissions or changed atmospheric CH_4 uptake of this sandy soil compared to the long-term application of mineral fertilizer. Different fertilization rates changed neither N_2O nor CH_4 exchange rates. The results of our two-year field experiment show that N_2O emissions from this sandy soil are generally low and restricted by low soil moisture and the related good soil aeration. Overall, our results indicate that the hypothesis that OM accumulation in soils promotes N_2O emissions is not valid for the sandy soil at the Darmstadt long-term experiment site. However, our results should not be applied to soils with finer texture where organic matter accumulation may have a much stronger effect on O_2 availability and gas diffusivity.

5. Application of the DNDC Model to Predict N_2O Emissions from Sandy Arable Soils with Differing Fertilization in a Long-term Experiment

Abstract

Modeling crop growth and soil nitrogen dynamics is difficult due to the complex nature of soil-plant systems. In several studies, the DNDC model has been claimed to be well suited for this purpose whereas in other studies applications of the model were less successful. Objectives of this study were to test a calibration and validation scheme for DNDC model applications to describe a field experiment with spring wheat on a sandy soil in Darmstadt, Germany, using different fertilizer types (either application of mineral fertilizer and straw – MSI; or application of farmyard manure – FYM) and rates (low – MSI_L, FYM_L; and medium – MSI_M, FYM_M). The model test is based on a model parameterization to best describe the case MSI_L and applies this parameterization for a retrospective simulation of the other cases (MSI_M, FYM_L, FYM_M) including crop growth and N_2O emissions. Soil water contents were not accurately simulated using either the DNDC default values for a loamy sand or for the next finer texture class or using results from the pedotransfer function provided by ROSETTA. After successful calibration of the soil water flow model using a soil texture class that led to the best fit of the measured water content data, grain yield of spring wheat and cumulative N_2O emission were slightly underestimated by DNDC and were between 91% and 86% of the measured data. A subsequent calibration of the yields and cumulative N_2O emissions from soils of the MSI_L treatment gave a good prediction of crop growth and N_2O emissions in the MSI_M treatment, but a marked underestimation of yields of the FYM treatments. Cumulative N_2O emissions were predicted well for all MSI and FYM treatments, but seasonal dynamics were not. Overall our results indicated that for the sandy German site, site specific calibration was essentially required for the soil hydrology and that a calibration was useful for a subsequent prediction where greater amounts of the same fertilizer were used, but not useful for a prediction with a different fertilizer type.

5.1 Introduction of the Fourth Study

A thorough understanding of nitrogen dynamics in soil is crucial for sustainable crop management. Nitrogen dynamics directly influence crop growth, soil fertility and potential pollution problems such as ammonia volatilisation, soil acidification, increased nitrate loads of drinking water, eutrophication of surface water and emissions of the greenhouse gas N_2O.

Process-oriented models such as DAYCENT, CANDY, ExpertN or DNDC (Parton et al., 2001; Franko et al., 2007; Kaharabata et al., 2003; Li, 2009; for a review see Chen et al., 2008) may give a better insight into the interaction of N dynamics, soil hydrology and crop growth. Moreover, models may be useful to test a number of scenarios.

The DNDC model consists of sub-models for soil climate, crop growth and decomposition and calculates soil temperature, moisture, pH, redox potential (Eh) and substrate concentration profiles, which are affected by ecological drivers (e.g., climate, soil, vegetation and anthropogenic activity). Additionally, nitrification, denitrification and fermentation sub-models calculate emissions of carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), nitric oxide (NO), nitrous oxide (N_2O) and dinitrogen (N_2) from the plant-soil systems (Li, 2009). In the model, denitrification is calculated by assuming the presence of an "anaerobic balloon". Overall, the model relies on the assumption of universal microbial parameters for the kinetics of their growth and N_2O production (Li, 2009).

Several studies reported successful prediction of N and C dynamics in arable soils with the DNDC model (Smith et al., 2002, 2004; Farahbakhshazad et al., 2008; Wang et al., 2008). For instance, Smith et al. (2002) found for two arable sites in Canada that the DNDC model successfully estimated N_2O emissions with a slight average over-prediction of 3% for one site and an underestimation of 8% (footslope landscape position) for the second site. However, N_2O emissions for the shoulder position of the second site showed an overestimation of 46%, which was assigned to the fact that data input for the DNDC model were not sufficiently detailed to characterize the moisture difference between the landscape positions (Smith et al., 2002). Wang et al. (2008) reported a remarkable agreement between modelled and measured C stocks for a number of trials in China and claimed that they have validated the DNDC model for these sites.

Critical studies have also been published. Li et al. (2005) tested the model components that simulate N_2O emissions during soil nitrification and denitrification of three models, namely DNDC, Century (DAYCENT) and the Water and Nitrogen Management Model (WNMM), using a data set of an irrigated wheat-maize system on the North China Plain. For all data sets considered, the WNMM components consistently performed better in estimating N_2O emissions than the model components of the other two models. Abdalla et al. (2009) used the DNDC model for Irish agriculture and concluded that DNDC is unsuitable for predicting N_2O emissions from Irish grassland due to its overestimation of WFPS and effect of soil organic carbon (SOC) on the N_2O flux. Beheydt et al. (2008) reported for field experiments in Belgium a marked overestimation of N_2O emissions with DNDC (conventional tillage and maize), a good agreement (minimum tillage and oats) and an underestimation (minimum tillage and maize). Smith et al. (2008) evaluated the DAYCENT and DNDC models for Canadian arable soils and concluded that the hydrology and nitrogen transformation routines need to be improved in both models before further enhancements are made to the trace gas routines. Kröbel et al. (2010) tested the performance of the DNDC and Daisy model to simulate the water dynamics in a floodplain soil of the North China Plain. The use of default values did not result in satisfying simulation results for either model. Parameter optimisation and the use of site-specific van Genuchten parameters resulted in improved simulations of the Daisy model, whereas for the DNDC model, parameter optimisation failed to improve the simulation result (Kröbel et al., 2010).

Several efforts have already been undertaken to clearly describe the importance of key parameters for the use of the DNDC model. For instance, the manual (Li, 2009) highlights the possible calibration of crop growth by adjusting the crop heat/water/N demands, growth curve, biomass partitioning or yield. Moreover, several limitations have already been tackled. Li et al. (2006) added new water retention features to the DNDC model in order to more accurately simulate nitrate leaching in a row-crop field in Iowa, USA. Modified DNDC versions have been developed for forest and wetland ecosystems (e.g. PnET-ET-N-DNDC, Wetland-DNDC) and also for different regions (UK-DNDC, NZ-DNDC) and a sensitivity module has been implemented to explore the effect of some of the parameters on N_2O emissions (Li, 2009; Giltrap et al., 2010).

Nevertheless, there are still uncertainties regarding under which conditions (climatic regions, soil types and textures, crops and land use management) the model can be applied most accurately and how the model can be further improved. We believe that such an evaluation is mainly hampered by the fact that information on model parameterization is not always sufficiently presented. Such information should include a description on how the model was initialized to represent each considered field site, whether measured and modelled grain yields were compared or adjusted (and if so, why and how), and if any additional calibration was carried out.

Objectives were to test a proposed calibration and validation scheme for a field experiment with spring wheat on a sandy soil in Darmstadt, Germany, using different fertilizer types and rates in order to test the usefulness of the DNDC model for a description and prediction of crop growth and N_2O emissions.

5.2 Materials and Methods of the Fourth Study

5.2.1 Study Site

We tested the DNDC model with data from the Darmstadt long-term trial (Heitkamp et al., 2009). Briefly, the experimental trial is situated near Darmstadt, Germany (49°50′ N, 8° 34′E), with an elevation of 100 m a.s.l. The mean temperature is 9.5 °C and the mean annual precipitation is 590 mm. The soil is a Haplic Cambisol (WR*B*, 2006) which developed on alluvial fine sands of the river Neckar (Bachinger, 1996). For soil properties see Table 12.

Table 12: Site characteristics for the soils (0 – 25 cm) of the MSI and FYM treatments (means and standard deviation, n = 4).

	pH	Bulk density ($g\ cm^{-3}$)	SOC ($mg\ g^{-1}$)	N_t ($mg\ g^{-1}$)	Sand (%)	Silt (%)	Clay (%)
MSI_L	6.0	1.41 (0.04)	6.71 (0.30)	0.63 (0.05)	84.8 (1.8)	10.5 (1.8)	4.7 (0.4)
MSI_M	6.1	1.37 (0.07)	6.93 (0.84)	0.65 (0.09)	85.9 (0.9)	9.2 (0.9)	4.9 (0.5)
FYM_L	6.4	1.35 (0.06)	7.47 (0.74)	0.74 (0.09)	85.4 (1.0)	9.0 (0.8)	5.6 (0.3)
FYM_M	6.3	1.38 (0.02)	8.17 (0.67)	0.79 (0.08)	85.7 (0.7)	8.5 (0.5)	5.8 (0.2)

The experiment was initiated in 1980, where nine treatments (four replicates each) were arranged in a strip design, the factors being type of fertilizer and its application rate. With the exception of fertilization, all management actions were the same. The crop rotation consisted of legumes (mainly red clover, *Trifolium pratense* L. or lucerne, *Medicago sativa* L.), spring wheat (*Triticum aestivum* L.), root crops (mainly potatoes, *Solanum tuberosum* L.) and winter rye (*Secale cereale* L.). Residues of potatoes were incorporated into the soil.

Four treatments are considered in this study (Table 12). They have been in place since 1985 as follows:

(i) MSI_L: low application rate of mineral fertilizer (50 kg N ha^{-1} to root crops or 60 kg N ha^{-1} to cereals) plus straw incorporation. Thus, in 2007 N addition was 60 kg N ha^{-1} (mineral fertilizer) and 28 kg N ha^{-1} (N in the wheat straw).

(ii) MSI_M: medium application rate of mineral fertilizer (100 kg N ha^{-1} to root crops or 80 kg N ha^{-1} plus 20 kg N ha^{-1} as second application to cereals) plus straw incorporation. Therefore, in 2007 N addition was 100 kg N ha^{-1} (mineral fertilizer) and 47 kg N ha^{-1} (N in the wheat straw).

(iii) FYM_L: low application rate of rotted farmyard manure: 9 t fresh weight ha^{-1} as manure to root crops or cereals. The total N input corresponded to the N input by mineral fertilizer in the treatment MSI_L. Thus, in 2007 N addition was 60 kg N ha^{-1} as farmyard manure.

(iv) FYM_M: medium application rate of rotted farmyard manure: 18 t fresh weight ha^{-1} as manure to root crops or 12 t fresh weight ha^{-1} plus 20 kg N ha^{-1} with urine (second application) to cereals. The total N input corresponded to N input by mineral fertilizer in the treatment MSI_M. Thus, in 2007 N addition was 100 kg N ha^{-1} as farmyard manure and urine.

The mineral fertilizer consists of calcium ammonium nitrate, super phosphate and potassium magnesia. Farmyard cattle manure originated from deep litter housing and therefore contained considerable amounts of straw. It is left to rot for three (winter rye) or six months (spring wheat and root crops) before application. When legumes were planted, no fertilizers were applied. In 2007, C and total N contents of the manure after storage were 416 and 18.3 g kg^{-1} dry matter (dm), respectively. Contents of NH_4^+ in the manure were only 0.23 g NH_4^+-N kg^{-1} dm.

Crops grown in 2007 were oilseed radish as cover crop followed by spring wheat from the 21st of March to the 1st of August and ryegrass as cover crop (Table 13). In 2007, six soil management operations were carried out, either rotary tillage or moldboard ploughing down to 25 cm (Table 13).

5.2.2 Field N_2O Fluxes and Soil Moisture

Trace gas fluxes of N_2O were measured approximately once a week in 2007 (Figure 13) using the closed chamber method with one chamber on each of the four plots per treatment (thus n = 4 for each treatment). The method is described in detail by Ruser et al. (2001). Briefly, the circular chambers were made of dark PVC with an inner diameter of 29.5 cm and an initial height of 15 cm. By using extensions of the same material the height of the chamber could be adjusted to plant growth. For each gas measurement these chambers were placed on permanently installed PVC-soil collars with the same diameter and sealed with a lid.

On the same day as the flux measurements, soil moisture was determined with four replicates for each treatment. Briefly, soil samples were taken from five points in a radius of approximately 30 to 60 cm distance from the PVC-soil collars at a depth of 0 – 10 cm and composited to obtain one sample for each plot (thus n = 4 for each treatment). Composited samples were weighed, oven dried to constant mass at 105 °C, and reweighed. The dry weight and differences between fresh and dry weight were used to calculate the gravimetric water content. Water-filled pore space (WFPS) is calculated by WFPS = (soil gravimetric water content x bulk density) x (1 − (bulk density / particle density))$^{-1}$ (Linn and Doran, 1984) and by using a particle density of 2.65 g cm^{-3}.

5.2.3 DNDC Model

We used the DNDC model (model version 9.3; http://www.dndc.sr.unh.edu, downloaded on the 1st of September 2009) to describe and predict water dynamics, crop growth and N_2O emissions. The following model variants were considered:

Model variant v1 – no calibration, solely use of the measured initial data and default values

No calibration was carried out. For a prediction of soil water dynamics, crop growth and N_2O emission in the MSI_L treatment, the model used the input for the SOC content, pH and bulk density given in Table 12, the crop management given in Table 13 and the hydrology characteristics were calculated by the model using the implemented pedotransfer function for a loamy sand. For crop growth of oilseed radish, spring wheat and ryegrass, the default values for “radish”, “spring wheat” and “grassland” provided by DNDC were used. Weeding was not considered by the model, since the options were solely “no weed problem” or “moderate weed problems”.

Table 13: Summary of selected input data of the DNDC model for the MSI_L treatment.

Data	Value	Data	Value
Climate data		*Crop data*	
Latitude (degree)	49.871	First crop: radish (cover crop) (dates)	01.01. – 08.03.
Annual mean temperature in 2007 (°C)	10.9	Second crop: spring wheat (dates)	21.03. – 01.08.
Annual precipitation in 2007 (mm)	713	Third crop: ryegrass (cover crop) (dates)	09.10. – 01.03.
Atmospheric CO_2 concentration (ppm)	350		
N concentration in rainfall (ppm)	4.4	*Tillage*	
		Ploughing[b] down to 20 cm (dates)	09.03., 13.09.
Soil data[a]		Ploughing with disk or chisel[b] (dates)	05.03., 12.03., 14.08., 17.09.
Soil texture	loamy sand		
		Irrigation and weeding	
Fertilization		Irrigation (dates and mm)	02.05: 11, 16.10.: 13
NH_4NO_3 at the 15.03. (kg N ha^{-1})	60	Weeding (date)[d]	04.04.

[a]pH, bulk density and SOC are given in Table 12
[b]Ploughing depth was 25 cm (25 cm depth is not included in DNDC),
[c]soil was tilled using a rotary tiller (not included in DNDC, thus ploughing with disk or chisel was used in the model).
[d]not included in the model, since weed problems on the field were minimal.

Model variant v2 – adjustment of soil water dynamics using curve fitting

The model variant v2 was the same as model variant v1 except that we now used the soil texture class in the pedotransfer function that resulted in the best agreement between simulated water contents and measured WFPS data of the MSI_L treatment. All textures provided in the DNDC database were tested and the best results were obtained by using the default values for the texture class loam.

Model variant v3 – calibration of the yields using realistic maximum grain yields and calibration of the cumulative N_2O emissions by adjusting the initial SOC content

Model variant v3 was based on model variant v2, but included additional calibrations for grain yield of spring wheat and initial SOC content using the experimental treatment MSI_L. Maximum grain yield of spring wheat was optimized in the range between 1200 kg C ha^{-1} (default value in DNDC, 32.4 dt dm (including 14% water) ha^{-1}) and 2403 kg C ha^{-1} (65.0 dt dm ha^{-1}). The upper value corresponds to the maximum yield for a number of spring wheat varieties in Germany in 2003 (Aman and Ott, 2003). We carried out scenario testing and found that an optimum agreement between measured and modelled grain yield of wheat was obtained by setting the maximum grain yield to 1345 kg C ha^{-1} (36.4 dt dm ha^{-1}).

Finally, the initial SOC content was optimized in order to best match the cumulative N_2O emission of the MSI_L treatment. Optimum agreement was found for an initial SOC content in the surface soil of 6.83 mg g^{-1}.

Retrospective predictions were carried out for the remaining three treatments based on the parameters obtained by the calibrations and considering the fertilization scheme as described above.

5.2.4 Statistical analyses

The performance of the model calibration and retrospective prediction of the soil water dynamics was evaluated by calculation of the root mean square error RMSE, model efficiency EF, and relative error *E* as defined in Smith et al. (1997):

$$\mathrm{RMSE} = \frac{100}{\overline{O}}\sqrt{\sum_{i=1}^{n}(P_i - O_i)^2 / n}\ , \quad (1)$$

$$\mathrm{EF} = \frac{\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2}\ , \quad (2)$$

$$E = \frac{100}{n}\sum_{i=1}^{n}(O_i - P_i)/O_i\ , \quad (3)$$

where O_i are the observed (measured) values, P_i are the predicted values, $\overline{O}$ is the mean of the observed data and *n* is the number of paired values. RMSE ranges from 0 to ∞, EF from $-\infty$ to 1 and E from $-\infty$ to ∞. For an ideal fit, RMSE and E equal zero and EF equals 1.

5.3 Results and Discussion of the Fourth Study

5.3.1 Yields and N_2O Emissions

Measured grain yields of spring wheat ranged from 30.0 to 34.8 dt dm ha^{-1} and were similar for the different types of fertilizer (Table 14 and 15). Increase of the rate of fertilizer from 60 to 100 kg N ha^{-1} did not result in significant yield changes either for the MSI or for the FYM treatments (Table 14 and 15). These yields are low compared to the average yields in Germany, which reached 51 dt dm ha^{-1} in 2007 (Statistisches Bundesamt Deutschland, 2009). The main reasons for these reduced yields in Darmstadt are the relatively dry site conditions and the low soil fertility of the sandy Cambisol. Similarly, the few long-term experiments in Europe on low fertility sandy soils (Thyrow, Germany and Askov, Denmark) also indicate reduced yields of crops compared to those of more fertile soils with a finer texture (Edmeades, 2003).

Cumulative N_2O emissions were small for the sandy site for all four treatments and ranged from 721 to 813 g N_2O-N ha^{-1} for the period from March to December (Table 3 and 4). Jungkunst et al. (2006) reported that annual N_2O emissions from fertilized German arable soils ranged from 0.07 to 17.1 kg N_2O-N ha^{-1}. In our study, small cumulative emissions were expected because of the dry conditions. In 2007, cumulative precipitation was 713 mm (Table 2), which is close to the threshold (< 600 mm) given by Jungkunst et al. (2006) for low emission sites in Germany.

Seasonal dynamics of N_2O emissions were not pronounced. Increases of N_2O emissions were associated with ploughing in March and September and with the application of 60 (MSI_L, FYM_L) or 80 (MSI_M, FYM_M) kg N ha^{-1} in March (Figure 13).

Table 14: Measured (means and standard deviations, n = 4) and modelled yields of spring wheat and cumulative N_2O emission in the MSI_L treatment. Statistics on the measured and modelled soil water dynamics are also given. Modelled data refer to a retrospective prediction (model variant v1) and calibration results (model variants v2 and v3).

	measured	v1	v2	v3
Yields				
Spring wheat grain[a] (dt dm ha^{-1})	31.1 (1.8)	20.6	28.3	31.1
Spring wheat straw (dt dm ha^{-1})	45.1 (2.3)	28.2	38.6	42.5
N_2O emissions				
Cumulative N_2O emissions (g N_2O-N ha^{-1}) (Mar – Dec)	813 (191)	1040	703	813
Soil water in 0 – 10 cm (measured) and at 5 cm (modelled)				
Mean WFPS (%) for all sampling dates	32.1	11.9	32.4	32.6
RMSE (WFPS)	-	68.0	24.9	24.7
EF (WFPS)	-	-2.2	0.6	0.6
E (WFPS)	-	324	1.0	0.4

[a]Amounts include 14% water content for grain. Modelled yields were recalculated using a C content of 43 % (grains, straw) and considering the water content of 14 % (grains)

However, the second application of mineral (MSI_M) or organic (FYM_M) fertilizer did not affect N_2O emissions, probably because of the rather small N amount that was added. The increase of N_2O emission rate on the 21st of August could not be associated with either fertilization or rewetting of the soil, both being generally considered to be important determinants for N_2O emissions (Kaiser et al., 1996; Jungkunst et al., 2006). However, the tilling of the soil using a rotary tiller (Table 13), the warm temperatures and precipitation of 12 mm in the previous week may have contributed to this peak. Spatial variability, however, was large.

Table 15: Measured (means and standard deviations, n = 4) and predicted grain yields of spring wheat and cumulative N_2O emission in the MSI_M, FYM_L and FYM_M treatments. Statistics on the measured and modelled soil water dynamics are also given.

	MSI_M		FYM_L		FYM_M	
	measured	v3	measured	v3	measured	v3
Yields						
Spring wheat grain[a]	30.0		30.8		34.8	
(dt dm ha^{-1})	(2.0)	31.2	(3.1)	16.7	(0.8)	20.1
Spring wheat straw	50.5		38.1		41.8	
(dt dm ha^{-1})	(2.8)	42.6	(2.5)	22.8	(3.1)	27.4
N_2O emissions						
Cumulative N_2O emissions (g N_2O-N ha^{-1}) (Mar − Dec)	721 (181)	1141	812 (95)	625	735 (87)	660
Soil water in 0 – 10 cm (measured) and at 5 cm (modelled)						
Mean WFPS for all sampling dates	29.4	32.6	29.0	33.5	31.8	32.9
EF (WFPS)	-	0.6	-	0.3	-	0.6

[a]Amounts include 14% water content for grain. Modelled yields were recalculated using a C content of 43 % (grains, straw) and considering the water content of 14 % (grains)

5.3.2 Performance of Model Variant v1

Model variant v1, which is applied to provide an independent simulation without any parameter optimization, indicated that the default values given by DNDC may not always be useful. The pedotransfer function used for this site (loamy sand) resulted in large deviations between modelled and measured WFPS data (Figure 14, Table 14). Measured WFPS showed a large spatial variability for some dates, but the modelled WFPS was consistently smaller in almost the entire period (Figure 14). The measured and modelled mean WFPS from 39 sampling dates were 32% and 12%, respectively. The root mean square error RMSE and the relative error E were the largest of all three model variants tested (Table 14). The negative efficiency value EF indicated that the model variant described the WFPS data less well than the mean of the data.

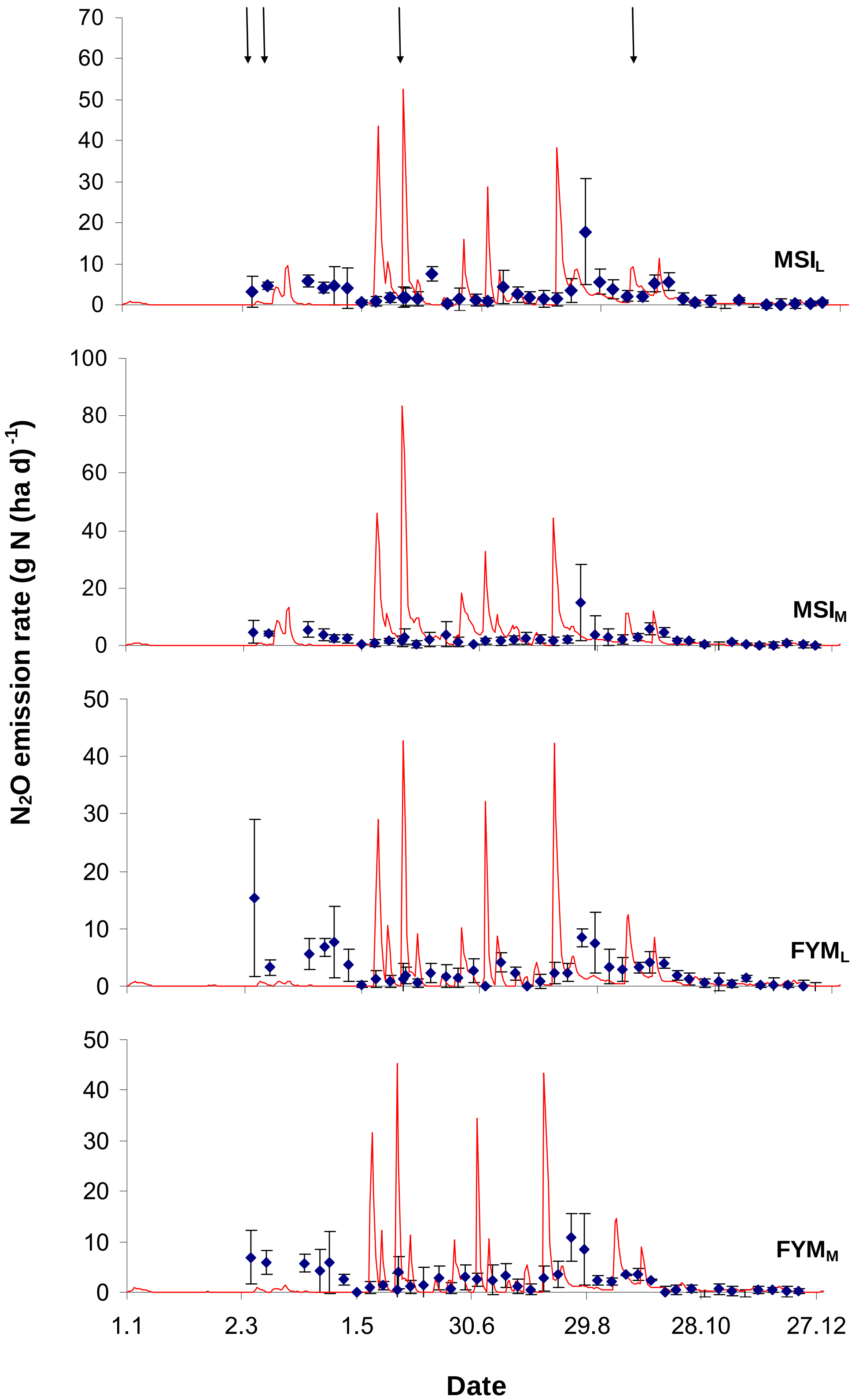

Figure 13: Modelled (lines, model variant v3) and measured (symbols, means and standard deviations) N_2O emissions from soils of the four treatments. Arrows indicate the timing of moldboard ploughing (09.03.), fertilization of 60 (MSI$_L$, FYM$_L$) or 80 kg N ha^{-1} (MSI$_M$, FYM$_M$, 15.03.), fertilization of 20 kg N ha^{-1} (MSI$_M$, FYM$_M$, 21.05.) and moldboard ploughing (13.09.).

We tested the use of the next finer texture class (sandy loam) in an additional model variant v1b (data not shown). Description of temporal dynamics of the WFPS was slightly improved, but overall, the performance of the model variant was also poor as indicated by a large RMSE, an EF value of −0.9 and a large relative error *E* of 128 (data not shown). Some of the deviations between the measured and modelled WFPS using the pedotransfer functions may be explained by the fact that most particles in the sand fraction of the sandy soil were fine sand (fine sand: 71.5%, medium sand: 12.7%, coarse sand: 0.5%).
The use of the pedotransfer function provided by ROSETTA (Schaap, 2002) by considering measured texture and bulk densities resulted in only slightly different WFPS at field capacity (28.5% WFPS) and at wilting point (9.9% WFPS) compared to model variant v1 (25 and 13% WFPS). Moreover, when we used these data as input for the DNDC model, the obtained EF (−1.5) also indicated a poor agreement between modelled and measured WFPS (not shown). Deviations between measured and simulated WFPS were also reported by Smith et al. (2008), Abdalla et al. (2009) and Kröbel et al. (2010) when applying the DNDC model to Canadian, Irish or Chinese sites. For instance, for an Irish grassland soil, WFPS was considerably overestimated by DNDC (version 9.2) (Abdalla et al., 2009). Similarly to our results, Smith et al. (2008) reported for Canadian sites that DNDC (as well as DAYCENT) underestimated soil water content particularly during the growing season. Our results also indicate that the use of a different pedotransfer function, in our case provided by ROSETTA, did not result in better simulations of soil water dynamics.

5.3.3 Performance of Model Variant v2

A test using each texture class provided by the DNDC model showed that the best agreement between measured and modelled WFPS data was achieved by the texture class loam (Figure 14): RMSE decreased to 24.9, E decreased markedly to 1.0, and EF increased to 0.6, indicating a good agreement between measured and calibrated data. The need for site specific calibrations has also been stated in other studies. For instance, Tonitto et al. (2007) applied the DNDC model to tile-drained Illinois agroecosystems and concluded that an accurate simulation of NO_3-N leaching and drainage dynamics required significant changes to key soil physical and chemical parameters relative to their default values.

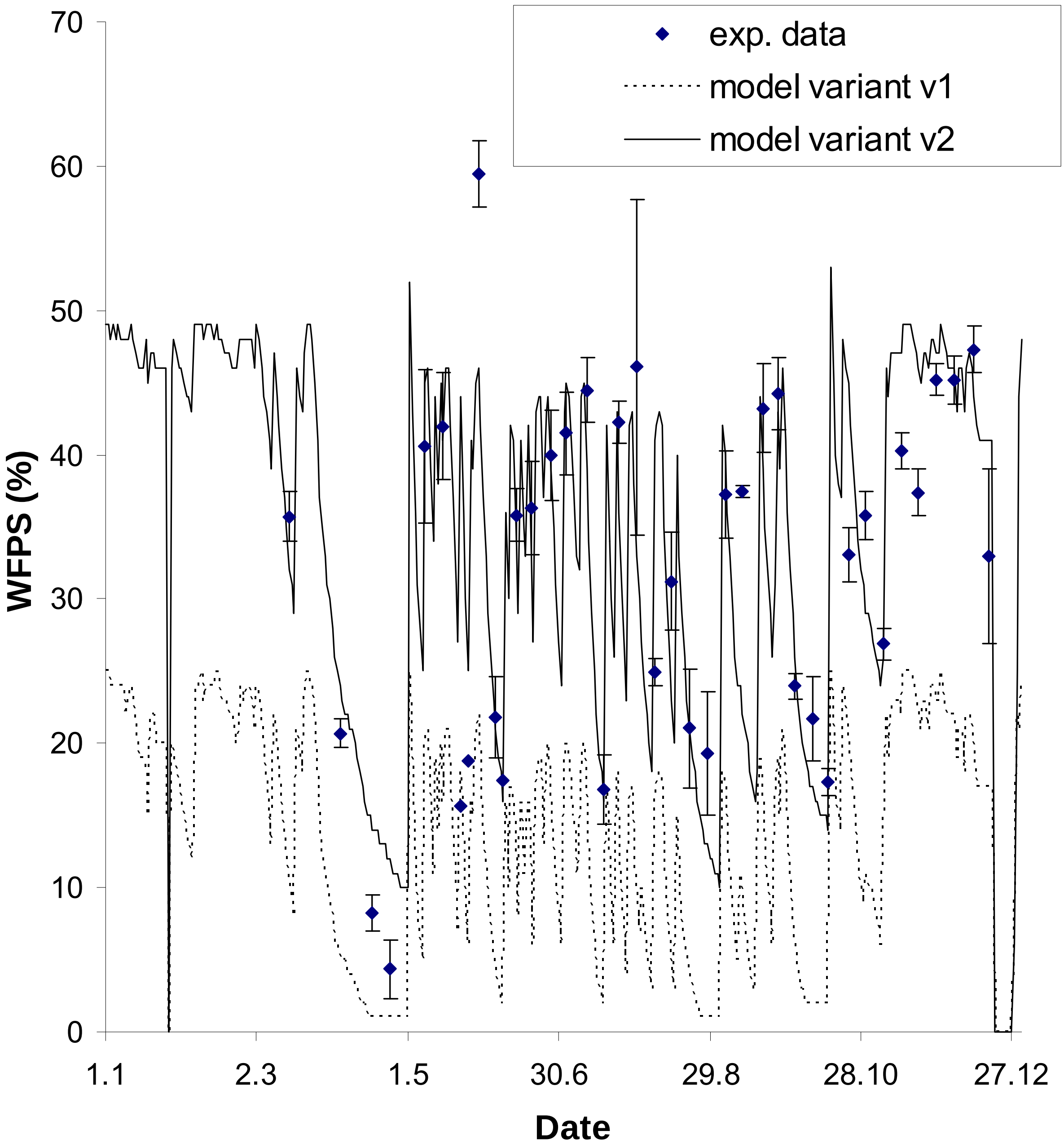

Figure 14: Modeled (at 5 cm depth, lines, model variants v1 and v2) and measured (in the 0 – 10 cm depth range, symbols, means and standard deviations) water-filled pore space in soils of the MSI_L treatment.

Overall, the results of model variants v1 and v2 indicate that it is essential – at least for the site studied – that the DNDC model is calibrated to the soil water dynamics. Since neither the default values for texture class of the studied soil using the DNDC pedotransfer function nor the additional use of the ROSETTA software gave satisfactory model efficiencies, we used a simple curve fitting procedure in model variant v2, the use of a different texture class. For a soil in the North China Plain, Kröbel et al. (2010) optimised in the DNDC model, besides other parameters, the WFPS at field capacity, clay fraction and bulk density for a calibration of soil water dynamics and noted that the optimised clay fraction no longer accurately represented the investigated system. Moreover, they concluded that the cascade model approach used by the DNDC model appeared to be unsuitable to simulate soil water dynamics at their specific site. Instead of using a very different texture class as in our study or instead of optimising the clay content and bulk density (Kröbel et al., 2010), it may be sufficient to test several adjustments of the WFPS at field capacity and wilting point, of the porosity and of the hydro-conductivity in the texture class of the studied soil. However, this was not tested in this study.

In our study, after the above parameterization of the soil water flow model, the model variant v2 simulated crop growth using the growth parameters implemented in DNDC quite successfully: predicted grain yield of spring wheat was 28.3 dt dm ha^{-1} (91% of the measured yield) and predicted yield of leaves and stems was 38.6 dt dm ha^{-1} (86% of the measured straw yield, Table 3). This agreement is surprising, since the yield performance between different varieties can vary strongly. Moreover, we could not find evidence in the literature for all of the default values that are given by DNDC for growth of spring wheat. For instance, Ehlers (1996) reported values of transpiration coefficients for wheat in the range of 169 to 488 kg water (kg dm) $^{-1}$, that are considerably higher than the default value in DNDC (150 kg water (kg dm)$^{-1}$). The default N demand (which depends on the biomass fractions and biomass C/N ratios of the compartments grain, leaves plus stem and root) is small (93 kg N ha^{-1}) compared to the range of the N fertilization recommendation for spring wheat in the range of 160 to 230 kg N ha^{-1} (KWS Lochow GmbH, 2010). In contrast, the default value of the thermal degree days for this crop (1800 days) is well in the range of 1500 to 2100 days given by Entrup and Oehmichen (2000).

Overall, the calibration of the soil hydrology in variant v2 resulted in different water fluxes and N and C fluxes compared to model variant v1. Due to the different pedotransfer function used, the model estimated an improved crop growth as discussed above and thus also an increased N uptake by the crops. Additionally, the model estimated that less water leaching and thus also less nitrate leaching occurred due to the assumed finer texture. The total effect of the different fluxes was a slight decrease in N_2O emissions in this model variant (Table 13).

5.3.4 Performance of Model Variant v3

Calibration of crop growth may be achieved by optimizing several combinations of parameters. In the DNDC manual (Li, 2009), it is suggested that for a calibration of crop growth, the crop heat/water/N demands, growth curve, biomass partitioning or yield may be adjusted. However, not all options of parameter optimization are meaningful. For instance, to increase simulated yields, a reduction of the water demand for spring wheat makes little sense, since the default value is already small compared to literature data. The simplest approach seems to be to optimize the maximum grain yield as we have done (model variant v3). The optimum maximum grain yield for winter wheat (36.4 dt dm ha^{-1}) obtained in the calibration indicates that a minor site-specific calibration was required to adjust for the biomass production; the data used was close to the default value for spring wheat in DNDC (recalculated to 32.4 dt dm ha^{-1}) but very different to the observed maximum yields of spring wheat in Germany (65.0 dt dm ha^{-1}, Aman and Ott, 2003).
Calibration of cumulative N_2O emissions in model variant v3 was achieved by slightly modifying the initial SOC content in the surface soil, which has a major effect on N_2O emission (Abdalla et al., 2009). Increase of the initial SOC content by only 0.12 mg g^{-1} in the model, a value within the standard deviation of 0.3 mg g^{-1}, resulted in an agreement of measured and modelled cumulative N_2O emissions (813 g N_2O-N ha^{-1}, Table 3). However, the annual distribution of N_2O emissions showed large deviations for the 9th of May, 22nd of May and 7th of August, where the model simulated emission rates of 44, 53 and 38 g N (ha day)$^{-1}$, all triggered by precipitation events (Figure 13), with the 22nd of May (34.8 mm) and the 9th of May (31.3 mm) being the days with the largest amounts of precipitation in 2007.
The overall successful performance of model variant v3 compared to variant v1 (except for the annual distribution of N_2O emissions) indicates the need for site-specific calibration of the DNDC model to describe the complex plant-soil-atmosphere interaction, thus emphasizing the relationship between model and site (Beven, 2002; Priesack et al., 2006).
Soil water dynamics were similar for all four treatments. Thus, the calibration made for the MSI_L treatment in model variant v3 was also successful for the MSI_M, FYM_L and FYM_M treatments with EF values for measured and predicted WFPS data ranging from 0.3 to 0.6 (Table 15).

In contrast, prediction of the yields of spring wheat grain and straw had variable success: for the MSI_M treatment, the model correctly predicted that increased N input for this site did not result in increased grain yield and it approximately matched the yield of straw. For the FYM treatments, however, the model markedly underestimated grain and straw yields (Table 15), indicating that calibration results could not be used for prediction of yields where a different fertilizer type was used. The use of additional model variants (not shown), where the SOC contents of the soils of the respective treatments (Table 12) were used in the model instead of the value of 7.1 mg g^{-1} obtained in the calibration procedure, did not result in marked improvements of the prediction accuracies: grain yield of spring wheat in the prediction increased only slightly to 20.6 (FYM_M) and 17.0 dt dm ha^{-1} (FYM_L).

Cumulative N_2O emissions from March to November 2007 were approximately matched for all three treatments with only a slight overestimation (1141 compared to 721 g N_2O-N ha^{-1} for MSI_M) or underestimation (625 compared to 812 g N_2O-N ha^{-1} for FYM_L and 660 compared to 735 g N_2O-N ha^{-1} for FYM_M, Table 15). However the model simulated several event-based emissions that were not observed to such an extent in the experiment (Figure 13).

5.4 Conclusions of the Fourth Study

The DNDC model is a very user-friendly model needing inputs that are generally easy to obtain. At present, we are not aware of any specific recommendation for modellers of how to calibrate the model to a specific site and we suggest to use an approach consisting of (i) using default values, adjusting (ii) soil hydrology, (iii) crop yields and (iv) cumulative N_2O emissions, before the model may be used for subsequent predictions. Moreover, a longer time span prior to the period of interest and a longer time span for the retrospective prediction than used in our study may give more detailed insights in the usefulness of the DNDC model at a specific site. However, our study indicates that the prediction accuracy may only be sufficient for similar treatments such as an increase of fertilizer rate, but not for a different fertilizer type. For the site studied, N_2O emissions were very low. DNDC (or other models) may be limited in their ability to accurately predict such a range of emissions.

Overall, we suggest that in modeling papers more space may be devoted to the description of the model parameterization and a discussion of its plausibility. Without such information, readers outside the modeling community may get a rather blurred idea of what can be achieved by predictive models.

6. General Discussion

6.1 Influence of the Fertilizer Type on N_2O Emissions

Many studies have shown that the use of fertilizer increases N_2O emissions and that the intensity of these emissions is dependent on the type of fertilizer (Bouwman, 1996; Eichner, 1990). We found that the effect of the fertilizer type on N_2O emissions depended on soil moisture. As long as soil moisture was below 60 – 70% WFPS N_2O emissions following mineral fertilizer application were lower than after application of organic fertilizer. Mineral fertilization increases mineral N contents in the soil, which may not necessarily increase N_2O emissions provided soil moisture is below a certain threshold. That means that in case soil moisture becomes favourable, N_2O emissions can increase markedly because of the high substrate availability. As a result, mineral fertilizer application in combination with higher soil moisture increases denitrification due to the low oxygen saturation.

This combined effect on N_2O emissions was also described in comparable studies. Velthof et al. (2003) performed an incubation experiment at field capacity and reported that the application of mineral fertilizer induced N_2O emissions in the same order of magnitude as compared to emissions induced by organic fertilizer. Dobbie et al. (1999) showed that the N_2O fluxes were low, when one of the variables like soil moisture, temperature and mineral N content was below a critical value. Dobbie and Smith (2001) reported N_2O emissions after ammonium nitrate application were negligible at low WFPS and increased with WFPS > 80%. Hence, it can be concluded that the amount of N_2O emissions is not solely determined by the type of fertilizer, and thus the form of N, but also by other factors like soil moisture. In addition, fertilizer induced emissions at different soil moisture depended on the fertilizer type. At low soil moisture, emissions were higher from the organically fertilized treatments than from the mineral fertilized treatments. But at high water saturation, highest emissions occurred from the treatments receiving nitrate.

The results of our laboratory studies described in chapters two and three show that N_2O emissions after organic fertilizer application were higher than after mineral fertilizer application, especially at low soil moisture levels. The addition of easily available C by organic fertilizers favours the O_2 consumption by higher microbial activity and anaerobiosis on soil microsites (van Groenigen et al, 2004; Calderón et al., 2005). Flessa and Beese (2000) explained the higher N_2O emissions induced by slurry, compared to mineral fertilizer with strongly increased microbial respiration, which favours anaerobic hotspots with high denitrification potential.

During the field study (chapter 4) the effect was not as clear, because the applied manure was composted for several months and tillage followed the organic fertilization, inducing N_2O emissions. This finding confirms results of former studies analysing the impact of organic fertilizer application on N_2O emissions. These studies revealed that higher emissions can occur directly after the application of manure with high contents of easily available N and easily mineralizable C (Comfort et al., 1990; Paul et al., 1993; Chadwick et al., 2000; Velthof et al., 2003; Petersen, 1999).

Many studies on N_2O emissions induced by organic fertilizer were performed with slurry (Rochette et al., 2000; Van Groenigen et al., 2004; Dendooven et al., 1997). They found higher emissions following slurry application than mineral fertilizer application. Dendooven et al. (1997) reported high emissions after pig slurry application. They again explained this finding with the additional and easily available C source and the high denitrification potential induced by microbial activity and indicated by higher CO_2 emissions. Higher N_2O emissions directly following the application of organic fertilizers might also be related to the amount of volatile fatty acids in the organic fertilizer (Velthof et al., 2003). Volatile fatty acids, which are built during digestion in the rumen, are an easily degradable C source (Canh et al., 1998). This easily available C source can be decomposed within days and increases the denitrification potential (Kirchmann and Lundvall, 1993; Paul and Beauchamp, 1989). Another C source contributing to N_2O production could be dissolved organic carbon (DOC). Velthof et al. (2005) studied the influence of different diets on manure quality and emission potential. They found out that N_2O emissions were correlated with volatile fatty acids but not with DOC. Saari et al. (2009) reported that not the concentration of DOC but the light molecular weight fraction of DOC was a major determinant of N_2O emissions. However, the effect of DOC and other C components on N_2O emissions is not fully understood.

In contrast to slurry, the effects of composted solid manure on N_2O emissions are less well studied. For this reason, the field experiment, presented in chapter four, was set up to analyse the impact of composted manure on N_2O emissions. Composted manure was applied each year and the results show that these applications were followed by N_2O emissions comparable to those from the mineral fertilized fields. These lower emissions on the manured treatments might be due to the fact that the composting of cattle manure results in a more advanced stage of organic matter oxidation and a greater enrichment in aromatic compounds (Gómez et al., 2007).

Additionally, Kirchmann (1991) reported that aerobically treated manure contains more stable C than fresh or anaerobically treated manure, which may lead to a lower denitrification potential. Compared to slurry, composted manure induced lower N_2O emissions as reported by Paul et al. (1993). This is in line with Calderón et al. (2005), who analysed the N losses of different manures and came to the conclusion that high ammonium contents of the manures led to higher N_2O emissions. Velthof et al. (2003) analysed different organic fertilizers and showed that manures contained higher organic N contents than slurries and the proportion of ammonium to total N was higher in solid manures. They reported that slurries with high mineral N contents and easily mineralizable C increased N_2O emissions whereas the organically bound N contents in manure led to a constant but slow supply of N (Chang et al., 1998; Gutser et al., 2005). This constant but slow release of mineral N may reduce the risk of N_2O emissions.

Former studies, comparing the effect of liquid slurry and solid manure on N_2O emissions do not provide a consistent picture. Loro et al. (1997) and Mogge et al. (1999) reported higher N_2O emissions following the application of solid cattle manure compared with application of liquid cattle manure whereas Chadwick et al. (2000) measured higher N_2O emissions from slurry compared with different manures. They explained that fact with the higher soil water content induced by liquid slurry application, the added fertilizer C and the high amount of NH_4^+. These effects on N_2O emissions also depend on soil properties as demonstrated by Velthof et al. (2005). Rochette et al. (2008a) found no difference in N_2O emissions following the application of liquid or solid manure and explain the differences reported in literature with the varying composition of organic fertilizers, the application technique and the soil type.

The application technique is another factor influencing the amount of N_2O emissions induced by organic fertilizers. There are several techniques to apply organic fertilizer, especially slurry, such as surface application followed by harrow or ploughing, narrow band spreading or injection. Former studies found out that injection of slurry enhances the denitrification potential (Wulf et al., 2002; Flessa and Beese, 2000; Thompson et al., 1987).

Moreover, the rate of the applied fertilizer is known to increase N_2O emissions (IPCC, 2007). However, during our field study we could not find such a correlation. N_2O emissions did not increase with the three fertilization rates. Such a lack of correlation has also been reported by Sehy et al. (2003) and Kaiser and Ruser (2000), indicating that at some sites factors other than N input may mainly govern N_2O emissions. Important factors, besides N input, may be soil moisture, temperature, soil nitrate contents and contents of available C. In our study, the effects of fertilizer rates on N_2O emissions were presumably low because of the high sand content.

Recently, biogas waste has been increasingly used as fertilizer because of the rising number of biogas plants in Germany (Gericke, 2009). Hence, one aim of the first laboratory incubation was to analyse the effect of biogas waste on the N_2O emissions from soils. During this study, described in chapter two, manure and mineral fertilizer application were compared with biogas waste application. The results of this experiment reveal that biogas waste induced very high N_2O emissions in our experiment. Additionally, the results show that C availability and the amount of ammonium are considerably greater than in farmyard manure. However, it is not clear, whether these results may be generalized for other biogas wastes. Most often biogas fermentation is compared with digestion in the rumen and related to manure and a more stable fertilizer with high nutrient use efficiency would be assumed (Möller and Stinner, 2009; Kirchmann and Lundvall, 1993). Large amounts of N in biogas waste are applied as ammonium (Gericke, 2009). Möller and Stinner (2009) found that biogas waste emits less N_2O after application than non-fermented liquid slurry. Several studies have shown that anaerobic digestion reduced N_2O field emissions induced by slurry application (Petersen, 1999; Clemens and Huschka, 2001; Amon et al., 2006, Möller and Stinner 2009). This was explained by a reduction of readily available OC, especially the soluble carbohydrates and protein fractions during fermentation (Vallejo et al., 2006). Therefore, composted manure and biogas waste, reduced in soluble organic fractions, emits less N_2O due to the reduced denitrification potential. Möller and Stinner (2009) reported emission reduction of 38% from digested slurry compared to undigested whereas Petersen (1999) determined a reduction of 20 – 40%. More research on biogas residues would elucidate the N_2O emission potential of biogas residues.

6.2 Influence of Long-term Organic Fertilization on N_2O Emissions

Increased organic C stocks led to slightly higher N_2O emissions under certain conditions. The second study described in chapter three revealed that increased organic C stocks induced by long-term application of farmyard manure resulted in slightly increased N_2O emissions at two of the three analysed soils (Methau and Spröda) at a soil moisture content of 60% water-holding capacity. However, this effect was small and only lasted as long as no other factors induced high N_2O emissions.

Chang et al. (1998) reported higher cumulative N_2O emissions after repeated application of organic fertilizer. They suggested that the repeated application of organic fertilizers leads to a "cumulative effect" by the long-term accumulation of nitrate and organic matter. The accumulated fertilizer C in the soil is a substrate for denitrifiers and increases microbial activity. Additionally, manure mobilizes organic N and constantly releases substrates for nitrification and denitrification over a longer time period (Mogge et al., 1999). The long-term application of manure successively fills up the organic C and N stocks, which can mineralize C and N over a longer time period. Webster and Goulding (1989) observed higher denitrification and higher N_2O emissions in treatments with higher C contents due to long-term manure application compared with mineral fertilized treatments. They justify their findings with the fact that C can be a factor limiting denitrification in the mineral fertilized treatments. Modeling studies with DNDC confirmed that C sequestration in soils increases N_2O emissions (Qiu et al., 2009; Li et al., 2005). Chirinda et al. (2010) compared conventional crop rotations receiving mineral fertilizer with organic crop rotations receiving organic fertilizer. They measured N_2O emissions from both systems in the same range although the N input was lower in the organic system.

However, our studies indicated that short-term events like fertilizer application or increased soil moisture, which induced high emissions, outweighed the effects of the long-term fertilization history as these emissions peaks were extraordinarily high. After these short-term events, differences between the long-term treatments were not detectable. Our studies showed that the substrate applied as fertilizer was a more important factor influencing short-term N_2O emissions than the SOC stocks. This is in line with Kilian et al. (1998) and Kaiser et al. (2000) who compared long-term application of mineral fertilizer with organic fertilization and came to the conclusion that organic fertilizers induced higher emissions. Kilian et al. (1998) confirmed that this effect was small in contrast to the short-term effects induced by fertilization.

However, two of the studies (chapter 4) presented in this thesis revealed no difference between the long-term fertilization treatments. During the field study (chapter 4) as well as during the first laboratory study (chapter 2), analysing the sandy soil (86% sand) from the Darmstadt site, N_2O emissions did not differ although the C stocks were higher in den organic fertilized treatments. Similar results were found by Meng et al. (2005), who also reported that organic C and N contents were higher in a sandy loam soil with long-term application of manure than with the application of mineral fertilizer but differences between N_2O emissions were not significant. Additionally, Stange and Neue (2009) found higher SOM contents following organic fertilization compared to mineral fertilization, but this fact did not increase N_2O emissions.

The low emissions in our studies, carried out with the sandy soil of Darmstadt, were probably mainly due to the very high sand content. The sandy soil texture led to constantly low soil moisture contents and constantly good aeration avoiding large denitrification losses. During the field study the soil moisture was too low to induce higher emissions from the organically fertilized treatments because the WFPS never exceeded 60%. This was reported to be the critical value to induce N_2O emission by denitrification (Dobbie et al., 1999; Khalil & Baggs, 2005). Rochette (2008) and Rochette et al. (2008b) concluded that the impact of increased organic matter stocks in coarse-textured soils on N_2O emissions is lower than in fine textured soils because these soils are well aerated.

Furthermore, the lack of an influence of SOC accumulation on N_2O emissions could be explained by the stability of the accumulated SOM. Heitkamp et al. (2009) reported that the partitioning of C inputs to labile SOC pools at the Darmstadt site was similar and independent from fertilization history but the accumulation of organic matter with intermediate stability was higher. Hence, the easily available, labile pool did not differ between the long-term fertilization treatments. C pool measurements at Methau and Spröda are not known.

Higher microbial activity induced by long-term fertilization was often reported to be one factor influencing N_2O emissions (Chang et al., 1998; Kilian et al., 1998; Li et al., 2005). For the sandy soil of the long-term trial at Darmstadt (chapter 2 and 4), there was no long-term effect of organic fertilization on N_2O emissions, although microbial activity was higher in the organically fertilized treatments (Heinze et al., 2009). A possible reason for this is that the difference of microbial activity in the fertilization treatments was too low to impact on N_2O emissions.

Enwall et al. (2005) found higher denitrification rates on a long-term field experiment in the plots treated with organic fertilizer than in those with mineral fertilizer. Rochette et al. (2000) also reported higher denitrification enzyme activity in the slurry treatments compared to the mineral fertilized treatments after 19 years of application. The emissions directly after application of slurry were higher compared to the mineral fertilizer. Nevertheless, they did not observe markedly increased long-term N_2O emissions in the organic fertilized treatments.

The second laboratory incubation presented in chapter three exhibits results which were contrary to our hypothesis that higher C stocks increase N_2O emissions. The unfertilized soil from the Bad Lauchstädt experiment exhibited very high N_2O emissions compared to the soil with extremely high manure application for 25 years. A possible explanation could be the degraded soil structure of the unfertilized soil. The soil structure resulted in a lower yield of water-stable macroaggregetes and probably reduced porosity and aeration because SOC is involved in the building of aggregation and acts as a binding agent and as a nucleus in the formation of aggregates (Bronick and Lal, 2005; Blair et al., 2006 a and b). This might have led to significantly higher N_2O emissions from the unfertilized soil although the total C and N contents were much lower compared to the manured soil with extremely high manuring rates. Cultivation decreases SOC, e.g. due to the nutrient removal and tillage and manure is a means to balance the removal. Permanently unfertilized soils are prone to soil degradation with low microbial activity and low amounts of macroaggregates (Bronick and Lal, 2005).

Several studies reported that fine-textured soils have a higher denitrification potential (Bouwman, 2002; Freibauer et al., 2003) and that the fine soil particles are more important for C stabilization (Hassink, 1997; Weigel et al., 1997). Rochette (2008) summarized data from different tillage experiments and came to the conclusion that well aerated soils react less to increased organic C stocks by minimum tillage than fine-textured soils. However, we could not confirm this finding in our laboratory study (chapter 3) when we analysed soils with different clay contents (Methau: 15% and Spröda: 6%). The more silty soil (Methau) did not consistently emit more N_2O than the more sandy soil. Our results support the conclusion by Skiba and Ball (2002) that the effect of soil texture on N_2O emissions is not consistent.

Furthermore, the results of the second study (chapter 3) show that the N_2O emissions are not necessarily related to the amount of C accumulation over the years. The difference between the fertilization treatments was higher in the fine-textured soils at Methau (C_{org} difference between the treatments of 55%) than in the coarse-textured soils at Spröda (C_{org} difference of 17%). This study revealed that the N_2O emissions were not higher from the soil with higher C accumulation and the higher absolute C contents (Methau: 9.9 – 15.3 mg C g^{-1}, Spröda: 7.1 – 8.3 mg C g^{-1}). Therefore, N_2O emissions might not only depend on the amount of C but also the availability of C is an important determining factor. Van Groenigen et al. (2004) stated that part of the differences in N_2O emissions during the incubation may have occurred because of differences in SOM quality. However, more research connecting SOM stability and N_2O emissions is needed.

7. Conclusions

The overall research question was whether or not organic fertilization leads to higher N_2O emissions due to increased SOC stocks. The results of our studies indicate that in long-term, organic fertilization may result in increased N_2O emissions, but only under certain conditions which strongly depend on soil and site-specific characteristics. However, this effect is low compared to the emissions induced by other factors like current fertlization management or climate. N_2O emissions after short-term events like fertilization outweighed the effect induced by higher organic C stocks. In contrast, a lack of fertilization for several years and, thus, reduced soil organic C stocks may have negative effects on soil structure and high N_2O emissions may be a consequence. Thus, the influence of organic C stocks strongly depends on the management and site-specific characteristics.

The results of the studies presented in this thesis show that the type of fertilizer strongly affected N_2O emissions in particular in the short-term. Mineral fertilizers tend to induce smaller N_2O emissions after their application at low soil moisture contents. But higher mineral nitrogen contents in the mineral fertilized soils could increase the risk of N_2O emission when soil moisture becomes increases. Organic fertilizers tend to increase N_2O emissions directly after application because of the higher denitrification potential induced by the easily available C applied. However, different organic fertilizers differently influence N_2O emissions. Manures, especially composted solid manures, may contain large amounts of organically bound C and N components and may slowly release nutrients so that the risk of N_2O emissions is reduced compared with slurries or fresh manures. Application of biogas waste resulted in very high N_2O emissions due to its large C and N availability. The composition of residues, the fermentation process and the storage have to be considered when organic materials are applied because they influence the C and N availability of the biogas residues.

A more stringent link of the research on SOM on the one hand and on N transformation on the other hand will be necessary. The determining factors for N_2O emissions are not only the amount of C stocks but also the availability, the form and the stability of C. More information about the stabilization process of long-term organic fertilization is helpful for a better determination of the feedback on trace gas emission. Not only the pool size but also the composition and the availability should be determined more in detail.

To reduce N_2O emissions humus preservation and a balanced nutrient management should be the target of sustainable agriculture. Although organic fertilization might lead to higher emissions on the short-term, a long-term application can contribute to humus preservation and soil fertility and, therefore, the additional N_2O emissions might be small. However, the application must be adapted to the crop demand to prevent high N_2O emissions.

8. References

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Declaration of the Author's Own Contribution to the Papers

The main part of the cumulative dissertation on hand is a series of manuscripts. The manuscripts will be published in peer-reviewed journals. I am the first author of three manuscripts and co-author of a fourth one. I took the soil samples, did the laboratory work with additional help of the technical staff, analyzed the data, evaluated them statistically, produced all tables and figures and wrote the text. Furthermore, I am corresponding author for the journal editors and reviewers. To the fourth article I contributed by supplying field measurement data for the evaluation of the model and by supporting the writing process.

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