

**Comparisons of N₂O and CH₄ fluxes
as affected by land use systems and climate
in small catchments in Korea**

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Summary

In the course of global and climate change humankind has to face extreme weather events with increased intensity and frequency and it has to deal with feeding an increasing number of people which is accompanied by shortage of resources such as water. Since half of humankind directly depends on freshwater and other ecosystem services provided by mountainous areas, it is essential to study such complex terrains and how natural as well as agricultural systems react to climatic and other anthropogenic changes.

Emissions of greenhouse gases like Nitrous oxide (N_2O) and Methane (CH_4) are of global concern, too, because they are involved in global warming and therewith: climate change. Major sources of N_2O are agriculturally managed soils, and very important sources of CH_4 are rice paddies. Thus, it is of great importance to study intensively managed agricultural systems and the effects of the management practices on greenhouse gas emissions.

The major focus of this thesis is to quantify dry crop fields' and forests' N_2O emissions as well as rice paddies' N_2O and CH_4 emissions and to identify climatic as well as management related factors and underlying processes which are driving the N_2O fluxes in a complex terrain.

A prolonged early summer drought in 2010 led to significant N_2O consumption in soil of three different forest sites. The following above-average monsoon rainfall period indeed turned the N_2O consumption into emission but could not turn the N_2O balance of a forest on sandy-loam substrate from negative into a positive one, which means that for the first time a negative N_2O balance was observed for a forest soil during the growing season. The N_2O emissions of those forest sites were clearly driven by soil moisture and temperature and there appeared to be an effect of the substrate on N_2O emissions as well, as it is increasingly often observed that sandy-loam soils show significant N_2O consumption.

Plastic mulching – a worldwide used method in agriculture to increase crop production by enhancing soil temperature, creating more stable soil moisture conditions and restricting arable weed growth – turned out to have a mitigating effect on N_2O emissions. DNDC (Denitrification and Decomposition) modeling results matched best with the measurement results when the maximum daily soil temperature and half of the daily precipitation was assumed to occur as dominating climate conditions underneath the impervious polyethylene (PE) film, suggesting that N_2O production underneath the plastic cover was driven by soil moisture and temperature. N_2O emissions from a non-fertilized soy bean field, which has Nitrogen fixation as an additional Nitrogen source, were similar to the N_2O emissions from a radish field after application of an intermediate amount of N fertilizer of 200 kg ha^{-1} .

Comparing N₂O and CH₄ emissions from rice paddies under different water management practices showed that intermittent irrigation (II) (no continuous flooding, no water logging) had the least global warming potential (GWP) which was only 30% of the global warming potential (GWP) of a traditionally irrigated (TI) paddy (continuous flooding and water logging). Another practice of 2.5 months of continuous flooding, followed by midseason drainage and reflooding which created moist but non-water logged conditions (FDFM) lead to 66% of the traditionally irrigated paddies combined CH₄ and N₂O emissions. These results suggest that a trend towards less flooding has a great potential to mitigate greenhouse gas emissions from a sandy or sandy-loam substrate, respectively. Studying the three paddies' subsoil conditions revealed that N₂O production and consumption processes had mainly taken place between 25 and 50 cm soil depth judging by N₂O concentrations and δ¹⁵N-N₂O values along the soil profiles of all the investigated paddies as well as gene abundances of denitrifying and nitrifying bacteria of the FDFM paddy.

Apart from these important findings on N₂O flux dynamics of three different land use systems, it is noticeable that the N₂O emissions of the study region are in general very low which is very pleasing and implies that the area deals with global change challenges and associated intensive agriculture in a way that comparatively only small amounts of N₂O degas. But this raises the question after the "why?" considering that large amounts of fertilizer are applied on the fields. This thesis does not have a final answer to that question but it discusses whether the sandy substrate may play a major role for the N dynamics of the whole area. There is evidence that NO₃⁻ - as the substrate for denitrification - leaches easily due to the soil conditions. To finally figure out why the N₂O emissions are that low a more detailed investigation on the fate of NO₃⁻ would be desirable.

Zusammenfassung

Im Zuge von Globalem Wandel und Klimawandel muss die Menschheit sich mit immer häufiger und heftiger werdenden extremen Wetterereignissen auseinandersetzen, sowie sie auch versuchen muss, eine immer zahlreicher werdende Weltbevölkerung zu ernähren bei zunehmender Verknappung von Ressourcen. Da die Hälfte der Menschheit angewiesen ist Ökosystemdienstleistungen aus den bergigen Gebiete der Erde, ist es essentiell, solche komplexen Landschaften zu studieren und zu verstehen, wie natürliche sowie auch landwirtschaftliche Ökosysteme sich auf Klimaänderungen und veränderte anthropogene Einflüsse einstellen.

Emissionen von Treibhausgasen wie Lachgas (N_2O) und Methan (CH_4) sind involviert in die Klimaerwärmung und den damit einhergehenden Klimawandel, was sie zu wichtigen globalen Angelegenheiten macht. Wichtigste Quellen von N_2O sind landwirtschaftliche Böden, CH_4 entstammt zu großen Anteilen aus Reisfeldern. Daher ist es von größter Wichtigkeit, solche landwirtschaftlichen Systeme, im Hinblick der Management-Praktiken und deren Einfluss auf Treibhausgasemissionen, zu studieren.

Das Hauptaugenmerk dieser Arbeit ist es, N_2O Emissionen von landwirtschaftlichen und Waldböden zu quantifizieren, sowie auch N_2O und CH_4 Emissionen von Reisfeldern und herauszufinden, welche Faktoren die Flüsse dieser Treibhausgase maßgeblich steuern.

Die verlängerte Frühsommertrockenperiode des Jahres 2010 führte zu signifikanter N_2O -Konsumption in Böden dreier Waldstandorte. Die darauffolgenden überdurchschnittlich heftigen Monsunregenfälle verursachten dann zwar N_2O -Emissionen, und leicht positive N_2O -Bilanzen in zwei der Wälder, jedoch waren sie nicht ausreichend um die N_2O -Bilanz des Waldes auf sandig-lehmigem Boden in eine positive umzukehren. Dies bedeutet, dass für einen Waldboden während der Vegetationsperiode zum ersten Mal eine negative N_2O -Bilanz beobachtet wurde. Die N_2O -Emissionen der Waldstandorte wurden gesteuert von Bodenfeuchte und Bodentemperatur und – wie zunehmend in der Literatur zu finden – schien es einen Einfluss der Bodentextur auf die N_2O -Flüsse zu geben.

Es stellte sich außerdem heraus, dass der Einsatz von Folie in der Landwirtschaft – eine weltweit immer häufiger eingesetzte Methode zur Steigerung der Ernten durch höhere Bodentemperaturen und stabilere Bodenfeuchte – eine lindernde Wirkung auf die N_2O -Emissionen der Felder hat. Modellierungen mit dem DNDC- (Denitrifikation und Dekomposition)-Model stimmten am besten mit den im Feld gemessenen N_2O -Flüssen überein, wenn Tageshöchsttemperaturen und die Hälfte des Tagesniederschlages als dominierende Klimafaktoren unter der Folie angenommen wurden, was impliziert, dass die N_2O -Produktion unter der Folie auch stark von Bodentemperatur und Bodenfeuchte

abhängig war. N₂O-Emissionen eines ungedüngten Sojabohnenfeldes, waren ähnlich den N₂O-Emissionen eines Rettichfeldes, welches eine mittlere Menge Stickstoff-Dünger von 200 kg N ha⁻¹ bekommen hatte.

Ein Vergleich von N₂O- und CH₄-Emissionen von Reisfeldern mit unter Bewässerungsstrategien ergab, dass eine zeitweise Flutung mit mehreren Trockenphasen das geringste Klimaschädigungspotential hat, welches nur 30% dessen beträgt, was ein traditionell bewässertes Reisfeld (fünf Monate kontinuierliche Flutung). Eine Intermediäre Bewässerungsstrategie (2.5 Monate Flutung, Austrocknung, Bewässerung ohne Stauen von Wasser) brachte im Vergleich zum traditionell gefluteten Reisfeld ein Klimaschädigungspotential von 60%. Diese Ergebnisse implizieren, dass ein Trend hin zu weniger Stauwasser auf Reisfeldern effektiv Treibhausgasemissionen senken kann, zumindest auf sandigen oder lehmig-sandigen Böden. Eine akribische Untersuchung der Reisfeldböden ergab, dass N₂O-Produktion und Konsumption hauptsächlich in 25 bis 50 cm Tiefe stattgefunden haben; die N₂O-Konzentrationen und δ¹⁵N-N₂O-Werte dieser Tiefen von allen untersuchten Reisfeldern sowie auch Gen-Häufigkeiten von Denitrifizierern und Nitrifizierern des Reisfeldes mit der Intermediären Bewässerungsstrategie deuten darauf hin. Abgesehen von diesen wichtigen Erkenntnissen über N₂O-Fluss-Dynamiken von drei verschiedenen Landnutzungssystemen, fällt auf, dass die N₂O-Flüsse des Studiengebietes generell niedrig sind. Dies ist erfreulich und zeigt, dass das Gebiet mit jenen Herausforderungen, die der Globale Wandel mit sich bringt und die mit Landwirtschaft assoziiert sind, so eingestellt ist, dass zumindest keine großen Mengen an N₂O produziert werden, was allerdings verwunderlich erscheint, führt man sich vor Augen welche großen Mengen an Dünger auf den Feldern ausgebracht werden. Die vorliegende Arbeit diskutiert an, ob möglicherweise der sandige Boden der Region eine schnelle Auswaschung der hochmobilen NO₃⁻-Ionen - dem Ausgangssubstrat für Denitrifikation - bewirken könnte, hat letztlich aber keine abschließende Antwort auf diese Frage. Um herauszufinden, wieso die N₂O-Flüsse so gering sind, wäre es wünschenswert, NO₃⁻-Flüsse und das Schicksal der NO₃⁻-Ionen genauer zu untersuchen.

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List of Abbreviations

BD	Bulk density
C	Carbon
CH ₄	Methane
CO ₂	Carbon dioxide
DFG	Deutsche Forschungsgemeinschaft
DNDC	Denitrification and Decomposition
EA-IRMS	Elemental Analyzer coupled with an isotope ratio mass spectrometer
FDFM	flooding-midseason drainage-reflooding-moist intermittent irrigation without water logging
GHG	Greenhouse gas
GIS	Geoinformationssysteme
GWP	global warming potential
II	Intermittent Irrigation
KIT	Karlsruhe Institute of Technology
KOSEF	Korea Science and Engineering Foundation
N	Nitrogen
N ₂	N gas, molecular N
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
N ₂ O	Nitrous oxide
NO	Nitric oxide
NO ₂	Nitrite
NO ₃ ⁻	Nitrate
O	Oxygen
PE mulch	Polyethylene mulch
PnET-N-DNDC	Photosynthesis and Evapotranspiration- Nitrification-Denitrification and Decomposition
PreCon-GC-IRMS	Pre-concentration-gas chromatography-isotope ratio mass spectrometry
R ²	Coefficient of Determination
RDA	Rural Development Administration of Korea

TERRECO	Complex <u>TERR</u> ain and <u>ECO</u> logical Heterogeneity
TI	Traditional Irrigation
WFPS	Water Filled Pore Space

Chapter 1

On this thesis

Background

The most important greenhouse gases

Greenhouse gases absorb infrared light in the atmosphere, thereby trap heat and cause a warming of the earth's surface. In terms of their global warming potential the three important greenhouse gases are Carbon dioxide (CO₂), Methane (CH₄) and Nitrous oxide (N₂O) (WMO 2006). In a 100-year horizon, unit masses of N₂O and CH₄ are considered to have 298 and 25 times the global warming potential, respectively, as a unit of CO₂ because of their longer lifespan (IPCC 2007). Furthermore, N₂O contributes to stratospheric ozone depletion (Cicerone 1987) and recently has even been identified as "the Dominant Ozone-Depleting Substance Emitted in the 21st Century" (Ravishankara et al. 2009). Other important gases are water vapor and halocarbon compounds but their emissions are not associated with agriculture and land use issues (Snyder et al. 2009). Even though the major greenhouse gas for the world's economy is CO₂, the most important greenhouse gas in agriculture is N₂O (Snyder et al. 2009) as well as its emissions are of ongoing interest in forest research and therefore it becomes the major focus of this thesis.

N₂O

N₂O is released in relatively small amounts during the microbial soil processes denitrification, nitrification and nitrifier denitrification (Bange 2000, Snyder et al. 2009, Wrage et al. 2001, Kool et al. 2011) depending on Oxygen (O₂) concentrations in the soil, soil temperature and moisture, soil texture, amount of nitrate (NO₃⁻) available for denitrification and amount of ammonium (NH₄⁺) available for nitrification (Firestone 1982, Granli and Bøckman 1994).

Denitrification names the reduction from NO₃⁻ into dinitrogen (N₂) gas as described in the following pathway: NO₃⁻ → NO₂⁻ → NO → N₂O → N₂ in an anoxic environment (Firestone 1982, Firestone and Davidson 1989, Robertson and Groffman 2007). The transformation of NO₃⁻ can be complete but it can happen that a small portion of N is emitted as N₂O gas.

Nitrification is the name of the conversion of NH₄⁺ into NO₂⁻ which is then transformed into NO₃⁻ (Norton 2008). N₂O as well as NO are by-products of the transformation from NO₂⁻ under oxygen-limited conditions (IFA/FAO 2001), but N₂O emissions resulting from nitrification have also been reported under fully aerobic conditions (Bremner and Blackmer 1978).

Nitrifier denitrification occurs when moisture conditions are suboptimal for denitrification, as a function of the soil moisture content, and likely of other environmental conditions as well. The

process is assumed to be a major contributor to N₂O emission from soils with sandy texture and recently calls for more and more attention (Kool et al. 2011).

Emissions of N₂O mostly occur sporadic throughout the whole year and N₂O emission peaks can be observed after previously well-aerated soils became moistened or saturated from precipitation or irrigation or during thawing of frozen soils (Snyder et al. 2009, Barton et al. 2008a, Goldberg et al. 2009).

Forest soils' N₂O emissions are known to be influenced by soil moisture and temperature, soil type and texture, aeration, tree species composition, pH, C:N ratio, atmospheric nitrogen deposition (Schindelbacher et al. 2004, Skiba et al. 2009, Butterbach-Bahl et al. 2002, Menyailo and Huwe 1999, Yamulki et al. 1997, Kesik et al. 2006, Morkved et al. 2007, Weslien et al. 2009, Klemetson et al. 2005, Pilegaard et al. 2006). Soil moisture and temperature often explain most of the temporal variation of the N₂O fluxes in daily to weekly timescales (Omerci et al. 1999, Schindelbacher et al. 2004, Kesik et al. 2006, De Bruijn et al. 2009) but when it comes to comparing annual N₂O emissions factors like nitrogen deposition and forest and soil type become much more important (Pilegaard et al. 2006).

N₂O emissions from croplands are known to be influenced by the amount of fertilizer applied (Cole et al. 1997, van Groeningen et al. 2010) and it is said that approximately 1% of the nitrogen fertilizer applied is emitted as N₂O (IPCC 2006). In addition to those management related factors, which also include type of crop with major differences between legumes and other annual crops, environmental factors such as climate, soil texture, soil drainage and abundance of NO₃⁻-N and pH have been identified as the most important drivers of N₂O fluxes (Eichner 1990, IFA/FAO 2001).

Recently, N₂O consumption is becoming a focal point of interest. Since the global N₂O balance is still not closed, knowing of soils which act as N₂O sinks could contribute to closing that balance (Billings 2008). The mechanisms behind this sink function and environmental factors leading to the sink function are still poorly understood. Chapuis-Lardy et al. (2007) summarized that it has mostly been reported under conditions of low mineral nitrogen availability and high soil moisture. However, significant consumption of N₂O in forest soils has also been observed by Kellman and Kavanaugh (2008), Goldberg and Gebauer (2009a, b), Inclán et al. (2012) under drought conditions.

CH₄

CH₄ is produced by methanogenic bacteria during decomposition of organic material in a process which is called methanogenesis. Those bacteria use CO₂ as terminal electron acceptor and convert it into CH₄ (Thauer 1998). These bacteria require environments with no oxygen (a situation present in flooded soils) and abundant organic matter, both of which are characteristics of wetlands (Zehnder, 1978). The CH₄ emitted into the atmosphere is only a small fraction of the much larger amounts of the gas that are consumed in the soils due to CH₄ oxidation (Bartlett and Harriss 1993, Rothfuss et al. 1996, Gilbert and Frenzel 1998).

Because CH₄ is such an important greenhouse gas and by being responsible for 10-25% of the global CH₄ emissions rice paddies are one of the major sources of CH₄ (Cicerone and Oremland 1988, Bartlett and Harriss 1993, Neue et al. 1997, Bousquet et al. 2006), much work has been and is still being done on CH₄ emissions from rice paddies. It turned out that CH₄ emissions can vary a lot with different water management strategies, mineralogy, rice cultivar, fertilization and local climate (Cai et al. 2001, Denier van der Con 2000, Neue et al. 1996, Liesack et al. 2000).

Why studying in Korea?

A huge percentage of humankind lives in mountainous areas, which account for 20% of the Earth's terrestrial surface, and depends on freshwater and other ecosystem services provided by these regions (Millenium Ecosystem Assessment 2005). Studying complex terrain, its surface properties, gradients in climate, transfer of materials, soil properties, patterning of land use according to human preferences and the resulting impacts on the environment is crucial for management of Earth's ecosystems and resources.

The Republic of Korea is a predominantly hilly and mountainous, as well as densely populated and developed country with a very high Human Development Index (HDI) score and very high living standards (Human development report 2011). Large areas are under intensive agricultural use. In comparison to Germany, Korea houses 61% of Germany's population on only 28% of Germany's total area which leads to a high population density of 491 inhabitants per km² (Germany has 229 inhabitants per km²) (Statistische Ämter des Bundes und der Länder: Bevölkerung am Monatsende, Korean Statistical Information Service). Thus, Korea is an interesting place to study as it can be regarded as a country which has to face and to deal with Global Change effects prior to other countries with a smaller population density, lower living standards, a larger area to flee from climate change driven natural catastrophes and extreme weather events and which are less exposed to such weather events. From studying Korea we could learn lessons for the whole world.

The TERRECO (Complex TERRain and ECOlogical Heterogeneity) project - a joint education and research activity between Germany and South Korea - aims to combine both, an achievement of a better understanding of the functioning of different land use and ecosystems in a complex terrain as well as an assessment of the ecosystem performances in terms of what we - the people - derive from them or how they cause or maybe mitigate environmental problems.

Study site

All the fieldwork for this thesis has been conducted in the Haean basin (see figure 1), which is located in Yanggu-county, Kangwon-province in the north-eastern part of South Korea between longitude 128° 5' to 128° 11' E and latitude 38° 13' to 38° 20' N. The punchbowl shaped area with an average altitude of about 400m at the valley-sites is surrounded by mountains reaching up to 1320 m. The average annual air temperature is ca. 7.5°C at the mountain ridges and 10.5°C at the valley sites and the average precipitation amounts to 1577 mm (11-year average) with about 70% falling during the summer monsoon (Lee, Tenhunen, Geyer, Seo, Li and Kang, unpublished). The mountain ridges as well as the areas with steep slope are covered with forest vegetation dominated by *Quercus dentata*, *Q. mongolica*, *Q. serrata*, *Betula davurica*, and *Tilia amurensis* as major tree species and understory are *Q. mongolica*, *Weigela florida*, *Stephanandra incisa*, *Ulmus laciniata*, *Symplocos chinensis*, *Euonymus alatus*, *Acer pseudosieboldianum*, and *Corylus heterophylla*. The valley sites are very intensively agriculturally used. 25% of this cropland area is covered with rice paddies, dryland farms include radish (20% of cropland area), potato (15%), cabbage (15%), soy bean (5%) and *Codonopsis pilosula* and ginseng (together 5%) as well as relatively new plantings of fruit trees and miscellaneous other crops. The typical soils of the agriculturally used area as well as the forest soils are terric cambisols (IUSS Working group WRB 2006). Due to very high soil erosion in the cropland area during the monsoon season and in order to compensate for the resulting high soil loss, the local farmers add sandy soil on top of their fields every few years. This long-term agricultural management technique modifies the soils to anthrosols (IUSS Working group WRB 2006). With its landuse pattern (50% forest cover, rice accounting for 25% of the cropland area and other major crops accounting for the residual harvested area) the Haean basin is somewhat representative of the world's pattern of landuse with 30% forest area and about 15% of the global cropland area used as rice fields (FAO 2005, Thenkabail 2010), which makes it a super study site when it comes to studying factors driving N₂O emissions on a landscape scale, delivering meaningful results for the broader, global picture.

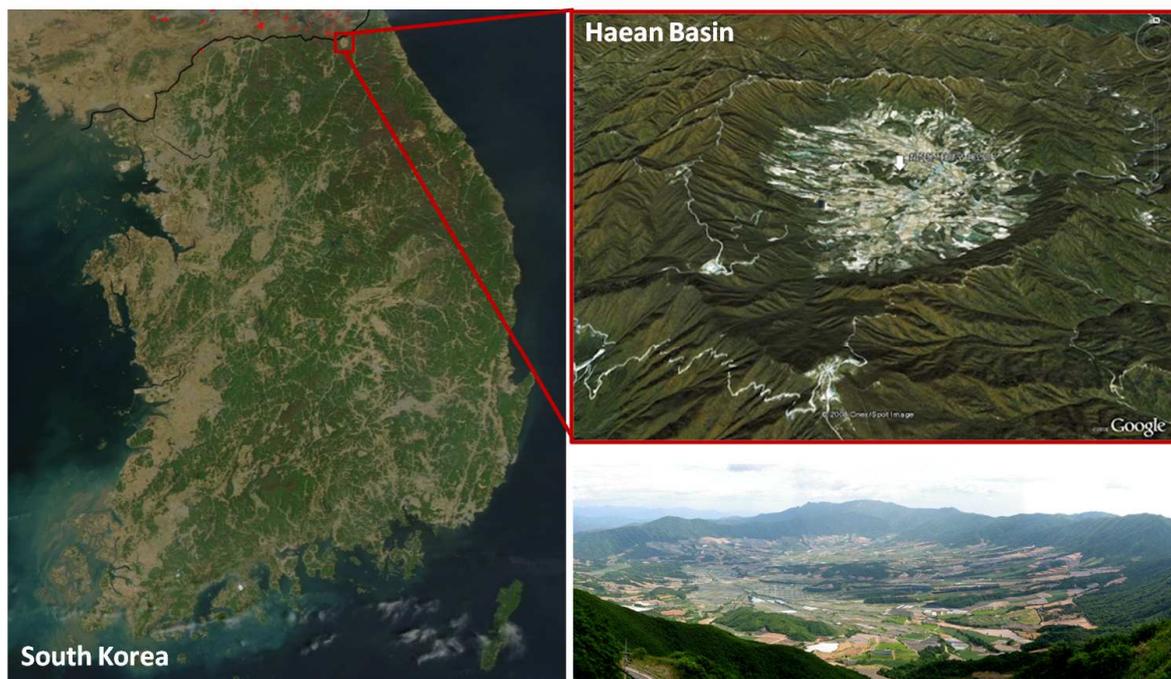


Figure 1: Satellite pictures of South Korea and the Haean Basin, photograph of the Haean Basin. (Pictures were downloaded from <http://www.worldofmaps.net/uploads/pics/satelliten-karte-sued-korea.jpg> on 17 September, 2012; downloaded from google-maps on 17 September, 2012; downloaded from http://www.bayceer.uni-bayreuth.de/terreco/de/top/gru/html.php?id_obj=67142 on 15 July, 2012)

Forest soil N₂O emissions as affected by environmental factors

Forest soils' N₂O emissions increase with soil moisture, soil temperature and nutrient availability (Davidson and Kinglerlee 1997, Ormecci et al. 1999, Papen and Butterbach-Bahl 1999, Brumme et al. 1999, Smith et al. 2003, Butterbach-Bahl et al. 2004, Schindlbacher et al. 2004, Pilegaard et al. 2006, Kesik et al. 2006, De Bruijn et al. 2009), as well as they are stimulated by high amounts of nitrogen deposition, intermediated by increased availability of inorganic N in the soil solution and a decrease in the soil C:N ratio (Butterbach-Bahl et al. 1998, Klemetsson et al. 2005, Pilegaard et al. 2006, Horváth et al. 2006). In general one can say that deciduous forests have lower N₂O emissions than coniferous ones (Butterbach-Bahl et al. 2002, Menyailo and Huwe 1999). pH causes maximum N₂O fluxes at values of 5.9 or lower, indicating that acid conditions favor N₂O production (Yamulki et al. 1997, Kesik et al. 2006, Morkved et al. 2007, Weslien et al. 2009). Soil texture has been assumed to play an important role in terms of driving N₂O fluxes, too (Skiba et al. 2009), and there is increasing recent evidence that poor sandy soils have a lower capability to produce N₂O than silty or loamy soils have (Włodarczyk et al. 2011). Studies by Barton et al. (2008a), Goldberg and Gebauer (2009a, b), Inclán et al. (2012), who all reported on very low and even negative N₂O fluxes on sandy loam soil, confirm that idea.

Because there are predicted changes in precipitation and temperature regimes which go along with an increasing occurrence of heavy rain events or extreme drought periods in the course of climate change (IPCC 2007), N₂O emissions are expected to be enhanced in the future (Potter et al. 1996; Skiba et al. 1998). Thus, studies of effects of such extreme weather events on N₂O emissions are absolutely necessary. During a long-term climate manipulation experiment in Germany it was found that a prolonged summer drought not only decreased N₂O emissions but even lead to significant N₂O consumption (Goldberg and Gebauer 2009a, b). However, the mechanism of that N₂O sink function in dry soils could not be found, yet. Chapuis-Lardy et al. (2007) summarized that the rate of N₂O consumption in soils (reduction to N₂ plus absorption by water) would depend on soil properties, such as the availability of mineral N (substrate for nitrification and denitrification), soil oxygen and water content, soil temperature, pH and redox conditions, and the availability of organic C and N, which are exactly the same parameters identified to drive N₂O emissions. It is a current research challenge to clear up the processes and environmental factors responsible for the N₂O uptake in soils.

Dry crop fields' soils' N₂O emissions as affected by management and environmental factors

The N₂O emitted from arable soils is known to increase linearly with amount of fertilizer applied (Eichner 1990, Kaiser et al. 1998). However, there is not yet a consensus reached on the type of N fertilizer which contributes the most to N₂O emissions (Eichner 1990, Granli and Bøckman 1994, Snyder et al. 2009). Tenuta and Beauchamp (2003) suggested that urea-based N fertilizer would cause greater N₂O emissions than other N fertilizers under aerobic conditions and that under conditions of higher soil moisture NH₄⁺-based fertilizers would produce greater amounts of N₂O. In contrast to that Harrison and Webb (2001) suggested that N₂O emissions from urea under warm and wet conditions may exceed those of NH₄⁺-based sources and that N₂O emissions from NO₃⁻-based fertilizers would be greater than those from NH₄⁺-based fertilizers. Bouwman (2002a), Tenuta and Beauchamp (2003), Velthoff et al. (2003), Venterea and Stanenas (2008) agreed that there are lower emissions for NO₃⁻-based fertilizer when compared to NH₄⁺-based fertilizers and organic or synthetic-organic ones.

Like for the fertilizer type's influence on N₂O emissions, there is no consensus yet on the tillage system's influence on the amounts of N₂O degassing from arable soils. Lal (2003), Gregorich et al. (2004), Venterea et al. (2005), Blanco-Conqui and Lal (2008) reported that

no or less tillage lead to increased N₂O emissions when compared to conventional or intense tillage, whereas Robertson et al. (2000), Halvorson et al. (2008a, b) observed the opposite.

Much work has been done on figuring out if N₂ fixing legumes, which have an additional N source, causes higher N₂O emissions from soils than other crops. In general one can say that during N₂ fixation less N is available for nitrification and subsequent denitrification and the resulting N₂O emissions during the time when the legumes are growing (Parkin and Kasper 2006) so that there are not necessarily greater N₂O emissions from N fertilized non-legume crops under similar climatic and management regimes (Helgason et al. 2005, Rochette and Janzen 2005, Parkin and Kaspar 2006, Stehfest and Bouwman 2006, Barton et al. 2008b).

In addition to those management related N₂O flux regulating factors, climatic factors also affect N₂O emissions from dry crop fields. Soil moisture and temperature are known to increase N₂O production (Dobbie et al. 1999, Ruser et al. 2006); however, it happened that no correlation between N₂O emission rates and soil moisture or temperature is found (Flessa et al. 1995). Even if it has frequently been observed that rain events triggered N₂O emissions from agricultural fields (Davidson et al. 1993, Scholes et al. 1997, Barton et al. 2008a), pH allows the most N₂O production at slightly acidic values and less sandy soil texture does so, too (IFA/FAO 2001).

Recently there is increasing use of an impervious polyethylene (PE) film (see figure 2) worldwide - but in East Asian countries such as Korea, China and Japan in particular - in order to increase crop production in the course of a growing world population and accompanying food scarcity (Kwon et al. 2006, Kyrikou and Briassoulis 2007). Due to a higher soil temperature and moisture underneath the PE mulch, conditions as in a greenhouse are created which promote crop growth, but that also raises the important question whether this method has negative side effects on the environment such as an increased N₂O production.



Figure 2: Impervious polyethylene (PE) film applied on an agricultural field. It covers the ridges and leaves only little holes open where the crops can emerge.

N₂O and CH₄ emissions from rice paddies as affected by management practices

Whereas rice paddies are one of the most important sources of atmospheric CH₄ (IPCC 1992, IPCC 2007), their contribution to global N₂O emissions was considered to be rather insignificant (Granli and Bøckman 1994). Due to the strong anaerobic conditions of rice paddy soils under the traditional rice irrigation method of continuous flooding - which was the dominating practice until the early 1980s (Geng et al. 2001) - N₂O as an intermediary product of denitrification would be further reduced to N₂ (Granli and Bøckman 1994). However, increasing water scarcity made and still makes farmers change their traditional irrigation practice to water-saving irrigation practices, including midseason drainages and non-water logged periods (Geng et al. 2001). It is well documented that such drainage, and the presence of non-water logging periods, enhance N₂O emissions in contrast to continuous flooding (Cai et al. 1997, Zeng et al. 2000, Jiang et al. 2003, Li et al. 2004, Xu et al. 2004, Li et al. 2005) because of changes in several N₂O production regulating factors, such as soil oxygen status, soil redox potential, moisture, temperature (Smith and Patrick 1983, Cai et al.

2001, Zou et al. 2005b, Johnson-Beebout et al. 2009, Liu et al. 2010, Peng et al. 2011). The good news about the new irrigation practices is that they significantly reduce CH₄ emissions; however, a clear trade-off relationship between CH₄ and N₂O emissions was found (Yagi et al. 1996, Hou et al. 2000), which is why it is scientists' challenge to find an irrigation method which would minimize the combined greenhouse effect by the two gases while ensuring maximum amounts of rice yields.

Obviously, some factors other than water regime also affect rice paddies' N₂O and CH₄ emissions, such as fertilizer type, soil moisture and soil temperature (Bouwman et al. 2002b, Granli and Bøckman 1994). So does the application of urea-based fertilizer cause the greatest CH₄ emissions but less N₂O emissions (Wang et al. 1992, Cai et al. 1997, Bufogle et al. 1998), in contrast to the effects of ammonium sulfate or ammonium bicarbonate fertilizer, which leads to higher N₂O emissions but lower CH₄ emissions (Cai et al. 1997, Zheng et al. 2000) at identical water management systems. The lowest CH₄ and N₂O emissions were observed after application of NO₃⁻-based fertilizer (Jugsujinda et al. 1995). This has to do with the redox potential which, after NO₃⁻-N application, was higher than -100mV (where CH₄ emissions occur), but lower than +200mV (where N₂O emissions occur) so that neither CH₄ nor N₂O emissions were promoted (Hou et al. 2000, Snyder et al. 2009).

Furthermore, a significant positive relationship between N₂O emissions and the WFPS (water filled pore space) ranging from 62.2 to 83.5%, while increasing the WFPS over 83.5% apparently reduces N₂O emissions, was observed by Khalil and Baggs (2005), Sey et al. (2008), Peng et al. (2011). At soil temperatures between 25 and 40°C there is increasing N₂O production (Granli and Bøckman 1994).

Objectives

This study was conducted within the framework of the International Research and Training Group (DFG-IRTG) TERRECO (Complex TERRain and ECOlogical Heterogeneity), comprising soil scientists, hydrologists, biologists and social scientists with the major aim of examining the way to carry out land management in mountain regions, in order to ensure sustainable yield of ecosystem services. The specific objectives of this thesis are:

- (1) to quantify the N₂O emissions of the deciduous forests' soils of the study area, to investigate how the East Asian summer monsoon affects the N₂O fluxes and to identify the processes which drive those forests' N₂O fluxes

Chapter 2

- (2) to quantify the N₂O emissions of representative dry crop fields of the study area with respect to effects of PE mulching, fertilizer amount and crop type

Chapter 3

- (3) to quantify the N₂O and CH₄ emissions from representative rice paddies of the study area, to investigate the different water management practices' effect on N₂O and CH₄ fluxes at the soil/atmosphere interface and to identify the underlying subsoil processes

Chapter 4

The following experiments were carried out by the Research group and aided me in achieving my objectives 1 and 2:

- (1) At four forest sites, of which three sites also served as my study sites, permanent sap flow measurements were carried out by Eunyoung Jung in addition to a meticulous recording of forest composition, vegetation type and structure, solar radiation, climate data, soil parameters such as soil moisture and soil temperature, which was mainly done by Eunyoung Jung, too, with my assistance. Furthermore, an intensive soil core and leaf sampling was carried out by Eunyoung Jung and me for further analysis of ¹³C and ¹⁵N abundances as well as C and N content; the soil samples were also analyzed with respect to bulk density, rock content, soil texture, root content, etc.
- (2) At a radish field, which also served as my dry crop field study site in 2010, an integrative experiment was carried out by Janine Kettering, Bora Lee, me, Steve

Lindner and Emily Martin, which was designed to investigate the effects of different amounts of N fertilizer on radish yields, and - with the help of a ^{15}N tracer experiment - to follow the fate of the fertilizer in a PE mulched ridge cultivation cropping system.

N_2O fluxes at the soil atmosphere interface were measured in intervals of two to seven days at the forest sites, the radish field study site and the 2010 rice paddy study site between 14 May and 24 October, 2010. At the three 2011 rice paddy study sites as well as at the bean field study site, N_2O flux measurements were carried out every two to three days between 6 May and 15 September, 2011. CH_4 fluxes of the rice paddies were determined every two weeks between 20 May and 28 August 2011.

In addition to the N_2O flux measurements, N_2O concentrations and N isotope signatures in soil air were determined from 10 to 60 cm soil depth at three points in time to identify areas along one forest and all of the rice paddies' soil profiles where N_2O was being produced or consumed.

NO_3^- concentrations as well as presence of O_2 along the rice paddies' soil profiles were analyzed once a week. Water levels and water temperatures of the 2011 rice paddy study sites were recorded from 1 June until 14 September, 2011.

Synopsis

Forest soil N₂O emissions as affected by early summer drought, heavy monsoon rains and other environmental factors (Chapter 2)

Unexpectedly the early summer drought led to significant negative N₂O fluxes at the soil/atmosphere interface in all of the three investigation sites. It was particularly pronounced at a site with sandy-loam topsoil texture where not even two and a half months of heavy monsoon rains could turn the N₂O balance into a positive one. Negative N₂O fluxes were observed again in September and October after the monsoon had stopped, while the soils dried up, again. At two more investigation sites a similar N₂O flux pattern was found, which was not that pronounced but still significant. Their N₂O balances were very low, too, with 0.084 and 0.063 mmol N₂O m². Since there is increasing evidence for the phenomenon of N₂O consumption of soils under dry conditions (Donoso et al. 1993, Yamulki et al. 1995, Klemedtsson et al. 1997, Verchot et al. 1999, Flechard et al. 2005, Goldberg and Gebauer 2009a, b), these findings also support this idea.

These results indicate an underestimation of the sink strength of the monsoon affected forests and considering the remarkable forest cover of such monsoon affected areas worldwide, these findings are very important.

One further aim was to identify processes and environmental factors responsible for the N₂O fluxes at the soil/atmosphere interface. Soil moisture and temperature explained most of the measured N₂O fluxes, which is not a surprise since Davidson and Kinglerlee (1997), Ormeci et al. (1999), Papen and Butterbach-Bahl (1999), Brumme et al. (1999), Smith et al. (2003), Butterbach-Bahl et al. (2004), Schindlbacher et al. (2004), Pilegaard et al. (2006), Kesik et al. (2006) and De Bruijn et al. (2009) pointed at those factors as major drivers of N₂O fluxes. What is exciting is that there appeared to be an effect of soil texture, as in sandy-loam soils significant N₂O consumption has recently been observed, too (Barton et al. 2008a, Goldberg and Gebauer 2009a, b, Włodarczyk et al. 2011, Inclán et al. 2012). The very low N₂O balances could also be a result of the forest type at the sites, as oak forests are known to have very low N₂O emissions (Brüggeman et al. 2005).

A closer look into the soil by using stable ¹⁵N-N₂O isotope abundances and N₂O concentrations as tools to evaluate N₂O production and consumption areas along the soil profile brought quite interesting results as the soil profiles looked very different from what literature provides so far. Goldberg and Gebauer (2009a, b) have found very high N₂O concentrations as well as ¹⁵N-N₂O abundances pointing at N₂O production in the subsoil,

whereas the soil profiles of the Korean forest did not show such a pattern at all, suggesting that all the occurring N₂O production and consumption took place in the topsoil.

N₂O emissions from dry crop fields as affected by PE mulching, amount of fertilizer, crop type and climate (Chapter 3)

Despite of the wide use of plastic mulching as an agricultural method in Korea, if not in Asia and worldwide, hardly any investigations have been conducted concerning its influence on N₂O emissions. The experiment which was conducted during the growing season of the first year at a radish field study site brought the result that there were significant differences between N₂O emissions from plant holes of PE-mulched ridges and furrows. Extraordinarily low amounts of N₂O degassed from those spots of the PE-mulched ridges which were totally covered with the plastic film, which raised the question whether less N₂O production occurred underneath the PE mulch film or there was horizontal diffusion of N₂O from the ridge soil covered with the mulch film to the adjacent furrows and plant holes, so that most of the N₂O produced underneath the PE mulch would have degassed from the furrows and plant hole spots. To tackle that question an additional experiment was conducted during the growing season of the second year. Comparative N₂O flux measurements of plant holes PE-mulched ridges and plant spots of non-PE-mulched ridges of a soy bean field brought the interesting but not statistically significant result that the N₂O cumulatively emitted from PE-mulched ridges' plant holes was only 68% (2.06 mmol m⁻²) of the N₂O emitted from plant spots of non-PE-mulched ridges (3.00 mmol m⁻²). These findings suggest that the use of plastic mulch in agriculture mitigates N₂O emissions.

The results are based on the assumption that the PE mulch is permeable for gas as Ou et al. (2007) and Nishimura et al. (2012) published, which was not tested by us.

Based on the radish field experiment, a modeling approach - by using the process-based models agricultural-DNDC (Denitrification and Decomposition) (Li et al. 1992, Smith et al. 2002, Giltrap et al. 2010) and PnET-N-DNDC (Photosynthesis and Evapotranspiration-Nitrification-Denitrification and Decomposition) (Li et al. 2000, Kesik et al. 2005, Kiese et al. 2011) - delivered the interesting result that the simulations agreed the best with the field measurements after the input information was adjusted according to the following parameters: only half of the annual precipitation and the maximum temperature was used for simulation of PE-mulch covered row conditions, whereas the actual weather data were used for the furrow simulations. These results strongly suggest that soil moisture and temperature are the major drivers of N₂O production even under the management practice of plastic

mulching, which is in agreement with earlier studies on agricultural fields without PE mulching (Dobbie et al. 1999, Ruser et al. 2006).

Measured cumulative N₂O emissions from the radish field increased with increasing N fertilization rates, ranging between 2.4 and 4.47 mmol m⁻² (ridges) and 2.04 and 6.1 mmol m⁻² (furrows). However the result was not statistically significant, which is contrast to the literature stating that there is a linear increase of N₂O emissions with amount of fertilizer applied (Eichner 1990, Kaiser et al. 1998). Compared with the IPCC approach (IPCC 2006) these values are also rather low which can be explained by high rates of by DNDC simulated and measured nitrate leaching across all N treatments (ridges: 214 - 240 kg N ha⁻¹ yr⁻¹; furrows: 259 - 263 kg N ha⁻¹ yr⁻¹).

The cumulatively emitted N₂O from the non-fertilized bean field amounted to 5.90 mmol m⁻² (2.06 mmol m⁻² for the PE-mulched ridges and 3.90 mmol m⁻² for the furrow), which is very similar to the amount of N₂O that had degassed from the radish field site in 2010, when an intermediate amount Nitrogen fertilizer was applied. This supports the general finding that N₂O fluxes from non-fertilized legume cropping systems, which have N fixation as an additional N source, do not necessarily exceed fluxes from N fertilized non-legume crops under similar climatic and management regimes (Helgason et al. 2005, Rochette and Janzen 2005, Parkin and Kaspar 2006, Stehfest and Bouwman 2006, Barton et al. 2008).

N₂O and CH₄ emissions from rice paddies as affected by water management (Chapter 4)

The combined global warming potential (GWP) of N₂O and CH₄ calculated in units of CO₂ equivalents over a 100-year time horizon (based on a radiative forcing potential relative to CO₂ of 298 for N₂O and 25 for CH₄ (IPCC 2001)) emitted from three investigated rice paddies was highest for the paddy undergoing traditional irrigation (TI) (5 months of continuous flooding) due to largest emissions of CH₄ (363.1 mol CO₂eq m⁻²). Intermittent Irrigation (II) turned out to have a GWP of 109 mol CO₂eq m⁻², which is only 30% of GWP of the Traditional Irrigation paddy. The paddy experiencing 2.5 months of flooding followed by midseason drainage and then reflooding-moist intermittent irrigation without water logging (FDFM) turned out to have a GWP of 240 mol CO₂eq m⁻². Thus, we conclude that the environmentally friendliest rice paddy water management practice is one with the least water use: Intermittent Irrigation. Among our rice paddy study sites it caused the lowest CH₄ as well as the lowest N₂O emissions. These results are somehow contrary to the literature which agrees on greatest CH₄ but lowest N₂O emissions from TI paddies, whereas less water use/logging is known to lead to less CH₄ but great N₂O emissions (Cai et al. 1997, Zeng et al.

2000, Jiang et al. 2003, Li et al. 2004, Xu et al. 2004, Li et al. 2005). These differences could be explained by the sandy soil texture where the highly mobile NO_3^- leaches even quicker than in less porous soils.

Besides looking at their soil/atmosphere exchange of greenhouse gases, more value was set on studying subsoil processes of the rice paddies. Considering that the fertilizer applied at all of the three paddies was composed of NH_4^+ -N and urea-N it seems not surprising that no correlation between NO_3^- concentrations along the soil profile and N_2O exchange at the soil/atmosphere interface was observed. Instead, $\delta^{15}\text{N}-\text{N}_2\text{O}$ values, N_2O concentrations along the soil profiles of all the investigated paddies and data on gene abundances of denitrifying and nitrifying bacteria for the FDFM paddy (Seo, Jang, Gebauer and Kang 2012, unpublished data) suggest N_2O production and consumption which led to the measured N_2O fluxes at the soil surface occur in the subsoil (25 and 50 cm soil depth). Such an investigation has not been done before and its results give us an exciting insight into subsoil processes involved in N_2O production and consumption occurring in rice paddies.

Concluding remarks

Even though the Haean Basin is an area under intensive agricultural use, cumulative N_2O emissions from different land use systems as presented in figure 3 are lower than expected considering the intensive management practices and wasteful amounts of fertilizer applied. As possible explanations for these low emissions this thesis brings up:

- 1) N_2O gets further reduced to N_2 gas which escapes into the atmosphere, or
- 2) large amounts of the highly mobile NO_3^- leach easily before a reduction to N_2O or N_2 gas can take place.

Explanation 2 seems more plausible regarding the sandy and well aerated soils of the study area, but to finally figure out why the N_2O emissions are that low, a more detailed investigation on NO_3^- leaching and its origin and fate could be very helpful.

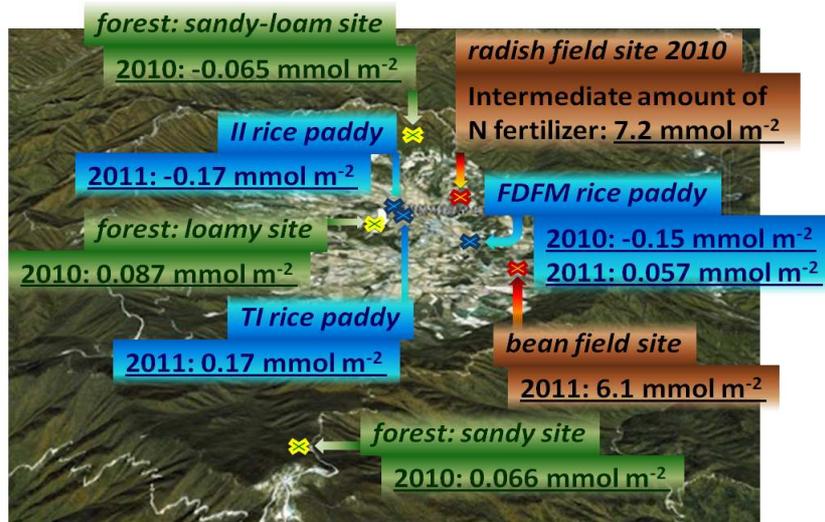


Figure 3: Amounts of cumulatively emitted N₂O presented in mmol m⁻² measured at the different sites during the growing seasons of 2010 and 2011.

Just like large areas of the world, in the course of global and climate change the study area has to face extreme weather events such as more severe early summer drought periods followed by heavier monsoon rains. This thesis showed that of such weather events were accompanied by very low and to some extent even negative N₂O balances of forest soils during the growing season.

Plastic mulching – a widely used practice in agriculture worldwide – turned out to have a potential to mitigate N₂O emissions, which should be subject to more studies.

Intermittent irrigation was identified as the best water management practice for the study region’s investigated rice paddies as it required the smallest amounts of water and caused the lowest N₂O as well as CH₄ emissions, which for the N₂O emissions is contrary to the literature but might be explained by the sandy soils and a high NO₃⁻ leaching potential.

These findings are important and also suggest that the study region deals with global and climate change effects in a good way at least with regard to its greenhouse gas emissions.

Record of contributions to this thesis

Chapter 1

Chapter 1 and the summary of this thesis were written by me. This dissertation includes four manuscripts of which three were written by me and one was written by Youngsun Kim. One of the manuscripts written by me is already published, the second one is resubmitted after revisions and the third one is submitted. The manuscript by Youngsun Kim is in preparation for submission. The contribution of me and all co-authors is listed below.

Chapter 2

Berger S, Jung E, Köpp J, Kang H, Gebauer G, 2013. Monsoon rains, drought periods and soil texture as drivers of soil N₂O fluxes – soil drought turns East Asian temperate deciduous forest soils into temporary and unexpectedly persistent N₂O sinks. *Soil Biology & Biochemistry* 57, 237-281.

Berger S: 60% (concepts, field and laboratory work, interpretation, discussion and presentation of results, manuscript preparation)
Jung E: 20% (concepts, field and laboratory work, discussion of results)
Köpp J: 5% (laboratory work, interpretation and discussion of results)
Kang H: 5% (field and laboratory work, logistics in Korea)
Gebauer G: 10% (concepts, discussion of results, contribution to manuscript preparation)

Chapter 3A

Berger S, Kim Y, Kettering J, Gebauer G, 2012. Plastic mulching in agriculture - friend or foe of N₂O emissions? *Agriculture Ecosystems & Environment* (Resubmitted after revisions, 12 January 2013)

Berger S: 70% (concepts, field and laboratory work, interpretation, discussion and presentation of results, manuscript preparation)
Kim Y: 15% (field and laboratory work, logistics in Korea)
Kettering J: 5% (field work)
Gebauer G: 10% (concepts, discussion of results, contribution to manuscript preparation)

Chapter 3B

Kim Y, Berger S, Kettering J, Tenhunen J, Kiese R, 2012. The simulation of N₂O emissions and nitrate leaching from different rates of N fertilizer in the radish field with the Landscape-DNDC model. (Manuscript in preparation)

Kim Y: 55% (concepts, discussion of results, manuscript preparation)

Berger S: 10% (field and laboratory work, discussion)

Kettering J: 5% (field and laboratory work)

Tenhunen J: 5% (discussion of results)

Kiese R: 25% (concepts, discussions of results, contribution to manuscript preparation)

Chapter 4

Berger S, Jang I, Seo J, Kang H, Gebauer G, 2012. A record of N₂O and CH₄ emissions and underlying soil processes of Korean rice paddies as affected by different water management practices. Biogeochemistry (Submitted, 19 September 2012)

Berger S: 75% (concepts, field and laboratory work, interpretation, discussion and presentation of results, manuscript preparation)

Jang I: 5% (field and laboratory work, logistics in Korea)

Seo J: 5% (field and laboratory work, logistics in Korea)

Kang H: 5% field work, logistics in Korea)

Gebauer G: 10% (concepts, discussion of results, contribution to manuscript preparation)

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Chapter 2

Forest soil N₂O emissions as affected by early summer drought, heavy monsoon rains and other environmental factors

;Monsoon rains, drought periods and soil texture as drivers of soil N₂O fluxes – soil drought turns East Asian temperate deciduous forest soils into temporary and unexpectedly persistent N₂O sinks

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Abstract

To quantify N₂O fluxes between soil and atmosphere and understanding those processes driving them, is crucial if we aim to reliably predict one of earth's important greenhouse gases' origin and fate. Soil moisture has been identified as one major driver of N₂O fluxes, drought has been observed to decrease soil N₂O emissions and accounts for soil N₂O consumption. We monitored N₂O fluxes occurring at the soil/atmosphere interface of three temperate deciduous Korean forest sites experiencing a pronounced early summer drought followed by heavy East Asian monsoon rains. Because soil texture can enhance or mitigate soil drought effects, we selected sites which were different in top soil texture. Therefore, we took closed chamber measurements of N₂O fluxes during the growing season 2010 and

determined N₂O concentrations and δ¹⁵N values along soil profiles in the dry and monsoon season for a sandy loam site. We observed N₂O consumption at all of our study sites during early summer drought, which turned into N₂O emission during the monsoon season. The N₂O balance of the sandy loam site remained slightly negative during the entire vegetation period. Soil moisture explained most of the measured N₂O fluxes. For a sandy-loam forest soil we calculated a switch between N₂O emission and consumption at an intermediate soil moisture (pF level of 3.02) which corresponds to a water filled pore space (WFPS) of 36.34%, but at half an order of magnitude moister soil (pF level: 2.57; WFPS 50.31%) at a loamy site. N₂O concentration and δ¹⁵N_{N₂O} values along the soil profiles suggest that those processes driving the N₂O fluxes at the soil/atmosphere interface most likely occurred in the topsoil. Our results contribute to our knowledge on the global N₂O budget, because monsoon affected forests cover large areas worldwide and their soils' N₂O emissions have so far been uninvestigated.

Keywords: N₂O emission, N₂O consumption, soil profile, δ¹⁵N, heavy rainfall, sand, loam, Korea

1. Introduction

N₂O is a powerful greenhouse gas which contributes to the global warming effect (WMO 2006) and is also involved in the destruction of the stratospheric ozone layer (Cicerone 1987). Important sources of N₂O are mainly agriculturally managed soils but also include (semi-)natural forest soils (Potter et al. 1996; Davidson and Kinglerlee 1997; Pilegaard et al. 2006). Microbial denitrification, nitrification and nitrifier denitrification are the N₂O producing processes (Kool et al. 2011). However, a significant N₂O sink function has recently been observed in managed northern forests in Canada (Kellman and Kavanaugh 2008), and in European forests (Goldberg and Gebauer 2009a, b; Inclán et al. 2012). Those findings are now of importance for further improvement of predictions on Earth's climate specifically under conditions of global climate change (Billings 2008), as soils as N₂O sinks had not been taken into account for global N₂O balances before.

Still little is known about the underlying processes of this N₂O sink function, which can temporarily be observed in different soils. Soil moisture and temperature have been identified as the most important drivers of N₂O fluxes between forest soils and atmosphere (Butterbach-Bahl et al. 2004; Pilegaard et al. 2006; Kesik et al. 2006). It is also known that an increasing amount of rainfall as well as increasing soil temperature are predicted to enhance N₂O emissions (Potter et al. 1996; Skiba et al. 1998; IPCC 2001). IPCC (2007) predicted changes in precipitation and temperature regimes, which raised the question how such changes actually affect N₂O emissions from forest soils. Goldberg and Gebauer (2009b) showed that an experimentally induced drought of 46 days could temporarily turn the soil of a coniferous forest in Germany from a source into a transient N₂O sink. East Asian climate is even more extreme than the simulated one: yearly recurring heavy monsoon rainfall periods after eight months of fair to extreme drought (Qian et al. 2002; Yihui and Chan 2005). This provides an extreme case of drying and rewetting cycles of soils and therefore we considered it as an adequate framework to field-test the above mentioned experimental results. And we intended to go one step further by investigating the effects of the those long drought and heavy rainfall periods on forest soils distinguished by different soil textures, which appears of great importance especially when considering most recent findings by Włodarczyk et al. (2011), who explicitly reported on loamy soils having a greater capacity to N₂O production and consumption than sandy soils.

Here we report on a monitoring study, to our knowledge investigating for the first time, how the N₂O fluxes of East Asian forests respond to the extreme fluctuations in soil moisture which we expected to be caused by heavy monsoon rains. Over and above the N₂O fluxes,

we determined several additional parameters such as soil moisture, soil temperature, soil and vegetation properties, N deposition and C/N ratio to see if there were any relationships with the occurring N₂O fluxes. Because the soil texture can enhance or mitigate drought effects, due to differences in water holding capacity, aeration and O₂ availability etc., the measurements were carried out on three forest sites differing in their top soil texture characteristics: each one predominantly consisted of sand, sandy-loam or loam, respectively. We hypothesized that the sandy site as the location with the most aerated and most quickly drying soil would show the least N₂O fluxes whereas the loamy soil with a greater water retaining capacity was expected to show higher emissions and less declining N₂O emissions during the drought period. Furthermore, we attempted to identify the switching point from N₂O emission to consumption and *vice versa* for each one of these soils.

2. Materials and Methods

2.1 Experimental sites

The measurements were taken in three forests in the Haean Basin which is located northeast of the city of Chuncheon in Yanggu County, South Korea, between longitude 128° 5' to 128° 11' E and latitude 38° 13' to 38° 20' N, with a range in altitude from ca. 400 to 1100 m a.s.l. The average annual air temperature is ca. 10.5°C at valley sites and ca. 7.5°C at the northern ridge line. Average precipitation is estimated at 1200 mm with 70% falling during the summer monsoon (Lee et al 2010, unpublished).

The most important characteristics of the three sites are summarized in Table 1. The solar radiation (provided by the TERRECO-site (<http://www.bayceer.uni-bayreuth.de/terreco/>), downloaded on 10 January 2011) at the sites is shown in figure 1. According to the FAO soil classification (IUSS Working Group WRB 2006) the soils of our research sites can be classified as Cambisols, even though they are different in soil texture of the first 20 cm topsoil layer.

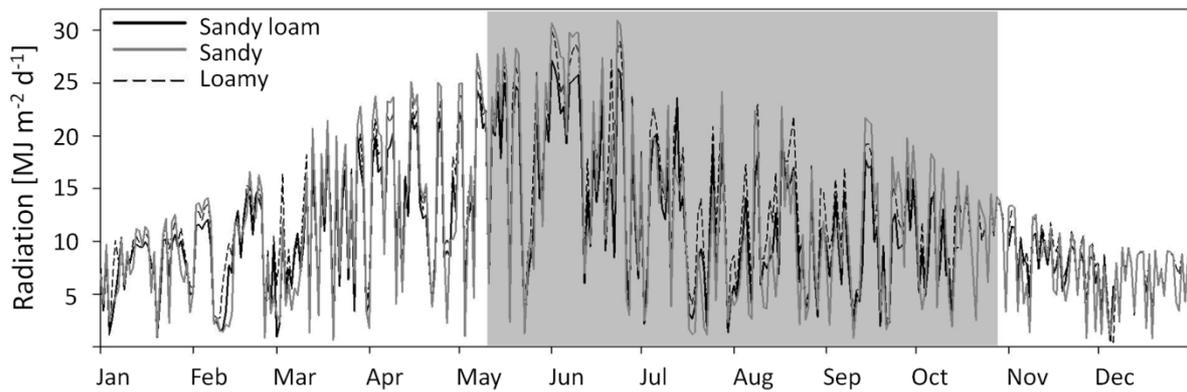


Figure 1. Daily sum of solar radiation during the entire year at the three study sites. The grey box indicates the time period when the N₂O flux measurements were carried out.

2.2 Measurement of soil moisture and soil temperature and determination of pF levels

On the sandy-loam site two ECH2O loggers and one ECH2O logger at both sandy and loamy site (EM50 Data logger, Decagon Devices, WA, USA) were installed at 10 cm depth logging volumetric soil water content [%] and soil temperature [°C] every 30 minutes from 10 May until 31 October 2010. Afterwards the mean daily water content and mean temperature of the soils at 10 cm depth were calculated.

In addition, on all of the three sites three top soil samples were collected using a soil corer. The samples' sand-, silt- and clay contents as well as their bulk densities were determined in the laboratory of the Soil Physics Department at the University of Bayreuth. The analysis method was wet sieving for sand and laser particle analyzer "Mastersizer S MAM5004" (Malvern Instruments, Herrenberg, Germany) for silt and clay. The samples were prepared by humus destruction (H₂O₂) and dispersion ((NaPO₃)₆). Based on the texture and bulk density data the computer program ROSETTA estimated the soil hydraulic parameters θ_r , θ_s , α and n which then defined the pF - water content - curve described by the Van-Genuchten function (Schaap et al. 2001) for each site. The pF level for each corresponding mean daily soil water content value was read out of that curve.

pF levels were determined because the topsoil characteristics of the study sites differed a lot and in order to make soil moisture site comparisons possible, a more independent factor stating soil moisture was needed. pF levels serve that purpose because they include soil characteristics such as soil texture and bulk density.

Table 1: Site characteristics of the studied forests, in Haean basin, South Korea.

Site	Location	Aspect	2010 monsoon precip. & mean air temp.	Soil charac- teristics	Dominant species Basal area	Subdominant species Basal area	Understory Basal area	Average tree height
Sandy- loam	128°8'27.13"E	220°	1223 mm	60% sand	10.3 m ⁻² ha ⁻¹	10.15 m ⁻² ha ⁻¹	2.46 m ⁻² ha ⁻¹	9.9 m
	38°18'57.067"N 650 m a.sl		8.5 °C	31% silt 9% clay BD: 0.90 g cm ⁻³	(<i>Quercus mongolica</i>)	(<i>Quercus dentata</i> , <i>Tilia mandshurica</i> , & others)	(<i>Q. dentata</i> , <i>Q. mongolica</i> & others)	
Sandy	128°6'0.86"E	70°	1616 mm	80% sand	16.13 m ⁻² ha ⁻¹	6.25 m ⁻² ha ⁻¹	1.02 m ⁻² ha ⁻¹	4.9 m
	38°14'43.374"N 950 m a.sl		7.5 °C	15% silt 5% clay BD: 1.11 g cm ⁻³	(<i>Q. mongolica</i>)	(<i>Fraxinus rhynchophylla</i> , <i>Euonymus hamiltonianus</i> , & others)	(<i>Acer pseudosieboldianum</i> , <i>Acer mono</i> & others)	
Loamy	128°7'50.091"E	70°	1326 mm	45% sand	11.43 m ⁻² ha ⁻¹	4.38 m ⁻² ha ⁻¹	8.28 m ⁻² ha ⁻¹	9.6 m
	38°17'18.636"N 450 m a.sl.		10.5 °C	42% silt 13% clay BD: 1.07 g cm ⁻³	(<i>Quercus serrata</i> , <i>Q. mongolica</i> , <i>Quercus aliena</i> , <i>Alnus japonica</i>)	<i>Q. dentata</i> , <i>Ulmus lacinata</i> & others)	(<i>Rhododendron yedoense</i> , <i>Euonymus alatus</i> , <i>Lespedeza cyrtotrya</i> & others)	

As dominant species we identified those which accounted for at least half of the canopy area.

Temperature and rainfall data were downloaded from the TERRECO-site (<http://www.bayceer.uni-bayreuth.de/terreco/>) on 31st of January, 2011. Sand, silt and clay were classified according to EN ISO 14688.

2.3 N₂O flux measurements

N₂O fluxes were measured from 14 May to 24 October of 2010 twice a week at the sandy-loam site and in weekly intervals at the sandy and loamy sites using the closed chamber technique in conjunction with a photoacoustic infrared gas analyser (Multigas Monitor 1312, INNOVA, Ballerup, Denmark) as described by Yamulki and Jarvis (1999) and Goldberg et al. (2008b). The sandy-loam site contained 8 polyvinylchloride (PVC) cylinders, with a total height of 15 cm and a diameter of 19.5 cm, which were installed 7 cm deep into the soil. The sandy and loamy site contained 5 of such PVC cylinders. Those cylinders served as connection pieces where the chamber heads were attached to. 4 of PVC cylinders of the sandy-loam site, and three cylinders of the sandy site contained only few small herbs. The other 4 PVC cylinders of the sandy-loam site, 2 cylinders of the sandy site and all five cylinders at the loamy site did not contain herbs. The cylinders were installed in a way that the herb abundance inside the cylinders was representative of the forest soil. The N₂O concentrations in the chambers' headspaces were measured after 0, 8, 16, 24 and 36 minutes at the sandy-loam site and in 0, 10, 20, 30 and 40 minute intervals at the loamy and sandy site. The reproducibility of one single N₂O concentration measurement was ± 32 ppb. From a linear increase or decrease of the N₂O concentration in the chambers' headspaces the N₂O flux was calculated taking into account the total chamber volume which includes the chamber headspace volume (chamber head 4000 ml + each individual PVC cylinder's volume of about 2000 ml), volume of the two 25 m long Teflon pipes (600 ml) and of the CO₂ and H₂O gas traps (38.2 ml).

According to the literature it is considered unlikely that daily or weekly measurements using manual chambers would sufficiently cover each after rain emission peak, especially in environments where N₂O emissions are strongly influenced by a small number of rainfall events, which are particularly unpredictable; an accurate measurement of all the N₂O fluxes ongoing would only be provided by an automated measurement system (Barton et al. 2008). We consider the climate that South Korea undergoes as suitable for N₂O flux measurements using manual chambers as rain-events as well as dry after-rain periods lasted 3-4 days, so that there was sufficient time to measure N₂O fluxes before, during and after each occurring and by weather forecast well-predicted weather-event.

Cumulative N₂O emissions were calculated as described by Tilsner et al. (2003), by multiplying the N₂O emission rates of two consecutive measurement days with the corresponding time period. These time weighted N₂O flux means were then summed up over the measurement period.

2.4 Gas sampling in the soil profiles

Soil gas was collected from the sandy-loam site following the procedure described by Goldberg et al. (2008a) on 6 June in the early dry season, on 1 August in the monsoon season, and on 23 October 2010 during the autumn drought season. Sub-surface soil gas tubes were installed in 10, 30, 40 and 60 cm depth. There were three replicates for each depth. Three samples of ambient air were collected as well. Gas sampling glass bottles (with an inlet, an outlet, and a septum and defined volumes of about 100 ml) were first flushed with N₂ gas, evacuated using a membrane vacuum pump (KNF Neuberger N026.3AN.18, Freiburg, Germany) and after measuring the vacuum by using a pressure gauge (TensioCheck TC 03S, Tensio-Technik, Geisenheim, Germany), connected to an opened stopcock of a soil gas tube before its inlet was opened.

2.5 Measurement of soil air ¹⁵N/¹⁴N ratios and N₂O concentrations

To measure N₂O concentrations and ¹⁵N/¹⁴N isotope ratios of the N₂O in soil gas and air samples a gas chromatograph-isotope ratio mass spectrometer coupling was used which was linked to a pre-GC concentration device (PreCon-GC-IRMS) (IRMS: delta V plus; Thermo Fisher Scientific, Bremen, Germany; gas chromatograph: GC 5890 series II; Hewlett-Packard, Wilmington, USA; Pre-Con: Finnigan MAT, Bremen, Germany) as described in detail by Brand (1995). The method enables to determine isotope ratios with a precision of ± 0.15‰. They are presented as δ¹⁵N-values which are defined as:

$$\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000 \quad [\text{‰}], \quad (1)$$

where R is the ratio of heavy isotope [atom percent, at %] to light isotope [at %] of the samples and the respective standard. The international standard is N₂ in the atmosphere (Mariotti 1983).

N₂O concentrations were calculated from the volume of the gas samples and the peak area in m/z on mass 44 with the help of a calibration curve. For further details on this method see Goldberg et al. (2008a).

2.6 Estimate of N deposition

N deposition data based on direct measurements are not available for the three forest sites of our investigation. For this reason we chose a correlation approach (Emmet et al. 1998) to estimate N deposition for the three sites from ^{15}N enrichment factors. On each site five sun and five shade leaves from five tall *Quercus mongolica* trees which were present in the forest canopy were collected. Also, from five understory *Q. mongolica* trees five leaves which grew approximately 1.5 m above ground were sampled. The collected samples were herbarized immediately after the harvest, and two months later dried at 75°C for two days. Furthermore, at each site five top soil samples were collected with a soil corer. Roots were removed by hand and subsequently the samples were dried at 75°C. Afterwards both, leaf and soil samples were ground in a ball mill (Retsch Schwingmühle MM2, Haan, Germany), weighed into tin capsules and stored in a desiccator before further analysis. The relative N isotope abundance as well as C and N concentrations were measured with an elemental analyzer (Carlo Erba 1108, Milano, Italy) connected to a delta S isotope ratio mass spectrometer via a ConFlo III interface (both Finnigan MAT, Bremen, Germany). For further details see Bidartondo et al. (2004). From the soils' C and N concentration C/N ratios were calculated. Isotope ratios are presented as δ values, which were calculated and defined according to the equation (1) given in 2.5.

Mean ^{15}N abundances of the leaves and soil samples from each site were identified and a N enrichment factor was calculated by subtracting the average $\delta^{15}\text{N}$ value of the leaves and the average $\delta^{15}\text{N}$ value of the soil from each other. To calculate N deposition the N enrichment factors were inserted into an equation empirically found for the relationship between N enrichment and N deposition in a set of European forest sites: $y = 0.1484x - 9.9472$ (Emmet et al. 1998).

Because the equation was only tested for coniferous forests, the results we derived were used carefully.

2.7 Statistical methods

N_2O flux curves were obtained by calculating mean N_2O flux values $\pm 1\text{SE}$ for every day of measurement and linear interpolation between two consecutive measurement days. The mean flux is based on $n=8$ for the sandy-loam site and $n=5$ for the sandy and loamy sites. The soil profiles' N_2O concentrations and $\delta^{15}\text{N}$ values are given as means of $n=3 \pm 1\text{SE}$. Statistical analyses were performed using the software R 2.12.0 for Windows (R Development Core Team, 2010). Via *t*-Test (normally distributed data) or Mann-Whitney *U*-

test (not normally distributed data) it was tested whether the measured N₂O fluxes are significantly different from 0 and whether the $\delta^{15}\text{N}$ and N₂O concentration profiles are significantly different from ambient air's ¹⁵N abundance and N₂O concentration. Site comparisons with regard to N deposition and C and N concentrations were done *via* ANOVA or the non-parametric Kruskal-Wallis-test. A multiple regression analysis was used to identify significant correlations between N₂O flux and other site parameters. Subsequently, Pearson correlations were done as posthoc tests.

3. Results

3.1 Soil moisture, soil temperature, C/N ratio and N deposition throughout the vegetation period

Depending on their soil texture and their precipitation and temperature characteristics the three sites showed differences in soil moisture (Fig. 2, a-c; Table 2). With a mean pF level of 3.02 the sandy-loam site turned out to be the driest site throughout the measurement period, during early summer drought reaching maximum pF levels of 3.62 on 11 June and 1 July 2010. The loamy site had the moistest soil with a pF average of 2.52. On 10 and 29 June the site's maximum pF level of 2.87 was reached, which means with a pF difference of 0.74 its soil was three-fourths orders of magnitude moister than the soils of the sandy-loam site during that drought period. The sandy site was of intermediate moisture (pF level 2.70). Whereas the sandy-loam and loamy sites showed huge moisture fluctuations throughout the measurement period, the sandy sites' soil humidity remained more or less constant from 1 May until 31 October. During the monsoon period (2 July until 13 September) the sandy-loam and loamy sites' soil moisture increased stepwise which is reflected by decreasing pF levels. The minimum pF level determined at the sandy-loam site was 2.44 and 2.11 at the loamy site. After the 2 ½ months of heavy monsoon rains the study sites' soils dried up again.

The soil temperature at all three sites increased gradually from the beginning of the measurement period until mid August and decreased afterwards. The mean soil temperature from May until October was highest at the loamy site (17.1°C; 450 m a.s.l.) and lowest at the sandy site (15.5°C; 950 m a.s.l.). The average soil temperature at the sandy-loam site (650 m a.s.l.) was 16.6°C.

The sites slightly differed in C/N ratio depending on the soil depth (Table 2).

Estimated N deposition ranges from $24 \pm 13.8 \text{ kg N ha}^{-1}$ at the most remote sandy site to $51 \pm 15.3 \text{ kg N ha}^{-1}$ at the most agriculture-affected loamy site in the middle of the Haeon basin (Table 2). There is no statistically significant difference for N deposition between the three sites ($P=0.102$), but the difference between the N deposition of the loamy site and the other two site's N deposition can be regarded as a trend.

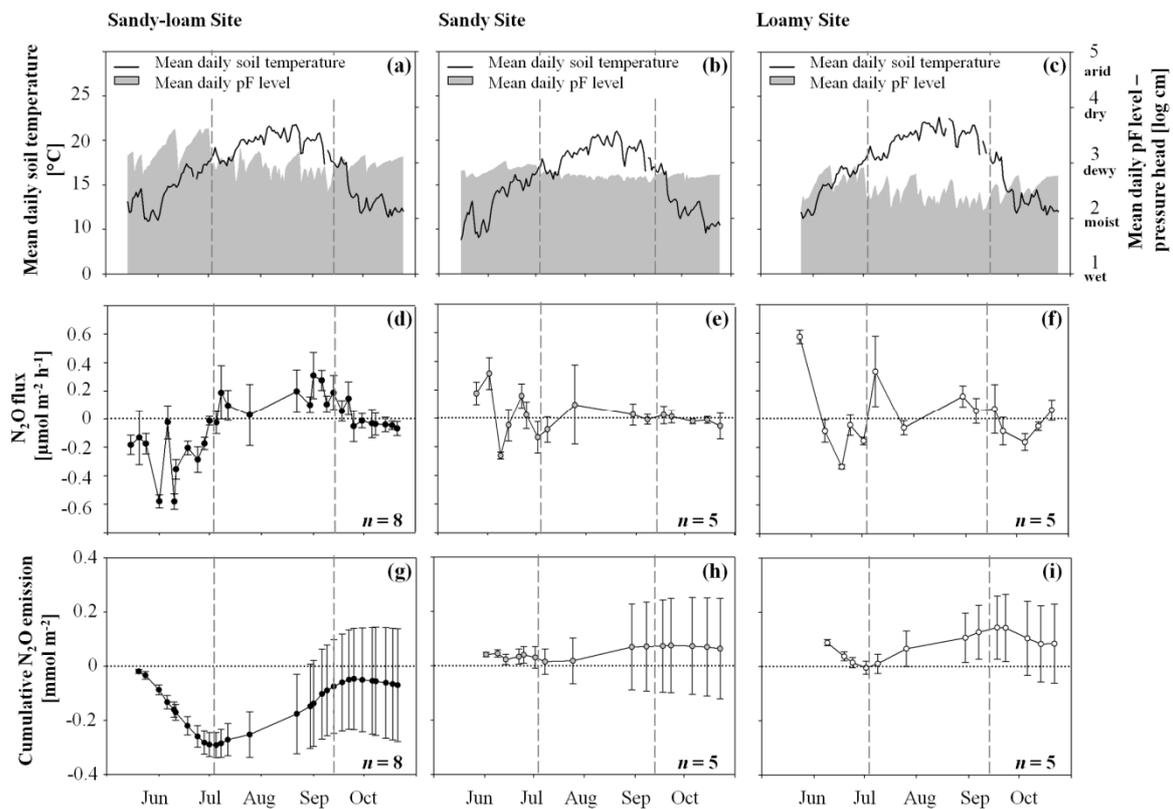


Figure 2. Mean daily soil temperature [°C] and mean daily pF level [log cm] (a-c), N₂O flux [$\mu\text{mol m}^{-2} \text{h}^{-1}$] (d-f) and cumulative N₂O emission [mmol m^{-2}] (g-i) at sandy-loam (a, d, g), sandy (b, e, h) and loamy site (g, h, i) as a function of time from 1 May until 31 October, 2010. The dashed vertical lines indicate beginning (2 July) and end (13 September) of the monsoon rains at the measurement sites. Error bars in N₂O flux- and cumulative N₂O emission- graphs represent the standard error of the mean ($n=8$ at sandy-loam site, and $n=5$ at sandy and loamy site).

Table 2. C/N ratios and N deposition of the study sites.

	Sandy loam	Sandy	Loamy
C/N at: 0-5 cm	14.35 <i>ab</i>	15.34 <i>a</i>	13.57 <i>b</i>
5-15 cm	15.23 <i>b</i>	14.21 <i>ab</i>	12.60 <i>b</i>
15-20	17.07 <i>a</i>	12.81 <i>b</i>	12.38 <i>b</i>
N deposition [kg ha⁻¹ yr⁻¹]	31 ±2.14 <i>a</i>	24 ±13.8 <i>a</i>	51 ±15.3 <i>a</i>

Different letters in each line indicate significant statistical differences ($P < 0.05$) for a comparison of C/N for each soil depth and they also state that there is no statistically significant difference between the N deposition at the three sites.

3.2 N₂O fluxes and cumulative N₂O emissions throughout the vegetation period

Before the monsoon, all three sites showed negative N₂O fluxes from the atmosphere into the soil (Fig. 2, d-f). The highest flux of all fluxes measured was negative on 31 May and 6 June at the sandy-loam site ($-0.57 \pm 0.05 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$) which - in addition to the exclusively negative fluxes during the dry period - makes the N₂O sink function at the sandy-loam site the most distinctive one. The sandy site's fluxes ranged between $+0.32 \pm 0.11$ and $-0.26 \pm 0.02 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$ and the loamy site's fluxes ranged between $+0.57 \pm 0.05$ and $-0.34 \pm 0.02 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$ during the pre-monsoonal drought period. The longer the drought period lasted the more pronounced the N₂O sink function appeared at the sandy and loamy site. After the monsoon start few negative N₂O fluxes could be observed. The sandy-loam and loamy sites' soils turned from a pronounced N₂O sink into an N₂O source; the sandy site no longer showed any significant N₂O fluxes. After the monsoon season, slightly negative net N₂O fluxes could be detected again in the sandy-loam and loamy site.

The mean N₂O fluxes of the three sites integrated over time from 1 May to 31 October (Fig. 2, g-i) are statistically significant ($*P < 0.05$). The fluxes amounted to $0.084 \text{ mmol N}_2\text{O m}^{-2}$ (equals $6.97 \text{ g N}_2\text{O ha}^{-1}$ or $0.237 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$) at the loamy, $0.063 \text{ mmol m}^{-2}$ (equals $27.73 \text{ g N}_2\text{O ha}^{-1}$ or $0.178 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$) at the sandy and $-0.07 \text{ mmol m}^{-2}$ (equals $-30.81 \text{ g N}_2\text{O ha}^{-1}$ or $-0.184 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$) at the sandy-loam site throughout 161 days of measurement period, respectively. Thus, the N₂O balance during the entire growing season at the sandy-loam site remained negative.

3.3 Correlation of soil moisture and soil temperature with the N₂O fluxes

The multiple linear regression analysis revealed that the N₂O fluxes would be explained the best with soil moisture, soil temperature, bulk density and δ¹⁵N values at 5 cm soil depth, when conducted as an overall site comparison ($R^2 = 0.53$, ** $p = 0.00013$, pF: *** $p < 0.001$, soil temperature: $p = 0.055$, δ¹⁵N: $p = 0.10$, bulk density: $p = 0.064$).

Further Pearson analyses testing correlations between N₂O fluxes and site parameters brought significant results for an influence of soil moisture on N₂O fluxes for the sandy-loam and loamy site (Fig. 3). With the soil moisture given as pF level instead of volumetric water content [%], the relation between N₂O flux and soil moisture is more pronounced (pF level $R^2=0.48$ at the sandy-loam site and $R^2=0.45$ at the loamy site). Mean daily soil temperature at the day of measurement explained 29% ($R^2=0.29$) of the measured N₂O fluxes at the sandy-loam site. No significant relation between soil temperature and N₂O flux for the other two sites could be found. Soil moisture and temperature of one, two, three and seven days prior to the measurement day have been correlated with the N₂O fluxes as well, but no significant correlations were found. A statistical comparison of the soil moisture-N₂O fluxes-regression lines of the sandy-loam and loamy sites showed that they are highly significantly different (*** $P<0.001$).

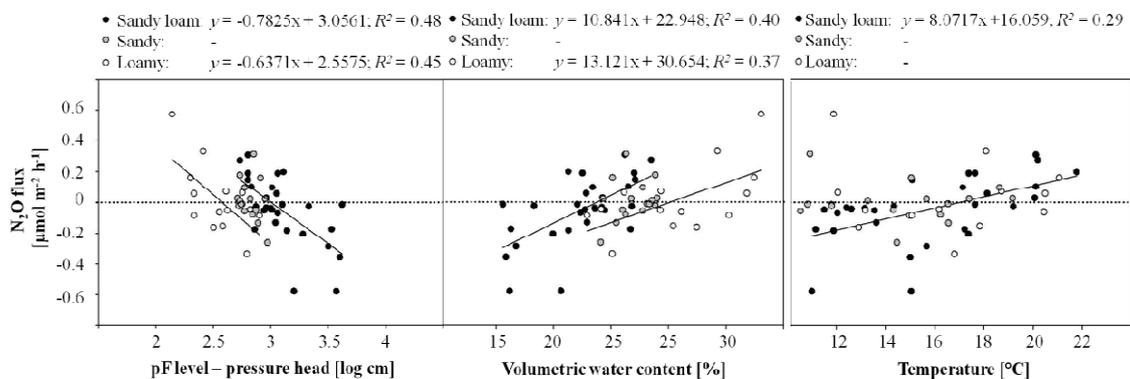


Figure 3. Regressions and correlations for soil moisture (pF-level and VWC), soil temperature and N₂O fluxes for the three sites ($n=30$ at the sandy-loam site, $n=16$ at the sandy site and $n=14$ at the loamy site.)

An attempt to determine the intersection point of the pF level/N₂O flux regression line with the line which indicated the zero-N₂O flux resulted in a pF level of 3.00 for the sandy-loam site (which conforms to a volumetric water content (VWC) of 24%, water filled pore space (WFPS) 36.34%) and 2.57 (= 30% VWC, WFPS 50.31%) for the loamy site.

3.4 N₂O concentration and isotope profiles during the dry and monsoon season at the sandy-loam site

The N₂O concentrations along soil depth profiles at the drought periods differ from the monsoon seasons' profile (Fig. 4). Whereas the N₂O concentrations on 6 June and 23 October (drought period) were slightly below the N₂O concentration of ambient air (in 40 cm depth reaching a minimum value of 220 ppb on 6 June), on 1 August (monsoon season) the concentration of N₂O in the soil air was slightly higher than in the ambient air (350 ppb) from 30 to 60 cm depth with 327 ppb in 10 cm depth not statistically different from the ambient air. The differences in soil air N₂O concentration between the first and the second sampling date are statistically significant ($*P<0.05$), whereas the N₂O concentrations of the third sampling did not differ significantly from pre-monsoonal and monsoon seasons' soil gas N₂O concentrations ($P>0.05$).

Even though the $\delta^{15}\text{N}$ enrichment of N₂O in June was slightly higher (3.3‰ in 10-30 cm depth) than in August (1.4‰ in 10-30 cm depth) and October (-1‰ in 10 cm depth but increasing up to 2‰ in 60 cm depth), the $\delta^{15}\text{N}$ values of the three sampling dates did not differ significantly ($P>0.05$).

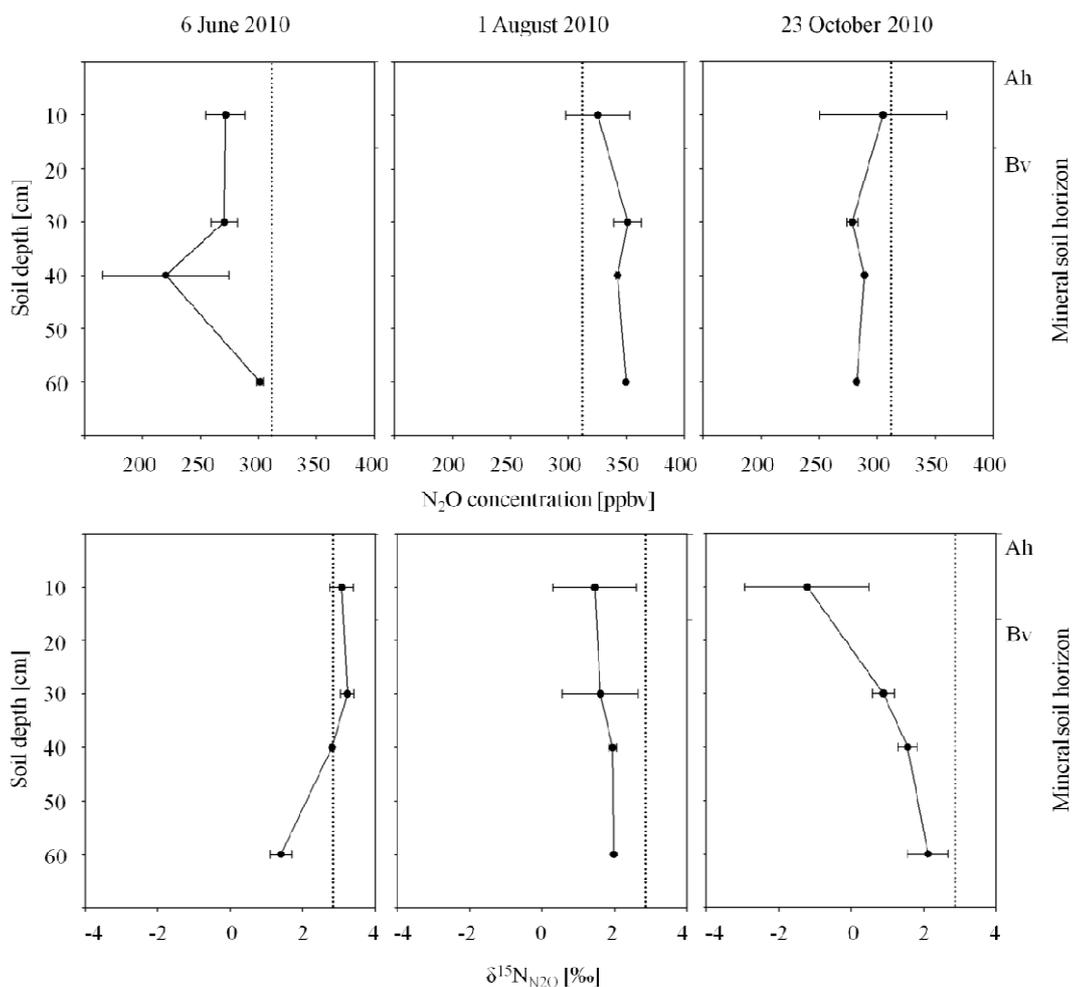


Figure 4. N₂O concentrations and δ¹⁵N values along soil profiles during the early summer drought period (6 June), monsoon season (1 August) and autumn drought season (23 October), 2010. Error bars represent the standard error of the mean ($n=3$). The dotted vertical lines indicate the respective values of N₂O in the ambient atmosphere.

4. Discussion

4.1 Site comparison of N₂O fluxes at the soil/atmosphere interface as influenced by soil moisture, soil temperature, C/N ratio, N deposition and vegetation related factors

Here we report for the first time on a forest soil that acts as a N₂O sink throughout an entire growing season. Up to now significant net N₂O fluxes from the atmosphere into the soil have been observed in various ecosystems under dry conditions from the tropics to temperate areas, in natural as well as in anthropogenic ecosystems (Chapuis-Lardy et al. 2007;

Kellman and Kavanaugh 2008; Goldberg and Gebauer 2009a, b; Inclán et al. 2012). For our study site with sandy-loam top-soil texture, soil moisture and soil temperature explained the measured N₂O fluxes well, which is in accordance with other groups' findings (Ormeçi et al. 1999; Schindlbacher et al. 2004; Pilegaard et al. 2006; De Bruijn et al. 2009). These groups agreed to the fact that soil temperature and moisture are the most important drivers of forest soil N₂O emissions in daily to weekly timescales. In addition, our data indicate that soil temperature and moisture serve also as drivers for forest soil N₂O consumption. So did the switching point between N₂O emission and consumption at the sandy-loam site emerge at a pF level of 3.02 (VWC 24%, WFPS 36.34%). At the loamy site soil moisture explained 45% of the measured N₂O fluxes (switching point between emission and consumption occurred at a pF of 2.57 (VWC 30%, WFPS 50.31%), which lies between “dewy” and “moist”), but there was no significant relation between the loamy sites' soil temperature and N₂O fluxes, neither any significant correlation could be found between the sandy sites' soil moisture, soil temperature and N₂O fluxes.

It is well known that a small C/N ratio and a high N deposition stimulate NO and most likely also N₂O emissions (Fenn et al. 1996; Davidson and Kinglerlee 1997; Butterbach-Bahl et al. 1998; Papen and Butterbach-Bahl 1999; Brumme et al. 1999; Jones et al. 2005; Klemmedtsson et al. 2005; Kitzler et al. 2006; Horváth et al. 2006). Therefore, it seems plausible that those two factors by increasing the available N to quite an amount could have affected the loamy site's N₂O emissions, because the loamy site has significantly different C/N ratios and by trend the highest N deposition (see table 2). For the sandy forest soil none of the mentioned factors, which are known to have an influence on N₂O emissions, was found to have a significant effect on that sites' N₂O fluxes. Neither the highest amount of 2010 monsoon precipitation, the highest amount of mean annual rainfall among the three sites nor soil nutrient availability and soil physical characteristics, respectively, affected significantly the forest soils' N₂O flux behavior.

However, deciduous forests are known to have lower N₂O emissions than coniferous forests (Menyailo and Huwe 1999; Butterbach-Bahl et al. 2002; Pilegaard et al. 2006; Inclán et al. 2012), with mean N₂O-N emissions ranging from 4.9 to 20.3 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ (Butterbach-Bahl et al. 1997, Kitzler et al. 2006, Pilegaard et al. 2006) for mainly beech forests. Oak forests were found to have lower N₂O emissions (Brüggeman et al. 2005). Recently, Inclán et al. (2012) observed mean N₂O-N emissions from oak forests in Spain that ranged between 2.2 and 4.1 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$. Our results suggest a much lower mean emissions between -0.07 and 0.084 $\text{mmol N}_2\text{O m}^{-2}$ (equals -0.05 and 0.06 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$), which we assume to be explained by the fact that our study sites' oak forests undergo that far more extreme climate in East Asia. With eight months of relative to extreme drought and 3-4 months of heavy rainfall (Qian et al. 2002; Yihui and Chan 2005) the soils are subject to an extreme

case of drying and rewetting cycles and thus, it seems not surprising that the N₂O emission balances of our sites remain very low or even negative. Goldberg and Gebauer (2009a) reported that soil rewetting after 46 days of induced drought took twice the time of their preceding drought experiment to turn the cumulative N₂O fluxes from negative into positive values.

The N₂O balances we calculated are based on six months of measurement and 31 measurement dates for the sandy-loam site, 16 measurement dates for the sandy and 14 dates for the loamy site and cover the entire growing season of the investigated forests; they also provide insights in how the forest soils N₂O fluxes reacted to monsoonal caused changes in soil moisture in 2010, but they happened to have a significant temporal variability, depended on environmental factors and might look different during other years' growing season with a different meteorological background.

4.2 Soil texture as an important driver of N₂O fluxes

The introductory hypothesis was that there would be less capacity to N₂O production in the sandy soil with the larger particles due to a smaller water holding capacity, whereas we expected a higher capacity to N₂O production in soils with a smaller particle size due to their higher water holding capacity. It emerged to require more factors taken into account and a more educated point of view to properly assess soil textures' influence on N₂O exchange at the soil/atmosphere interface.

Recently, there is an increasing number of studies reporting on very tiny or even negative N₂O fluxes at a substrate with sandy loam soil texture, suggesting that soil texture - be it in interaction with other soil parameters such as gas diffusivity, N and O₂ concentrations etc. - might also be an important driver of forest soils' N₂O fluxes (Goldberg and Gebauer 2009a, b, Włodarczyk et al. 2011, Inclán et al. 2012). We are well aware that our study does not allow to draw the conclusion that soil texture does indeed drive N₂O fluxes as the effect of soil texture is hard to separate from other parameters, but we want to emphasize that the very tiny N₂O fluxes that we measured also occurred on a sandy loam substrate, which points at the importance of clarifying how soil texture actually affects N₂O fluxes.

4.3 N₂O concentration and $\delta^{15}N$ profiles along the sandy-loam sites' soil profile

Along the profile of the sandy-loam site we detected sub-ambient N₂O concentrations (220 ppb) during the early summer drought period down to 40 cm depth but an increasing concentration in 60 cm depth, which suggests that N₂O consumption could have taken place down to 40 cm soil depth. The ¹⁵N abundance of the soil gas N₂O was similar to the ¹⁵N

signature of ambient N₂O, which suggests an N₂O flux from the atmosphere into the soil. On 1st of August (during the monsoon season) the N₂O concentration and ¹⁵N abundance pattern along the soil profile is not that clear. N₂O concentrations in the soil gas only slightly higher than the N₂O concentrations of the ambient air, as well as a ¹⁵N-signature that was not significantly different from ambient-N₂O's δ¹⁵N values allow the conclusion to be drawn that only very tiny N₂O emissions have taken place on that sampling date, neither has occurred any N₂O consumption along the soil profile.

N₂O concentrations and δ¹⁵N values along the soil profiles are in agreement with the N₂O fluxes measured at the soil/atmosphere interface *via* chamber measurements and give further insights into the N₂O production concerning processes, even though the values we observed are very different from other studies.

Goldberg and Gebauer (2009a, b) detected N₂O concentrations up to 5000 ppb and δ¹⁵N gradients between +7 and -24 ‰ in deeper soil layers (50 cm and deeper). Our study sites are exposed to fair or even severe drought during eight months a year, which means increased soil aeration and thus unfavorable conditions for N₂O production by denitrification (Castaldi 2000) or nitrifier denitrification during most of the year. Drought is also known to reduce the amount of N cycled in the ecosystem by reducing the overall activity of N metabolizing microorganisms (Kieft et al. 1987). Given that the sandy-loam sites' N₂O emissions during the monsoon period were very low and that the fluxes at the soil/atmosphere interface result from dynamic production and consumption processes in the soil, it appears likely that just not much of such processes are going on in Korean deciduous forests' soils and that a time span of 3-4 months of rainfall per year is too short to establish conditions favorable for N₂O producing or consuming microorganisms at the site.

Up to now there was the concept of not much of the N₂O being produced within the soil column ever reaching the soil surface (Seiler and Conrad, 1981; Arah et al. 1991; Neftel et al. 2000; Goldberg and Gebauer, 2009a, b), but the concept of not having ongoing N₂O production down to 60 cm soil depth is rather uncommon. Yoh et al. (1997) suggested that most of the N₂O produced in the topsoil may easily escape to the atmosphere without residing in the soil for a long time, and since we identified the top-soil texture as a probable major factor driving our sites' N₂O fluxes between soil and atmosphere, since we detected N₂O fluxes at the soil/atmosphere interface while neither having strongly increased or decreased N₂O concentrations nor enriched or depleted ¹⁵N_{N₂O} abundances along the soil profile, our data agree with this hypothesis.

4.4 Concluding remarks

Given Korea's frontier-like location between Pacific Ocean and Asia, it is not surprising that climate change hits the country harder than for example Europe. The mean annual temperature in Korea increased not only by 1°C as globally observed but by 1.8°C during the last 100 years, summers are now two to three weeks longer, moister and extreme rainfall events are occurring more frequent (Lee et al. 2012). Considering those facts – which are known to increase N₂O emissions (Potter et al. 1996; Skiba et al. 1998; IPCC 2001, Butterbach-Bahl et al. 2004; Pilegaard et al. 2006; Kesik et al. 2006) – and that the 2010 monsoon season was unusually long and rain-laden (Zhao 2010, unpublished data), our data provide further insight in the N₂O flux behavior of forest soils under global climate change. Taking into account all the previously discussed ideas and facts about dry forest soils acting as N₂O sinks or at least not as huge N₂O emitters, one would expect a climate change towards moister conditions to increase N₂O emissions. But interestingly our study sites happened to have N₂O balances which are extremely low or even negative which is an unexpected finding. Still 30% of the global N₂O budget remains uncertain by either overestimating N₂O sources or underestimating N₂O sinks (Billings 2008). Our data now show that one year of extreme monsoon precipitation in Korea's rapidly changing environments did not result in a strong N₂O emission of forest soils which may suggest that forest soils as N₂O sinks play a bigger role for the global N₂O budget than considered up to now. Climate change is still proceeding and the development of Korea's climate, which was observed during the last 100 years, will emerge in a more intensive way in the next 100 years (Lee et al. 2012), so it would be of great interest to put more effort in studying the N₂O flux behavior of Korean forest's soils and to also study forests of other East Asian countries such as Japan or the Eastern regions of China, which undergo the same climate.

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Chapter 3

N₂O emissions from dry crop fields as affected by PE mulching, amount of fertilizer, crop type and climate

Part A

Plastic mulching in agriculture - friend or foe of N₂O emissions?

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Abstract

Polyethylene (PE) mulching is a very common method in agriculture worldwide because the use of PE films can improve product quality and yield by mitigating extreme weather changes, optimizing growth conditions and extending the growing season. Other than the problem with disposal of the plastics hardly any other of its effects on the environment are known. To determine whether covering fields with PE films affects N₂O emission, we

conducted two experiments: first, comparing N₂O emissions of furrows and PE-mulched ridges of a radish field which had received different amounts of N fertilizer and second, assessing whether PE mulching increases N₂O emissions from PE-mulched ridges in comparison to non-PE-mulched ridges and furrows of a non-fertilized field. To achieve those aims we took comparative closed chamber measurements in conjunction with a photoacoustic infrared trace gas analyzer during the growing seasons of 2010 and 2011 at a radish and soy bean field site in South Korea. For the radish field site we found significant differences between the N₂O emitted by furrows and PE-mulched ridges and found extraordinarily low N₂O fluxes from those spots of the ridges which were totally PE-mulch-covered between plant hole openings. At the soy bean field we observed that plant holes of PE-mulched ridges showed only 68% of the emission measured of soils around soy bean plants of non-PE-mulched ridges, implying that PE mulching may decrease N₂O emissions. Since our result is contrary to very recent findings we consider the extremely low soil moisture at our sites as explanation for the differences. Because knowledge on how PE mulches affect production and emissions of greenhouse gases is very limited, our study contributes greatly to understanding N₂O emission behavior of PE-mulched, poor sandy soils in a temperate monsoon climate.

Keywords: N₂O flux, polyethylene (PE) film, soil moisture, soil temperature, NH₄⁺ fertilizer

1. Introduction

Nitrous oxide (N_2O) is a greenhouse gas of special concern due to its high global warming potential per molecule (Rodhe, 1990), its high contribution to the observed global warming at present (WMO, 2006) and its involvement in the destruction of the ozone layer in the stratosphere (Cicerone, 1987), although its atmospheric concentration of 323 ppb (global mean concentration in 2005 (IPCC, 2007)) is rather low. Major sources of N_2O are agriculturally managed soils (Vitousek et al., 1997), which produce and release N_2O through microbial denitrification, nitrification and nitrifier denitrification (Wrage et al., 2001; Kool et al., 2011). An overall aim should be to reduce N_2O emissions from such soils.

Plastic mulching - covering soil with polyethylene (PE) plastic films - is being established worldwide as a method in agriculture to increase crop production not only by keeping soil temperature and water content high but also by restricting arable weed growth. One obvious drawback of the method is the problem with the disposal of the plastic film (Kyrikou and Briassoulis, 2007), but other side effects of the method such as its influence on greenhouse gas emissions are still hardly investigated.

N_2O emissions from arable soils are known to increase both with fertilizer application and after heavy rainfall events (Flessa et al., 1995), but emissions are also driven by soil temperature and moisture parameters (Sheperd et al., 1991). Many studies have been published on how plastic films increase soil temperature and improve soil water dynamics (e.g., Ban et al., 2009; Díaz- Pérez, 2010; Katan and Devay, 1991; Zhang et al., 2011), which in combination with high inorganic N and organic matter contents and low O_2 concentration in the soil (e.g., Akiyama and Tsuruta, 2003a, 2003b; Hayakawa et al., 2009; Yanai et al., 2011), may increase the N_2O production of such covered soils. Recently, Arriaga et al. (2011) and Nishimura et al. (2012) reported on increased N_2O production from agricultural soils covered with plastic mulch films.

Here we present two consecutive experiments: the first attempts to provide an overview on the amounts of N_2O emitted from agricultural soils under plastic mulching and second, assesses the effect of plastic mulching on N_2O emissions from poor and rapidly drying sandy soils in a temperate monsoon climate. Therefore, in 2010 we took comparative measurements of N_2O emissions at the soil/atmosphere interface of PE-mulched ridges and uncovered furrows of a radish field's plots which had received different amounts of nitrogen fertilizer and because of unexpected results we conducted one further experiment in 2011, comparing the N_2O emissions of PE-mulched and non-mulched ridges of an unfertilized soy bean field. Both experiments were conducted in East Asia (Korea), where plastic mulching is an extensively used method in agriculture. We hypothesized that the plastic mulching would

cause higher N₂O emissions due to the mentioned conditions underneath the plastic film which are considered to be favorable for N₂O production.

2. Methods

2.1 Study site

The study sites were located in the Haean-myun Catchment in Yanggu County, Gangwon Province, South Korea . The agricultural soils of the catchment are mainly characterized as terric cambisols or even as anthrosols (IUSS Working Group WRB, 2007) because of an artificial long-term addition of sandy soil on the top of the fields.

The 2010 experiment was conducted at the Punchball Tongil Agricultural Experimental Farm (38°17'42.471"N, 128°8'28.088"E, 420 m asl), the 2011 experiment was conducted at a conventionally treated soy bean field (38°16'26.211 "N, 128°8'45.354"E, 452 m asl).

The study area falls within the East Asian monsoon climate and has an 11-year (1999-2009) average annual air temperature of 8.5°C and an annual precipitation of approximately 1577 mm, with 70% of the precipitation occurring as heavy rainfall between June and August. In recent decades, a shortening of the monsoon season, as well as an increase in the amount of precipitation, and the number of heavy rainfall days, was observed (Chung et al., 2004).

However, the months of June and July in 2010 had precipitation amounts of only 67 mm and 216 mm, respectively, which were exceptionally low compared to the 11-year averages. Very dry periods, each with less than 20 mm precipitation in total, were observed from June 14 to July 1, July 6 to July 15, and from July 19 to August 1. In contrast, the months of August and September were extremely wet, with precipitation amounts of 458 mm and 415 mm, respectively. Due to clearly colder temperatures in March, April and May than during the 11-year mean there was a delay in the start of cropping by approximately two to four weeks.

The 2011 mean air temperature (8.4°C) was in accordance with the 12-year (1999-2010) average whereas precipitation amounts (1440 mm) were slightly lower. Most precipitation occurred in June (372 mm), July (596 mm) and August (148 mm).

2.2 Experimental design in 2010

On May 15, the previously fallow field was tilled. On May 31, a commonly used basal fertilizer (30% mineral NPK fertilizer with 4.2-2-1, 70% organic fertilizer, with C/N ratio 4.1:1 and an N content 186.7 kg / ha, SamboUbi, South Korea) was applied as granules and mixed in the top 15 cm of the soil to enhance soil fertility. On June 1, additional NH₄⁺-urea fertilizer in a ratio of 7:3 was applied as a one-time top dressing (mineral NPK fertilizer 11-8-9

+3MgO+0.3B, KG Chemicals, South Korea) at 4 fertilizer N rates on June 1: N50, N200, N250, and N350, reflecting the application of 50, 200, 250, and 350 kg N ha⁻¹. The recommendations for highland radishes provided by the Rural Development Administration of Korea (RDA, 2006) was 250 kg/ha. The plots (7x7 m) were arranged in a randomized block design with three replicates for the applied fertilizer amounts N50, N250 and N350 and there was one more additional plot which received the N200 treatment (Fig. 1). On June 9, the top 20 cm of the soil was ploughed, implementing a ridge system (35 cm width and about 15 cm height) with a distance of 70 cm between the rows. The ridges were covered with impervious black PE mulch (see Fig. 2) that contained one row of holes with a diameter of 6 cm every 25 cm along the ridge. Finally, on June 14, radishes were sowed on the top ridges at a rate of two - three seeds for each hole (Hungrong Seeds, South Korea). Weeding during the experiment was performed manually without the application of herbicides. This is not the common practice in this area as farmers usually seem to apply herbicides, but in order not to add any more chemicals and potentially N₂O-emission-causing substances, it was decided to do manually weed. The weeding was done weekly during the month after the seeding of the radish. On August 27, the radish was harvested, the PE mulch was removed and the field lay fallow.

Each N50-, N250- and N350-radish field plot contained three polyvinylchloride (PVC) cylinders (see Fig. 1). There were two of those cylinders on the PE-mulched ridge: the first one surrounded a hole with one radish plant (*plant hole* cylinder) and the second one was installed on the PE mulch (*PE mulch* cylinder). The PE mulch cylinder was accomplished by cutting a hole of the size of the PVC cylinder in the PE mulch, installing the PVC cylinder and then placing the PE mulch in the PVC cylinder. The PE mulch which surrounded that PVC cylinder was placed on the PVC cylinder from its outside so that the PE mulch of the ridge remained impervious. The third cylinder of each plot was installed in the furrow (*furrow* cylinder). The N200 plot had nine PVC cylinders, three in the furrow, three in the PE mulch and three more surrounding plant holes. Prior to seeding and after the harvesting N₂O flux measurements were taken on the fallow soil.

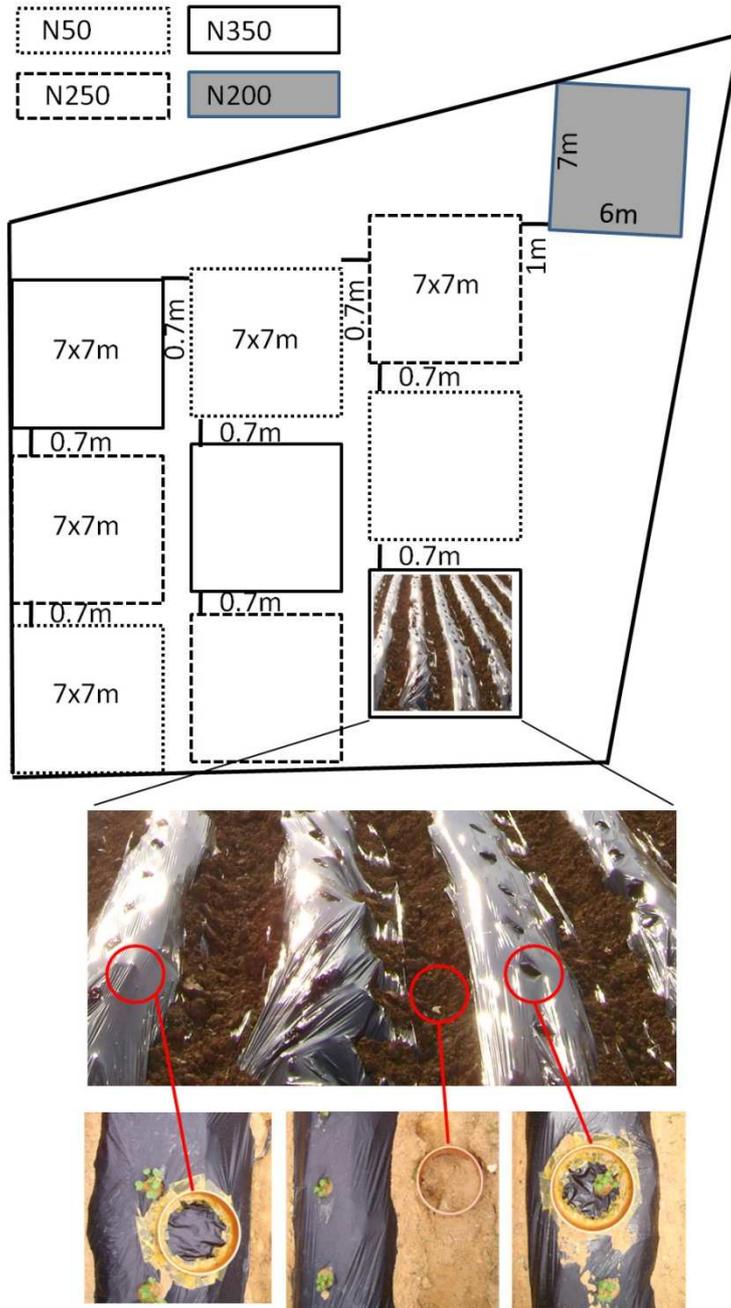


Figure 1: Schematic drawing of the experimental design of the radish field site in 2010.

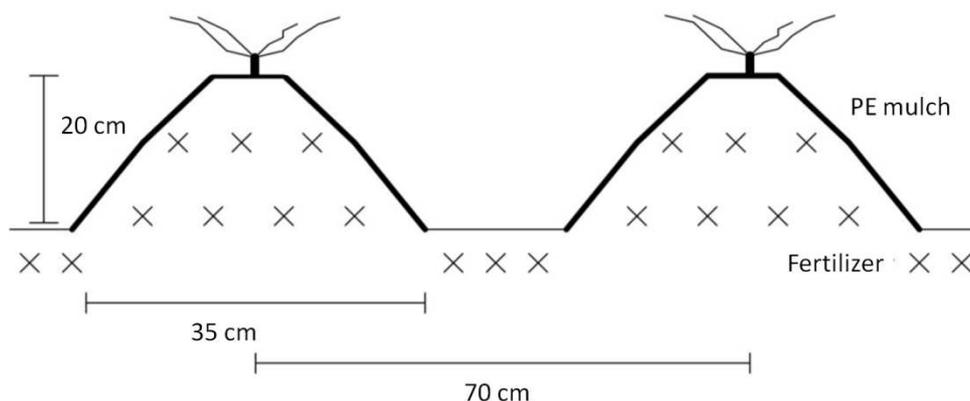


Figure 2: Scheme of a typical ridge cultivation system with plastic mulching in a temperate South Korean area with summer monsoon (Kettering unpublished). Shown are the distribution of N fertilizer in the system and width, height and distance of the ridges.

2.3 Experimental design in 2011

Before the experiment started, the field in which radish had grown the previous year, was ploughed by the farmer without applying any fertilizer in 2011. The ridge and furrow system was implemented (35 cm wide and 15-20 cm high (Fig. 2)), the ridges were covered with impervious black PE mulch that contained one row of holes every 25 cm along the ridge with a diameter of 6 cm. On May 29, soy beans were sowed on top of the ridges at a rate of two - three seeds for each hole. Some ridges remained uncovered. Weeding during the experiment was performed manually without the application of herbicides. This is not the common practice in this area as farmers usually seem to apply herbicides, but in order not to add any more chemicals and potentially N₂O-emission-causing substances, it was decided to manually weed. The weeding was done one time, on June 15, 2011.

N₂O fluxes were measured using nine PVC cylinders: three surrounded soy bean plants which grew on ridges covered with PE mulch, three surrounded soy bean plants which grew on ridges which were not covered with PE mulch and three installed in the furrows which were randomly distributed next to PE-covered and non-PE-covered ridges.

2.4 Measurements of N₂O fluxes

N₂O fluxes were measured every three to seven days from May 13 through October 22, 2010 at the radish field site and from May 16 through September 14, 2011 at the soy bean field site using the closed chamber method in conjunction with a photoacoustic infrared gas analyser (Multigas Monitor 1312, INNOVA, Ballerup, Denmark) as described by Yamulki and

Jarvis (1999) and Goldberg et al. (2008). Each site contained the amount of PVC cylinders described above with a diameter of 19.5 cm and a height of 15 cm, which were installed 7 cm deep in the soil. They served as connecting points to attach the chambers in whose headspaces the N₂O concentrations were determined in 0, 10, 20, 30 and 40 minute intervals. The reproducibility of one single N₂O concentration measurement was ± 32 ppb. From a linear increase or decrease of the N₂O concentration in the chambers' headspaces the N₂O flux was calculated taking into account the total chamber volume which includes the chamber headspace volume, volume of the two 25 m long Teflon tubes and of the CO₂ and H₂O gas traps.

Cumulative N₂O emissions were calculated as described by Tilsner et al. (2003a), by multiplying the N₂O emission rates of two consecutive measurement days with the corresponding time period. These time weighted N₂O flux means were then summed up over the measurement period.

2.5 Measurement of soil moisture and soil temperature

To measure volumetric soil water content [%] and soil temperature [°C] ECH2O loggers (EM50 Data logger, Decagon Devices, WA, USA) were used. They logged soil moisture and temperature values every 30 minutes from May 13 through August 31, 2010 at the N200 treatment of the radish field and from May 16 through September 14, 2011 at the soy bean field.

At the N200 treatment of the radish field one sensor was installed 5 cm deep in the furrow and a second sensor was installed 5 cm deep in one of the holes of the PE mulch.

At the soy bean field one sensor was installed 5 cm deep in a furrow, one more sensor was installed 5 cm deep in one of the plant holes of a ridge that was covered with PE mulch and a third sensor was installed next to a plant of a ridge which was not covered with PE mulch.

2.6 Statistical methods

N₂O flux curves were obtained by calculating mean N₂O flux values ± 1 SE for every day of measurement and linear interpolation between two consecutive measurement days. The mean flux was based on $n=3$ for furrows, PE mulches and plant holes at each amount of fertilizer applied. Statistics were conducted with R 2.12.0. *Via t-Test* (normally distributed data) or Mann-Whitney *U-test* (not normally distributed data) it was tested whether the measured N₂O fluxes are significantly different from zero and whether the soil moisture and temperature conditions underneath the PE mulch were different from those in the furrow. After the t-Test had not shown a difference between the soil temperatures of PE-mulched

ridges and furrows, a paired t-Test was conducted. To determine whether furrow-, PE mulch- and plant hole N₂O fluxes of the radish field's N50, N200, N250 and N350 plots and also the N₂O fluxes of the soy bean field's PE-mulched and non-PE-mulched ridges, as well as soil moisture or soil temperature of the soy bean field's furrows, PE- and non-PE-mulched ridges were statistically different from each other, t-Tests, ANOVAs or the non-parametric Kruskal-Wallis-tests were calculated. Pearson or Spearman analyses were performed to identify potential correlations between N₂O fluxes and volumetric soil water content and soil temperature and between the cumulative N₂O emissions and the amount of N fertilizer applied.

3. Results

3.1 N₂O fluxes and cumulative N₂O emissions at the radish field in 2010

With increasing amount of fertilizer applied there appeared to be a higher N₂O emission rate of the plant hole-spots at all the plots' ridges. The N₂O-emissions of the furrow showed a more complicated pattern: for those plots which had received a lower amount of N fertilizer (N50 and N200), the N₂O emissions of the furrows exceeded the emissions of the plant holes. For the N250 and N350 plots the opposite N₂O emission pattern could be observed.

The N₂O fluxes of ridges with PE mulch were almost zero for all of the treatments during the time of the experiment, except for June 23, when they reached their maximum (N50: 3.15 $\mu\text{mol m}^{-2} \text{h}^{-1}$; N200: 1.85 $\mu\text{mol m}^{-2} \text{h}^{-1}$; N250: 1.21 $\mu\text{mol m}^{-2} \text{h}^{-1}$; N350: 2.84 $\mu\text{mol m}^{-2} \text{h}^{-1}$). On that day, the plant holes and furrows also showed the highest N₂O fluxes.

Before June 16 and after July 24 only very tiny to zero N₂O fluxes could be measured.

There were significantly different N₂O fluxes (* $P < 0.05$) between PE mulch and plant holes in PE mulch as well as furrows for almost all of the plots (see Table 1 in the appendix for all statistical differences). No differences were found among ridges, furrows and PE mulches of the differently fertilized plots.

The measurement period's cumulative N₂O emissions of the furrows and plant holes in PE mulch range between 2 to 6 mmol m^{-2} (equals 880.3 to 2640.8 $\text{g N}_2\text{O ha}^{-1}$ or 5.5 to 16.4 $\text{g N}_2\text{O ha}^{-1} \text{d}^{-1}$), whereas the highest cumulative N₂O emissions degassed from the furrows of the N50 plots (6 mmol m^{-2} , equals 2640.8 $\text{g N}_2\text{O ha}^{-1}$ or 16.4 $\text{g N}_2\text{O ha}^{-1} \text{d}^{-1}$). Among all of the different amounts of fertilizer applied the N₂O fluxes of the PE mulches integrated over time amounted to comparably low values of 0.2 to -0.8 mmol m^{-2} (equals 88.0 to -352.1 $\text{g N}_2\text{O ha}^{-1}$ or 0.5 to -2.2 $\text{g N}_2\text{O ha}^{-1} \text{d}^{-1}$).

- N₂O fluxes of furrows
- N₂O fluxes of ridges – plant holes in PE mulch
- N₂O fluxes of ridges – PE mulch
- N₂O fluxes of bare soil prior to seeding and after the harvesting
- cumulative N₂O emissions of furrows
- cumulative N₂O emissions of ridges – plant holes in PE mulch
- cumulative N₂O emissions of ridges – PE mulch

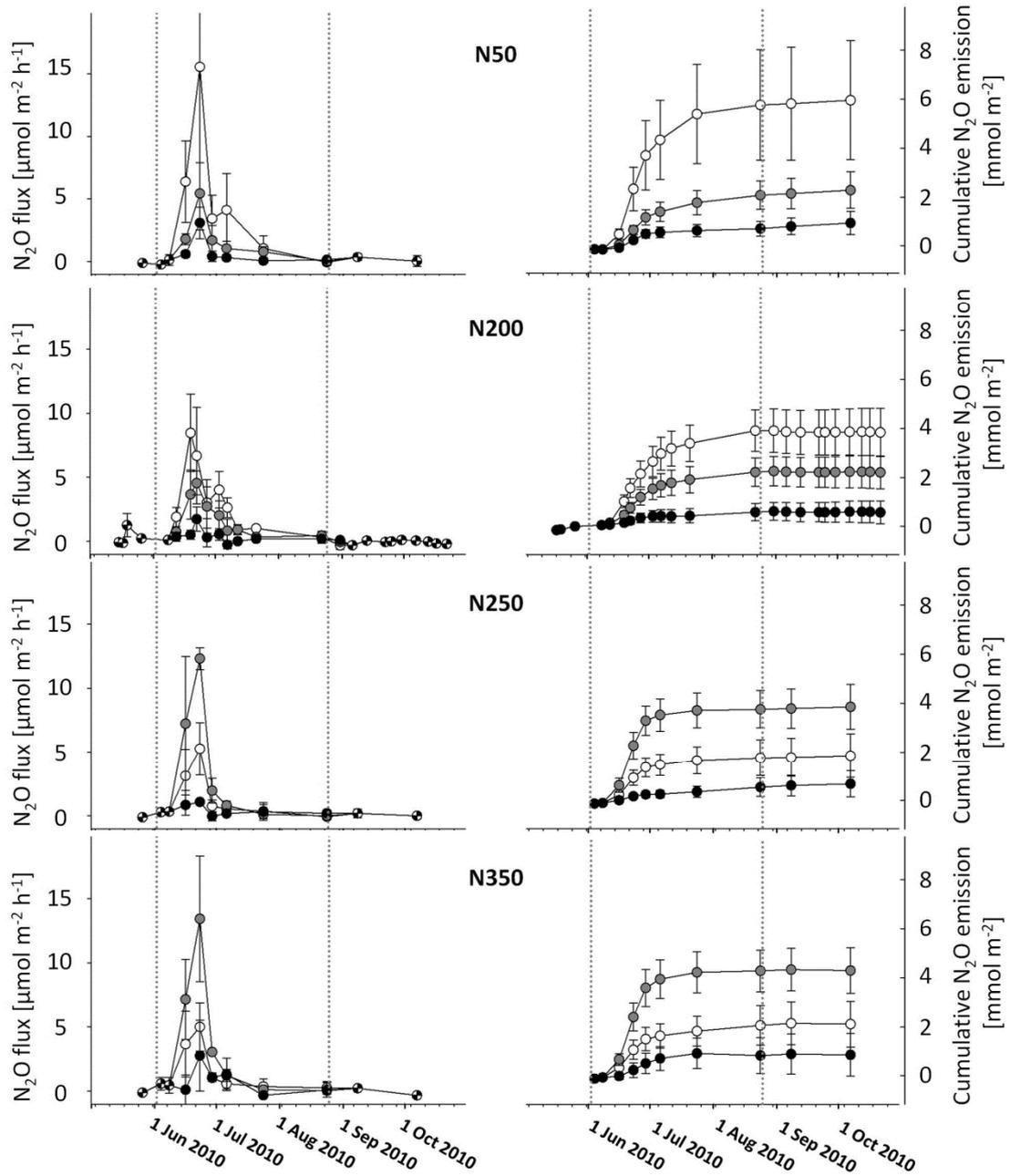


Figure 3: N₂O flux [$\mu\text{mol m}^{-2} \text{h}^{-1}$] and cumulative N₂O emission [mmol m^{-2}] of the radish field site from May 13 until October 22, 2010. The first dotted line indicates the day when the N fertilizer was applied (June 1) and the second dotted line indicates the day when the radish was harvested, the PE mulch was removed and the ridge and furrow system was dissolved. Error bars in N₂O flux- and cumulative N₂O emission- graphs represent the standard error of the mean ($n=3$).

3.2 Soil moisture and temperature of the PE-mulched ridges and furrows at the N200 plot

There appeared to be higher temperature fluctuations in the PE-mulched ridges than in the furrows; however, the mean soil temperature during the time of the experiment was 24.80°C (± 2.14) in PE-mulched ridges and 24.30°C (± 1.58) in furrows (Fig. 4) which makes a very significant difference of 0.5°C (**P = 0.005). In contrast, the mean volumetric soil water content in ridges and furrows differed with a mean value of 19.80% (ranging from 10% to 32%) in the furrows and 15.62% (ranging from 5% to 15%) in the ridges underneath the PE mulch, which makes a highly significant difference (**P < 0.001) of 4.18%.

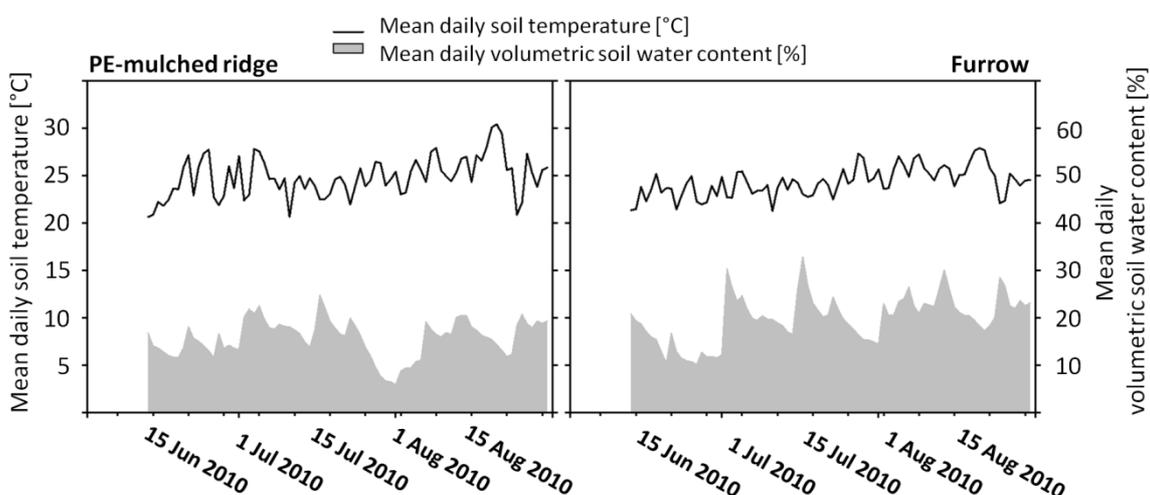


Figure 4: Mean daily volumetric water content [%] and mean daily soil temperature [°C] from June 14 until August 31 of the N200 plot at the radish field site in 2010.

3.3 N₂O fluxes and cumulative N₂O emissions at the soy bean field in 2011

The N₂O fluxes at the soy bean field site's PE-covered and non-PE-covered ridges ranged from slightly negative to 5.2 $\mu\text{mol m}^{-2} \text{h}^{-1}$ (Fig. 5). During the time of the experiment they were comparatively low: flux peaks occurred on May 22, June 6, July 6, August 23 and August 30; however, statistically significant differences between the PE-mulched and non-PE-mulched ridges could not be found. For the furrows there is a similar pattern; however, their average N₂O exchange at the soil/atmosphere interface most of the times was higher than that of the ridges (Tab. 2).

For the cumulative N₂O emissions the graph (Fig. 5) shows a difference between the amount of N₂O degassed from PE-covered and non-PE-covered ridges which is not statistically significant. Also, the amount of N₂O degassed from the furrows (Tab. 2) exceeds both the cumulative N₂O emissions of the PE-covered and non-PE-covered ridges. The N₂O fluxes of

the non-PE-mulched ridges amounted to 3 mmol m⁻² (equals 1320.4 g N₂O ha⁻¹ or 10.9 g N₂O ha⁻¹ d⁻¹), which is 50% more than the emission from the PE-mulched ridges. The highest cumulative N₂O emissions were found for the furrows (3.9 mmol m⁻² equals 1716.5 g N₂O ha⁻¹ or 14.2 g N₂O ha⁻¹ d⁻¹).

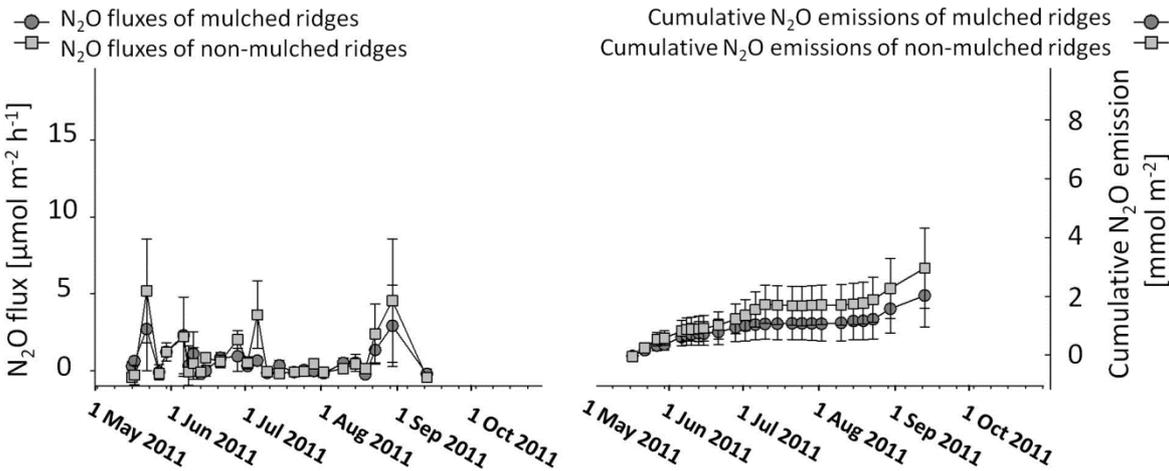


Figure 5: N₂O flux [μmol m⁻² h⁻¹] and cumulative N₂O emission [mmol m⁻²] of the soy bean field site from May 15 until September 14, 2011. Error bars represent the standard error of the mean (n=3).

Table 2: N₂O flux [$\mu\text{mol m}^{-2} \text{h}^{-1}$] and Standard Error ($n=3$) as well as cumulative N₂O emission [mmol m^{-2}] and Standard Error ($n=3$) of the soy bean field site's furrows from May 15 through September 14, 2011. Those N₂O fluxes are a mixture of N₂O fluxes from furrows which were located next to PE-mulched and such which were located next to non-PE-mulched ridges so that they cannot be included into Figure 5.

Date	Measured N ₂ O flux [$\mu\text{mol m}^{-2} \text{h}^{-1}$]	$\pm 1\text{SE}$	Cumulative N ₂ O emission [mmol m^{-2}]	$\pm 1\text{SE}$
16.05.2011	-0.29	0.18		
17.05.2011	0.40	0.56	0.00	0.00
22.05.2011	7.83	4.62	0.50	0.09
27.05.2011	0.23	0.41	0.98	0.19
30.05.2011	1.24	0.69	1.03	0.20
06.06.2011	3.03	2.12	1.34	0.32
08.06.2011	0.42	0.15	1.42	0.36
10.06.2011	0.95	0.09	1.46	0.39
13.06.2011	0.55	0.18	1.51	0.42
15.06.2011	1.02	0.08	1.55	0.43
21.06.2011	0.97	0.54	1.69	0.45
28.06.2011	1.95	1.58	1.93	0.50
02.07.2011	1.35	1.37	2.09	0.53
06.07.2011	3.30	2.53	2.31	0.54
10.07.2011	0.52	0.18	2.50	0.54
15.07.2011	0.50	0.43	2.56	0.56
21.07.2011	0.05	0.05	2.60	0.57
25.07.2011	-0.09	0.10	2.60	0.58
29.07.2011	0.14	0.30	2.60	0.59
02.08.2011	0.38	0.30	2.63	0.61
10.08.2011	0.53	0.49	2.71	0.63
15.08.2011	2.83	2.19	2.91	0.66
19.08.2011	-0.05	0.47	3.05	0.67
23.08.2011	2.16	1.09	3.15	0.69
30.08.2011	2.19	1.91	3.51	0.84
13.09.2011	0.15	0.36	3.91	1.09

3.4 Soil moisture and temperature of the PE mulched ridges, the non-PE-mulched ridges and furrows at the soy bean field

The lowest mean soil temperature ($21.47^{\circ}\text{C} \pm 2.44$) as well as the smallest temperature fluctuations occurred in the furrows (Fig. 6), whose soil temperatures were only by trend ($P = 0.103$) different from mean daily soil temperatures in the PE mulched and non-PE-mulched ridges. The temperature fluctuations and averaged mean daily soil temperature were very similar in PE-mulched ($21.96^{\circ}\text{C} \pm 2.57$) and non-PE-mulched ridges ($22.00^{\circ}\text{C} \pm 2.56$). Volumetric soil water content was very similar and statistically not differentiable in the furrows ($30.22 \pm 0.11\%$) and non-PE-mulched ridges ($28.36 \pm 0.08\%$), whereas the ridges which

were covered with the PE film were much drier and statistically different (19.03 ± 4.98 %), which is reflected in a highly significant statistical result of $P < 0.001$, $H = 86.684$.

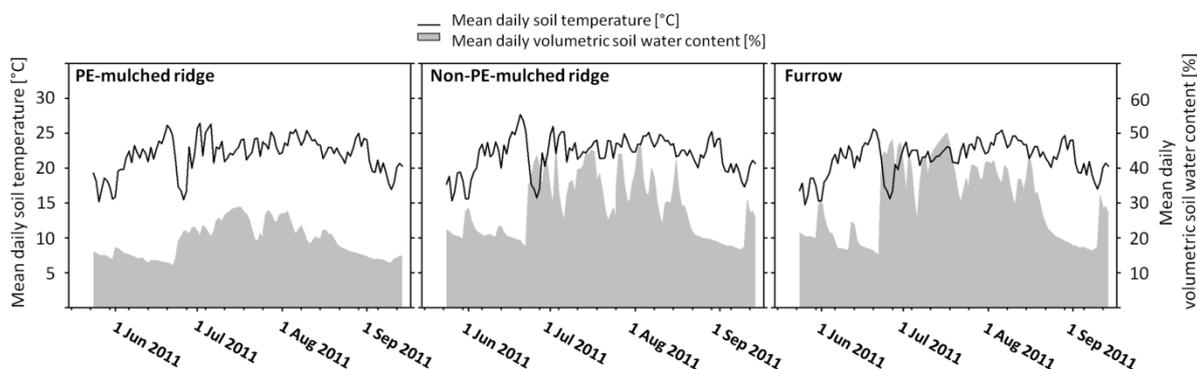


Figure 6: Mean daily volumetric water content [%] and mean daily soil temperature [°C] from May 15 until September 14 at the soy bean field site in 2011.

3.5 Correlations between N_2O fluxes and soil moisture, soil temperature and amount of N fertilizer applied

Neither soil moisture nor soil temperature affected the N_2O fluxes at the radish or soy bean field site significantly ($R^2 < 0.1$, $P > 0.05$) even though the rain event from June 12 through June 14 apparently triggered the N_2O fluxes and the July 2 through July 5 rain event preceded one more, smaller, N_2O peak at the radish field site in 2010.

No correlation could be found between applied N fertilizer amounts and sum of N_2O emitted from the radish field.

4. Discussion

4.1 General comments on crop yields of the study region

The average yield of radish in the study area in 2010 was 33.1 t/ha and in 2011, 32.5 t/ha; average yield of soy beans was 1.85 t/ha in 2010 and 1.56 t/ha in 2011 (Yanggu County office statistic 2010, 2011, unpublished data sheets). For radish the average yield data given in the literature varies between 60 and 160 t/ha and for soy beans the average yields are 0.6-4.9 t/ha (Batti et al., 1983; Morgan and Midmore, 2003; Khairul Alam et al., 2010; Lindner, 2012, personal communication). Therefore, the yields of soy beans of the study region were on average whereas radish yields were below average. For other crops of the study area which also experience the PE mulching practice such as potato and cabbage, the yields are

well on average in comparison to other areas' yields (Horton et al., 1988; Hassal and Associates, 2003; Rahemi et al., 2005; Bohl and Johnson, 2010).

Also, it is known that the PE mulch - through performing as a greenhouse - in general has a positive effect on the plant productivity, which is the main reason why it is widely used worldwide. The purpose of our study was not to reconfirm it but we took the already well-investigated positive PE mulching effect on crop yields (Kyrikou and Briassoulis, 2007) as given and furthermore tried to broaden our knowledge on side effects of the PE mulch, such as its impact on N₂O as its impact on N₂O emissions.

4.2 Discussion of the results

An unexpected result was that the soil moisture of the PE-mulched ridges of the radish field as well as those of the soy bean field was much lower than we had expected and as other publications predict (Kyrikou and Briassoulis, 2007; Nishimura et al. 2012). Nishimura et al. (2012) observed that during the summer the soil moisture under the PE mulch at their experimental site ranged from 26% to 33%, which is in contrast to the considerably lower soil moisture values underneath the PE mulch that we found at our study sites: during the early summer drought period in 2010 it ranged from 9% to 22% at the radish field site and during the early summer drought of the year 2011 it ranged from 12% to 20%. The reason for those low soil moistures could be the soil conditions of the study area. According to Kettering et al. (2013), the soils of the study region were very sandy, as were the soils of our experimental sites. Such soils show a fast infiltration and seepage of water; thus due to quick seeping of water it appears plausible to us that the PE mulch at our experimental sites could not keep the soil moisture high and the soils of our experimental sites were dryer as in the previous studies.

This unexpected finding may be the main reason why our initial hypothesis could not be corroborated. We were assuming that plastic mulch films covering agricultural fields would lead to increased N₂O emissions due to higher soil temperatures and moisture but the two experiments which we conducted were not in line with this hypothesis.

The 2010 experiment at the radish field site provided an indication that ridges which are being covered with PE mulch films show very tiny N₂O emissions from the PE mulch surface whereas the adjacent plant hole spots and furrows showed quite high emissions. This raised the question whether less N₂O production occurred underneath the PE mulch film or there was horizontal diffusion of N₂O from the ridge soil covered with the mulch film to the adjacent furrows and plant holes, so that most of the N₂O produced underneath the PE mulch would have degassed from the furrows and plant hole spots. Recently, Nishimura et al. (2012) published that the N₂O flux by permeation through the mulch film was much higher than that

by horizontal diffusion to the furrow, that N₂O permeates through PE mulch film and that its permeability increased with increasing ambient temperature in a way that extremely huge amounts of N₂O degassed through the PE mulch film from the field during midday temperatures in the summer. Ou et al. (2007) also found that another gas the fumigant methyl bromide injected to the soil covered with a PE film was emitted to the atmosphere by permeation through the film to a great extent.

Considering that the PE mulch is permeable for gas at high temperatures and the high mean daily soil temperatures of up to 30°C at our site, we conclude that the amount of N₂O degassing from the PE mulch surface to a great extent must have been in accordance with the amount of N₂O that had been produced underneath.

To us it makes sense that low soil moistures as well as high soil temperatures (the conditions underneath the PE mulch at our study sites) lead to a decreased N₂O production even though there are recent previous studies (Arriaga et al., 2011; Nishimura et al., 2012), that suggest otherwise, although at higher soil moistures. Assuming that N₂O is mainly produced during microbial denitrification (Tilsner et al., 2003b) and the recently attention attracting process of nitrifier denitrification (Wrage et al., 2001; Kool et al., 2011), processes which are known to occur at conditions of low oxygen - however the first process mainly takes place at low soil moisture, whereas the latter process takes place when moisture conditions are sub-optimal for denitrification (Linn and Doran, 1984; Kool et al., 2011) - there would be less production of N₂O underneath the PE cover.

Interestingly, we neither found significant correlations between N₂O fluxes and soil moisture or temperature nor between N₂O fluxes and amount of fertilizer applied, which would have been an expected result since soil water content, soil temperature and fertilization rates have been identified as main drivers of N₂O fluxes (Dobbie et al., 1999; Ruser et al., 2006; Kool et al., 2011; Nishimura et al., 2012). A previous study which had been conducted in nearby forest sites had shown that there were significant correlations between N₂O fluxes and soil moisture and temperature (Berger et al., 2013).

However, despite not finding a correlation between moisture and N₂O fluxes, it was obvious that the rain event from June 12 to June 14, 2010 had triggered the N₂O fluxes of the radish field. This is consistent with previous studies reporting on greatest N₂O fluxes after the first of summer rains (Davidson et al., 1993; Scholes et al., 1997; Barton et al., 2008).

Because the 2010 experiment left so many questions unanswered, we conducted the soy bean field experiment in the following year in order to directly compare whether covered or uncovered ridges of a non-fertilized field would show higher N₂O emissions. The interesting result was that the amount of N₂O cumulatively emitted from plant holes of ridges which were covered with the PE mulch (2 mmol m⁻²) was only 68% of the emission of soils around soy

bean plants of non-PE-mulched ridges (3 mmol m^{-2}) and it was only 50% of the N_2O emitted from the furrows (3.9 mmol m^{-2}) even though hardly any statistical significant differences could be found between N_2O fluxes at both PE-mulch-covered and –non-covered ridges on the single measurement days. The difference between soil moisture of the PE-mulched ridges and the non-PE-mulched ridges and furrows was even more pronounced than the differences between furrows and PE-mulched ridges in 2010.

Thus, our results suggest that PE mulch may reduce N_2O emissions from agricultural fields on sandy soils in temperate areas with summer monsoon like in Korea because the PE mulch keeps the covered soils between the plant holes, where no water can infiltrate into the ridges, at lower soil moisture and higher soil temperatures.

Only taking into account the radish field data, one may argue that there might have occurred a strong N_2O diffusion to, and stack effect through, the adjacent plant holes and furrows. But since a direct comparison of N_2O emissions of plant holes of PE-mulched ridges and plant spots of non-mulched ridges in the following year showed that mulched ridges certainly do not have higher emissions (if not even lower ones), we believe that PE mulches and the way they are used in Korea (application of fertilizer and PE mulching long before the most of the rainfall occurs, so that most of the fertilizer can get assimilated by the crops) can reduce N_2O emissions from agricultural soils.

To finally answer the title question: “Plastic mulching in Agriculture – friend or foe of N_2O emissions?”, it would be necessary to take comparative N_2O flux measurements of furrows located next to PE-mulched ridges would behave in comparison to furrows located next to non-PE-mulched ridges, which has not been done so far.

Considering that the PE mulching is a very common method in agriculture in East Asian countries such as Korea, Japan and China, and that its use is increasing in Africa, in the Middle East and also in Germany by 15-20% annually (Kwon et al., 2006; Kyrikou and Briassoulis, 2007; FBAW information, 2007; unpublished data sheet), it is very important to acquire detailed knowledge on the PE mulch’s effects on the environment.

Our results support the general finding that N_2O fluxes from non-fertilized legume cropping systems, which have N fixation as an additional N source, are not necessarily greater than fluxes from N fertilized non-legume crops under similar climatic and management regimes (Helgason et al., 2005; Rochette and Janzen, 2005; Parkin and Kaspar, 2006; Stehfest and Bouwman, 2006; Barton et al., 2008). The N_2O emitted from the non-fertilized soy bean field site in 2011 amounted to 5.90 mmol m^{-2} (2.06 mmol m^{-2} for the PE-mulched ridges and 3.90 mmol m^{-2} for the furrow), which is very similar to the amount of N_2O that had degassed from

the N200 plots at the radish field site in 2010, which had received an intermediate amount of nitrogen fertilizer.

Conclusions

Comparative N₂O flux measurements were conducted at a radish field in 2010 and at a soy bean field in 2011 in order to elucidate if PE mulching of agricultural fields affected N₂O emissions. Whereas the PE-mulched rows of the radish field showed rather low N₂O emissions, the adjacent furrows and plant holes showed higher emissions among different amounts of nitrogen fertilizer applied, we considered the extremely low soil moisture at our study site to be responsible for the comparatively low N₂O emissions which could neither be correlated with soil temperature and moisture, nor amount of fertilizer applied. The experiment at the soy bean field in 2011 brought the interesting result that PE-mulching might decrease N₂O emissions from agricultural soils if applied on sandy soils located in a temperate climate including an early summer drought and monsoon rains. One additional result was that the N₂O emitted by a non-fertilized PE-mulched legume field did not exceed the N₂O emitted by a non-legume field which had received an intermediate amount of nitrogen fertilizer, which supports earlier findings which state that cultivation of nitrogen fixing plants does not cause N₂O emissions above cultivation of non-nitrogen fixing plants and common nitrogen fertilizer use.

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Appendix

Table 1: Statistically significant differences between N₂O fluxes of PE mulches, plant holes and furrows of the N50, N200, N250 and N350 plots of those measurement days when such differences occurred. * indicates P < 0.05, ** indicates P < 0.01 and *** indicates P < 0.001.

N50	16.06. 2010			23.06. 2010			29.06. 2010			06.07. 2010			24.07. 2010		
		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole
	Plant hole	* p = 0.036		Plant hole			Plant hole	p = 0.138		Plant hole	p = 0.173		Plant hole		
	Fur-row		Fur-row			Fur-row	* p = 0.044	p = 0.158	Fur-row	* p = 0.017	p = 0.093	Fur-row			
N200	12.06. 2010			19.06. 2010			22.06. 2010			03.07. 2010			07.07. 2010		
		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole
	Plant hole			Plant hole	p = 0.063		Plant hole	p = 0.121		Plant hole	p = 0.131		Plant hole	**p= 0.003	
	Fur-row	p = 0.163		Fur-row	* p = 0.029	* p = 0.029	Fur-row	* p = 0.036		Fur-row			Fur-row	p = 0.151	p = 0.074
	12.07. 2010			21.07. 2010											
		PE mulch	Plant hole		PE mulch	Plant hole									
Plant hole	* p = 0.022		Plant hole												
Fur-row	* p = 0.018		Fur-row	***p< 0.001	**p= 0.006										
N250	16.06. 2010			23.06. 2010			29.06. 2010			06.07. 2010			24.07. 2010		
		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole
	Plant hole			Plant hole	p = 0.057		Plant hole	* p = 0.036		Plant hole	p = 0.056		Plant hole		
Fur-row			Fur-row	* p = 0.029	* p = 0.011	Fur-row	p = 0.109	p = 0.167	Fur-row			Fur-row			
N350	16.06. 2010			23.06. 2010			29.06. 2010			06.07. 2010			24.07. 2010		
		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole		PE mulch	Plant hole
	Plant hole	* p = 0.021		Plant hole	* p = 0.026		Plant hole	**p< 0.005		Plant hole			Plant hole	***p< 0.001	
Fur-row			Fur-row	p = 0.064		Fur-row	* p = 0.015	***p< 0.001	Fur-row			Fur-row			

Given are those p-values which indicate a statistically significant difference as well as P-values which indicate a trend (P =/ < 0.1). There were more measurement days but the table only provides the statistical results of such measurement days on which statistical differences between plant holes, PE-mulch and furrows could be found.

Part B

The simulation of N₂O emissions and nitrate leaching from different rates of N fertilizer in the radish field with the Landscape-DNDC model

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Abstract

The Landscape-DNDC-model was used to estimate N₂O emissions, nitrate concentrations and leaching from 50, 150, 250 and 350 kg N ha⁻¹ fertilizer treatments of a radish field study site in Korea. Half of the daily precipitation and the daily average maximum temperature were assumed to be the climatic conditions in rows, which were covered with impervious black polythylene (PE) mulch during the growing period of radish, in order to consider the effects of the plastic mulch on soil biogeochemistry in rows and differentiate N₂O emissions, nitrate concentrations and leaching in interrows which were not covered with the plastic mulch. Simulation results showed that the model was capable of predicting the dynamics of N₂O emissions, nitrate concentrations and leaching in rows and interrows. The simulated N₂O emissions in rows were increased with increasing amount of N fertilizer applied but underestimated during the monsoon season. The model predicted more N₂O emissions in rows than in interrows. About 0.94 and 0.97% of applied N fertilizer were lost by N₂O emissions from rows and interrows, respectively. The simulation results of nitrate

concentrations at 45 cm depth in rows ranged from 137.1 (50 kg N ha⁻¹) to 149.6 mg N l⁻¹ (350 kg N ha⁻¹). Lower nitrate concentrations were simulated for 45 cm depth in interrows as compared with rows, ranging from 91.1 (50 kg N ha⁻¹) to 124.7 mg N l⁻¹ (350 kg N ha⁻¹). These results were in good agreement with measured nitrate concentrations at 45 cm depth in rows and interrows. ME was positive (ME > 0) for all N treatments and r² was also high (eg., 0.89, 0.89 and 0.52 for 50, 150 and 250 kg N ha⁻¹) at 45 cm depth of interrows. Nitrate leaching simulated by the model was increased following the rainfall events and applied N fertilizer rates. In general, interrows which were not covered with the plastic mulch show high nitrate leaching rates as compared with rows under the plastic mulch. The model simulated about 13.2% more nitrate leaching in interrows than in rows, ranging from 403.4 to 452.3 kg N ha⁻¹ yr⁻¹. About 72.2% of applied N loss by nitrate leaching from interrows and about 62.5% N loss from rows were predicted by the model.

Keywords: Landscape-DNDC, N fertilizer, Plastic mulch, N₂O, Nitrate leaching

Introduction

Agriculture is the major anthropogenic source of nitrous oxide (N₂O) (McCraw and Motes 1991; Smith and Conen 2004). Of global anthropogenic greenhouse gas (GHG) emissions, agriculture accounts for about 60% of N₂O (IPCC 2007b). N₂O emissions are directly connected to the amounts of nitrogen application (Smith and Conen 2004) and have been increased by 11% since 1990, primarily due to the increase in fertilizer use and the aggregate growth of agriculture (IPCC 2007a). In Korea, agricultural N₂O is estimated about 12 x 10³ tons, which accounts for about 24% of the total N₂O emissions. Agricultural soils are the major source of N₂O emissions, contributing about 58.3% to the total agricultural N₂O emissions (KEEI 2009). N₂O emissions are influenced by environmental factors such as soil temperature and water content, radiation, pH, Eh, and substrate concentration gradient, as well as management practices such as plastic mulch, tillage, manure and fertilizer application and incorporation of crop residues (LI 2007; Smith et al. 2002).

For many years the use of impervious black and clear plastic (polyethylene) films as a mulch has been widely utilized for various crops. In the traditional plastic mulching system the crop is sown under the plastic film which is held tightly across the soil surface by covering the edges. The crop emerges through perforations in the plastic mulch, which are usually made at the time of seeding. The plastic mulch is discarded after harvest and new a mulch is laid in following season (Fisher 1995). In arid and semi-arid regions, crop growth is limited by water. Amount of available water in soil can be increased by mulching (Wang et al. 2009). The plastic mulch is effective in reducing 3 to 11% crop water use and improves its efficiency by 25% (Chakraborty et al. 2010). The plastic mulch can also provide other benefits such as weed control, reduction in soil compaction and erosion, production of staple food crops (Fisher 1995), and an increase in soil temperature (Liakatas et al. 1986; Wan and El-Swaify 1999). The plastic mulch performs like a glass house by capturing and retaining daytime solar radiation and reducing heat loss at night, producing a mini-greenhouse effect (Kwabiah 2004). Many studies have reported that soil temperature is increased under the plastic mulch. The temperature of the black plastic mulch is greater than that of the soil surface during the day (Ham and Kluitenberg 1994). The net effect of the mulch is to increase the daily mean temperature of the soil by 3°C (Liakatas et al. 1986) and the maximum temperature is increased by 7°C for soil due to the plastic mulch (Kwabiah 2004). Less rainfall can pass through the root zone under the plastic mulch because the rain that falls onto an impervious plastic film covering a planting bed can run into the furrows, immediately (Haraguchi et al. 2004). The total amounts of precipitation and surface runoff for two months under the full-mulching condition were 112.5 and 50.3 mm, respectively. Neglecting the water that is kept on leaves and the plastic film this result suggests that almost a half of the

rain that falls into the lysimeter infiltrated into the soil through a hole on a plastic film for seeding (Haraguchi et al. 2003).

The black plastic mulch is the most commonly used for crop cultivation in Korea as well. The main purposes of using plastic mulch are weed control and water retention. The row is covered with the black plastic mulch before seeding or transplanting and the mulch is removed after harvest. The plastic mulch is one of the typical agricultural practices in Korea, however, the model is incapable of simulating the mulching effect, yet. Therefore, the daily mean maximum temperature as the daily mean temperature and a half of the precipitation as the total precipitation were hypothesized for the row condition. In contrast, the real climate information was used for the interrow condition.

Objectives

The process-based models can be used to predict the impact of various agricultural management practices on net greenhouse gas (GHG) emissions by analyzing the interactions between management practices, primary drivers such as climate, soil properties, crop types, etc., and biogeochemical reactions (Smith et al. 2010). So far the process-based model agricultural-DNDC (Denitrification and Decomposition) (Giltrap et al. 2010; Li et al. 1992a; Smith et al. 2002) and PnET-N-DNDC (Kesik et al. 2005; Kiese et al. 2011; Li et al. 2000) have been tested on the various types of ecosystems since its development. The Landscape-DNDC model, which is combined the Agricultural-DNDC with the Forest-DNDC, has been developed at Karlsruhe Institute of Technology (KIT), IMK-IFU in order to simulate the C and N turnover, GHG emissions, nitrate leaching and plant growth for arable, forest and grassland ecosystems on site and regional scales (Haas et al. 2012). However, little or no attention has been given to apply the DNDC model for arable or forest ecosystems of Korea. In this study, we applied the Landscape-DNDC to test the effects of different rates of N fertilizer on N₂O emissions, nitrate concentrations and leaching and plant growth for arable fields in Korea.

Materials and methods

Site description

The model was tested with data from summer radish fields (38.3°N, 128.14°E, 420 m a.s.l) in Haean-myun Catchment, located in the northeast of Yanggu County, Gangwon Province, South Korea. The annual average air temperature is 8.5°C and the annual precipitation is

approximately 1,500 mm (Fig. 1). More than half of the annual precipitation occurs during the monsoon season.

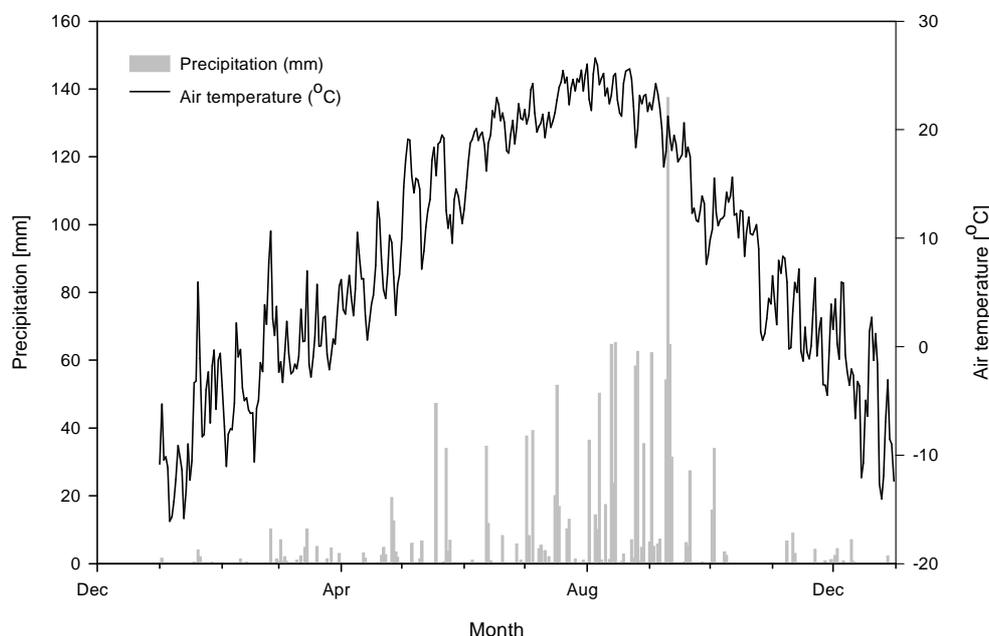


Fig. 1 Daily precipitation and daily average temperature at the study site. The data was collected from the automatic weather station on site in 2010.

The soil is loamy sand at 0 - 40 cm depth and sandy loam from 40 - 60 cm (Kettering et al. Submitted to *Nutrient Cycling in Agroecosystems* 2012) and classified as Anthrosols (FAO 2006) with 80.7% sand; 16.3% silt; 3.0% clay; pH 5.08; bulk density 1.64 g cm⁻³. The detailed information for soil characteristics of the study site is given in Table 1.

Table 1 Soil properties for 50, 150, 250 and 350 kg N ha⁻¹ treatments in radish fields at 0-20 cm depth soils

N rates [kg N ha ⁻¹]	OM [g kg ⁻¹] ^a	pH	BD [g cm ⁻³] ^b	SOC [%] ^c	N [%]	Sand [%]	Silt [%]	Clay [%]
Average	29.7	5.08	1.64	0.21	0.038	80.7	16.3	3.0
50				0.29	0.037	80.3	16.7	3.0
150				0.20	0.036	79.5	17.4	3.2
250				0.21	0.041	81.6	15.6	2.8
350				0.20	0.038	81.6	15.5	2.9

^a Organic Matter

^b Bulk Density

^c Soil Organic Carbon

N fertilizer treatments

186.7 kg N ha⁻¹ fertilizer was manually applied to the total field as basal fertilizer two weeks before seeding and the field was plowed with about 15 - 20 cm depth at the time of the fertilizer application. To examine the impacts of different rates of N fertilizer on N₂O emissions, nitrate leaching and crop growth, at first, the field was divided into four different N treatment plots with 196 m² size. Each N treatment plot had 4 replicated subplots (49 m² size in each). 50, 150, 250 and 350 kg N fertilizer were applied to the plots as a top dressing, respectively. All treatment plots were tilled again about one week after additional N fertilizer application in order to make rows and interrows. The rows were covered with the black plastic mulch prior to radish seeding and the mulch had continuously covered the row until harvest. About 2 or 3 seeds of summer radish (*Raphanus sativus* L.) were sown per one plant hole at rows in mid-June. Detailed information for crop management is shown in Table 2.

Table 2 Crop managements and four different rates of N fertilizer application

Seeding date [dd/mm]	Basal fertilization		Tillage		Additional fertilization		Harvest date [dd/mm]
	Date [dd/mm]	N rate [kg N ha ⁻¹]	Date [dd/mm]	Depth [cm]	Date [dd/mm]	N rate [kg N ha ⁻¹] ^a	
14/06	31/05	186.7	31/05 09/06	15 - 20	01/06	50/150/250/350	31/08

^a 50, 150, 250 and 350 kg N ha⁻¹ were applied to each N treatment plot with 4 replicates.

Field measurements

The field measurements were conducted in the radish field in 2010. The N₂O fluxes were measured by the closed chamber in conjunction with a photoacoustic infrared trace gas analyzer (Multigas Monitor 1312, INNOVA, Ballerup, Denmark) (Berger et al. Submitted to Agriculture, Ecosystems & Environment 2012) from May (before seeding) to October (after harvest) in rows and interrows of each N treatment plot with 3 replicates. ECH₂O loggers (5TE Soil Moisture Sensor, Decagon Devices, USA) connected with data loggers (EM50, Decagon Devices, USA) were installed in each N fertilizer treatment row in order to measure soil temperature and water content at 15 and 30 cm depth every 30 minutes with 2 replicates. Suction lysimeters connected with a soil hydrological monitoring network of standard tensiometers (Kettering et al. Submitted to Nutrient Cycling in Agroecosystems 2012) were installed at 15 and 45 cm depth in rows and at 45 cm depth in interrows in 50, 150, 250 and 350 kg ha⁻¹ N treatment plots to estimate N losses in seepage water. The seepage samples were collected once a week. Suction lysimeters are able to be used to

determine the nitrate concentrations in seepage water but provide no information on water fluxes (Kettering et al. Submitted to Nutrient Cycling in Agroecosystems 2012).

To examine the biomass production and the nutrient contents at different developmental stages, 8 radishes per each plot were randomly selected and harvested manually at 25, 50 and 75 days after seeding. Fresh weight of radish was measured immediately after harvest and dry weight was determined after drying in the oven at 70°C for 48 hours. Daily meteorological data such as precipitation, average temperature, wind speed, relative humidity and radiation was collected from the automatic weather station on site.

The Landscape-DNDC

Model description

The Landscape-DNDC is an ecosystem model developed at KIT, IMK-IFU to simulate biogeochemical C and N turnover, plant growth, and the water cycle at site and regional scales. Two main process-based models the Agricultural-DNDC (Giltrap et al. 2010; Li et al. 1992a; Smith et al. 2002) and the Forest-DNDC (Kesik et al. 2005; Kiese et al. 2011; Li et al. 2000) are incorporated and further developed into the Landscape-DNDC. The Landscape-DNDC is able to simulate ecosystem C and N turnover, changes in soil C and N stocks and associated GHG emissions and nutrient leaching for agricultural, grassland and forest ecosystems. Daily meteorological data (eg., air temperature, precipitation, radiation, wind speed, etc) as well as management data (e.g, seeding and harvest dates, fertilizer rates and types, tilling date and depth, etc) as drivers and information on soil and vegetation properties (eg., soil texture, pH, crop types, etc) as initialization parameters are used in the model in order to calculate daily rates of plant N uptake, litter production, mineralization, nitrification and denitrification. In the model, the soil chemistry module explicitly considers nitrification, denitrification as well as chemo-denitrification as processes of N₂O production and consumption in soils (Haas et al. 2012).

The process-based Landscape-DNDC model is used to simulate N₂O emissions, nitrate leaching and crop growth with different rates of N fertilizer application to the arable fields. To consider the effects of plastic mulch on N₂O emissions and nitrate concentrations and leaching in rows and examine the differences between rows and interrows, weather conditions such as average air temperature and precipitation were modified in this study. As the rows were covered with the black plastic mulch from seeding (14th of June) to harvest (31st of August), a daily average maximum air temperature and half of the daily precipitation were assumed to be row conditions. Except for growing periods of radish, a daily average air temperature and a daily precipitation were used for the periods of before seeding and after

harvest. The actual weather data taken from the automatic weather station on site was applied for interrow conditions without the plastic mulch.

Model evaluation

The model performances were evaluated by the normalized root mean square prediction error (RMSPE), coefficient of determination (r^2) and model efficiency (ME). The following equations were used to calculate RMSPE, r^2 and ME:

$$RMSPE = \sqrt{\frac{1}{N} \sum (X_{mea} - X_{sim})^2}$$

$$r^2 = \frac{(\sum (X_{mea} - \bar{X}_{mea})(X_{sim} - \bar{X}_{sim}))^2}{(\sum (X_{mea} - \bar{X}_{mea})^2 \sum (X_{sim} - \bar{X}_{sim})^2)}$$

$$ME = \frac{\sum (X_{mea} - \bar{X}_{mea})^2 - \sum (X_{sim} - X_{mea})^2}{\sum (X_{mea} - \bar{X}_{mea})^2}$$

Where X_{mea} is the measured value and X_{sim} is the simulated value. \bar{X}_{mea} is the average value of field measurements and \bar{X}_{sim} is the average value of model simulations. The coefficient of determination value of 1 indicates that there is strong correlation between measured and the simulated values (Chirinda et al. 2011). ME provides a comparison of the efficiency of the chosen model to the efficiency of describing the data as the mean of the measurements. A positive value of ME indicates that the simulated values describe the trend in the measured data better than the mean measured values (Smith et al. 1997).

Model validation

The Landscape-DNDC model was tested against the field measurement data: (1) soil water content and temperature, (2) N fluxes and leaching and (3) crop growth. The crop cultivation with row and interrow is the most common agricultural practice at dry fields in Korea. However, row and interrow are not implemented into the Landscape-DNDC model yet.

Therefore, the weather data was modified in order to examine the effects of row and interrow on soil biogeochemistry. The maximum temperature and a half of the precipitation were considered for the row conditions, since the row was covered with the black plastic mulch. On the other hand, the actual weather data was used for interrow conditions. As the radish was not grown in interrows but in rows, the radish cultivation was simulated only for rows. No crop was implemented into the simulation of interrows. Except the weather conditions and the radish cultivation, the simulations for rows and interrows were conducted under the same soil and management conditions. The radish field was simulated by the Landscape-DNDC model on a daily basis and simulation results were compared with daily mean measured data.

Results

Soil temperature and water content

The Landscape-DNDC simulated daily mean soil temperature and water content at 15 and 30 cm depth in rows for all N treatment plots. No measurements were at interrows and the model only simulated soil temperature and water content for rows.

Fig. 2 shows the measured and the simulated soil temperature at 15 and 30 cm depth in rows. Soil temperature was simulated with the daily average maximum air temperature in order to consider row conditions which were covered with the black plastic mulch during the whole growing periods of radish. Except for periods between seeding and harvest, the daily average air temperature was used. To examine the ability of model to predict the effects of plastic mulch with the maximum air temperature on soil temperature, the model simulated soil temperature again with the average air temperature. Simulated soil temperature with the maximum and average air temperature were compared with the measurement values, respectively. Comparisons between measured soil temperature and simulated soil temperature with the maximum and average air temperature indicated that the model predicted soil temperature well with the maximum air temperature. The simulation results of soil temperature with the maximum air temperature showed higher coefficient of determination (r^2) and more statistically significant for all N treatments than with the average air temperature (Table 3).

Table 3 Measured and simulated soil temperature at 15 and 30 cm depth in rows

	Mean			r^2	
	Measured	Simualted_max. temperature ^a	Simulated_avg. temperature ^b	Simualted_max. temperature	Simulated_avg. temperature
Soil temperature [°C] at 15 cm depth					
50 kg N ha ⁻¹	24.01	25.88	21.90	0.28 ^{***}	0.03
150 kg N ha ⁻¹	23.69	25.84	21.84	0.14 ^{**}	0.00
250 kg N ha ⁻¹	23.91	25.81	21.82	0.05 [*]	0.03
350 kg N ha ⁻¹	23.96	25.79	21.78	0.32 ^{***}	0.03
Soil temperature [°C] at 30 cm depth					
50 kg N ha ⁻¹	23.00	25.00	21.24	0.66 ^{***}	0.38 ^{***}
150 kg N ha ⁻¹	22.85	24.95	21.15	0.39 ^{***}	0.18 ^{***}
250 kg N ha ⁻¹	23.43	24.90	21.11	0.50 ^{***}	0.20 ^{***}
350 kg N ha ⁻¹	23.37	24.86	21.05	0.37 ^{***}	0.15 ^{***}

^a Simulated soil water content with the maximum temperature from seeding to harvest

^b Simulated soil water content with the average temperature

* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

The model overestimated soil temperature for both 15 and 30 cm depth by 7.5% and 7.1%, respectively. As comparisons of simulated mean soil temperature between 15 and 30 cm depth, the model predicted soil temperature at 30 cm depth better than at 15 cm depth. The root mean square prediction error (RMSPE) was relatively low and r^2 (eg., 0.66 and 0.50 for 50 and 250 kg N ha⁻¹) was high at 30 cm depth for all N treatments as compared with soil temperature at 15 cm depth (Table 6).

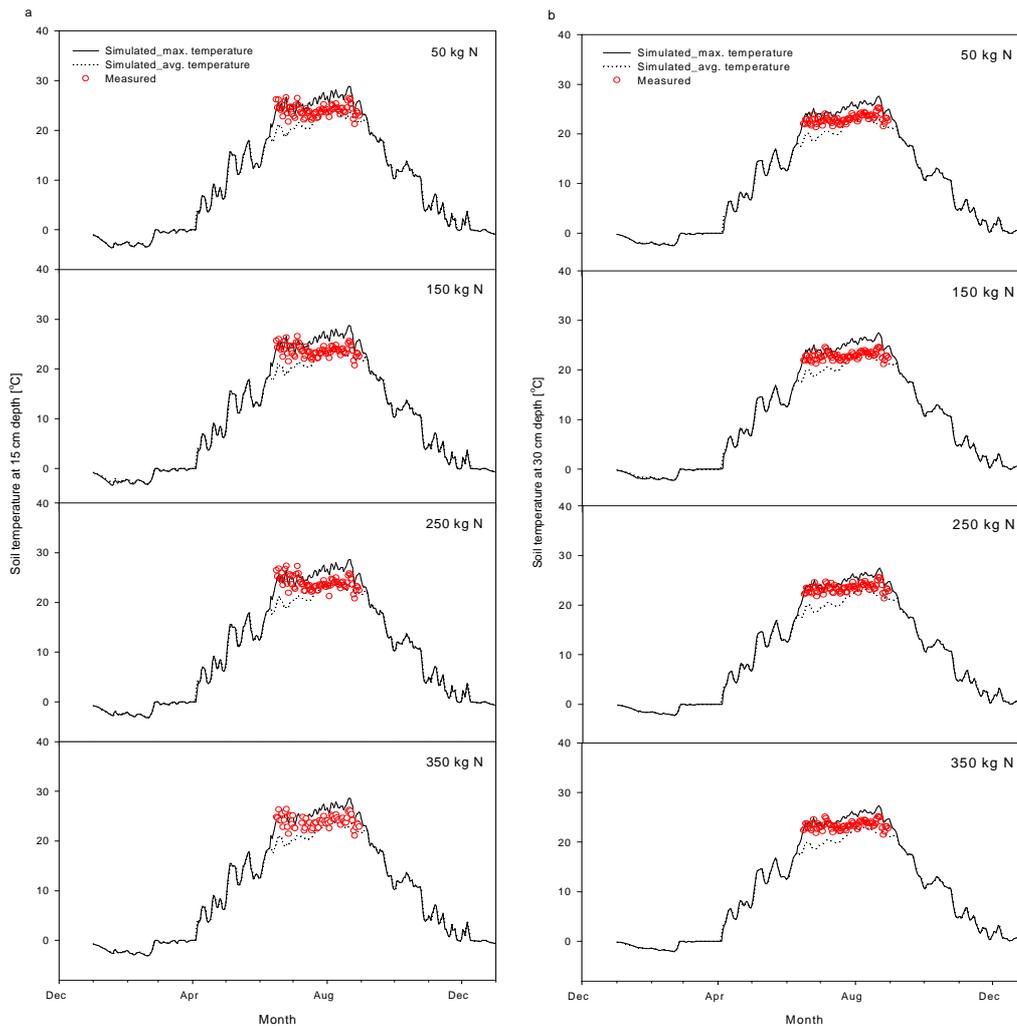


Fig. 2 Measured (circle) and simulated (line) soil temperature at 15 (a) and 30 cm (b) depth in rows with four different rates of N fertilizer. Solid lines represent the simulated soil temperature with the maximum air temperature which is assumed to be row conditions covered with the black plastic mulch during the whole growing periods of radish. Dotted lines indicate the simulated soil temperature with the average air temperature.

The model simulated soil water content with a half of the daily precipitation due to less rainfall into the hole on the plastic mulch in rows. Except for growing periods of radish when rows were covered with the black plastic mulch, the daily precipitation was used for periods of before seeding and after harvest. Soil water content was simulated again with the daily precipitation. Simulated soil water content with 50% of the daily precipitation and with the daily precipitation were compared with the measured values (Fig. 3), respectively, in order to evaluate the reliability of the model to simulate soil water content with 50% of the daily precipitation. Although the model was not able to simulate soil water content for 250 kg N ha⁻¹ ($r^2 = 0.02$) well, most simulation results indicated that the model generally predicted soil

water content with 50% of the daily precipitation better than with the daily precipitation. Simulated soil water content with 50% of the daily precipitation showed the relatively high r^2 as compared with values with the daily precipitation at 30 cm depth (Table 4).

Table 4 Measured and simulated soil temperature at 15 and 30 cm depth in rows

	Mean			r^2	
	Measured	Simulated_50% precipitation ^a	Simulated_annual precipitation ^b	Simulated_50% precipitation	Simulated_annual precipitation
Soil water content [vol %] at 15 cm depth					
50 kg N ha ⁻¹	18.61	20.61	21.81	0.22 ^{***}	0.33 ^{***}
150 kg N ha ⁻¹	19.30	22.37	24.21	0.32 ^{***}	0.43 ^{***}
250 kg N ha ⁻¹	17.92	22.35	24.43	0.02	0.20 ^{***}
350 kg N ha ⁻¹	27.73	29.21	27.03	0.36 ^{***}	0.36 ^{***}
Soil water content [vol %] at 30 cm depth					
50 kg N ha ⁻¹	25.06	25.28	25.56	0.33 ^{***}	0.20 ^{***}
150 kg N ha ⁻¹	24.49	25.16	26.35	0.36 ^{***}	0.33 ^{***}
250 kg N ha ⁻¹	22.02	25.42	26.49	0.48 ^{***}	0.46 ^{***}
350 kg N ha ⁻¹	18.68	24.92	29.05	0.41 ^{***}	0.23 ^{***}

^a Simulated soil temperature with 50% of the annual precipitation from seeding to harvest

^b Simulated soil water content with the annual precipitation

* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

The model overestimated soil water content at 15 and 30 cm depth over all N treatments by 12.1 and 10.5%, respectively. Of all simulations for soil water content, a high overestimation was observed in 250 kg N ha⁻¹ treatment at 15 cm (19.8%) and in 350 kg N ha⁻¹ treatment at 30 cm (25.0%). Differences between measured and simulated soil water content at 15 and 30 cm depth were 2.7 and 2.6 vol. %, respectively.

As compared the simulation results of soil water content between 15 and 30 cm depth, simulated soil water content at 30 cm depth agreed well with measurements. The simulation results of 15 cm depth from 50, 150 and 250 kg N ha⁻¹ treatments had the negative ME (ME < 0) and r^2 was also relatively low as compared with the results of 30 cm depth (Table 6). Of all simulations for soil water content at 15 cm depth, 350 kg N ha⁻¹ treatment only showed the positive ME (ME > 0) and the high r^2 (0.41).

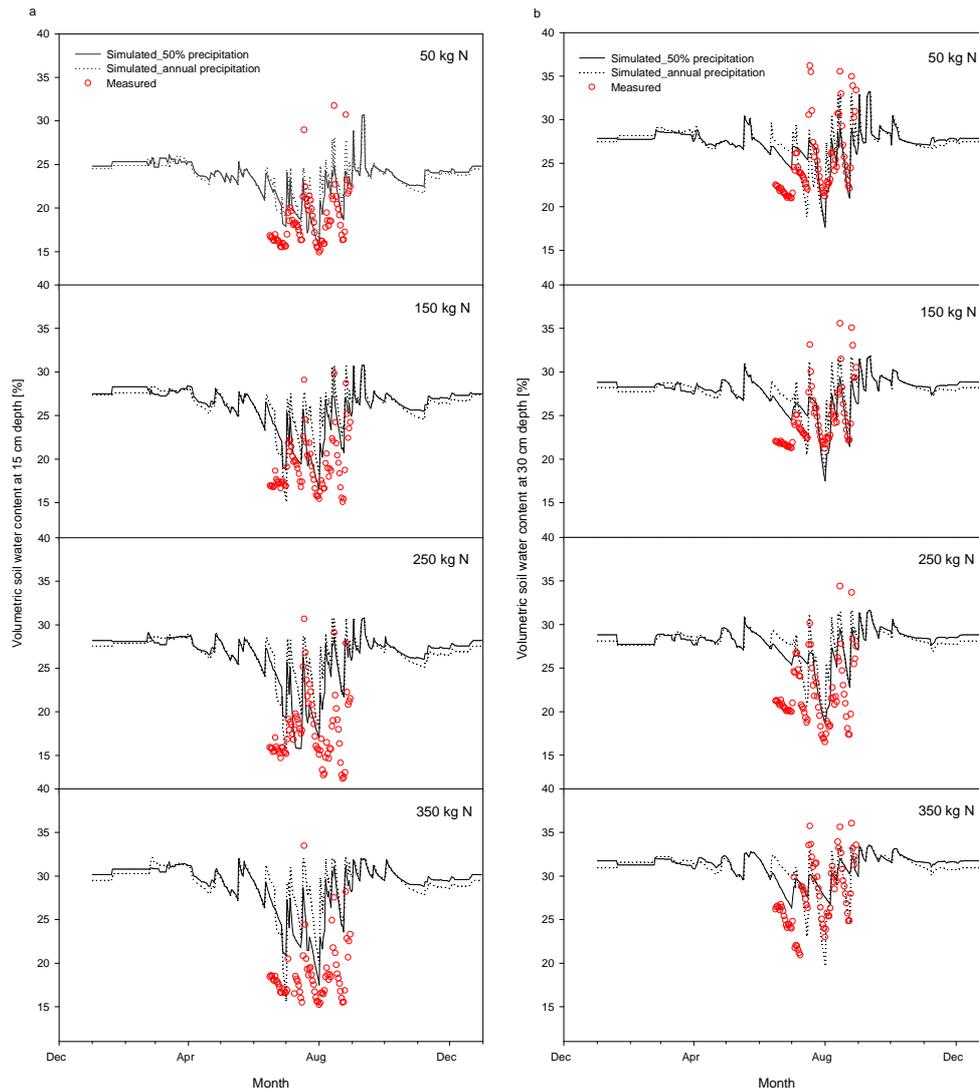


Fig. 3 Measured (circle) and simulated (line) soil water content at 15 (a) and 30 cm (b) depth in rows with four different rates of N fertilizer. Solid lines represent the simulated soil water content with 50% of the precipitation in order to consider row conditions covered with the black plastic mulch during the whole growing periods of radish. Dotted lines indicate the simulated soil temperature with the annual precipitation.

Radish biomass

Radish is a cool-season and fast-maturing crop (El-Desuki et al. 2005) that grows well in spring and autumn (Sirtautas et al. 2011) in Korea. Korean ecotypes of radish are cold sensitive so that radish is cultivated during the autumn when ambient temperatures goes down to 5 - 6°C (Curtis 2003). Radish needs a high demand for nutrients even though it is a rapidly growing and a short duration crop (Akoumianakis et al. 2011; Hegde 1987). For example, radish requires 183 kg N, 120 kg P₂O₅, 232 kg K₂O, 103 kg CaO, and 54 kg MgO ha⁻¹ in order to produce 49,280 kg ha⁻¹ (Park et al. 2006).

The Landscape-DNDC is capable to simulate above- and belowground biomass separately. The aboveground biomass includes leaves and stems and the belowground biomass stands for roots. The simulation results of radish biomass for all N treatments were compared with the measured biomass at 25, 50 and 75 harvest days. Dry weights of measured and simulated radish biomass at the last harvest day (75 days after seeding) are listed in Table 5. Both measured and simulated radish biomass were increased as the increase of the N fertilizer application rates. This positive relationship between radish biomass and N application rates has been reported in several researches. Maximum radish root yield (16.6 kg) per plant was produced with 200 kg N ha⁻¹ followed by 150 and 100 kg N ha⁻¹ (Pervez et al. 2004). Radish root yield was 5.7 and 6.9 t ha⁻¹ at 56 and 168 kg N ha⁻¹, respectively (Sanchez et al. 1991). The maximum yield (89.2 t ha⁻¹) of total radish was recorded at 200 kg N ha⁻¹ and the minimum yield (60.3 t ha⁻¹) was produced at 50 kg N ha⁻¹ treatments (Jilani et al. 2010).

Simulated belowground biomass was underestimated for 50 kg N ha⁻¹ treatment and slightly overestimated for 150, 250 and 350 kg N ha⁻¹ treatments. In contrast, the model overestimated the aboveground biomass at 50 and 150 kg N ha⁻¹ treatments and underestimated at 250 and 350 kg N ha⁻¹ treatments. Total biomass indicates the sum of above- and belowground biomass. The model overestimated the total biomass for 50 (2.0%) and 150 (2.0%) kg N ha⁻¹ treatments. In contrast, the total biomass from 250 and 350 kg N ha⁻¹ treatments was underestimated by 1.5 and 1.2%, respectively.

Table 5 Measured and simulated radish biomass at the last harvest day (75 day)

N rates [kg N ha ⁻¹]	Aboveground [kg DW m ⁻²] ^a		Belowground [kg DW m ⁻²] ^b		Total [kg DW m ⁻²] ^c	
	Measured	Simulated	Measured	Simulated	Measured	Simulated
50	0.1264	0.1443	0.2724	0.2680	0.3988	0.4123
150	0.1547	0.1614	0.2971	0.2997	0.4518	0.4612
250	0.1817	0.1735	0.3217	0.3222	0.5034	0.4958
350	0.2005	0.1894	0.3393	0.3517	0.5399	0.5411

^a Leaves and stems were included.

^b Roots were included.

^c Sum of above- and belowground biomass

Fig. 4 shows that the model overestimated both above- and belowground biomass at first harvest day (25 day) and well predicted the last harvest day (75 day). At the second harvest day (50 day), the model overestimated the belowground biomass but underestimated the aboveground biomass over all N treatments. The growth and the development of simulated

radish were faster and they reached the mature stage earlier than the field radish so that the model might overestimate both above- and belowground radish biomass at first two harvest days. In addition to this, the less available field data might also result in inaccurate predictions for radish biomass by the model in this study.

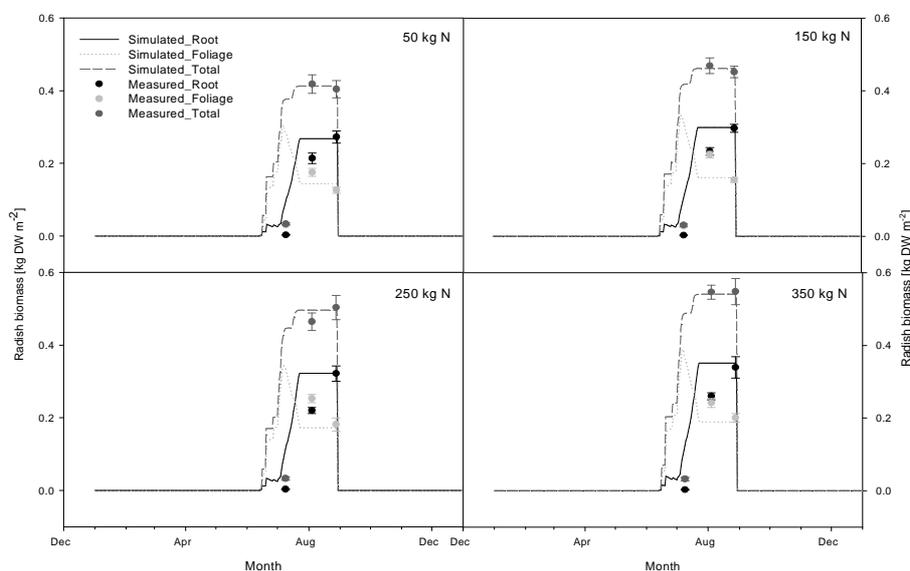


Fig. 4 Comparison of measured (circle) and simulated (line) radish biomass in rows with four different rates of N fertilizer. Bars represent standard errors of measurements.

N₂O emissions from agricultural soils

N₂O emissions depend on application of N fertilizer as well as other factors such as soil conditions and managements, precipitation and temperature (Roelandt et al. 2005). In this study, the measurements of N₂O emissions were conducted at 50, 150, 250 and 350 kg N ha⁻¹ treatments in rows and interrows and compared with the simulated N₂O emissions. Both measured and simulated N₂O emissions were increased as the increase of applied N fertilizer rates in rows; 350 > 250 > 150 > 50 kg N ha⁻¹ treatments (Fig. 5).

Similar results were shown in interrows, except for 50 kg N ha⁻¹ treatment. Of all measurements of N₂O emissions in interrows, the highest N₂O emissions were observed in 50 kg N ha⁻¹ treatment (77.97 ug N m⁻² h⁻¹) and followed by 350, 250 and 150 kg N ha⁻¹ treatments. The model simulated more N₂O emissions from 50 kg N ha⁻¹ treatment (56.54 ug N m⁻¹ h⁻¹) than for 150 and 250 kg N ha⁻¹ treatments as well. In contrast with measurements, the model predicted the highest N₂O emissions from 350 kg N ha⁻¹ treatment (73.08 ug N m⁻² h⁻¹). The high N₂O emissions from measurements at 50 kg N ha⁻¹ treatment might be caused by uncertainties in field measurements. The reason is that about 3.1 times more N₂O emissions were observed in 50 kg N ha⁻¹ treatment (435.3 ug N m⁻² h⁻¹) than in 350 kg N ha⁻¹

treatment ($147.6 \text{ ug N m}^{-2} \text{ h}^{-1}$) in 23th of June. As compared with 150 and 250 kg N ha⁻¹ treatments, N₂O emissions from 50 kg N h⁻¹ treatment were still 2.4 and 2.9 times high, respectively. In this sense, these high N₂O emissions are also considered to result in the least correlation between measured and simulated N₂O emissions from 50 kg N ha⁻¹ treatment. Comparison between measurement and simulation results of N₂O emissions from 50 kg N ha⁻¹ treatment shows the highest RMSE (124.5) and the lowest r^2 (0.07) of all N treatments in interrows (Table 6). Except for 50 kg N h⁻¹ treatments, N₂O emissions from interrows were increased as the increase of N application rates. The simulation results showed that the model overestimated N₂O emissions for all N treatments in rows. N₂O emissions in interrows were overestimated as well, except for 50 kg N ha⁻¹ treatment. The model underestimated N₂O emissions from 50 kg N ha⁻¹ treatment by 37.9%. As compared with simulated N₂O emissions between rows and interrows, the model predicted N₂O emissions better in rows than in interrows. r^2 was low and ME was negative (ME < 0) for almost all N treatments in interrows.

Comparison between measured and simulated N₂O emissions in rows and interrows showed that measured N₂O emissions from rows were generally higher than from interrows, except for 50 kg N ha⁻¹ treatment. In case of 50 kg N ha⁻¹ treatment, about 2.8 times more N₂O emissions were measured in interrows than in rows. In contrast, simulated N₂O emissions from rows were always higher than from interrows for all N treatments. The second tillage and the plastic mulch are considered to induce the first high peak of N₂O emissions in the measurements and the maximum peak of simulated N₂O emissions is associated with N fertilizer application. Because added N fertilizer as a top dressing mixed into the soils during the second tillage for creating rows and interrows and then the rows were continuously covered with the black plastic mulch during the whole growing periods of radish in this study. The plastic mulch intercepts sunlight which warms the soil (McCraw and Motes 1991). The mulch keeps the soil warm and promotes N mineralization of the applied N fertilizer. The soil temperature at 5 cm depth under plastic mulch showed extensive diurnal fluctuation, mostly from 25 to 50°C in summer season (Nishimura et al. 2012) and the mean temperature under plastic mulch was 4°C higher than under bare soil (Liakatas et al. 1986). In general, high soil temperature, high soil moisture and hence high decomposition rates promote high N₂O emissions during the summer season (Li et al. 1992b). Since soil covered with plastic mulch right after fertilizer application is under high N content and low O₂ concentration, a significant amount of N₂O can be produced and emitted to the atmosphere (Nishimura et al. 2012). Simulated N₂O emissions were increased following the fertilizer application and then gradually decreased. N₂O emissions are generally increased with the increase of rainfall flux (Li et al. 1992b) and the N₂O emission peaks usually coincide with rainfall events (Smith et al. 2002). The rain that falls onto the impermeable plastic mulch is able to run into the

interrow immediately and the less rainfall can pass through the root zone in the row (McCraw and Motes 1991). The simulation results showed that the model was capable of simulating N₂O emissions during heavy rainfall. As seen in Fig. 5, slightly increased N₂O peaks were simulated during the monsoon season (June - August). Measured and simulated mean values of N₂O emissions were presented in Table 6.

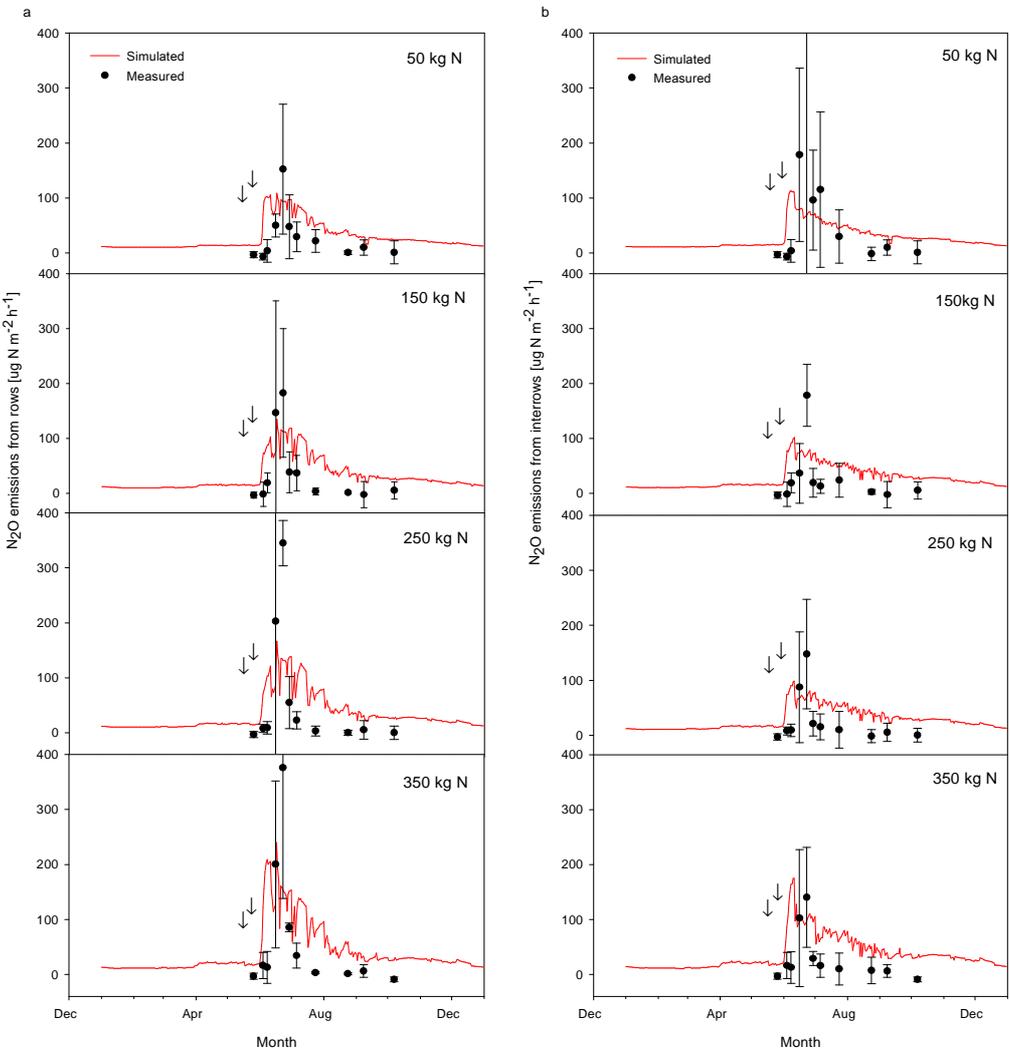


Fig. 5 Measured (circle) and simulated (line) N₂O emissions from four different rates of N fertilizer in (a) rows and (b) interrows. Arrows indicate time and date of N fertilizer application. Bars represent standard deviations of measurements.

The model simulated N₂O emissions in interrows with the same rates of N fertilizer and tilling events as rows. The only one difference between rows and interrows was that there was no crop in interrows. It means that there is no N loss by the plant uptake in interrows. Therefore, most of added N was lost by N₂O emissions, nitrate leaching and ammonia volatilization in interrows as compared with rows. N₂O emissions by both permeation through the plastic

mulch and the horizontal diffusion to the adjacent interrow may be important. The significant amounts of N_2O emissions were observed from the unfertilized interrow between rows, which were covered with plastic mulch after fertilization, indicating the horizontal diffusion of N_2O from rows to the adjacent interrow (Nishimura et al. 2012). In this study, the same rates of N fertilizer were added to rows and interrows because rows and interrows were created after fertilizer application. Therefore, it was not able to detect the horizontal diffusion of N_2O in interrows in this study.

Nitrate concentrations and nitrate leaching in agricultural soils

Calculation of soil nitrate concentrations in soil layers takes into account the mineralization, nitrification and denitrification as well as nitrate leaching. In addition, nitrate deposition from the atmosphere is also considered in the first soil layer (Kiese et al. 2011). In this study, nitrate concentrations in seepage water were measured at 15 and 45 cm depth of rows covered with the black plastic mulch and at 45 cm depth of interrows without the plastic mulch for 50, 150, 250 and 350 kg N ha^{-1} treatments and compared with the simulation results.

The mean measured nitrate concentrations were increased as the increase of applied N fertilizer rates in both rows and interrows. The simulated nitrate concentrations at 45 cm depth of rows and interrows were increased as the increase of N fertilizer rates as well (Fig. 6). The simulation results of nitrate concentrations at 45 cm depth of rows ranged from 137.1 (50 kg N ha^{-1}) to 149.6 mg N l^{-1} (350 kg N ha^{-1}). The less nitrate concentrations were simulated for 45 cm depth of interrows as compared with rows, ranged from 91.1 (50 kg N ha^{-1}) to 124.7 mg N l^{-1} (350 kg N ha^{-1}). These results were in good agreement with measured nitrate concentrations at 45 cm depth of rows and interrows. The measurements for nitrate concentrations at 45 cm depth in rows were more than of interrows. In contrast, simulated nitrate concentrations at 15 cm depth in rows decreased as the increase of N fertilizer rates. The model simulated the high nitrate concentrations at 50 kg N ha^{-1} treatment (173.7 mg N l^{-1}) and the low concentrations at 350 kg N ha^{-1} treatment (158.1 mg N l^{-1}).

The model was able to predict nitrate concentrations in rows and interrows. For example, ME was positive (ME > 0) for all N treatments and r^2 was also high (eg., 0.89, 0.89 and 0.52 for 50, 150 and 250 kg N ha^{-1}) at 45 cm depth of interrows. The simulation results of nitrate concentrations in rows were generally in good agreement with measured nitrate concentrations as well. In case of rows at 45 cm depth, for instance, r^2 was 0.73 for 50 kg N ha^{-1} and 0.53 for 150 kg N ha^{-1} (Table 6). In addition, the model was capable of estimating nitrate concentrations following the rainfall events. The high nitrate concentrations were

observed in early growing stage of radish during the monsoon season than late growing stage over all N treatments.

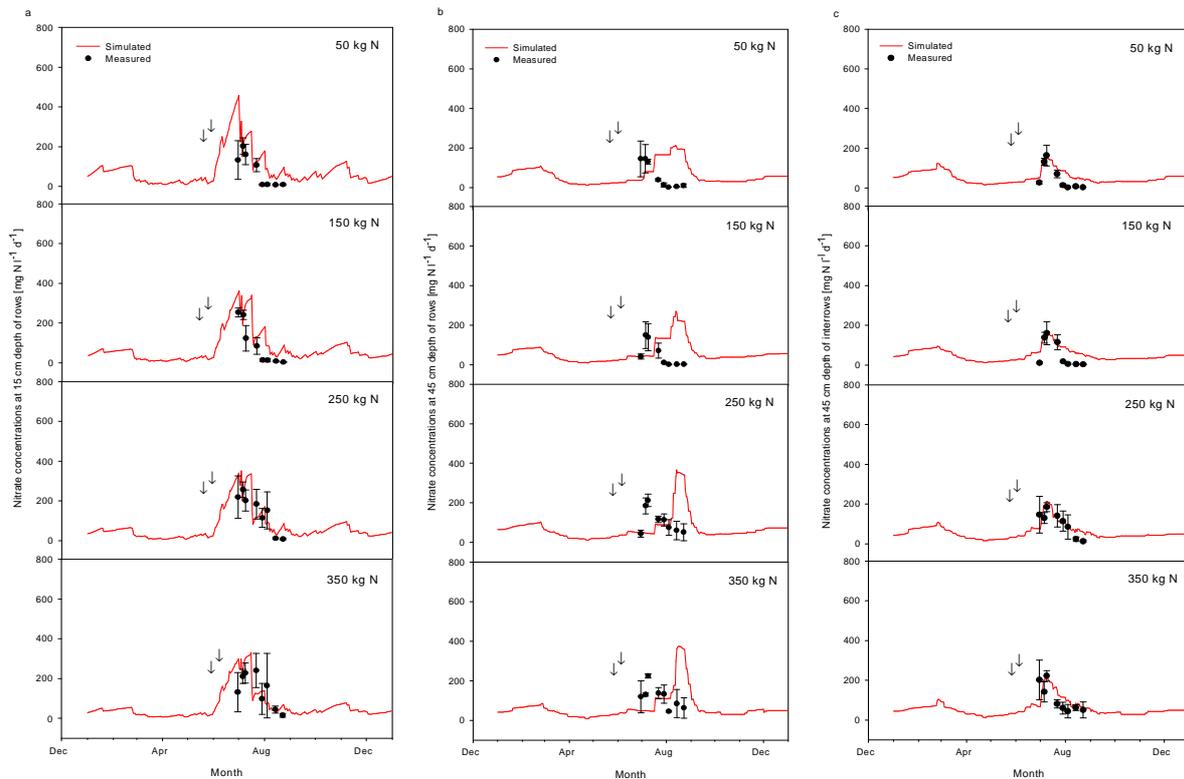


Fig. 6 Comparison of nitrate concentrations between rows and interrows with four different rates of N fertilizer; measured (circle) and simulated (line) nitrate concentrations at (a) 15 cm depth in rows, (b) 45 cm depth in rows and (c) 45 cm depth in interrows. Arrows indicate time and date of N fertilizer application. Bars represent standard deviations of measurements.

Nitrate leaching rate was most sensitive to fertilizer application rate and precipitation (Li et al. 2006). The amount and the time of N fertilizer application have significant impacts on the nitrate leaching (Hansen et al. 2000). The high input of N fertilizer and low use efficiency may certainly result in the increase of the N loss from leaching (Qiu et al. 2011). In general, nitrate leaching rates increased under high nitrogen level and the low N level led to lower nitrate leaching (Liu et al. 2003). However, the simulations of nitrate leaching in this study showed the different results. Simulated nitrate leaching was decreased as the increase of N fertilizer rates in rows and interrows; $350 < 250 < 150 < 50$ kg N ha⁻¹ treatments. Simulated annual nitrate leaching ranged from 352.6 (350 kg N ha⁻¹) to 382.6 kg N ha⁻¹ yr⁻¹ (50 kg N ha⁻¹) in rows. The model simulated about 13.2% more nitrate leaching in interrows than in rows, ranged from 403.4 (350 kg N ha⁻¹) to 452.3 ha⁻¹ yr⁻¹ (50 kg N ha⁻¹) in interrows.

Table 6 The model performance of Landscape-DNDC for simulation of radish fields with four different N treatments

	Mean		Model Performance		
	Measured	Simulated	ME	RMSPE	r ²
Soil temperature [°C] at 15 cm depth					
50 kg N ha ⁻¹	24.01	25.88	-2.62	2.23	0.28 ^{***}
150 kg N ha ⁻¹	23.69	25.84	-3.86	2.55	0.14 ^{**}
250 kg N ha ⁻¹	23.91	25.81	-2.38	2.51	0.05 [*]
350 kg N ha ⁻¹	23.96	25.79	-2.61	2.13	0.32 ^{***}
Soil temperature [°C] at 30 cm depth					
50 kg N ha ⁻¹	23.00	25.00	-4.91	2.11	0.66 ^{***}
150 kg N ha ⁻¹	22.85	24.95	-7.53	2.28	0.39 ^{***}
250 kg N ha ⁻¹	23.43	24.90	-2.80	1.67	0.50 ^{***}
350 kg N ha ⁻¹	23.37	24.86	-3.69	1.74	0.37 ^{***}
Soil water content [vol %] at 15 cm depth					
50 kg N ha ⁻¹	18.61	20.61	-0.23	3.58	0.22 ^{***}
150 kg N ha ⁻¹	19.30	22.37	-0.74	4.15	0.32 ^{***}
250 kg N ha ⁻¹	17.92	22.35	-2.05	6.58	0.02
350 kg N ha ⁻¹	27.73	29.21	0.19	3.29	0.36 ^{***}
Soil water content [vol %] at 30 cm depth					
50 kg N ha ⁻¹	25.06	25.28	0.33	3.28	0.33 ^{***}
150 kg N ha ⁻¹	24.49	25.16	0.30	2.80	0.36 ^{***}
250 kg N ha ⁻¹	22.02	25.42	-0.38	4.32	0.48 ^{***}
350 kg N ha ⁻¹	18.68	24.92	-3.73	6.67	0.41 ^{***}
N ₂ O emissions [ug N m ⁻² h ⁻¹] in Rows					
50 kg N ha ⁻¹	27.88	61.53	-0.35	50.83	0.27
150 kg N ha ⁻¹	38.91	66.79	0.13	57.41	0.33
250 kg N ha ⁻¹	58.83	73.48	0.27	91.13	0.34
350 kg N ha ⁻¹	65.82	98.02	0.12	106.7	0.21
N ₂ O emissions [ug N m ⁻² h ⁻¹] in Interrows					
50 kg N ha ⁻¹	77.97	56.54	0.04	124.5	0.07
150 kg N ha ⁻¹	26.56	55.41	-0.24	55.22	0.11
250 kg N ha ⁻¹	27.12	54.49	-0.24	50.08	0.15
350 kg N ha ⁻¹	29.89	73.08	-0.99	63.31	0.16
Nitrate concentrations [mg N l ⁻¹] at 15 cm depth in Rows					
50 kg N ha ⁻¹	79.81	173.7	-2.17	134.1	0.35
150 kg N ha ⁻¹	92.50	172.1	-0.03	99.10	0.69 [*]
250 kg N ha ⁻¹	143.2	165.4	0.37	69.03	0.59 [*]
350 kg N ha ⁻¹	141.6	158.1	-0.14	84.57	0.34
Nitrate concentrations [mg N l ⁻¹] at 45 cm depth in Rows					
50 kg N ha ⁻¹	61.24	137.1	0.69	44.29	0.73 ^{**}
150 kg N ha ⁻¹	52.01	125.8	-5.31	145.3	0.53 [*]
250 kg N ha ⁻¹	107.6	139.9	-7.22	168.2	0.30
350 kg N ha ⁻¹	116.9	149.6	-8.94	163.4	0.32
Nitrate concentrations [mg N l ⁻¹] at 45 cm depth in Interrows					
50 kg N ha ⁻¹	53.00	91.05	0.43	44.54	0.89 ^{***}

150 kg N ha ⁻¹	56.75	96.87	0.38	50.05	0.89 ^{***}
250 kg N ha ⁻¹	104.8	118.3	0.41	43.36	0.52 [*]
350 kg N ha ⁻¹	108.0	124.7	0.07	64.12	0.25

$P < 0.05$, $^{**} P < 0.01$, $^{***} P < 0.001$

N fertilizer applied early in the crop growing stage has a high potential of being lost by leaching (Errebhi et al. 1998; Romić et al. 2003). The crop was not able to use up all nitrates, which usually linked to heavy rainfall, resulted in nitrate leaching (Romic et al. 2003). Frequent rainfall may cause rapid movement of nitrate from the rooting zone through the intermediate soil layer (Islam et al. 1994). The rainfall for 15 days induced more than 50.0% of nitrate leaching during the crop growing stage (Vázquez et al. 2006). The results from previous studies are in good agreement with simulated nitrate leaching in this study. Heavy rainfall in early growing stage of radish had significant effects on nitrate leaching. About 34.6% (510 mm) of the total precipitation was observed during the measurements of nitrate concentrations (from 30th of June to 23rd of August). The model simulated about 18.5% and 52.2% of the total nitrate leaching in rows and in interrows during this heavy rainfall, respectively.

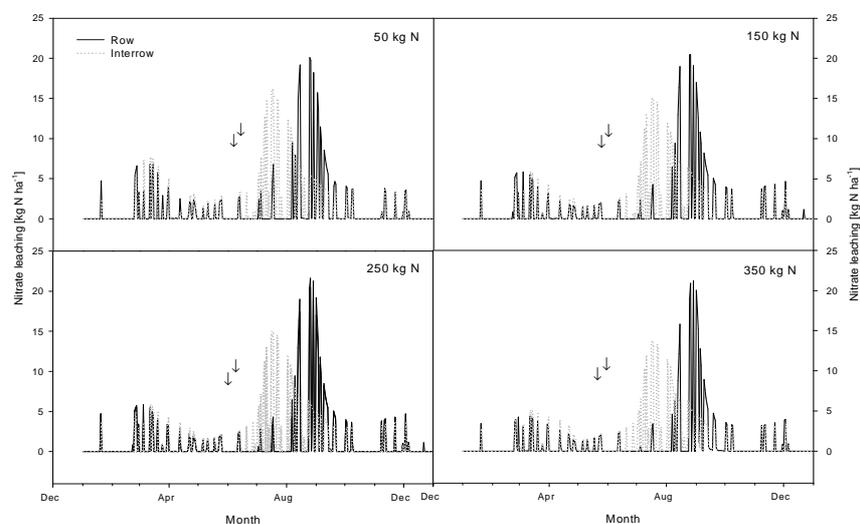


Fig. 7 Simulated nitrate leaching in rows and interrows with four different rates of N fertilizer. Solid lines represent nitrate leaching in rows with the black plastic mulch. Dotted lines indicate nitrate leaching in interrows without the black plastic mulch. Arrows indicate time and date of N fertilizer application.

Several studies have shown that the plastic mulch has a positive effect on the reduction of nitrate leaching. Nitrate leaching in the plot with the mulch was less than without the mulch. The plastic mulch protects soil from the direct infiltration of precipitation so that nitrate

leaching from the root zone is reduced (Islam et al. 1994; McCraw and Motes 1991; Romic et al. 2003; Zhang et al. 2012). For example, a nitrate leaching rate of 7% from the total water was shown in the plot with mulching and 10% without mulching (Romic et al. 2003). This result is in good agreement of simulation results of nitrate leaching in this study. Comparison of simulated annual nitrate leaching between rows and interrows showed that the model was able to predict nitrate leaching under the plastic mulch (Fig. 8). The model simulated about 13.2% more nitrate leaching in interrows without the plastic mulch than in rows with the plastic mulch. The differences of nitrate leaching between rows and interrows ranged from 50.78 (350 kg N ha⁻¹) to 69.65 kg N ha⁻¹ yr⁻¹ (50 kg N ha⁻¹).

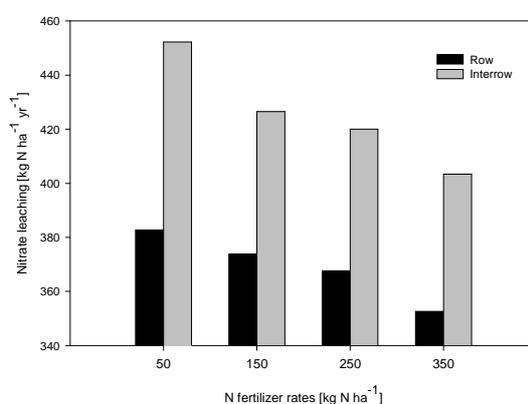


Fig. 8 Comparison of simulated annual nitrate leaching between rows and interrows with four different rates of N fertilizer

Table 7 shows the annual N₂O emissions and nitrate leaching from 50, 150, 250 and 350 kg N ha⁻¹ treatments by the model. The total N₂O emissions were high in rows with 350 kg N ha⁻¹ treatment (3.472 kg N yr⁻¹) and in interrows with 350 kg N ha⁻¹ treatment (3.155 kg N yr⁻¹). The high nitrate leaching rates were shown both in rows and interrows with 50 kg N ha⁻¹ treatments.

About 0.94% of applied N fertilizer was lost by N₂O emissions and more than a half of applied N fertilizer was lost by nitrate leaching in rows. As compared with rows and interrows, the model predicted more N lost by nitrate leaching in interrows (72.2%) than in rows (62.5%). Considering both the ratio of total N₂O emissions and nitrate leaching to the total biomass, 250 kg N ha⁻¹ was recommended to apply for the radish cultivation.

Table 7 Simulated annual N₂O emissions and nitrate leaching from 4 different N treatments by the Landscape-DNDC model

N treatment [kg N yr ⁻¹]	Direct N ₂ O [kg N yr ⁻¹]	Indirect N ₂ O ^a [kg N yr ⁻¹]	Total N ₂ O ^b [kg N yr ⁻¹]	Nitrate leaching [kg N yr ⁻¹]	Total N ₂ O / Total N Input ^c	Nitrate leaching / Total N Input	Total N ₂ O / Total Biomass ^d	Nitrate leaching / Total Biomass
50								
Row	2.435	2.870	5.304	382.6	0.0114	0.8230	0.00129	0.0928
Interrow	2.365	3.392	5.757	452.3	0.0124	0.9728	-	-
150								
Row	2.682	2.803	5.485	373.8	0.0097	0.6617	0.00119	0.0811
Interrow	2.441	3.199	5.640	426.5	0.0100	0.7550	-	-
250								
Row	2.883	2.757	5.640	367.7	0.0085	0.5529	0.00114	0.0742
Interrow	2.457	3.150	5.607	420.0	0.0084	0.6317	-	-
350								
Row	3.472	2.645	6.117	352.6	0.0080	0.4610	0.00112	0.0644
Interrow	3.155	3.026	6.181	403.4	0.0081	0.5274	-	-

^aN₂O emissions from leaching and runoff. Indirect N₂O emissions were calculated with the IPCC's default value, EF₅ (0.0075) (IPCC 2006).

^bSum of direct and indirect N₂O emissions

^cTotal N input indicates the amount of applied N fertilizer.

^dSum of above- and belowground radish biomass

Discussion

Agricultural soils are one of the important sources of N₂O due to their great contribution to the anthropogenic N₂O emissions. N fertilizer, soil and crop managements and precipitation have a great impact on N₂O emissions (Mosier and Freney 2002).

Radish is the main dry field crop, accounting for about 21% of the total crop production in Haean Catchment. In this study, soil temperature and water content, N₂O emissions, nitrate concentrations and leaching across four different rates of N fertilizer (50, 150, 250 and 350 kg N ha⁻¹) in radish fields by the Landscape-DNDC model. Simulation results of nitrate concentrations at both 15 and 45 cm depth soils showed the relatively precise prediction for all N treatments. In contrast, the model overestimated N₂O emissions after application of N fertilizer and then underestimated during the monsoon season when the high peak of N₂O emissions were observed in the measurements, which resulted in negative ME (ME < 0) and low r² in interrows. The model simulated N₂O emissions in rows better than interrows. ME was positive (ME > 0), except for 50 kg N ha⁻¹ treatment, and r² was also relatively high as compared with interrows.

The plastic mulch restricted the penetration of rainfall into the soil (Nishimura et al. 2012) and kept soil warm (McCraw and Motes 1991; Nishimura et al. 2012). In addition, since the row covered with plastic mulch right after fertilizer application is under high N content and low O₂ concentration, a significant amount of N₂O can be emitted to the atmosphere (Nishimura et al. 2012). The most challenging of this study was to consider the impacts of the plastic mulch on soil systems. However, the plastic mulch was not implemented into the model yet and precipitation and temperature were adjusted to test the effects of the plastic mulch on soil systems. Several studies have reported that N₂O emissions are high (Nishimura et al. 2012) and nitrate leaching rates are low under the plastic mulch compared with under bare soil (Haraguchi et al. 2004; Islam et al. 1994; Nishimura et al. 2012; Romić et al. 2003). This result was in good agreement with simulation results of N₂O emissions and nitrate leaching in this study. The model simulated about 8.9% more N₂O emissions from rows than from interrows, ranged from 0.07 (50 kg N ha⁻¹) to 0.43 kg N ha⁻¹ yr⁻¹ (250 kg N ha⁻¹). Simulated nitrate leaching in interrows without the plastic mulch were 13.2% higher than rows with the plastic mulch. Differences of nitrate leaching between rows and interrows ranged from 50.78 (350 kg N ha⁻¹) to 69.65 kg N ha⁻¹ yr⁻¹ (50 kg N ha⁻¹). The model predicted most of the applied N lost by nitrate leaching and ammonia volatilization. For example, about 72.2% of the total added N was lost by nitrate leaching and 1.9 % by ammonia volatilization in interrows. In case of rows, about 62.5% of the total applied N was lost by nitrate leaching and 1.7% by ammonia volatilization.

Increased N fertilizer rates and continuous rainfalls during the monsoon season may result in the high nitrate leaching rate. Significant losses of N from urea and ammonium fertilizers result from ammonia volatilization (Sommer et al. 2004). Therefore, applied urea and NH_4^+ -N fertilizers are responsible for the significant amount of ammonia volatilization by the model. Several studies have shown that the significant amount of N_2O is emitted from the soil covered with the plastic mulch (Nishimura et al. 2012) and nitrate leaching from the plastic mulch is less than from the bare soil (McCraw and Motes 1991; Romic et al. 2003; Zhang et al. 2012). In this respect, simulation results indicated that the model was able to differentiate between rows with the plastic mulch and interrows without the mulch. The model predicted more N_2O emissions but less nitrate leaching in rows for all N treatments as compared with simulation results of interrows. Many studies have reported the relationship between fertilizer N rates and GHG emissions. 0.39% of applied N fertilizer was emitted as N_2O -N from radish field (Xiong et al. 2006). In this study, the model simulated relatively high N_2O emissions, which were induced by N fertilizer. About 0.94% and 0.97% of added N fertilizer were emitted as N_2O in rows and interrows, respectively.

N_2O emissions by both permeation through the plastic mulch and the horizontal diffusion to the adjacent interrow may be important (Nishimura et al. 2012). The current version of the Landscape-DNDC is capable of simulating vertical movements of trace gases in the soil layers, however, the model is incapable of capturing the horizontal diffusion. Therefore, horizontal diffusion is needed to consider in the further development of the model in order to have more precise prediction for N fluxes.

Conclusion

The Landscape-DNDC was able to predict N_2O emissions, nitrate concentrations and leaching and biomass production from the radish field with four different N treatments. To consider the effects of the black plastic mulch, which has covered the rows during the whole growing periods of radish, on soil biogeochemistry, modified weather data such as the maximum average air temperature and 50% of the daily precipitation was applied for the simulations of rows. The actual weather data taken from the automatic weather station on site was used for interrows which were not covered with the plastic mulch. In general, the plastic covered row showed more N_2O emissions than the interrow under the bare soil (Nishimura et al. 2012). This result was in good agreement with simulation results of N_2O emissions in this study. The model predicted more N_2O emissions from rows than from interrows. It should be noted that the model simulated significant amounts of N losses by nitrate leaching and ammonia volatilization. Therefore, appropriate functions for the plastic

mulch are needed to adopt in the further improvement of the Landscape-DNDC in order to have more accurate prediction.

The simulation results showed the possibility of application of the Landscape-DNDC for simulating arable ecosystems in Korea. The model can be used to estimate N₂O emissions, nitrate leaching and plant growth from different types of ecosystems such as grassland and forest and simulate on regional scale with GIS data base in the further research.

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Chapter 4

N₂O and CH₄ emissions from rice paddies as affected by water management

A record of N₂O and CH₄ emissions and underlying soil processes of Korean rice paddies as affected by different water management practices

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Abstract

Rice is staple food of half of mankind and paddy soils account for the largest anthropogenic wetlands on earth. Ample of research is being done to find cultivation methods under which the integrative greenhouse effect caused by CH₄ and N₂O emissions would be mitigated. Whereas most of the research focuses on quantifying such emissions, there is a lack of studies on the biogeochemistry of paddy soils. In order to deepen our mechanistic understanding of N₂O and CH₄ fluxes in rice paddies, we also determined NO₃⁻ and N₂O concentrations as well as N₂O isotope abundances and presence of O₂ along soil profiles of paddies which underwent three different water managements during the rice growing season(s) in (2010 and) 2011 in Korea. Largest amounts of N₂O (2 mmol m⁻²) and CH₄ (14.5 mol m⁻²) degassed from the continuously flooded paddy, while paddies with less flooding showed 30-60% less CH₄ emissions and very low to negative N₂O balances. In accordance, the global warming potential GWP was lowest for the Intermittent Irrigation paddy and highest for the Traditional Irrigation paddy. The N₂O emissions could the best be explained

(*P<0.05) with the $\delta^{15}\text{N}$ values and N_2O concentrations in 40-50 cm soil depth, implying that major N_2O production/consumption occurs there. No significant effect of NO_3^- on N_2O production has been found. Our study gives insight into the soil of a rice paddy and reveals areas along the soil profile where N_2O is being produced. Thereby it contributes to our understanding of subsoil processes of paddy soils.

Keywords

Nitrous oxide, ^{15}N , NO_3^- , traditional irrigation, intermittent irrigation, Korea

Introduction

Nitrous oxide (N_2O) is a significant long-living greenhouse gas and it currently contributes about 6% to the annual increase in radiative forcing (WMO 2006). Worldwide, sources of N_2O are dominated by agriculture (Potter et al. 1996, Robertson and Grace 2004), with the amount of N fertilizer applied as one of the key drivers of the N_2O emission (Sheperd et al. 1991).

Rice is the staple food of almost 50% of the earth's population and 20% of the agriculturally managed soils are rice planting areas (Frolking et al. 2002). Whereas rice paddies are known to be among the most important sources of methane (CH_4) (IPCC 1992, Neue and Sass 1998; Yan et al. 2009), their N_2O emissions are considered negligible, in particular under conditions of 4-6 months of continuous flooding (Cai et al. 1997; Smith and Patrick 1983; Zou et al. 2005a) because such strong anaerobic conditions lead to a further reduction of the intermediary denitrification product N_2O to N_2 , so that no degassing of N_2O can occur (Granli and Bøckman 1994), whereas that irrigation method has the great disadvantage of producing great amounts of CH_4 (IPCC 1992; Neue and Sass 1998; Sass et al. 1999; Yan et al. 2009). However, it is the scientists aim to find irrigation methods which would cause the least integrative greenhouse effect by mitigating CH_4 and N_2O emissions as much as possible by ensuring enough rice yields (Chapagain and Yamaji 2010; Miyazato et al. 2010; Sato et al. 2011; Peng et al. 2011). Controlled irrigation practices which leave rice paddies under non-water logged conditions 40-80% of the time, are subject of plenty of studies (Cai et al. 1997; Wu 1999; Mao 2002; Zou et al. 2007; Quin et al. 2010; Peng et al. 2011). This not only saves water but also mitigates CH_4 emissions, however at stronger N_2O emissions due to changes in soil oxygen status, soil redox potential, moisture, temperature etc. (Smith and Patrick 1983; Cai et al. 2001; Zou et al. 2005b; Johnson-Beebout et al. 2009; Liu et al. 2010; Peng et al. 2011). Such controlled irrigation methods are intermittent irrigation, flooding-midseason drainage-frequent water logging with intermittent irrigation (FDF), and flooding-midseason drainage-reflooding-moist intermittent irrigation but without water logging (FDFM) (Mao 2002; Wu 1999; Zou et al. 2007).

This is a monitoring study comparing not only N_2O and CH_4 fluxes at the soil/atmosphere interface of three rice paddies in South Korea, which were under different water management practices, but it even more focuses on a couple of biogeochemical soil factors which are known to affect N_2O emissions, such as NO_3^- and N_2O concentration, $\delta^{15}\text{N}-\text{N}_2\text{O}$ values, presence or absence of oxygen along soil profiles in addition to paddy water level and water temperature during the vegetation period of 2010 and 2011. The investigated water management practices were 1) 'traditional irrigation' (TI) with 5 months of flooding, 2) 'flooding-midseason drainage-reflooding-moist intermittent irrigation without water logging'

(FDFM) with only 2.5 months of continuous flooding before the drainage and 3) 'intermittent irrigation' (II) without continuous flooding. Our objectives were to test how the different water management practices would affect the biogeochemistry of the rice paddies with respect to N₂O production and emission. According to the literature, we hypothesized that the most N₂O would degas from the paddies experiencing less flooding and most CH₄ would be emitted from the continuously flooded paddy; but furthermore we were expecting to see great changes in N₂O, NO₃⁻ and O₂ concentrations, as well as in δ¹⁵N-N₂O values along the soil profiles in dependence of the water levels especially in the FDFM and II fields.

2. Methods

2.1 Study region and experimental sites

All the field work was conducted in the mountainous Haean Basin between longitude 128° 5' to 128° 11' E and latitude 38° 13' to 38° 20' N in Yanggu County, Gangwon Province in the north-eastern part of South Korea. The average annual air temperature at the valley sites is 10.5°C and the average precipitation is approximately 1500mm, with 70% falling during the summer monsoon from June to August. Rice paddies cover over 507 ha which is 25% of the cropland area in the Haean Basin, which makes rice the most important crop of the region.

Three rice paddies have been selected as research sites (see Table 1).

The first one was undergoing flooding-midseason drainage-reflooding-moist intermittent irrigation without water logging (FDFM) with only 2.5 months of continuous flooding; the second one was exposed to intermittent irrigation (II) and the third one experienced traditional irrigation (TI) of 5 months of continuous flooding.

Measurements have been taken from 11 May 2010 until 23 October, 2010 at the FDFM paddy and from 6 May until 15 September 2011 at all three paddies.

The three paddies had a substrate of sandy-loam texture and the soils were characterized as terric cambisols or even as anthrosols (IUSS Working Group WRB 2007) because of an artificial long-term addition of sandy soil on the top of the fields.

The paddies were treated in the following way: the first irrigation occurred between end of April and the first days of May. Between 8 and 10 May the paddies were fertilized (see Table 1) on their moist soils. Between 10 and 15 May the continuous flooding as well as the irrigation of the paddies started. The transplanting of the rice seedlings took place between 25 and 30 May. Herbicides and pesticides were spread by end of June. The harvest was between middle and end of October. The owners of the three paddies followed that traditional procedure in 2011 as well as the farmer of the FDFM paddy did in 2010.

In 2010 the measurements were taken at the edge of the FDFM rice paddy, and potential edge effects could not be excluded. To avoid those edge effects, the 2011 measurements were taken within the paddies 5-8 m away from the paddies' edges. Walkways were used to access the experimental sites in 2011. These walkways aimed to minimize disturbances of the sites from stepping onto the soil leading to soil compaction and pushing of gas bubbles from the sub-soil.

Furthermore, the paddies differed in their soil horizons which were investigated until 60 cm soil depth. The FDFM paddy had an Apg-horizon from 0 until 22 cm soil depth, followed by an Arp horizon. The II paddy had two different Apg-horizons (the first one reached from 0 to 11cm and from 11 to 34cm), followed by two different Arp-horizons. The II paddy's sequence of horizons was quite different from the other two paddies' sequence of horizons: the thin (0-15cm) Apg-horizon was followed by a thin (15-33cm) Arp-layer which was followed by two different B-horizons with Bg1 reaching from 33 to 55cm and Bg2 starting at 55cm, reaching deeper. Ap-horizons may be oxic or anoxic, Arp-horizons are characterized by the absence of free oxygen since they represent the puddled but compacted layer. B horizons may either be aerobic or anaerobic (IUSS working group WRB, 2006).

Table 1: Site characteristics of the experimental sites in Haean Basin, South Korea

Site	FDFM <i>Flooding-midseason Drainage- reFlooding-Moist intermittent irrigation without water logging</i>	II <i>Intermittent Irrigation</i>	TI <i>Traditional Irrigation</i>
Location	128° 8' 33.532" E 38° 17' 5.008" N 411 m a.sl.	128° 7' 53.123" E 38° 17' 26.175" N 440 m a.sl.	128° 7' 51.632" E 38° 17', 26.78" N 440 m a.sl.
Fertilizer	N-P-K: 21-17-17 N: 127 kg ha ⁻¹ NH ₄ -N: 76 kg ha ⁻¹ ; urea-N: 51 kg ha ⁻¹	N-P-K: 21-17-17 N: 109 kg ha ⁻¹ NH ₄ -N: 65 kg ha ⁻¹ ; urea-N: 44 kg ha ⁻¹	N-P-K: 18-8-9 N: 109 kg ha ⁻¹ NH ₄ -N: 65 kg ha ⁻¹ ; urea-N: 44 kg ha ⁻¹
Yield	7118 kg/ha	4638 kg/ha	4356 kg/ha

2.2 Measurements of water level and water temperature

From 1 June until 14 September 2011 water level and temperature of the three paddies were recorded every 30 minutes using Levelloggers Junior Edge (Model 3001, Solinst Canada). From these data mean daily water level and temperature were calculated.

2.3 Measurements of N₂O fluxes

To measure N₂O exchange at the soil-water/atmosphere interface we took closed chamber measurements in conjunction with a photoacoustic infrared gas analyzer (Multigas Monitor 1312, INNOVA, Ballerup, Denmark) (for further details see Yamulki and Jarvis 1999 and Goldberg et al. 2008b) every two days at each experimental site. One day before the measurement, we installed 8 polyvinylchloride (PVC) cylinders (20 cm long and 19.5 cm wide) 6 cm deep in the soil, so that – depending on the water level of the rice paddy – they poked out of the paddy water at least 2 cm. At each rice paddy, four of them contained rice plants, the other four were installed on spots without rice plants. For the measurement days we connected them to chambers with a tubing connection to the gas analyzer which determined the N₂O concentration of the chambers headspaces after 0, 8, 16, 24 and 36 minutes. The reproducibility of one single N₂O concentration measurement was ± 32 ppb. From a linear increase or decrease of the N₂O concentration in the chambers' headspaces the N₂O flux was calculated taking into account the total chamber volume of the gas analyzing system, including the chamber headspace volume, volume of the two 25 m long Teflon tubes and of the CO₂ and H₂O gas traps. N₂O flux measurements were done between 11 May 2010 and 23 October, 2010 at the FDFM paddy and between 6 May and 15 September 2011 at all three paddies.

Cumulative N₂O emissions were calculated according to Tilsner et al. (2003) by multiplying the N₂O emission rates of two consecutive measurement days with the corresponding time period. These time weighted N₂O flux means were then summed up over the measurement period.

2.4 Measurements of CH₄ fluxes

CH₄ fluxes were measured by closed chamber measurements, too, but instead of a field determination of the CH₄ concentrations, gas samples were collected in the field and later analyzed *via* FID (flame ionization detector) gas chromatography (gas chromatograph: CP-3800 Varian, USA) at the laboratory of the School of Civil and Environmental Engineering of the Yonsei University in Seoul. 10 ml gas samples were collected out of the chambers which

had an inlet with a septum, using 10 ml syringes. The collecting of the samples took place every two weeks.

Cumulative CH₄ emissions were calculated after the same method which served for the calculation of the cumulative N₂O emissions (see 2.3).

2.5 Determination of presence or absence of oxygen

The presence or absence of oxygen in the paddies' soils was evaluated as described by Reiche et al. (2007). PVC cable funnels (9 x 9 x 9 mm) were poured with melted 2% agar containing c. 80mM particulate black FeS (FeSO₄ • 7 H₂O mixed with Na₂S • nH₂O in a ratio of 1 : 1, solved in deionized water). Just after the solidifying 3 FeS probes were placed vertically until 60 cm soil depth in each rice paddy, nearby the experimental sites. Once a week, FeS probes were removed and the color was determined using the Munsell color chart and classified into three groups: A change in color from black to brownish, orange and red caused by oxidized FeS to Fe(III)-oxyhydroxide indicated the presence of oxygen. *Black* implied "no oxygen", *dark brown* was interpreted as "small or intermediate amount of oxygen" and *red* or *orange* was regarded as "high amount of oxygen". In general, the change in color was very sharp, occurred mostly within a few millimeters and only in few cases stretched over a few centimeters.

2.6 Determination of NO₃⁻ concentrations in the paddies' waters and soils

To enable us to collect soil water of the paddies' soils we installed suction lysimeters. They consisted of a ceramic cup, a PVC tube, and a PE suction tube. The latter was connected to samplers (brown glass bottles), which were connected *via* air tight and high density PVC tubing to a self-constructed portable vacuum pump. At each rice paddy we installed 9 suction lysimeters in total: 3 of them reaching into 50 cm depth, 3 reaching into 30 cm depth and 3 more in 10 cm depth. The suction lysimeters were installed by following the recommendations of UMS (2008).

Once a week the brown glass bottles were evacuated. On the following day they had sucked up soil water from the suction lysimeters due to the underpressure in the glass bottles. The soil water was filled into sampling devices, treated with Spectroquant® quick tests based on the photometric method (Nitrate test photometric, DMP 0.10 - 25.0 mg/l NO₃-N 0.4 - 110.7 mg/l NO₃ Spectroquant®, MERCK, South Korea) and by using a photometer (LP2W Digital Photometer, Dr. Lange, Germany) the optical density (leading to NO₃⁻ concentrations) was determined.

2.7 Soil gas sampling

At each rice paddy, three passive diffusion gas samplers containing six sampling cylinders were installed to collect soil gas from between 0 and 10 cm, 10 and 20 cm, 20 and 30 cm, 30 and 40 cm, 40 and 50 cm and 50 and 60 cm depth. Each PVC cylinder (ID, 70 mm, OD, 79 mm; 0.1 m height) had a total sampling volume of 35.34 ml using 5 m of silicon tubing (ID, 3 mm; OD, 5 mm). The sampling was done from the soil surface using gas impermeable polyurethane (PUR) tubing (ID, 1.8 mm; OD, 3 mm) fitted with stopcocks (Luer Lock, Value Plastics, Fort Collins, CO, USA). To the one end of the two tubing-stopcock-links 100 ml glass bottles - which were first flushed with N₂ gas, then evacuated using a membrane vacuum pump (KNF Neuberger N026.3AN.18, Freiburg, Germany) and whose vacuums were then measured by using a pressure gauge (TensioCheck TC 03S, Tensio-Technik, Geisenheim, Germany) - were connected, to the other end an air bag filled with N₂ gas at ambient pressure. Subsequently, gas was sampled into the bottles directly from the various soil depths, replacing the extracted volume with N₂ gas. Samples of ambient air were collected (n=3) on the respective sampling dates at approximately 2 m above the soil surface. Sampling dates were 14 June, 18 July and 27 August, 2011. For more details about the air sampling method along water-logged soil profiles see Goldberg et al. (2008a).

2.8 Determination of N₂O concentrations and δ¹⁵N-N₂O values along soil profiles

The gas samples collected from the soil profiles were analyzed for N₂O concentration and ¹⁵N/¹⁴N ratios of N₂O using a gas chromatograph-isotope ratio mass spectrometer coupling which was linked to a pre-GC concentration device (PreCon-GC-IRMS) (IRMS: delta V plus; Thermo Fisher Scientific, Bremen, Germany; gas chromatograph: GC 5890 series II; Hewlett-Packard, Wilmington, USA; Pre-Con: Finnigan MAT, Bremen, Germany) as described in detail by Brand (1995). The reproducibility of the method is ± 0.15‰. Isotope ratios are presented as δ-values relative to air nitrogen for δ¹⁵N (Mariotti 1983):

$$\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000 \quad [\text{‰}], \quad (1)$$

where R is the ratio of heavy isotope [atom percent, at %] to light isotope [at %] of the samples and the standard.

N₂O concentrations were then calculated from the volume of the gas samples and the peak area on m/z 44 with the help of a calibration curve, considering the exact amount of the samples' additional N₂ gas out of the air bags, which was subtracted. For further details on this method see Goldberg et al. (2008a).

2.9 Statistical methods

We obtained N₂O and CH₄ flux curves by calculating mean N₂O flux values \pm 1SE for every day of measurement and linearly interpolated between two consecutive measurement days. The mean flux is based on n=8 for each rice paddy. Statistics were conducted with R 2.12.0. Via *t*-Test (normally distributed data) or Mann-Whitney *U*-test (not normally distributed data) it was tested whether the measured N₂O fluxes are significantly different from 0 and whether the $\delta^{15}\text{N}$ and N₂O concentration profiles are significantly different from ambient air's N₂O concentration and ¹⁵N abundance. Comparisons of total gas fluxes, water level and water temperature between the three paddies, as well as NO₃⁻, N₂O concentrations and $\delta^{15}\text{N}$ -N₂O values along the soil profiles of the paddies were done by ANOVA or the nonparametric Kruskal-Wallis test. Analysis of correlation between N₂O fluxes, CH₄ fluxes, concentrations of N₂O and NO₃⁻, $\delta^{15}\text{N}$ -N₂O values, water level and water temperature were done by using the correlation test after Pearson.

3. Results

3.1 Water level and water temperature

Due to different irrigation methods the three paddies underwent quite different water level fluctuations (see Fig. 1). The TI paddy was flooded continuously until end of September with huge water level fluctuations mostly driven by heavy monsoon rain events. The field fell dry only twice for two days each, at 22 and 23 June and 5 and 6 September. The II paddy fell dry very often and it never showed water levels as high as the TI paddy. Until beginning of August, the FDFM pattern faced water level heights which were similar to those of the TI paddy but during August and September it stood dry for almost half of the time. During the remaining time it showed very low water levels, except for the period from 7 until 11 September 2011. There is a statistical significant difference (**P* = 0.048) between the water levels of the experimental sites.

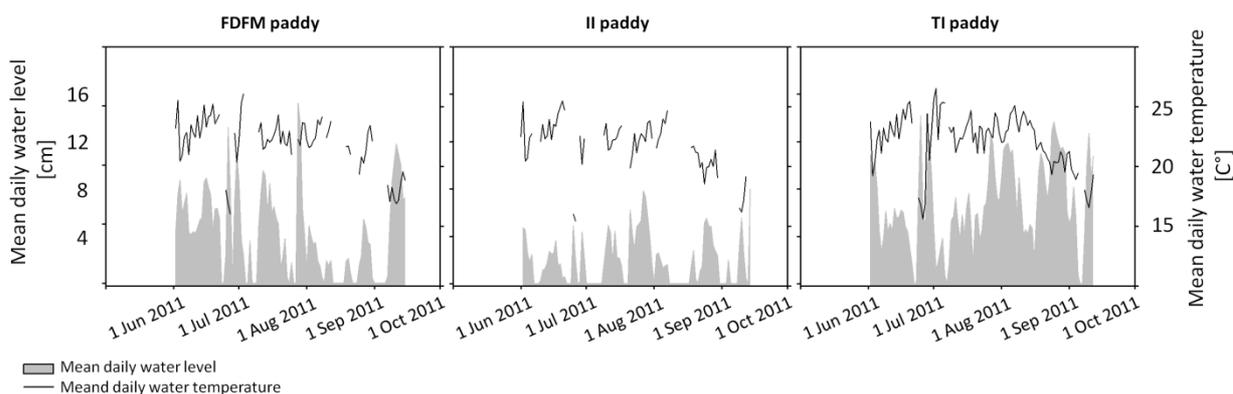


Fig. 1: Water level and water temperature between 1 June and 14 September 2011 at the experimental sites. When the water level was 0, no water temperature could be measured.

3.2 N_2O fluxes and cumulative N_2O emissions

In general the N_2O fluxes at the three rice paddies were quite low (Fig. 2). The FDFM paddy's fluxes in 2010 and 2011 were very similar; Statistics revealed that there is no difference ($P = 0.332$, $t = 0.978$) in N_2O fluxes between both years. On 5 July and 12 August the TI paddy showed pronounced emission peaks of 1.49 and $2.0 \mu\text{mol m}^{-2} \text{h}^{-1}$. It is also the TI paddy which showed the highest cumulative N_2O emissions of 2 mmol m^{-2} (equals $880.2 \text{ g N}_2\text{O ha}^{-1}$ or $6.57 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$), which is exactly the amount of N_2O that has been consumed by the II paddy (which has an emission balance of -2 mmol m^{-2} (equals $-880.2 \text{ g N}_2\text{O ha}^{-1}$ or $-6.57 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$). The emission balance of the FDFM paddy in 2011 (when the measurement period ended by 14 September) is slightly positive (0.05 mmol m^{-2} , equals $22.05 \text{ g N}_2\text{O ha}^{-1}$ or $0.16 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$), whereas in 2010 (when the measurements continued until 23 October) the balance was negative with $-1.47 \text{ mmol m}^{-2}$ (equals $-646.95 \text{ g N}_2\text{O ha}^{-1}$ or $4.83 \text{ g N}_2\text{O ha}^{-1} \text{ d}^{-1}$).

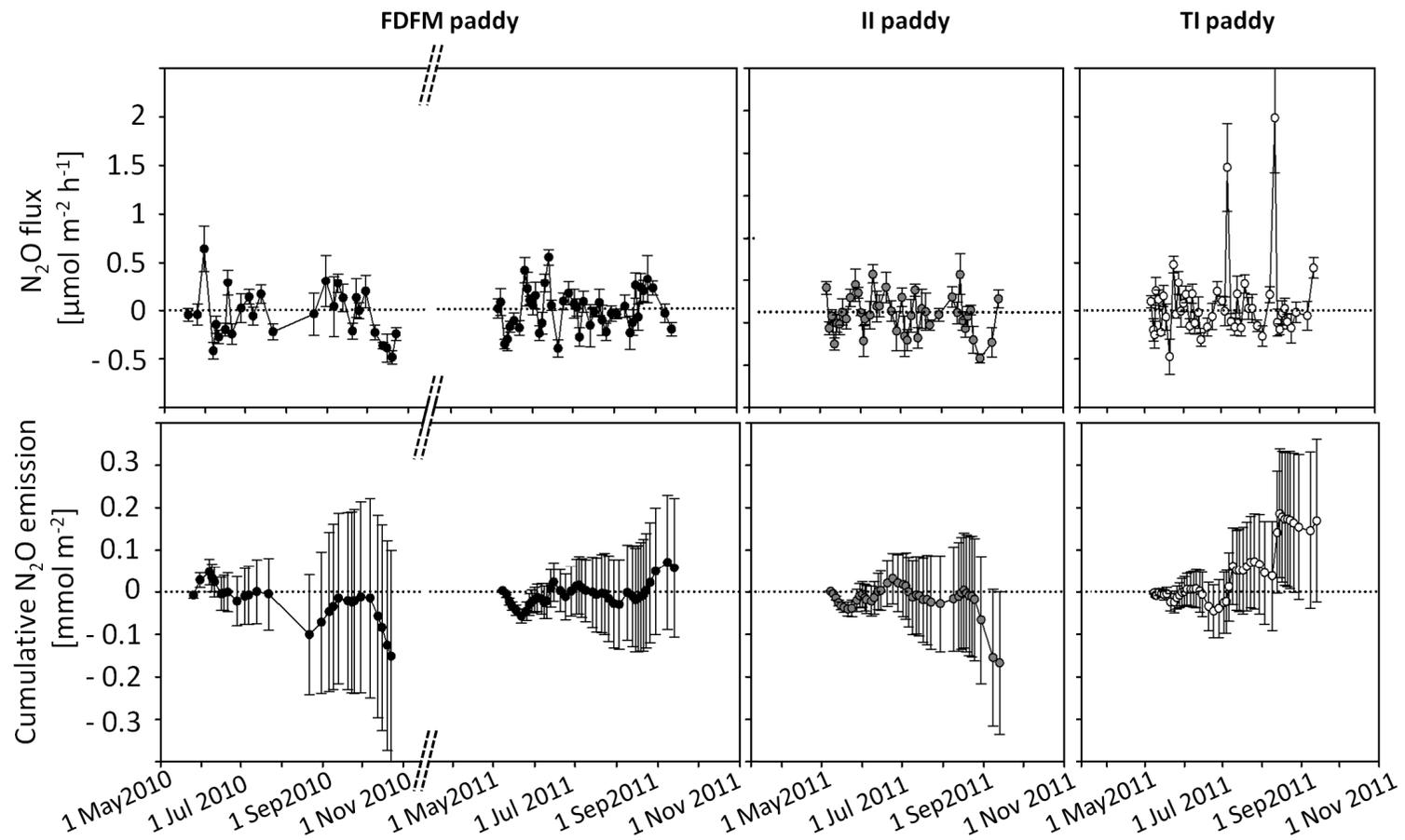


Fig. 2: N₂O flux and cumulative N₂O emissions as a function of time from 11 May to 23 October 2010 and 5 May to 14 September 2011 at the experimental sites.

Error bars in N₂O flux- and cumulative N₂O emission- graphs represent the standard error of the mean (n=8).

3.3 CH₄ fluxes and cumulative CH₄ emissions

While the CH₄ fluxes of the II paddy were comparably low, there were quite huge amounts of CH₄ degassing from the TI and FDFM paddies (see Fig. 3). There was a decline to zero-fluxes at the II and FDFM paddies on 12 July.

During the measurement period, the paddy with the highest CH₄ emission balance was the one with TI (14.5 mol m⁻²; equals 2328 kg CH₄ ha⁻¹ or 19.4 kg CH₄ ha⁻¹ d⁻¹), followed by the FDFM paddy (9.6 mol m⁻²; equals 1541 kg CH₄ ha⁻¹ or 12.8 kg CH₄ ha⁻¹ d⁻¹). The lowest CH₄ emission balance was found for the II paddy with 4.4 mol m⁻² (equals 706.42 kg CH₄ ha⁻¹ or 5.89 kg CH₄ ha⁻¹ d⁻¹).

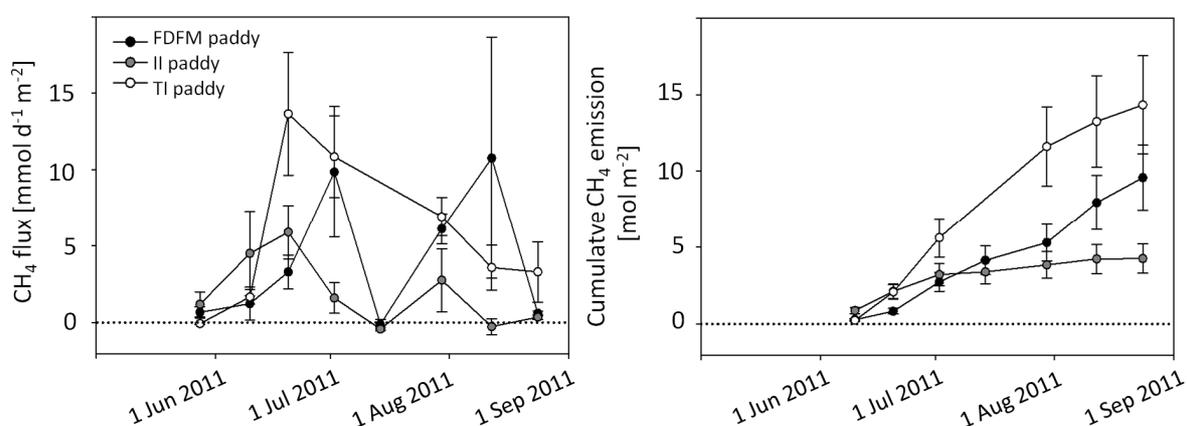


Fig 3: CH₄ flux and cumulative CH₄ emissions as a function of time from 29 May to 28 August 2011 at the experimental sites. Error bars in N₂O flux- and cumulative N₂O emission- graphs represent the standard error of the mean (n=5).

3.4. Presence of O₂ along the paddies' soil profiles

The O₂ profiles of the rice paddies look very different (Fig. 4). The FDFM paddy did not seem to contain any O₂ from the starting point of the O₂ investigation until mid of August when abruptly huge amounts of O₂ occurred from the topsoil until deep down in the paddy's soil. The II and TI paddies had a more complex O₂ situation than the one with FDFM. Whereas II had high to low amounts of O₂ from the topsoil down to 30 cm depth during the whole measurement period and almost no O₂ occurred in the deeper soil layers, TI did not have any O₂ in the topsoil during half of the O₂ investigation period but it did have some O₂ between 40 and 70 cm depth during more than half of the time of the investigation period.

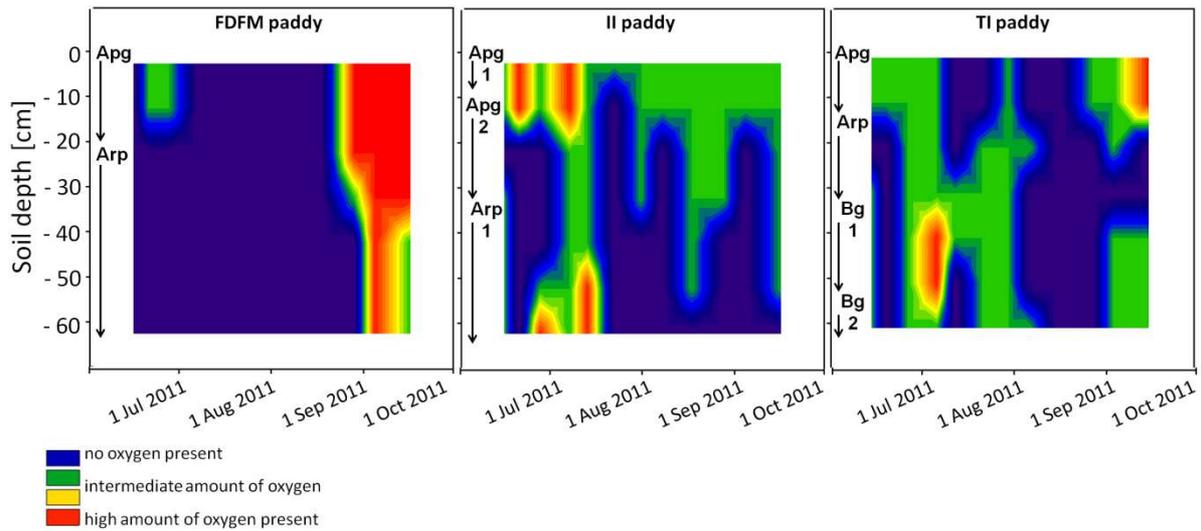


Fig. 4: Presence or absence of oxygen (O_2) as a function of soil depth and time from 10 June to 13 September at the experimental sites.

3.5 NO_3^- concentrations of the paddies' soil profiles

The NO_3^- pattern of the three paddies is similar (Fig. 5). All of them show high concentrations of NO_3^- (about 40 mg/l; in 50 cm depth at the TI paddy there were 100mg/l) in June. From 10 June until 1 August, the NO_3^- concentrations along all depths of the FDFM and II paddies decreased to minimum values of 5 mg/l, then increased up to 55 mg/l and decreased again. The TI paddy showed slightly increased NO_3^- concentrations (35mg/l) on 17 July but then a strong decrease down to 3 mg/l. There were no statistical differences ($P > 0.05$) of the NO_3^- concentrations of the three paddies at each measurement day.

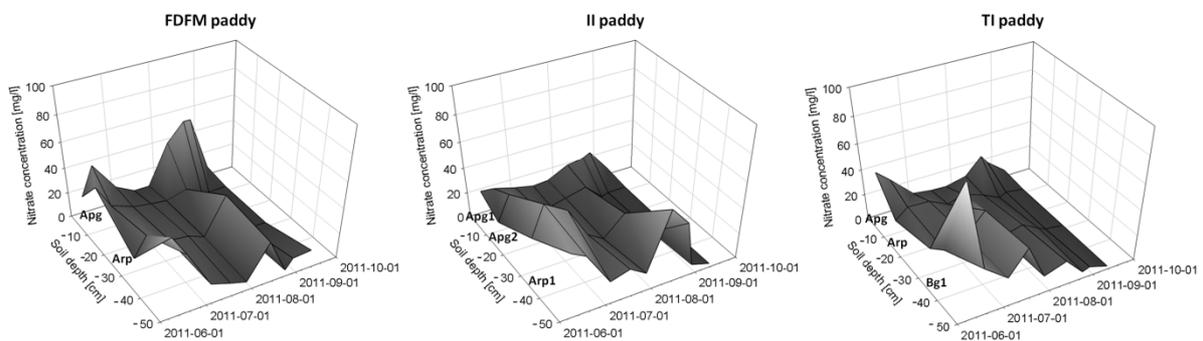


Fig. 5: NO_3^- concentration as a function of soil depth and time from 10 June to 11 September 2011 at the experimental sites. [For deviations from mean values see standard errors in Table 2 in the Appendix.]

3.6 N₂O concentrations and $\delta^{15}\text{N-N}_2\text{O}$ values along the paddies' soil profiles

In general, the N₂O concentrations along the paddies' soil profiles are quite low, except for beginning of June 2011 at the FDFM and II paddy, where maximum values of 6700 and 9900 ppb were reached (Fig. 6). At the other measurement days N₂O concentrations in the soils of these two paddies were similar to the N₂O concentration of ambient air (about 320 ppb). For the paddy undergoing TI, no huge changes in soil N₂O concentrations could be observed; the lowest concentrations were around 460 ppb and the highest ones around 2085 ppb. The 2010 and 2011 N₂O concentration profiles of the FDFM paddy differ a lot. Whereas there were huge fluctuations in 2011, they were almost stable in 2010, ranging from 425 to 1420 ppb. In addition to the statistical differences between the dates at each site, which are given in Fig. 6, comparisons of all three paddies' N₂O concentrations in June, July and August were done, too. They revealed that there were no statistical differences ($P > 0.05$) in June and July, but there were such differences in August ($*P = 0.018$, $F = 5.706$) with the paddy undergoing FDFM on the one hand having significantly higher N₂O concentrations than the II paddy, but on the other hand not different from the TI paddy.

The $\delta^{15}\text{N-N}_2\text{O}$ curves at all sites in 2011 as well as in 2010 varied statistically significant (Fig. 6). While the TI and II paddy's curves started with $\delta^{15}\text{N}$ values down to -11.85‰ , for the following two dates the II paddy's values increased up to -0.51‰ and the TI paddy's values even turned into positive ones (3.8‰). For the FDFM paddy in 2011 the opposite pattern could be observed: the June initial values were positive or less negative ones (ranging from 1.51‰ down to -5.68‰), remained stable in July, but declined in August down to -11.84‰ . A statistical comparison of the 2010 and 2011 $\delta^{15}\text{N-N}_2\text{O}$ values of the FDFM paddy showed that there were no statistical differences between June and July, but the differences were very significant ($P = <0.001$, $t = -5.405$) for the last measurement date, which was 24 August in 2011 and 23 October in 2010. A direct comparison of the $\delta^{15}\text{N}$ values of each measurement day among the three paddies revealed that there were very significant differences in June ($**P = 0.004$, $F = 9.109$; FDFM different from II but not from TI), significant differences in July ($P = 0.012$; II different from TI but not different from FDFM) and highly significant differences in August ($P = <0.001$, $F = 31.146$; differences between all of the three paddies).

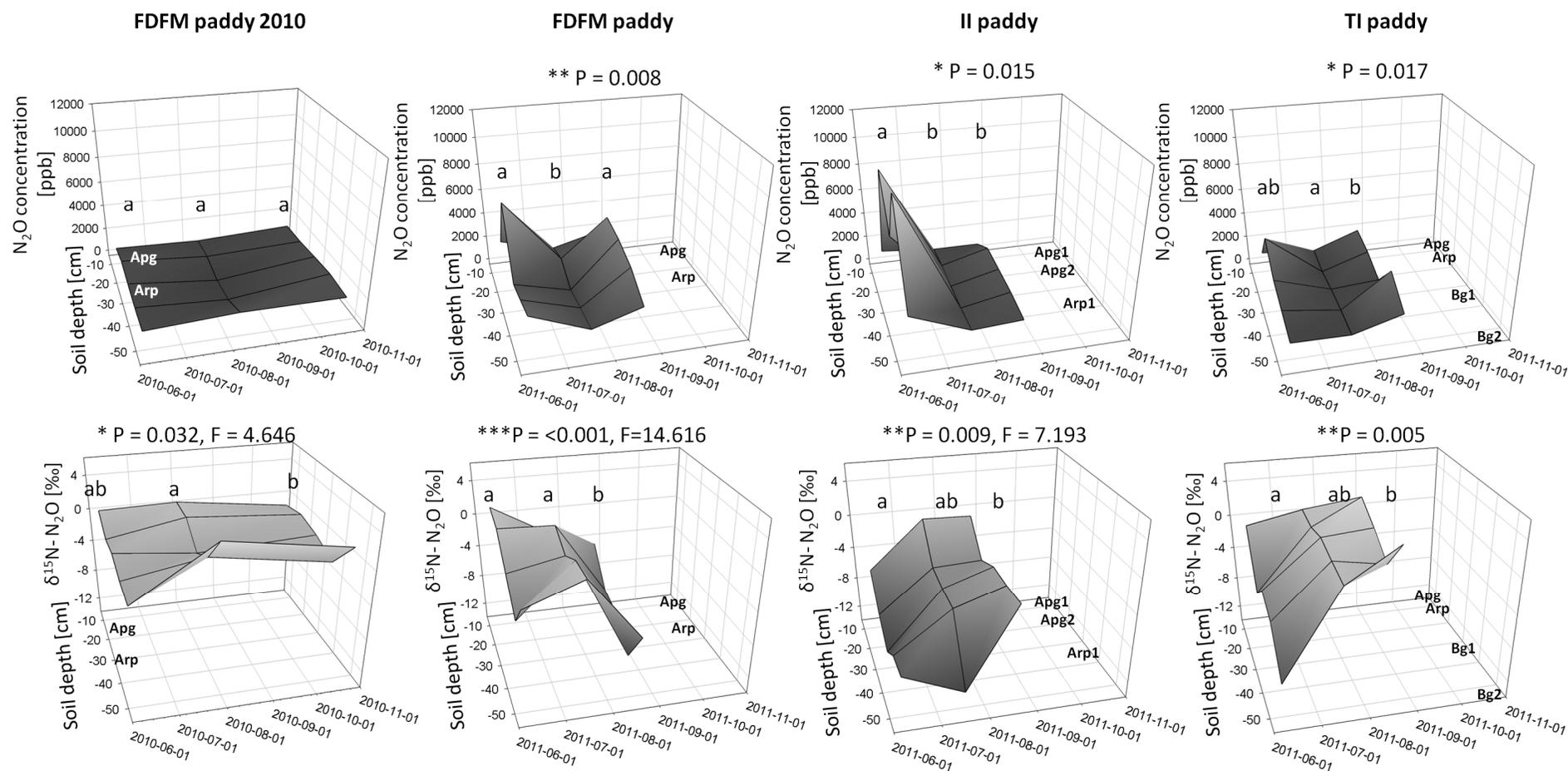


Fig. 6: N₂O concentrations and δ¹⁵N-N₂O values on 6 June, 1 August and 23 October 2010 at the FDFM paddy and 14 June, 18 July and 24 August 2011 at the three experimental sites. Letters indicate statistical differences. [For deviations from mean values see standard errors in Table 3 in the Appendix.]

3.7 Correlations of N₂O fluxes at the soil/atmosphere interface and water level, CH₄ fluxes, the soils' N₂O concentrations and δ¹⁵N-N₂O values

For each experimental site a correlation between N₂O- and CH₄ fluxes could be found, as well as there were correlations between N₂O fluxes and water level at the individual sites. Over all sites correlations revealed relations between N₂O fluxes and N₂O concentrations in different soil depths as well as δ¹⁵N-N₂O values at 50 cm depth (see Table 4).

Table 4: P- and R² values of correlations of N₂O fluxes with those parameters (CH₄ fluxes, water level, N₂O concentration in 10, 20, 40 and 50 cm soil depth, δ¹⁵N value at 50 cm depth) which resulted in a statistical trend (P =/ < 0.1) or were significant (*P < 0.05) or very significant (**P < 0.01).

Correlations at individual experimental sites - N₂O flux vs. :				
<u>CH₄ flux (FDFM)</u>	<u>CH₄ flux (II)</u>	<u>CH₄ flux (TI)</u>	<u>Water level (II)</u>	<u>Water level (TI)</u>
P = 0.1089; R ² = 0.39	*P = 0.0285; R ² = 0.39	**P = 0.0092; R ² = 0.81	P = 0.0839; R ² = 0.10	P = 0.0760; R ² = 0.10
negative correlation	negative correlation	positive correlation	negative correlation	negative correlation
Correlations over all experimental sites - N₂O flux vs. :				
<u>N₂O conc. 10</u>	<u>N₂O conc. 20</u>	<u>N₂O conc. 40</u>	<u>N₂O conc. 50</u>	<u>δ¹⁵N 50</u>
P = 0.1011; R ² = 0.25	P = 0.1061; R ² = 0.24	*P = 0.0450; R ² = 0.30	*P = 0.0386; R ² = 0.30	**P = 0.0079; R ² = 0.47
positive correlation	positive correlation	positive correlation	negative correlation	negative correlation

4. Discussion

4.1 Evaluation of the N₂O and CH₄ fluxes and emissions with respect to water management

The first of the two initial hypotheses was that the most N₂O would degas from the paddies experiencing less flooding and the least N₂O but the highest amount of CH₄ would be emitted from the continuously flooded TI paddy. This hypothesis could not be corroborated for N₂O, where the opposite result was found, but it could be corroborated for CH₄. The TI paddy emitted the most N₂O (2 mmol m⁻², equals 880.2 g N₂O ha⁻¹ or 6.57 g N₂O ha⁻¹ d⁻¹) as well as the highest amounts of CH₄ (14.5 mol m⁻²; equals 2328 kg CH₄ ha⁻¹ or 19.4 kg CH₄ ha⁻¹ d⁻¹), whereas the II paddy consumed exactly that amount of N₂O and emitted only 30% of the CH₄ emitted from the TI paddy, which still sums up to a considerable amount of 4.4 mol m⁻² (equals 706.42 kg CH₄ ha⁻¹ or 5.89 kg CH₄ ha⁻¹ d⁻¹) during the measurement period. The FDFM paddy showed 65% of the TI paddy's CH₄ emissions; its N₂O emissions in 2011 summed up to almost zero, but in 2010, when the N₂O flux measurements continued until end of October, the FDFM paddy consumed 1.47 mmol N₂O m⁻², which corresponds to 72% of the amount that the II paddy consumed in 2011.

In general, previous studies have shown that N₂O fluxes in rice paddies are strongly affected by source and rate of fertilizer applied (Clayton et al. 1997; Cai et al. 1997; Bouwman et al. 2002; Zou et al. 2005a; Ma et al. 2007) as well as by the irrigation method (Smith and Patrick 1983; Cai et al. 2001; Zou et al. 2005b; Johnson-Beebout et al. 2009; Liu et al. 2010; Peng et al. 2011), whereupon it's the cumulative N₂O emission that can be correlated with irrigation method (Zou et al. 2007), but it is not the N₂O flux which is related to the water level, as our present result confirms, regardless of observations of N₂O emission peaks during midseason aeration, which – when incorporated into statistics – do not bring significant results (Zou et al. 2007, Li et al. 2011, Yao et al. 2012).

Traditionally irrigated paddies (which experience continuous flooding) have been found to show the least N₂O emissions, which were consistent with the N₂O emissions we measured in our experimental sites (Zou et al. 2007; Peng et al. 2011). For FDFM paddies (which are flooded for a shorter time of 2 to 3 months in the beginning of the rice growing period, experience midseason-drainage and stand moist but not flooded until the harvest) cumulative N₂O emissions range between 1.21 and 6.17 kg N₂O-N ha⁻¹ (Zheng et al. 2000; Zheng et al. 2004; Zou et al. 2005a,b; Zou et al. 2007; Peng et al. 2011), which in any case exceeds the emissions we have measured. Other water management practices lead to cumulative N₂O emissions of 0.17 to 2.5 kg N₂O-N ha⁻¹ (Cai et al. 1997; Cao et al. 1999; Zou et al. 2005; Peng et al. 2011). The N₂O balances found in our study are considerably low, especially the ones of the II and FDFM paddies, which had been expected to be high, are lower than the TI paddy's cumulative emission and even negative. N₂O consumption in rice paddies was observed recently, too, (Ferré et al. 2012) occurred under flooded and water-logged conditions and might be explained by a more and more declining availability of NO₃⁻, which had served as electron acceptor before; and when nitrate became limited, microbes metabolized NO₂⁻, NO and N₂O instead, resulting in the production of N₂, which degassed from the soil into the atmosphere very quickly (Kögel-Knabner et al. 2010). This denitrification process, leading to decreased N₂O emissions but increased N₂O consumption and N₂ emission, would only occur under anoxic conditions (Khalil and Bags 2005; Sey et al. 2008; Kögel-Knabner et al. 2010) which we thought our II experimental site did not have to face; so we can only speculate that, either our rice paddy's soil did remain wetter than we thought it was, or another process – metabolizing NH₄⁺ to NO₃⁻ and further to N₂ under aerobic conditions – could have taken place: nitrifier denitrification (Wrage et al. 2001; Kool et al. 2011). In fact, it is known that in rice paddy soils a tight coupling between nitrification and denitrification processes exists (Arth et al. 1998). Since it is also known that the application of NH₄⁺ fertilizer stimulates ammonium oxidizing bacteria (Cai et al. 1997; Kögel-Knabner et al. 2010), we assume that in our II site favorable conditions for NH₄⁺ oxidation and further processing under aerobic conditions to N₂ could be found, which may also have

lead to the use of N_2O and its being processed to N_2 . The TI paddy experienced water-logging during the whole rice growing season, whereas FDFM was flooded continuously for 2.5 months, so they underwent the procedure which typically leads to a thin layer of ammonium oxidizing bacteria in the upper few cm of the paddies' soils and underneath, where it is supposed to be anoxic, there would be the denitrifying bacteria (FAO 2006; Kögel-Knabner et al. 2010) all together causing the processing of NH_4^+ via NO_3^- to N_2 . This would have caused very low N_2O fluxes, which is indeed what we have measured, except for two unexpected N_2O emission peaks which boosted the TI paddy's N_2O balance. But fluctuations of the amount of N_2O emitted from paddies with identical water management and fertilizer application have been observed before (Zheng et al. 2004) are not to be over-interpreted.

The quite high CH_4 emissions at our sites may be explained by the NH_4^+ fertilizer, too, because the presence of a high NH_4^+ concentration also leads to a decreased CH_4 oxidation, which may cause higher CH_4 concentrations in the soil and finally leads to high CH_4 fluxes (Cai et al. 1997). On the other hand one must be aware that we measured CH_4 fluxes rather infrequent and seldom in contrast to our N_2O emission measurements, so we may have missed CH_4 peaks as well as days with low CH_4 fluxes, which makes the CH_4 flux results less robust.

Thus, both seems possible, increasing N_2O emissions with increasing CH_4 emissions (as we found for the TI paddy) according to the preceding, to NH_4^+ referring explanation, as well as the common opinion and our introductory hypothesis that contrary N_2O and CH_4 fluxes would occur (as found for FDFM and II), meaning larger emissions of one gas would cause less emissions of the other one, as favorable conditions for the production of the two gases, are assumed to be mutually exclusive (Granli and Bøckman 1994, Klüber and Conrad 1998).

When considering the combined Global Warming Potential (GWP) of CH_4 and N_2O , calculated in units of CO_2 equivalents over a 100-year time horizon (based on a radiative forcing potential relative to CO_2 of 298 for N_2O and 25 for CH_4 (IPCC 2001)), it turns out that the traditional irrigation lead to the highest GWP of $363.1 \text{ mol } CO_2\text{eq m}^{-2}$, followed by FDFM, which lead to degassing of $240 \text{ mol } CO_2\text{eq m}^{-2}$. Intermittent Irrigation turned out to have a GWP of $109 \text{ mol } CO_2\text{eq m}^{-2}$. Thus, we would conclude that intermittent irrigation caused the least greenhouse gas emissions.

4.2 Evaluation of the N_2O fluxes at the soil/atmosphere interface with respect to the soil parameters: presence or absence of O_2 , NO_3^- and N_2O concentration and $\delta^{15}N-N_2O$ values

We hypothesized great changes in N_2O , NO_3^- and O_2 concentrations, as well as in $\delta^{15}N-N_2O$ values over time and along the soil profiles especially in the FDFM and II paddy, whereas we had expected the TI paddy to have rather stable soil conditions. This hypothesis could partly

be corroborated. In terms of O_2 presence the FDFM and II paddy behaved exactly as expected, so the FDFM paddy soil was anaerobic until mid August and afterwards experienced aerobic conditions, and II was infiltrated with O_2 from the top downwards during the whole measurement period. TI was riddled with O_2 in its deeper soil layers in particular, which at first sight appears odd, regarding that TI is the paddy with the smallest Ap-horizon (the horizon which contains oxygen (Frenzel et al. 1992; FAO 2006; Yu et al. 2007; Kögel-Knabner et al. 2010)), but at second sight one notices the paddy's B-horizon which may have oxic conditions, too (Kögel-Knabner et al. 2010). We speculate that the TI paddy's deeper soil layers contain O_2 because they may have access to ground water providing them with O_2 . In contrast to that, the other two paddies' oxygen-containing horizons reach down to 20 and 35 cm, respectively, and get filled up with O_2 every time when the water level declines. Regarding the NO_3^- concentrations along the soil profiles we got anything but the expected result. Instead of great differences and concentration changes among study sites we found no statistical differences between NO_3^- concentrations of the experimental sites. Furthermore, no relations detected between N_2O fluxes and NO_3^- concentrations of different soil layers makes us conclude that NO_3^- concentrations in the soils only play a minor role for the N_2O production and exchange at the paddies' soil/atmosphere interfaces. To our knowledge there are no other lysimeter studies investigating NO_3^- leaching from rice paddies, but there are such studies on DOC-leaching revealing that there are extremely large fluxes from top- to subsoil (Michalzik et al. 2001; Katoh et al. 2004; Maie et al. 2004). In general, one assumes that the highly mobile NO_3^- can leach easily to deeper soil layers or is metabolized by microbes under anoxic conditions, quickly (Kögel-Knabner et al. 2010), which drastically reduces N fertilizer use efficiency in rice paddies in comparison to other agricultural systems (DeDatta 1981; Cao et al. 1984a,b; Roy and Misra 2003). Thus, we conclude that the water management of the three paddies had no effect on their NO_3^- concentrations throughout the measurement period. In the short term there might have been significant differences between the paddies' NO_3^- concentrations, which we failed to detect, because NO_3^- is highly mobile and it might have leached or metabolized by microbes too quickly.

With regard to N_2O concentrations and $\delta^{15}N-N_2O$ values along soil profiles, introductorily it needs to be said that that high N_2O concentrations together with depleted $\delta^{15}N-N_2O$ values are interpreted as N_2O production, whereas low N_2O concentrations and positive $\delta^{15}N-N_2O$ values are regarded as N_2O consumption (Goldberg et al. 2010). The FDFM paddy showed high N_2O concentrations in June and by end of August 2011, at the same time when its $\delta^{15}N-N_2O$ values (in June in the deeper soil layers) were fairly negative (down to -11.84‰), which is regarded indicative of N_2O production and further reduction to N_2 gas. The II paddy possessed high amounts of N_2O (9977ppb) as well as fairly negative $\delta^{15}N-N_2O$ values (-

11.85‰) in June, which we also interpret as N₂O production and subsequent reduction to N₂ gas whereas the rest of the measurement period showed δ¹⁵N-N₂O values around -3‰ and N₂O concentrations between 957 and 2106 ppb, indicating less N₂O production than in June. The TI paddy's soil was depleted in ¹⁵N-N₂O in June (-9.94‰), but comparably enriched (δ¹⁵N-N₂O values up to 3.41‰), at comparably low N₂O concentrations (567-3904ppb) throughout the measurement period, suggesting that after a short N₂O production period in June, hardly any N₂O had been produced anymore during the following measurement days. These profiles explain the N₂O exchange we have measured at the soil/atmosphere interface to a good extent; so we identified the deeper soil layers' (40-50 cm soil depth) N₂O concentrations and ¹⁴N/¹⁵N ratios to have a significant effect on the N₂O fluxes. Unpublished data on gene abundances of denitrifying and nitrifying bacteria at our FDFM paddy study site by Seo and Kang (2012) revealed a higher nirK / nosZ ratio at the subsoil (between 25 and 65 cm soil depth), suggesting that N₂O might be produced in the subsoil, which supports our findings.

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Appendix

Table 2: Average NO₃⁻ concentrations [mg/l] and corresponding Standard errors.

	FDFM paddy				II paddy				TI paddy			
	water	10	30	50	water	10	30	50	water	10	30	50
10.6 NO ₃ ⁻ conc	13.21	35.98	10.97	62.37	17.91	7.41	27.60	50.53	34.86	10.50	20.97	112.62
SE	1.90	24.95	3.45	52.57	6.53	1.78	9.72	22.01	1.04	2.27	7.76	23.82
19.6 NO ₃ ⁻ conc	35.86	18.13	26.39	46.04	17.01	27.35	50.65	44.80	25.86	18.50	15.89	36.79
SE	2.56	3.41	8.67	11.45	3.38	13.65	14.70	18.40	7.55	6.08	0.08	4.80
4.7 NO ₃ ⁻ conc	12.90	11.59	16.20	16.23	12.43	14.42	40.25	18.16	9.13	17.69	21.28	22.99
SE	1.72	1.38	3.38	2.69	7.18	8.33	23.24	10.49	0.86	6.18	2.50	11.64
17.7 NO ₃ ⁻ conc	5.23	9.25	14.42	11.03	9.31	6.98	15.76	22.62	7.07	10.50	36.88	41.00
SE	0.55	3.71	8.49	6.36	2.22	1.15	7.06	12.02	1.04	1.59	14.97	25.16
28.7 NO ₃ ⁻ conc	5.30	7.88	9.38	7.23	10.28	9.94	7.82	14.45	6.51	14.89	10.81	13.89
SE	0.64	1.99	6.88	4.40	1.65	0.33	1.02	7.72	1.30	1.70	1.54	3.39
12.8 NO ₃ ⁻ conc	36.54	12.37	37.69	33.12	18.32	14.08	23.18	58.13	10.16	8.82	15.33	19.56
SE	26.07	1.98	14.06	25.13	9.23	2.41	8.70	30.07	2.16	1.62	3.59	2.90
24.8 NO ₃ ⁻ conc		3.18	2.87	5.39	20.28	1.56	0.62	43.30	22.99	2.34	7.60	5.61
SE		1.37	0.81	3.46	1.33	0.20	0.19	36.56	0.92	0.76	2.91	2.06
29.8 NO ₃ ⁻ conc		3.68	4.02	13.18	23.12	3.21	3.99	7.82	16.26	5.26	5.11	7.71
SE		0.60	0.78	3.70	1.41	0.35	0.64	2.14	1.82	1.30	0.95	3.01
11.9 NO ₃ ⁻ conc	6.54	3.96	3.93	14.39	5.92	3.58	2.74	3.18	5.20	3.30	3.18	2.80
SE	0.09	0.45	1.03	6.53	1.07	1.25	0.30	0.64	1.01	0.14	0.53	0.96

Table 3: Average N₂O concentrations [ppb] and δ¹⁵N values and corresponding standard errors.

depth	FDFM paddy					II paddy					TI paddy				
	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
10.6 N ₂ O conc	2139	6691	1744	2283	2894	1324	9189	5542	9977	2874	1174	3904	2086	1431	805
SE	813	5612	147	308	1809		4609	1523	4448		180	1679	495	331	
18.7 N ₂ O conc	1071	1703	687	1002	1179	957	1094	999	987	1122	836	567	755	816	739
SE	78	971	134	149	241		80	82	203		44	19	44	29	20
24.8 N ₂ O conc	2030	4667	4348	3705	2377	957	2106	1919	1729	1352	2167	1790	1020	3418	1815
SE	937	3353	2414	2200		142	227	539	223		1774	1355	842	2661	1370
10.6 δ ¹⁵ N	1.51	0.79	-2.43	-5.68	-1.86	-6.12	-9.61	11.85	-9.49	-9.07	-0.51	-6.77	-4.18	-5.41	-9.94
SE	3.88	0.92	2.86	5.55	2.01		0.05	1.58	2.11		1.37	0.34	2.78	1.53	
18.7 δ ¹⁵ N	-2.24	0.53	-1.07	0.51	0.67	-0.35	-4.39	-4.75	-4.73	12.05	0.80	0.50	1.22	0.65	0.21
SE	-1.30	0.31	-0.62	0.29	0.39		-2.53	-2.74	-2.73		0.46	0.29	0.70	0.37	0.12
24.8 δ ¹⁵ N	-4.28	-8.28	-8.99	11.84	-6.78	-0.52	-4.09	-2.77	-2.77	-2.46	1.50	3.41	1.71	-0.34	3.80
SE	-2.47	-4.78	-5.19	-6.84		-0.30	-2.36	-1.60	-1.60		0.86	1.97	0.99	-0.20	2.19

Hiermit erkläre ich, dass ich die vorliegende Promotionsarbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Bayreuth, 21.09.2012_____

Sina Berger

Hiermit erkläre ich, dass ich nicht bereits anderweitig versucht habe, diese Dissertation ohne Erfolg einzureichen oder mich einer Doktorprüfung zu unterziehen.

Bayreuth, 21.09.2012_____

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