

NORWEGIAN UNIVERSITY OF LIFE SCIENCES



Abstract

The agricultural sector has been identified as a major anthropogenic source for the greenhouse gases N₂O, CH₄ and CO₂ by the Intergovernmental Panel on Climate Change (IPCC, 2007). Although N₂O only accounts for around 0.03% of total greenhouse gas emission, its radiative forcing is much higher since it absorbs 310-340 times more radiation than CO₂. Therefore the effect of cultivation strategies on soil borne N₂O emissions is an important issue for reducing greenhouse gas (GHG) emissions from food production. In the present study, N₂O emissions were measured in a long-term (since 1989) agricultural plot trial on a clay soil on the campus of Norwegian University of Life Sciences in Ås, comparing the combined effect of fertilizer rate and spring versus autumn plowing on cereal yields. N₂O emissions were measured periodically throughout the growing season 2010 using a static chamber method. Integrated over the measurement period (April to October 2010), cumulative N₂O emissions clearly increased with increasing fertilizer rate (0-120 kg N ha⁻¹ yr⁻¹). Although not perfectly linear, the increase in cumulative N_2O emissions suggested that ~1% of the applied N is lost as N_2O -N which is identically to the Tier 1 emission factor devised by IPCC (2007) for national GHG inventories. Time of plowing had no significant effect on N₂O emissions when integrated over the entire growing season. However, seasonal fluxes showed that emissions were higher in spring plowed soil before plowing as compared with soils that had been plowed in the previous autumn, presumably because autumn plowing leads to more N loss throughout winter. The opposite was the case after spring plowing, i.e. soils that were not plowed in spring had higher emissions which might have been associated with plowing-induced changes in soil structure. Together, both effects cancelled each other out so that no effect of plowing time could be seen on an annual basis. Irrespective of the mechanisms involved, it may be concluded that permanent (> 30 years) spring versus autumn plowing had no fundamental effect on N₂O emission in the studied soil, suggesting that time of plowing is not a relevant tool for mitigating fertilizer induced N₂O emissions. On the other hand, this means that the plowing time can be chosen to meet other environmental goals (e.g. erosion control) without jeopardizing the goal by undesirable effects on N₂O emissions.

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1. Introduction

1.1 Nitrous Oxide and Agriculture

Nitrous oxide (N₂O) is one of the increasing GHGs in the atmosphere. N₂O, commonly known as laughing gas, is a colorless and non-toxic gas, discovered over 200 years ago that has since been used as an anesthetic and fuel additive, and its atmospheric mixing ratios have risen from 270 ppb to 316 ppb within the time period between the industrial revolution and the year 2000. N₂O is a powerful greenhouse gas and an important catalytic agent for ozone destruction in the stratosphere (Ravishankara, Daniel et al. 2009) that can persist for up to 150 years in the atmosphere. The only sink for atmospheric N₂O is photolytic destruction in the stratosphere. Although N₂O only accounts for around 0.03% of global GHG emissions, the radiative absorption potential is 310-340 times higher than that of CO₂. Therefore, it has a 300 fold greater potential for global warming (P érez-Ram érez, Kapteijn et al. 2003).

Agricultural soils are the main source of N_2O , accounting for 50% of global anthropogenic nitrous oxide (IPCC, 2007). N_2O emissions from agriculture are mainly derived from the microbial processes of nitrification and denitrification in soil (Meng, Ding et al. 2005). Therefore attempting to reduce N_2O emissions should focus on refining agriculture soil management practices.

Although the N₂O is produced through natural pathways, lot of the atmospheric increase is considered to be due the ever increasing rates of nitrogen loading, be it through atmogenic deposition of reactive N (NH₄⁺, NO₃⁻), mineral N-fertilizer application or increased cultivation of legumes. However, due to the multitude of physical, chemical and biological process in soil, many factors such as weather, soil structure, soil management and soil cultivation history control N₂O emissions. Therefore, there are many uncertainties about how cultivation strategies affect N₂O emissions from cultivated soils on the long run. Long-term data of direct N₂O emissions have been established recently within the project "Creating an empirical basis for an integrated evaluation of soil-borne GHG emissions in Norwegian agriculture". The present study reports measurements conducted in a field experiment in a SE Norwegian cereal cropping system, focusing on the effects of N-fertilization rate and time of plowing (autumn vs. spring plowing) on N₂O emissions in cereal cropping and to explore temporal variability of N₂O emission rates as affected by soil moisture, temperature and cereal yields.

1.2 The soil nitrogen cycle: a brief overview

Nitrogen is a polymorphous and dynamic element that is transformed chemically or biochemically through some complex reactions referred to as the global N cycle. Much attention is paid to reactive forms of nitrogen because of their essentiality to life and their impact on environmental quality. The soil N cycle (Fig. 1) has been described as a subset of the global N cycle. The soil N cycle includes transformations of organic N forms to inorganic N, a process mediated by heterotrophic microbes and referred to as "N mineralization" and transformation of inorganic forms to organic N, a process referred to as "N immobilization". N immobilization by microbes competes with the plant N demand which is the most limiting factor in food production. Overall, soil N cycling is driven by the chemical composition of soil organic materials and the nutrient demand of microbes and plants (Manzoni and Porporato 2007). The soil N cycle is an open system where N can enter through anthropogenic inputs such as organic and inorganic fertilizers, or through microbial symbiotic and non-symbiotic N fixation. Conversely, N can be lost from soils due to leaching of NO₃⁻, volatilization of NH₃, or denitrification of NO₃⁻ to N₂O and N₂.



Figure 1. N₂O formation in soil as part of the soil nitrogen cycle (after Firestone and Davidson, 1989).

1.3 Pathways of nitrous oxide production

Globally, 70% of N_2O emissions to the atmosphere are estimated to derive from soils. Soils are rarely observed to be a sink for N_2O (Smith, Ball et al. 2003). Production of N_2O in the soil is a natural process occurring during red/ox reactions within the N cycle such as nitrification and denitrification.

Nitrification

Nitrification is the oxidation of NH_4^+ to NO_3^- via NO_2^- carried out by ammonium oxidizing bacteria (AOB) and ammonium oxidizing archaea (AOA) under oxic conditions (Equ.1). Nitrification is an important source of N₂O in the soil (Robertson and tiedje 1987). The nitrification rate is strongly depending on the availability of the NH_4^+ and N_2O_1 production therefore increases with increasing NH_4^+ availability (Bøckman and Olfs 1998). However, the concentration of NH_4^+ is quite low in agricultural soils, because the NH_4^+ produced by mineralization of soil organic matters is utilized by soil microorganisms and plants, thus limiting nitrification rate in soil; however, nitrification becomes an important process in soils to which fertilizers containing urea and ammonium have been applied. A number of environmental factors have been identified to affect rates of nitrification and N2O:NO3 product ratios, including substrate availability, soil water content, O₂ availability, pH, and temperature (Ruser, Flessa et al. 2006). NH₄⁺ availability for nitrification is affected by rates of organic N mineralization and fertilizer N application (Zaman, Di et al. 1999). In general, nitrification rates increase with soil moisture up to 60% water-filled pore space (WFPS). As WFPS exceeds 60%, availability of O_2 and CO_2 substrate for nitrifies declines due to severely restricted diffusion rates (Linn and Doran 1984).



Equation 1: Pathway of nitrification

Denitrification

Denitrification plays a special role in the soil N cycle by being the main process that returns nitrogen to the vast pool of atmospheric N_2 . Denitrification is the microbial process of

dissimilatory reduction of nitrate (NO₃⁻) via nitrite (NO₂⁻) to the gases nitric oxide (NO) and nitrous oxide (N₂O), and then to the inert gas dinitrogen (N₂) (Richardson, Felgate et al. 2009) (Equ.2). Many bacteria can grow under anaerobic conditions by performing denitrification instead of oxygen (O₂) respiration. Oxic respiration is energetically superior by allowing the complete oxidation of a growth substrate and the concomitant conservation of the large amounts of energy released. Denitrification is most likely to occur when soil water content and NO₃⁻ contents are high and diffusion rates of O₂ into the soil are lower than the O₂ demand by oxic respiration. Most denitrifiers are heterotrophic organisms; therefore the process is dependent on availability of oxidizable C.



Equation 2: Pathway of denitrification

Both of processes, denitrification and nitrification produce N_2O . Furthermore, nitrification supports denitrification by supplying the substrate (NO_3^-) for this process. The complexity of microbial processes and the multitude of physical and chemical factors are given by soil type, climate and crop management results in a great deal of uncertainties about N_2O emissions from agricultural soils. Because it is evident that agriculture's contribution to N_2O in the atmosphere is of general concern, the complexity of processes and controlling factors has to be studied.

1.3.1 Nitrous Oxide emission from cultivated soils

Effect of Tillage

Primarily, plowing increases the accessibility of crop residues and soil organic matter (SOM) for soil microbes and enhances C and N mineralization. In the long run, tillage is known to diminish the capacity of the soil to immobilize N due to decreased C availability (Gregorich, Rochette et al. 2006). Theoretically, this should reduce the denitrification capacity. Secondly, tillage changes soil environmental conditions, which more directly affect the production and emission of soil biogenic gases (CO₂, N₂O, and CH₄). Plowing loosens the soil and decreases the water filled-pore space (WFPS). On the other hand, evaporation decreases. Fresh organic matter plowed into the soil is mineralized quickly promoting the production of NH_4^+ and NO_3^-

through subsequent nitrification. Last but not least, soil tillage also causes major changes in below-ground environmental conditions and the distribution of nutrients in the soil profile.

Compared to tilled soils, no-till soils have different temperature regimes, and are often more compacted and dense at the surface, leading to relatively poor drainage and aeration so that gases diffuse more slowly through them. Under no-till systems, a larger fraction of the crop residues is left at, or close to the soil surface, where they are prone to slower decomposition because of limited mixing with other soil constituents and organisms. All in all, tillage may affect direct N₂O emissions significantly. Depending on soil type, type and timing of plowing, N₂O emissions may increase or decrease (Pu, Saffigna et al. 2001). Timing of plowing (spring versus autumn plowing) may be expected to affect N₂O emissions during the growing season by affecting mineralization of crop residues during winter, thereby controlling the amount of mineralized N available in spring. Moreover, there might be a more direct effect on off-season emissions, since cold soils have been frequently reported to emit huge amounts of N₂O (Flessa, Dorsch et al. 1995; Dorsch, Palojarvi et al. 2004).

Mineral fertilization

Soils rarely supply sufficient N for productive cereal or grass cultivars to achieve their potential yields. Application of mineral N fertilizers has been the key factor in bringing about the very substantial increase in crop productivity that has been achieved since the beginning of industrialization. Increased N fertilization, on the other hand, may increase the release of N₂O from soils through nitrification and denitrification and thereby contribute to the global warming. Among soil management practices, N fertilization application plays a major role for the absolute magnitude of N_2O emission. Also, N_2O emission dynamics are largely determined by the type and timing of N fertilization and the application rate. Surprisingly, continued fertilizer application, although producing a higher total N content, does not increase the denitrification potential (Abbasi and Adams 2000) as often indicated by high residual NO₃⁻ concentrations after harvest. Although numerous studies have shown that fertilizer and manure increase gaseous nitrogen emissions from soils, there are indications that the rate of denitrification is not increased and may even be depressed by the addition of nitrogen (Blackmer and Bremner 1978). Similarly, while some studies have revealed the dependence of N₂O emission rates on the type of N-fertilizer used (Eichner 1990) others have shown no particular trend in N₂O emission with fertilizer type (Stehfest and Bouwman 2006). In the

present study, focus will be given among others on the effect of fertilization rate on N_2O emission.

Soil moisture and temperature

Soil moisture controls the aeration of soil by affecting the proportion of air filled pores. Oxygen (O₂) diffuses much slower in water-filled pores than in air-filled pores. Therefore, soil moisture in studies on nitrification/denitrification is often given as % water filled pore space (WFPS) which denotes the proportion of the total soil porosity occupied by water. WFPS is a central factor for the anoxic volume in soil, and therefore controls the distribution of nitrification and denitrification. Further, WFPS controls the diffusion of N₂O from the soil to the atmosphere.

Soil moisture may become limiting for microbial activity during summer droughts. Rewetting of dry soil has been reported to lead to the release of large quantities of N_2O from the soils to the atmosphere (Davidson 1992). Commonly soil moisture corresponding to 50-60% of water holding capacity is considered as being optimal for both nitrification and denitrification (Linn and Doran 1984). With increasing moisture content, the production of N_2O increases. Above 90% WFPS, probably N_2O emissions decrease because N_2O is reduced to N_2 on its way to the atmosphere.

Like all biological processes, nitrification and denitrification depend on temperature. However, there seems to be no clear relationship for N_2O emission rates which often are episodic after climate induced perturbations like drying-rewetting or freezing-thawing (Flessa, Dorsch et al. 1995).

2. Materials and Methods

2.1 Site description

The measurements were conducted during the growing season of 2010 in a long term field trial established in 1989 with three fertilization rates (0, 60 and 120 kg N ha⁻¹ yr⁻¹) and spring or autumn plowing arranged in a randomized split plot design. The crop rotation consisted of cereals only (spring wheat, barley). Average rainfall in 2010 was 807 mm, which is 2.5% higher than the long-term (1961-1990) annual mean. Average temperature in 2010 was 3.7 C, which was 1.6 C higher than the long-term (1961-1990) annual mean average (Grimenes, 2011). Soil type was loamy clay with a pH of 6.2. Basic soil properties are listed in table 1.

Soil pH	6.2
Soil type	clay loam
Bulk density (g cm ⁻³)	1.19
Organic C (%)	1.74
Total nitrogen (%)	0.21
Soil C/N	8.7
P (mg/100g)	4.2
K (mg/100g)	7.6
Mg (mg/100g)	13.5
Ca (mg/100g)	211
Na (mg/100g)	2.2

Table 1: Chemical and physical properties of the topsoil at experiment field A95 (fromBørresen, T. 1993).

Management details are given in table 2. Autumn plowing plots were plowed in October 2009 and left fallow during winter while spring plowing plots had stubbles until plowed in April 2010 right before sowing. Both plowing treatments received a single dose of NPK fertilizer in the beginning of June.

 Table 2: Agricultural management at A95 throughout 2010
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Management	date
Spring plowing	26th of April 2010
autumn plowing	21st of September 2010
sawing	11th of May 2010
fertilization	1st of June 2010
harvest	8th of September 2010
	(all straw removed from the plots)

2.2 Experimental design

The experimental field was organized as a fully randomized split plot experiment in two blocks with 2 plowing dates (spring and autumn) $\times 3$ fertilization rates(0, 60, 120 kg ha⁻¹ yr⁻¹) $\times 4$ catch crops (no catch crop, ryegrass, white clover and mixture of ryegrass and white clover) in 1989 (Fig. 2). N₂O fluxes were measured for all combinations of fertilizer levels and plowing dates. An additional treatment including ryegrass (spring plowing; with 120 kg N ha⁻¹ yr⁻¹) was included to investigate the effect of a non-legume catch crop with the highest fertilizer level. N₂O measurements were set up for in total 7 treatments, in each two replicate plots were chosen on the basis of an 8-year time series of yield data, to make sure that similar plots with respect to soil fertility and weeds were picked for each treatment. In each plot, two micro plots (0.5 × 0.5 m) for gas measurements were established by driving aluminum frames into the soil (to be used as bases for chamber measurements, see below), giving 30 micro plots for gas sampling all together. The micro plots for emission measurement were established after April 2010. A field map of the experiment is given in figure 2, showing the location of the micro plots used for gas measurements.

A95				a: no cat	ch crop											
Kjerringjordet			b: ryegrass N0: 0kg N						Nfertilizer	tilizer 1989						
	AP = auto	umn plowing	9	c: white	clover					N1: 60 I	kg N / ha					
	SP = spri	ing plowing		d: mixture of ryegrass and white clover				N2: 120 kg N / ha								
	<u>a</u>	С	b	d	С	d	а	b	b	а	d	С	d	b	С	а
6m	1	7	13	19	25	31	30 37	43	49	<u>2</u> 55	61	67	73	79	85	91
	NU	N2	N1	NÜ	N2	N1	²⁹ N2	N0	N1	21 N1	N2	NO	N1	N0	N2	N1
	2		14	20	2(32	²⁸ 38	44	50	²⁰ 56	6?	38	74	80	36	72
N	N1 4	NO	N2	N1	N		27 N1	N1	NO	¹⁹ N2	NO	N1	N0	N1		N2
	3	9	15	21	27	33	²⁶ 39	²⁴ 45	51	18 .57	63	69	75	81	87	93
	N2	N1	NO	N2	NO	N2	²⁵ NO	²³ N2	N2	17 NO	N1	N2	N2	N2	N1	N0
↓ 44m 8m																
	ı d	b	а	С	а	b	d	С	d	С	b	а	b	а	С	d
	4	1 10	3 16	22	28	34	40	46	52	58	64	70	76	82	88	94
	N1	² N2	4 N1	NO	NO	N1	N2	N0	N2	N1	N1	NO	N2	N1	N2	N0
	5	11	7	23	7 29	1 5	D 41	47	53	55	¹¹ 65	71	77	83	89	95
	N2	NO	N2	N1	8 N2	N	N1	N1	N1	NO	12 N2	N1	NO	12	N1	N2
	6	12	5 18	24	9 30	36	42	48	54	60	66	¹³ -72	78	84	90	96
'	NO	N1	- ⁶ N0	N2	¹⁰ N1	N2	NO	N2	NO	N2	NO	¹⁴ N2	N1	NFO	N0	N1
	4m							64r	n							

Figure 2: Field map of the A95 experiment; numbers in red are micro plots for N_2O flux measurements

2.3 Sampling methods

2.3.1 Gas sampling and analysis

N₂O emission were taken by the static chambers method (Hutchinson and Mosier, 1981) using $50 \times 50 \times 20$ cm aluminum chambers equipped with a sampling port with 3-way stop cock and a 3 mm diameter pressure equilibration tube. 50×50 mm (width \times length) metal frames were pressed 10 cm into the soil in April 2010 and remained there until plowing in October 2010. The frames were equipped with a U-shaped groove at the top, to be filled with water prior to chamber deployment to achieve a gas tight seal between chamber and soil. For each N₂O flux measurement, the aluminum chambers were set on the permanently installed frames. Extensions (30 cm high) were used towards the end of the growing season when crops were higher than 30 cm. After chamber deployment, gas samples were taken at 1, 15, 30 and 45 min with a 25 ml polypropylene syringe from the sampling port which was located on the top of chamber (Fig. 3). Before taking the samples, the plunger of the syringe was pulled and pushed three times to mix the gas in the chambers. The samples were transferred to evacuated 12.5 ml vials crimped with rubber septa (10-CV-Crimp, Chromacol, Herts, UK). After the last sample was taken, the temperature inside the chamber was measured. Flux sampling was carried on 17 occasions throughout 2010, in weekly to biweekly intervals. Longer periods without flux sampling were due to agricultural management in spring and autumn.

The gas samples taken in the field were transferred to the laboratory. A gas chromatograph (Model 7890A, Agilent, Santa Clara, CA, US) coupled to a headspace auto-sampler (GC - PAL, CTC Analysis AG, Switzerland) was used to analyze the gas samples for CO₂, CH₄ and N₂O mixing ratios. The GC is equipped with a 250 μ l sampling loop, a packed haysep precolumn with back flush (to prevent water from entering the column and detectors) and a 30 m 0.53 mm Poraplot U capillary column to separate CO₂, CH₄ and N₂O from air. He 5.0 was used as a carrier gas and the oven temperature was 50 °C. CO₂ was measured by a thermal conductivity detector (TCD), CH₄ by a flame ionization detector (FID), and N₂O by an electron capture detector (EC3) operated at 340 °C with Ar/CH₄ (17 ml min⁻¹) as make up gas. EZchrome software was used for data acquisition and peak integration, whereas the auto-sampler was controlled by in-house software. A house standard close to ambient trace gas concentrations was used for calibration. Drift correction was performed on the basis of interspersed standards.



Figure 3: Photograph of soil frame with open channel and flux sampling.

2.3.2 Soil sampling and analysis

Soil samples were taken at each gas sampling date by a 30 mm diameter soil corer from 0-20 cm depth. 8 soil cores distributed over the replicate plots belonging to one treatment were taken and mixed to give one representative composite sample per treatment. The soil samples were stored in a cooled box until transferred to the laboratory for processing and analysis. Every sample was divided immediately into two parts; 20 g fresh soil was weight in for soil moisture measurement; another 45 g fresh soil was weight into extraction bottles and frozen for later analysis of NH_4^+ and NO_3^- . The gravimetric soil moisture was determined by drying at 105 °C for at least 24 hours. These soils moisture values were used to convert to NH_4 -N and NO_3 -N concentrations to g N g dry soil¹. The 45 g fresh soil samples were extracted in 50 ml 2 M KCl solution immediately after thawing by shaking the bottles horizontally for 1 hour at 100 rpm. Blanks were included. Both the soil-KCl solutions and blank samples were filtered through Whatman blueband filters (Whatman International, Maidstone, UK). The resulting filtrates were frozen at -18 °C for later NH_4^+ and NO_3^- analysis by flow injection analyzer (FIA Star 5010 analyzer Tecator, Sweden).

2.4 N₂O flux calculation

The N_2O concentration from GC is expressed by the peak areas, so we had to convert the peak areas to the known concentration (in ppm) through calibration with the air. The N_2O concentrations were plotted over time in excel, the data were then fitted to a 1st order (linear) or 2nd order (curve-linear) polynomial, the slop of which gives the relative change in concentrations per chamber volume and minute. The concentration change was transformed into flux rates by using equation 3

$$F_{N2O} = d [N_2O]/dt * V/A * M_N/V_M * 60 * 1000$$
(Equ.3)

Where F_{N2O} is the emission flux (µg N₂O-N m⁻² h⁻¹), d [N₂O]/dt the change of N₂O concentration in the chamber (ppmv min⁻¹), V is the chamber volume (L), A is the area covered by the chamber (m²), and M_N is the molecular mass of N in N₂O (g mol⁻¹) and V_m is the molecular volume (L mol⁻¹) at chamber temperature. Fluxes were cumulated for each micro plot assuming average flux between each measurement. Treatment effects were tested by analysis of variance (SAS) using averaged cumulative fluxes per treatment.

2.5 Water filled pore space (WFPS)

Volumetric water content was calculated from gravimetric soil moisture by multiplying with the average bulk density (1.19 g cm⁻³). WFPS was calculated based the bulk density and a particle density of 2.653 g cm⁻³ using equations 4 and 5:

$$WPFS = \frac{volumetric water content}{soil porosity}$$
(Equ.4)

And the soil porosity is based the bulk density and particle density.

Soil porosity =
$$1 - \frac{bulk \, density}{particle \, density}$$
 (Equ.5)

3. Result

3.1 Soil and air temperature, precipitation and soil moisture

Soil temperature was measured with a handheld digital thermometer. A temperature probe was inserted 2.5 and 5 cm deep into the soil next to each chamber and temperatures were recorded manually. Figure 4 shows soil temperatures together with average daily air temperature (Grimenes, 2011) during the whole study period from 1st of April to 25th of December, 2010 and average temperatures for all treatments in -2.5 cm depth recorded at the time of N₂O emission measurements. In the growth period, from May to August 2010, the average daily air temperatures varied from 2 $\$ to 20 $\$. Surface soil temperatures measured during chamber deployment in this period were mostly above average daily air temperature as flux measurements were carried out during the middle of the day. However, from September on, surface soil temperatures converged with average daily air temperatures. April and October 2010 were fairly dry months with <50 mm precipitation, whereas August 2010 was exceptionally wet with almost 150 mm rain (Fig. 4).



Figure 4: Average daily air temperature (from meteorological station), average soil temperature at 2.5cm depth and daily precipitation throughout the investigation period

Figure 5 shows water-filled pore space (WFPS) together with daily precipitation in all 7 treatments throughout the study period. Due to the agriculture management (plowing, sowing, harvest, fertilization), no soil and flux samples were taken in May and September. Soils were

wet early in April, but the WFPS decreased quickly by 0.2 units because of little rainfall in April. Low WFPS values below 0.5 were recorded in June and July followed by steep increases after rainfall events. WFPS values were highest in late August and towards the end of the year, reaching almost 0.9. No systematic differences in WFPS were seen in plots with autumn and spring plowing.



Figure 5: Dynamics of WFPS of the topsoil (0-20cm) and daily precipitation in all 7 treatments during the investigated period. S: sowing; SP: spring plowing; F: fertilization; AP: autumn plowing; H: harvest.

3.2 Mineral nitrogen (NO₃⁻-N and NH₄⁺-N)

Figure 6 shows the temporal dynamics of NO₃–N and NH₄-N concentrations in 0-20 cm depth for all 7 treatments. Mineral N contents after spring thaw were generally low with values under 10 μ g N g dw soil⁻¹ for NO₃ and NH₄ (Fig. 6). After fertilization in April, 2M KC1 extractable NH₄-N and NO₃-N tended to be higher than before fertilization except for NO₃-N in the N0 treatments which never exceeded 10 µg N g dw⁻¹. NH₄-N contents during the period of intense crop growth were very variable but still showed distinct temporal patterns with fertilization treatments. Surprisingly, NH₄-N contents were highest in the N0 treatment after fertilization, but dropped rapidly to very low levels thereafter. The N60 and the N120+CC treatments showed a more gradual increase in NH₄-N contents throughout June and July, whereas the N120 treatment increased steadily, reaching highest NH₄-N contents in the end of July, before dropping to values around 5 µg NH₄-N on the 3rd of August. The N60 treatment showed higher NH₄-N contents in the spring plowing treatment, whereas no such effect was seen in the N0 and N120 treatments which showed practically identical dynamics in NH₄-N content. NO₃-N contents followed a temporal pattern similar to NH₄-N with permanently low NO₃-N in the N0 treatment, peaking NO₃-N in early June in the N60 and a more stable NO₃-N content during summer in the N120 treatment. Again, the N60 treatment was the only one showing a spring plowing effect with higher NO₃-N contents in the spring plowed plots before converging with the autumn plowed plots in the middle July. Overall, NO₃-N content was somewhat higher than NH₄-N content in the various treatments throughout summer.

3.3 Temporal dynamics of N₂O emission

N₂O fluxes showed a strongly fluctuating pattern in time with no clear relation to season (Fig. 7). High emissions were observed in spring after snowmelt and after fertilization. Two marked emission tops were recorded during summer on 16^{th} of June and 14^{th} of August. N₂O emissions after harvesting were generally low. Despite difference in magnitude, daily N₂O emission followed an identical temporal pattern in all treatments except for the N0 spring plowing treatment which had consistently low N₂O emissions. N₂O emission rates ranged from 0 to 180 µg N₂O-N m⁻² h⁻¹. During the episodic flux peaks in summer, there was a clear positive relation between the magnitude of N₂O emission flux and fertilization level. Generally, highest N₂O emissions were recorded in the N120 treatment.



Figure 6: Dynamics of ammonium (upper panel) and nitrate N (lower panel) in 0-20 cm soil depth in all 7 treatments from 13^{rd} of April to 13^{rd} of October, 2010 (after 13^{rd} of October, no soil samples were taken because the soil was frozen). Note the different scales for ammonium and nitrate N. S: sowing; SP: spring plowing; F: fertilization; AP: autumn plowing; H: harvest.

After snowmelt (before spring plowing), N_2O emission fluxes were consistently lower in the autumn plowed plots as compared to the not yet plowed plots belonging to the spring plowing treatment (see insert in Fig. 7). Interestingly, N_2O emission right after spring thaw was highest in the 120N+CC treatment, suggesting that residual mineral N from the previous year or nitrogen mineralized during winter fueled N_2O emissions early in spring. Emissions

declined in all treatments during April, probably due to decreasing WFPS (Fig. 5) and low mineral N levels (Fig. 6). After fertilization and spring plowing, N₂O emissions were still higher in the spring plowed plots as compared to the autumn plowed ones. This pattern reversed during June, after which higher N₂O emission rates (particularly during periods of high flux) were observed in the autumn plowed treatment. After harvest, N₂O emissions were generally low (< 20 μ g N₂O-N m⁻² h⁻¹), irrespective of fertilizer level or plowing treatment.



Figure 7: Temporal dynamics of average N_2O emission in each treatment. Error bars are not shown in order not to overcrowd the figure. Insert shows N_2O emission fluxes after spring thaw during April 2010. S: sowing; SP: spring plowing; F: fertilization; AP: autumn plowing; H: harvest.

3.4 Treatment effects (fertilizer rate and spring plowing vs. autumn plowing)

Figure 8 shows the cumulative N_2O emissions in the different treatments and fertilizer levels throughout the 220 days of the study. Cumulative N_2O emissions increased with increasing fertilizer rate irrespective of the date of plowing. However, the cumulative emissions in the three fertilizer regimes (0kg, 60kg and 120 kg N ha⁻¹ year⁻¹) were not significantly different from each other, except for the spring plowed N120 treatment which emitted significantly more N₂O than the spring-plowed N0 treatment (Tab. 3). The lack of significant differences was mainly due to a high variability among the four replicate micro plots as can be seen from the high standard deviation in Tab. 3 and Fig 8 (except for spring plowed N0). In contrast to these results from a t-test (Tab. 3), the regression between cumulative N₂O emission and fertilizer rate (Fig. 8) was highly significant ($R^2 = 0.75$; p= 0.012 combined for both plowing treatments), confirming that N-fertilization rate had a significant impact on cumulative N₂O emission by 30% relative to the other treatments receiving 120 kg N ha⁻¹, but this effect was not statistically significant.

Time of plowing had no significant effect on cumulative N_2O emissions (Fig. 8, Tab. 3). This was mainly because of the counteracting plowing effects described above (higher N_2O emissions in spring plow treatments before spring cultivation and higher in autumn plowed treatments thereafter) which compensated each other when cumulated over the entire year.

Figure 8 (lower panel) gives the emission factors (kg N₂O-N kg fertilizer N⁻¹) for spring and autumn plowing, respectively as the slope of the regression between N-input and N₂O-N emission. In spring plowing, the emission factor was 0.96 % and for autumn plowing 0.73 % of applied N. Both values were not significantly different from each other and are within the uncertainty range given by the IPCC Tier 1 (2007) emission factor of 1% (0.3% to 3 %).

Figure 9 plots the N_2O emission response to fertilization rate together with the yield curve. The yield response started to decrease from 70-80 kg N ha⁻¹ yr⁻¹, whereas the N_2O emission response increased.



Figure 8: Mean cumulative N_2O emissions (n=4) throughout 220 days during the vegetation period in 2010 in the different treatments (upper panel). The lower panel shows the cumulative emission as a function of fertilizer rate in spring plowing and autumn plowing treatments.

Table 3: Cumulative N₂O emissions and grain dry matter yields in A95 (April 5th – Nov. 11th 2010). Numbers followed by different letters are statistically different at a significance level of $p \le 0.05$

treatment	cumulative N ₂ O emission (kg N ha ⁻¹ period ⁻¹) [#]	dry matter yield (t ha ⁻¹)*
autumn plowing+0kg N/ha	0.852 (0.129) ^{ad}	2.3
spring plowing+0kg N/ha	0.806 (0.035) ^a	1.7
autumn plowing+60kg N/ha	1.097(0.233) ^{abd}	3.9
spring plowing+60kg N/ha	1.023(0.277) ^{abc}	3.8
autumn plowing+120kg N/ha	1.725(0.336) bcd	4.7
spring plowing+120kg N/ha	1.958(0.799) ^{cd}	4.3
spring plowing+120kg N/ha + catch crop	1.321(0.387) ^d	5.0

Standard deviation (n=4) in parentheses. *data from T. Børresen (unpublished)



Figure 9: Effects of fertilizer rate on the cumulative N_2O emission and dry matter yield in spring and autumn plowing

3.5 Environmental controls on N₂O emissions

3.5.1 The effects of WFPS and soil and air temperatures on N2O emission

 N_2O emissions were very variable in time, fluctuation over three orders of magnitude (Fig. 7). Figure 10 groups N_2O emissions together with WFPS, temperature and precipitation to explore the impact of these variables on N_2O emission dynamics. WFPS fluctuated by up to 0.2 units during summer indicating pronounced drying-rewetting cycles during summer 2010. During this period, N_2O emissions appeared to follow the fluctuations in WFPS, with peaking fluxes in response to increasing WFPS after rainfall. This response was however not uniform. On some occasions there was a delay in N_2O emission response after rising WFPS (e.g. middle of July). In autumn, after harvest, WFPS exceeded 0.85, but the N_2O emissions were low, indicating that other factors (mineral nitrogen, soil temperature) became limiting. Moreover, at the high WFPS values observed in autumn, N_2O flux might have been diffusion limited.

Figure 11 shows the individual flux values measured in all treatments throughout the investigation period, plotted against WFPS values. Even though there was no clear correlation between WFPS and N_2O emission flux, the figure illustrates that high N_2O emission at each fertilization level were confined to a WFPS range between 0.50 and 0.70.

3.5.2 The effects of mineral fertilizer (NO₃-N and NH₄-N) on N₂O emission

Figure 12 shows N₂O emissions together with measured NO₃-N and NH₄-N contents in 0-20cm soil depth in the all treatments. In general, high N₂O emission rates went along with higher mineral N contents during summer. However, there was no clear correlation between N₂O and neither NH₄⁺- nor NO₃⁻-N contents during this period. For instance, the first maximum in N₂O emission recorded in June 2010 occurred at fairly high NO₃⁻-N concentrations (> 30 μ g N g dry soil⁻¹) but a similar N₂O emission peak was observed in the middle of August, when NO₃⁻-N concentrations in 0-20 cm soil had declined to below 10 μ g N g dry soil⁻¹



Figure 10: Temporal dynamics of average N_2O emission, WFPS, daily precipitation, air and soil (-2.5cm) temperature. S: sowing; SP: spring plowing; F: fertilization; AP: autumn plowing; H: harvest.



Figure 11: The relationship between temporal dynamics of average N_2O emission and water filled-pore space (WFPS).



Figure 12: Temporal dynamics of average N_2O emission, NO_3 -N and NH_4 -N contents in all treatments in the investigated period. S: sowing; SP: spring plowing; F: fertilization; AP: autumn plowing; H: harvest.

4. Discussion

This study was conducted to investigate the effects of plowing time, fertilizer level and catch crop on N_2O emission in arable soil in SE Norway. I studied N_2O emission fluxes throughout the vegetation period in 2010 in a long-term field trial with three fertilizer levels (0, 60 and 120 kg N ha⁻¹) and spring versus autumn plowing, organized in a factorial design. Flux rates were measured by closed chamber technique on 17 occasions and extrapolated linearly to the entire snow free period. Since emission rates were found to be very variable in time (Fig. 7), this approach likely missed important flux events (moments of high or low emission flux) and the accumulated N_2O emissions over the entire measurement period have to be considered as a first estimate for N_2O emissions in SE Norwegian cereal cropping systems. However, periodic measurements by manual closed chamber techniques yield valuable information about relative treatment effects on N_2O emission and are the only way to cover multiple treatments in agronomic plot trials. Moreover, most of the data used to estimate the emission factor for N_2O (as a fraction of applied nitrogen) are based on closed chamber measurements (Stehfest and Bouwman 2006) as used here.

4.1 Temporal variability of N₂O emissions

N₂O emissions recorded in 2010 were very variable in time ranging in flux intensity from below 10 to 180 μ g N₂O-N m⁻¹ h⁻¹. Emission peaks were associated with rainfalls on dry soil. Similar emission patterns have been reported previously (Flessa, Dorsch et al. 1995; Dobbie and Smith 2003). They found that N₂O emission rates increased with increasing WPFS in a certain range, while decreasing when soil moisture approached saturation. In the present study, maximum N₂O emission rates were recorded at WFPS values between 0.5 and 0.7 (Fig. 11), whereas N₂O emission rates at WFPS below 0.5 were uniformly lower, independent of fertilizer level. Low N₂O emissions at low WFPS may have been dominated by nitrification which has a much lower N₂O yield than denitrification (Jiang and Bakken 1999; Mørkved, Dörsch et al. 2007). (Dobbie, McTaggart et al. 1999) concluded that nitrification is the main source of N₂O emission at WFPS less than 0.5. Also, at lower soil moisture contents, diffusion of substrate (NH_4^+) to nitrifiers may become rate-limiting, explaining low N₂O emissions during drought. Highest N₂O emission rates were recorded at WFPS values between 0.5 and 0.7, and the maximum values increased with increasing fertilization rate, indicating that the fertilizer effect on cumulative N₂O emission is mainly due to denitrification of added NO_3^- and nitrified NH_4^+ (see below). Low emission rates were

observed at WFPS values above 0.7 which is consistent with the idea that moisture saturation of soils slows down the diffusion of N₂O out of the soil, thereby increasing the change for N₂O to be reduced all the way to N₂ (Bateman and Baggs 2005). However, WFPS was highest in autumn after soil temperatures had fallen to values between 0 and 5°C (with occasional freezing during night) and NO₃⁻ contents were low (< 5 μ g N g dw⁻¹), both of which would be expected to limit microbial activity in general and denitrification in particular.

Together, this suggests that denitrification was the dominant source for peak N_2O emission rates observed during summer. However, due to the interaction of different factors (NO₃⁻ availability or temperature) there was no clear relationship between WFPS and N_2O emission rate (many low rates were observed in this range, Fig. 11). In addition, some of the highest N_2O emission rates at WFPS between 0.5 and 0.7 were measured right after heavy rainfall on dry soil. Rewetting of dry soil has been shown to produce high pulses of N_2O emissions (K im, Vargas et al. 2011), which level down some time after the rewetting event. This means that in soils with frequent drying-rewetting as observed in my study, no linear relationship between WFPS and N_2O emission rate can be expected. As seen from Fig. 11, there was no clear difference in the pattern of N_2O as a function of WFPS between spring and autumn plowed plots, except for the highest fertilization rates which showed two emissions peaks which were higher in the autumn plowed than the spring plowed plots.

Fertilization rate did not have any clear effect on the temporal dynamics of N_2O emissions in my study. All treatments followed the same temporal pattern, despite some difference in mineral N contents (Fig. 12), particularly between the 0N and the fertilized plots. This means that the temporal dynamics were ruled by other factors such as fluctuating WFPS driven by drying and rewetting.

As can be seen in figure 10, soil temperature had no straight forward effect on N₂O emissions. Relatively high emissions were recorded early in spring when soils were close to the freezing point, whereas low emissions were found in the beginning of July when soil temperatures reached their maximum (25° C). High emissions after spring thaw have been reported earlier (Flessa, Dorsch et al. 1995; Teepe, Brumme et al. 2001; Dorsch, Palojarvi et al. 2004) and have been attributed to frost induced release of protected organic matter. Moreover, low soil temperatures after thawing have been shown to result in higher N₂O/(N₂O+N₂) ratios in some soils (Holtan-Hartwig, Dörsch et al. 2002; Dörsch and Bakken 2004). On the other hand, low

during summer which leads to high soil aeration thereby restricting the anoxic volume in the soil in which denitrification occurs. WFPS values as low as 0.45 as recorded in my study may in addition limit microbial activity (Iovieno and Baath 2008). Drying rewetting cycles may lead to N_2O emission pulses (Rudaz, Davidson et al. 1991; Ruser, Flessa et al. 2006). Together, this explains why N_2O showed no ordinary temperature response in my study.

In summary, no single factor could explain the observed seasonal pattern of N_2O emissions (Fig. 7). Factors such as soil temperature, WFPS, mineral nitrogen and others likely interacted and different factors may have been dominant in controlling N_2O emissions at different time points. For example, after fertilization, there were enough substrates for nitrification and denitrification, so WFPS and temperature controlled the N_2O flux; during summer, WFPS was periodically high (after rain falls) and soil were warm (Fig. 4), which resulted in conditions conductive to high N_2O emission from denitrification despite the low mineral nitrogen concentration (Fig. 6). After harvest, in the late autumn, in contrast, soil temperature seemed to limit N_2O emission fluxes in addition to low mineral N contents.

4.2 Treatment Effects on N₂O emission

4.2.1 Timing of plowing

Before spring management (plowing, sawing, fertilization), all chamber bases had to be removed and could not be reinstalled before end of May. Therefore, no flux measurements could be carried out directly after plowing and the effect of incorporation of the crop residues on N_2O emissions could not be investigated. Plowing exerts a strong mechanical perturbation on the soil which could be expected to result in a pronounced N_2O emission response. However, only few studies have examined the direct effects of soil tillage right after mechanical disturbance. High N_2O fluxes have been reported right after seed bed preparation (van der Weerden, Sherlock et al. 2000). One study has examined the instantaneous effects of cultivation (Kessavalou, Mosier et al. 1998), showing that N_2O concentrations above the soil (40 cm) increased by 9–31% within 1 min after tillage but had decreased to background concentrations within 2 h.

In my study, I found adverse effects of spring versus autumn plowing throughout the investigation period; N_2O emissions tended to be higher in spring plowed plots before plowing (April 2010) irrespective of fertilizer level in the previous year (plots were not fertilized yet). The possible reasons for this may be as follows: firstly, the spring plowing

treatment retained more easily available organic matter throughout winter fuelling N₂O emissions after spring thaw, while crop residues in the autumn plow treatment may have been mineralized and lost throughout the winter after being incorporated earlier in the previous autumn, so that less organic material was available after spring thaw to fuel nitrification and denitrification (Mørkved, Dörsch et al. 2006). Secondly, the autumn plowed soil might have had a greater porosity and possibly more macro-pores as compared with the denser spring plowing plots, allowing for better aeration condition thus reducing denitrification (Schurgers, Dorsch et al. 2006). Thirdly, crop residues were concentrated on the soil surface in the not yet plowed spring plowing treatment, possibly hindering O₂ from entering the soil by creating a zone of high respiratory O₂ consumption. No visible differences in mineral nitrogen had been lost or was immobilized during winter irrespective of plowing treatment, explaining that higher emissions in the not yet plowed spring treatment possibly more irrespective of plowing treatment, explaining that higher emissions in the not yet plowed spring treatment on mineral N status.

After spring plowing, the effect of plowing time seemed to be reversed. Now, plots plowed in autumn of the previous year showed a tendency for higher N_2O emissions than the recently spring plowed plots, particularly during rainfall-driven emission peaks in the high fertilization plots (Fig. 7). Again, changes in soil structure could be an explanation for this; spring plowing likely increased drainage and aeration thereby lowering the anoxic volume in which denitrification could occur (Philippe). This interpretation is supported by the observation that the difference in N_2O emissions between the two plowing treatments increased with fertilizer amount, suggesting that soil structure may have been the dominating factor in the presence of equal amounts of NO_3^- (Fig. 6).

After autumn plowing in 2010, there was no difference in N_2O emission between the plowing treatments. Due to low temperatures and low mineral N concentrations, N_2O emission fluxes were generally low (less than 20 µg N_2O -N m⁻² h⁻¹; Fig. 7). Obviously, the low temperature prevented instant mineralization of incorporated crop residues in the autumn plow treatment, explaining why no N_2O emission peak was observed after plowing.

In summary, timing of plowing had some effect on N_2O emissions throughout the year, but the effects were adverse and cancelled each other out, so that there was no significant effect on overall cumulative emission (Tab. 3).

4.2.2 Fertilizations rate

Soils rarely supply sufficient N for the crops to achieve their potential yield. Therefore, providing mineral N fertilizers has been the significant factor in sustaining crop productivity. Increased mineral N fertilization, however, provides substrates for soil nitrifying and denitrifying bacteria (NH₄ and NO₃), which may increase N_2O emission from nitrification and denitrification.

In my study, N₂O emission increased near-linearly with fertilization rate irrespective of plowing regime (Fig. 8). Linear relationships between fertilizer rate and cumulative N₂O emission have been found previously (Dobbie and Smith, 2003) which has given rise to the emission factor concept by which annual N₂O emissions are estimated as a constant fraction of applied fertilizer N (IPCC, 2007). The emission factors found on the present study were 0.73% and 0.96% for autumn plowing and spring plowing, respectively. This is very close to Bouwman's (1996) emission factor of 1.25% and IPCCs current Tier 1 factor of 1.0% (IPCC, 2007), and well within the great uncertainty range (0.3% to 3%).

However, as can be seen from Fig. 8, the slope of the regression between N₂O emission and N input was depending highly on "background emissions" in the N0 treatment. Background emissions were 0.81 and 0.85 kg N₂O-N ha⁻¹ period⁻¹ (220 days), for spring and autumn plowing respectively, which is lower than the default value given by IPCC (2007) for annual emissions from arable soils. On the other hand, background emission seemed to be higher than what could have been expected from back-extrapolating the emission response from 60 and 120 kg N addition (Fig.8). The relative higher expected emission potential of unfertilized soil may be due to exceptionally low yield (and high occurrence of weeds), possibly favoring microbial N turnover relative to plant uptake in the N0 treatment. It should be noted that the present study was conducted in a long-term experimental field trail in which treatments (such as N rate) have been applied to the same plots for 30 yrs. From this, one would expect that the N0 treatment was depleted in organic matter because of consistently low return of crop residues (due to low yields), which would suggest a lower background emission than that in IPCC Tier 1.

 N_2O emission intensity appeared to relate to the yield curve in that N_2O emission became relatively higher when the yield response started to decrease (Fig 9.). This indicates that N_2O emissions were controlled by the competition with plants for available N, suggesting that N_2O emissions per unit harvest could be reduced by increasing nitrogen use efficiency. However, the cut-off value (highest yield with lowest N_2O emissions) appeared to be very low (70-80 kg N ha⁻¹ yr⁻¹) as compared to other studies (Millar, Robertson et al. 2010; Liu, Li et al. 2011), which limits this conclusion to the long term field trial. Possible reasons are as follows: identical cultivation, no crop rotation, other nutrition factors are limiting it, such as, phosphorous, organic carbon and so on.

4.2.3 Effect of catch crop on N₂O emission

The effect of catch crop was studied in only the highest fertilizer level (120N, SP). Ryegrass was chosen over leguminous catch crops studied in the same trail, in order to not confound the fertilizer N_2O response with additional nitrogen brought into the soil by N-fixation. Over entire investigation period, the ryegrass treatment emitted 30 % less N_2O as compared with the same treatment without. Ryegrass reduced N_2O emissions particularly during times of peak emissions (after drying-rewetting, 16th of June and 14th of August, Fig. 7), suggesting that grass crops can lower peak emission by binding available mineral nitrogen. However, no effect of catch crop was seen on mineral N contents. In contrary, NO_3^- and NH_4^+ values were particularly high in early summer after plowing without giving rise to high N_2O emissions. This suggests that growing catch crops might play a role especially during drying rewetting by having an active root layer in place competing more efficiently for available nitrogen when the soil rewets. After spring thaw, before fertilization, N_2O emissions in the catch crop treatment were very high probably because there was more available fresh plant material as compared with the stubbles on the non-plowed treatment without catch crop.

5. Conclusions

The flux measurements performed in my study covered a whole growing period of spring wheat. The results showed that N_2O emission flux is very variable in time and controlled by several factors such as drying-rewetting, temperature, time of plowing and fertilizer level. N_2O emissions responded almost linearly to fertilizer rate, if cumulate over the entire investigation period and this response was in the range reported by IPCC (2007). Time of plowing did not have any significant effect on total N_2O emissions, because of temporarily inverse effects which cancelled each out. N_2O emissions appeared to increase with decreasing yield response within the studied range of fertilization rates, suggesting that increasing N use efficiency can be an interesting tool to reduce N_2O emissions per unit food produced.

6. References

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