



Swedish University of Agricultural Sciences
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ABSTRACT

Because of the increasing concentration of methane (CH₄) and nitrous oxide (N₂O) in the atmosphere, there is an increasing concern about the emissions of these two gases from agricultural land. Both CH₄ and N₂O are major contributors to the greenhouse effect and agricultural lands constitute a large contributor of the anthropogenic load of these gases. Agricultural land is also something that will always be needed, so a long term view towards sustainability is needed. *In situ* measurements of CH₄ and N₂O emissions were conducted on a long-term fertilizer experiment in Uppsala. The aim was to compare the emissions from the different fertilizing regimes. The fertilizers investigated were ammonium sulphate ((NH₄)₂SO₄), manure and sewage sludge in comparison to unfertilized plots. The emissions were related to the differences in soil properties and weather conditions at the site at the time of sampling. The emission measurements were conducted on two occasions. Negative CH₄ emissions indicated that the soils were net sinks and there was no difference between treatments and time points. The two sampling occasions showed slightly different results regarding N₂O with higher emissions in February, but there were no statistically significant differences. In April 2008 the sewage sludge amended soil had the highest emissions while the results from February 2009 showed that the manure fertilized soil had highest emissions.

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INTRODUCTION

Methane (CH₄) and Nitrous oxide (N₂O) are the most important greenhouse gases (GHG) apart from carbon dioxide. Studies of ancient ice cores have shown that an unprecedented significant CH₄ concentration increase started around 150 years ago (Rasmussen et al 1984; Jiule et al 2010). Methane concentrations in the atmosphere have increased with over 100 % since pre-industrial times from around 700 ppb to above 1700 ppb in modern times (Etheridge et al. 1992). The N₂O concentration in the atmosphere increased approximately with around 50% from pre-industrial times to 1990 (Houghton et al. 1990). The last two decades have shown a nearly linear increase of 0.26% N₂O concentration per year and N₂O now account for 7% of atmospheric radiative forcing compared to 18 % of radiative forcing for CH₄ (Forster et al. 2007). The Intergovernmental panel on climate change (IPCC) estimate that the anthropogenic load of N₂O from agriculture is between 2.0-5.8 mt per year and that the total agricultural load of CH₄ is between 175-350 mt CH₄ (Forster et al 2007).

Arable soils are the main source of N₂O in the agricultural sector, whereas ruminants are the major contributor of CH₄. However, soils also produce CH₄, although most upland soils are sinks of CH₄. The process of CH₄ and N₂O production in soil is dependent upon various factors, mainly oxygen (O), soil organic matter (SOM), pH and temperature. The question of how microbial activity and gas fluxes responds to different fertilizing regimes have been assessed in various reports (Vermoesen, A. et al. 1996; Enwall et al. 2005; Hallin et al. 2006; Jones et al. 2007; Schils et al. 2007), of these only the two latter have made in situ measurements of GHG emissions.

The aim in this study was to compare emissions of CH₄ and N₂O from soils subjected to different fertilizing regimes. The hypothesis was that there is a difference in emissions of N₂O and CH₄ in soils fertilized with different fertilizers. N₂O and CH₄ fluxes were measured from unfertilized soil and soils fertilized with (NH₄)₂SO₄, manure and sewage sludge. The plots have been fertilized in this manner since 1956. Hence, the measurements show the long-term effect of different fertilizer regimes on GHG emissions.

CH₄ production and consumption in soils

CH₄ is produced in anaerobic conditions during decomposition of SOM by a guild of archaea called methanogens. When the soil is aerobic the opposite process occurs and methane is oxidized to CO₂ by methanotrophic bacteria. Hence, CH₄ production is highly influenced by soil water filled pore space (WFPS). Areas with high precipitation or dense soils produce more CH₄ and wetlands are considered to be the main natural source of atmospheric CH₄, (Hütsch 2001; table 1).

N₂O production and consumption in soils

The production of N₂O in soil is due to two major processes: nitrification and denitrification. Nitrification occurs under aerobic conditions. It is a two-step process. First ammonia NH₃ is oxidized to nitrite (NO₂⁻) via the intermediate hydroxylamine (NH₂OH), which makes it possible for N₂O to be released. The first step is conducted by ammonia-oxidizing bacteria (AOB) and ammonia oxidizing archaea (AOA). The second step when NO₂⁻ is further oxidized to nitrate NO₃⁻ is made nitrite-oxidizing bacteria (NOB). There are no microbes capable of carrying out the whole process of nitrification. Denitrification is an anaerobic process in which N₂O is an intermediate when NO₃⁻ is reduced to N₂ by facultative aerobes. The amount of N₂O that is accumulated from this process depends on the gaseous movement in the soil and the availability of other electron acceptors. There is also fungal denitrification that only leads to N₂O since most fungi lacks N₂O-reductase enzyme (Flecharde et al. 2007). Denitrification seems to be the most important process for the development of N₂O since poorly drained soils give higher emissions than well-drained soils (Bouwman et al. 2002), although denitrification can be a sink for N₂O.

Denitrification is dependent upon soil carbon availability and higher emissions have been recorded when crop residues have been incorporated into soil (Shelton et al 2000). Smaller amounts of N₂O may also be produced by other biochemical oxidation and reduction reactions such as N₂-fixation. Abiotic production of N₂O is also possible through chemodenitrification (Morkved et al. 2007).

Table 1. Estimated amounts of CH₄ from different sources or sinks on a global scale. Source: Hütsch 2001 (from UNEP, 1993).

Sources/Sinks	Best estimates	Range
	(Tg CH₄ per year)	(Tg CH₄ per year)
Sources:	515	
<i>Natural</i>	155	
Wetlands	115	(100-200)
Termites	20	(10-50)
Oceans	10	(5-20)
Fresh water	5	(1-25)
CH ₄ hydrate	5	(0-5)
<i>Anthropogenic</i>	360	
Coal mining and natural gas	100	(70-120)
Rice paddies	60	(20-150)
Enteric fermentation	80	(65-100)
Animal wastes	25	(20-30)
Domestic sewage treatment	25	?
Landfills	30	(20-70)
Biomass burning	40	(20-80)
Sinks:	500	
<i>Atmospheric</i>	470	(420-520)
<i>Removal by soils</i>	30	(15-45)
Atmospheric increase	32	(28-37)

METHODS

Site description

Measurements of CH₄ and N₂O were made on a long-term soil fertility experiment that was initiated in year 1956 (Kirchmann 1994). The soil is described as a Eutric cambisol according to the FAO-system. It is a loamy clay with 37 % clay and an average SOM content of 2.3 %. The experiment was divided into four blocks with treatments in plots of 2 by 2 meter separated by impregnated wooden frames. The wooden frames were merged 50 cm into the ground and placed 20 cm above ground so that soil movement between plots can be neglected. One of the

four blocks does not have randomized plots and hence is omitted from this study. All plots have been cultivated with maize since year 2000. Before that a common six-year crop rotation was used. The whole experiment has been managed and harvested by hand. In this study the B, D, J and O plots with three replicates were investigated. B was an unfertilized control plot with crop, D was fertilized with NH_4SO_4 , J was fertilized with manure and O was fertilized with sewage sludge. All treatments received 22 kg of phosphorous and 38 kg potassium ha^{-1} year $^{-1}$. The mineral fertilizers were applied in spring to the amount of 80 kg ha^{-1} year $^{-1}$. Organic fertilizers were applied every second year in autumn to the amount of 8 tons ha^{-1} .

Soil properties and climatic conditions

The soil properties pH, nitrogen content and carbon content have been measured yearly since the beginning of the field experiment in 1956. Weather data was obtained from a climate station approximately 4 km away from the site. Department of Earth Science and Meteorology at Uppsala University are responsible for collecting the data and publishing the graphs (<http://big.met.uu.se/default.aspx?pageid=31&lan=0>). For calculations of emissions, the air temperature was measured at ground level on site at each sampling occasion.

Gas sampling

The fluxes were measured at each replicate plot at two occasions: the 24th of April 2008 and the 25th and 26th of February 2009 at the same time of day. For measuring gas emissions, a static manual stainless steel chambers method was used. The chambers, covering 0.037 m^2 and with the volume of 7.4 l, were merged into the soil and luted with suspended soil. The chambers were equipped with butyl rubber septa through which gas was sampled with a double-needle. Five gas samples were taken during two hours, one every half hour, by circulating the air for 30 seconds between the chamber and a glass vial with butyl rubber septa.

Analysis of CH_4 and N_2O

For the gas analysis, a chromatograph equipped with an electron capture detector and a flame ionization detector was used to analyze CH_4 and N_2O concentration in the vials. The gas fluxes were calculated from the time versus concentration data. All calculations were made with Excel 2007.

Calculations of emissions

The data retrieved from the chromatograph in parts per million volumes (ppmV) were converted to moles using the ideal gas law.

$$pV = nRT$$

The law expressed in words is the atmospheric pressure (P), in Pascal, times the volume (V), in cubic meter, equals moles (n) times the universal gas constant (R) times the temperature (T), in Kelvin. After dividing the gas exchange rates with the bottom area of the chamber, moles were then multiplied with the molarities of the gas molecule and extrapolated to hectare.

RESULTS

Soil properties

The pH has remained rather stable above 6 in the manure and control treatments in contrast to the pH in the $(\text{NH}_4)_2\text{SO}_4$ and sewage sludge treated soils which have declined to around 4 and 5 respectively (Fig 1). The carbon content of the top soil substantially increased in the sewage sludge and manure amended soils while the $(\text{NH}_4)_2\text{SO}_4$ and control treatment decreased in carbon content (Fig 2). The soil nitrogen content in the sewage sludge treatment exceeded all

other treatments followed by the manure treatment and the $(\text{NH}_4)_2\text{SO}_4$ and control treatment that were equally low in nitrogen content (Fig 3). According to the results from 2007, the carbon nitrogen ratio (C:N) of B, D, J and O was 9.9; 8.5; 10.55 and 9.93 respectively.

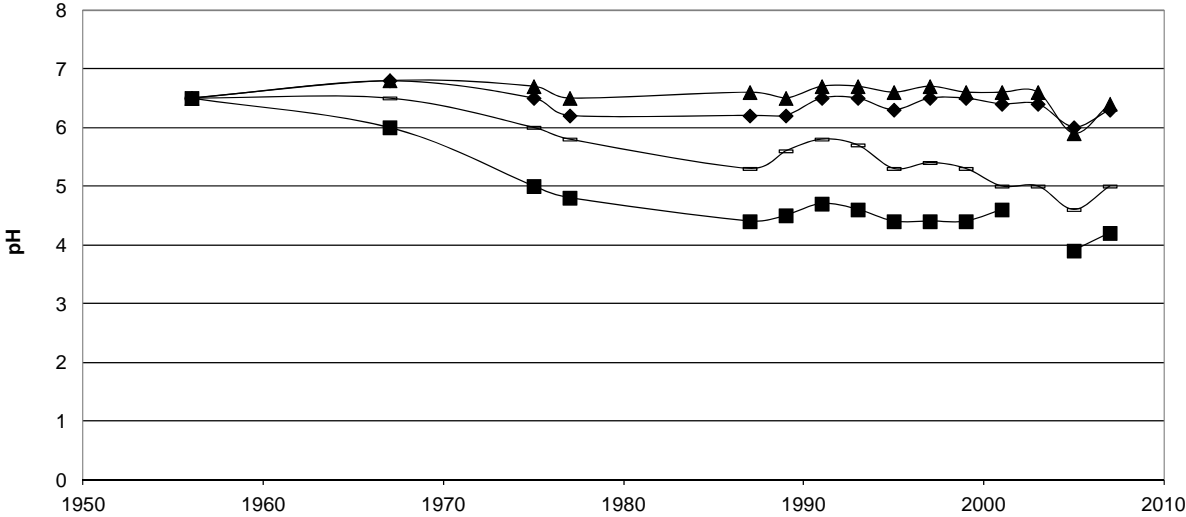


Figure 1. pH-H₂O in soils under different fertilizer regimes at *The Ultuna long-term soil organic matter experiment* since year 1956. ▲:Manure, ◆:Control, —:Sewage sludge, ■: $(\text{NH}_4)_2\text{SO}_4$.

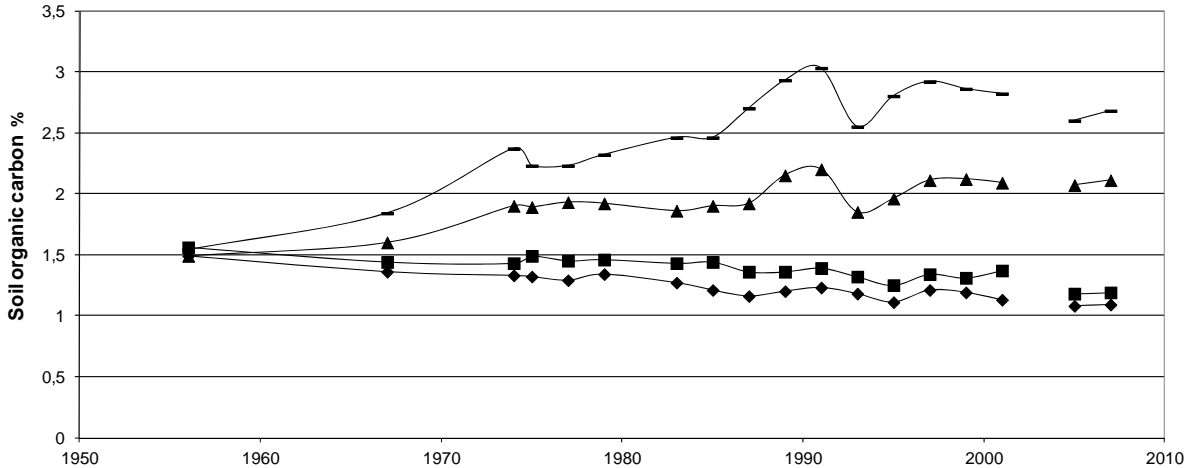


Figure 2. Carbon content percentage in the top 20 cm layer of soils under different fertilizer regimes at *The Ultuna long-term soil organic matter experiment* since year 1956. ▲:Manure, ◆:Control, —: Sewage sludge, ■: $(\text{NH}_4)_2\text{SO}_4$.

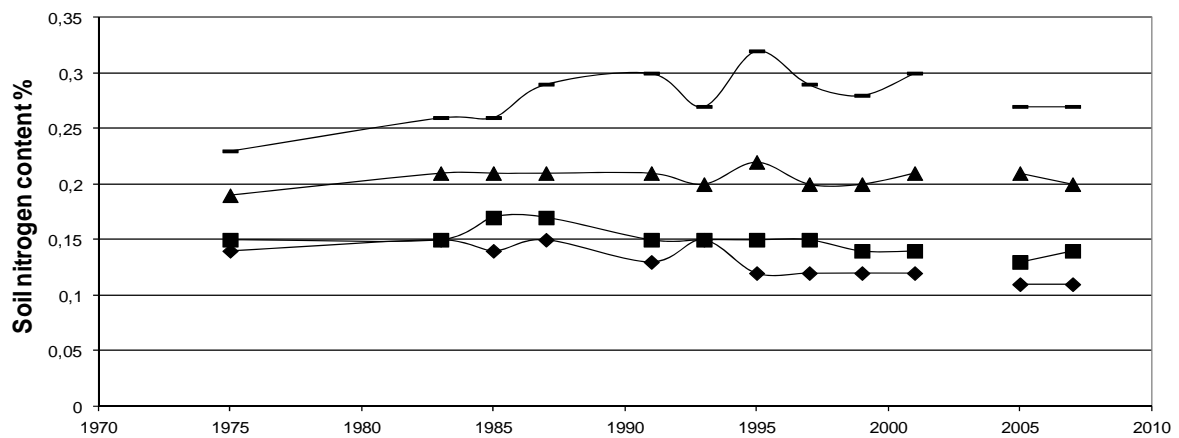


Figure 3. Nitrogen content percentage in the top 20 cm layer of soils under different fertilizer regimes at *The Ultuna long-term soil organic matter experiment* since year 1975. ▲:Manure, ◆:Control, — :Sewage sludge, ■: $(\text{NH}_4)_2\text{SO}_4$.

Weather conditions

The air temperature at ground level was 12-17 °C in April 2008 and 4.9-5.2 °C in February 2009. Figure 4 shows the variations in ground temperatures during the months of sampling. In April 2008 there were daily variations in the top layer with soil temperatures constantly rising after the 9th. In February 2009, the top soil temperature was constantly below zero. Around the time of the second sampling, there was some precipitation in the form of rain where as for the first sampling time in April 2008, there had been ten days without rainfall (Fig 5). The mean relative humidity, i.e. percentage of air moisture in relation to its maximum carrying capacity at actual air temperature, for the sampling months is displayed in figure 7. When the first measures were conducted it was around 50% and at the second occasion it was above 90%.

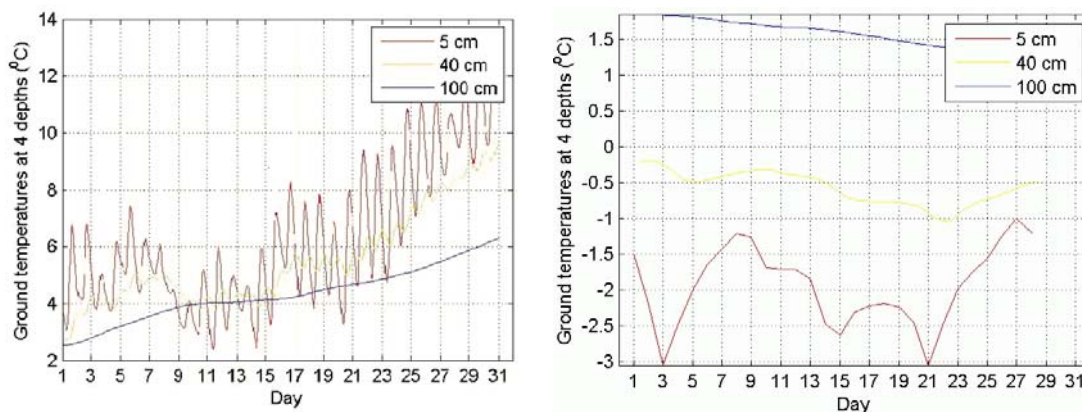


Figure 4. Soil temperatures at different depths. Left: April 2008. Right: February 2009 Source: Department of Earth Science and Meteorology, Uppsala University.

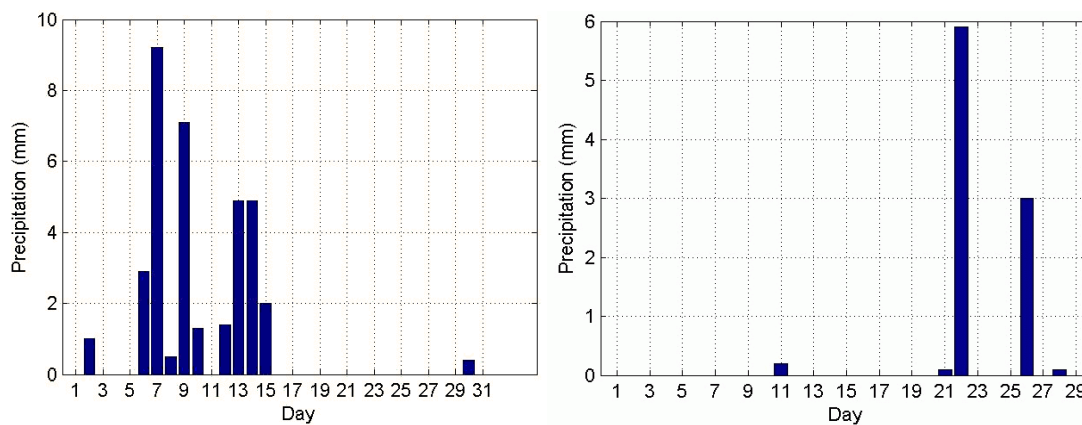


Figure 5. Precipitation per square meter. Left: April 2008. Right: February 2009. Source: Department of Earth Science and Meteorology, Uppsala University.

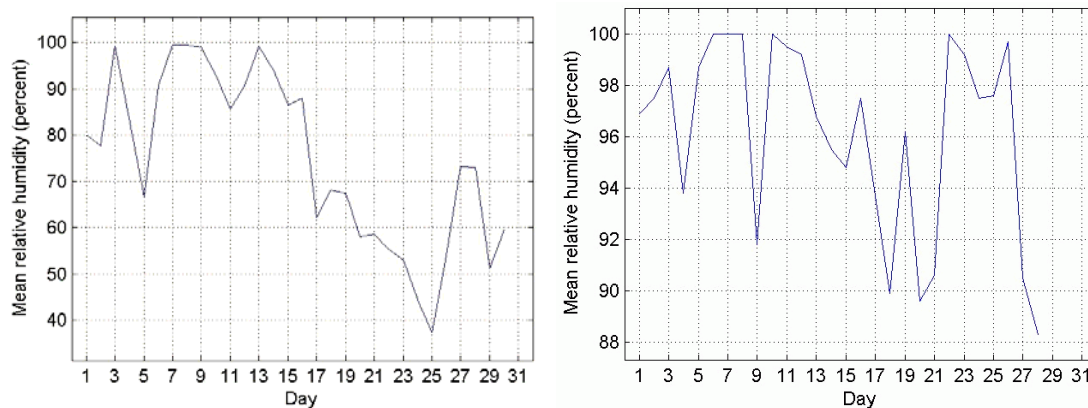


Figure 6. Mean relative humidity. Left: April 2008. Right: February 2009. Source: Department of Earth Science and Meteorology, Uppsala University.

CH₄ and N₂O emissions

In April 2008 only the NH₄SO₄-fertilized plot had a positive flux regarding methane, whereas the other treatments were net sinks (Table 2). In February 2009 there were only negative methane fluxes if any. By contrast, all soils emitted N₂O and the highest emissions were determined in February, although the difference was not statistically significant. Plots amended with sewage sludge or (NH₄)₂SO₄ displayed the highest emissions in April, whereas the manure treatment showed the highest N₂O emissions in February.

Table 2. Net CH₄ and N₂O-N fluxes in fertilized soils from *The ultuna long-term soil organic matter experiment* (n=3 ±SD). B: Control. J: Sewage sludge. O: Manure. D: (NH₄)₂SO₄

Treatment	CH ₄ (g ha ⁻¹ h ⁻¹)		N ₂ O-N(g ha ⁻¹ h ⁻¹)	
	April 2008	February 2009	April 2008	February 2009
B	-0.05±0.066	-0.03±0.027	0.02±0.042	0.09±0.164
J	-0.03±0.054	0±0	0.01±0.020	0.53±0.914
O	-0.27±0.355	-0.05±0.040	0.16±0.144	0.29±0.510
D	0.15±0.206	0±0	0.09±0.101	0.23±0.214

Discussion

The negative fluxes of CH₄ in this investigation indicate that oxidation of atmospheric CH₄ is occurring at the site. It is common for upland soils to be annual sinks for CH₄ (Regina et al. 2006; Castro et al. 1995). The strength of agricultural soils as sink or source of CH₄ depends upon its porosity or water filled pore space (WFPS) according to Regina et al (2006). They studied various soils in Finland and found that the CH₄ oxidation decreased in the order: loamy sand > well drained peat > clay > poorly drained peat and that the total agricultural area of Finland constitutes an annual sink for CH₄ with -19 Gg of CO₂ equivalents. Bowden et al (1998) reported a CH₄ consumption maximum at 60% WFPS and suggested that consumption decreases at higher WFPS due to diffusion limitation and decreases at lower WFPS because drought negatively affects the CH₄ oxidizing bacteria. The highest CH₄ oxidation observed was in the sewage sludge treatment. Hütsch (2001) reported that long-term application of nitrogen reduced CH₄ oxidizing capacity of soil but when nitrogen was applied in the form of manure or slurry this negative effect was reduced, suggesting that it might be due to the increased microbial community size following the increased SOM content. The (NH₄)₂SO₄ treatment which had the lowest pH was the only treatment with a positive although small CH₄ flux. The reason could be that the methanotrophs are more sensitive to low pH than methanogens (Dunfield 1993). Temperature has been found to also affect CH₄ consumption at certain levels. Castro et al (1995) reported that low temperatures had a negative effect on CH₄ consumption between -5^o C and 10^o C but above 10^o C there was no longer any correlation between temperature and CH₄ consumption. Instead WFPS and soil fertility affected CH₄ consumption. The same authors also found that higher concentrations of NH₄ and NO₃ decreased CH₄ consumption and suggested the reason to be that the microbial community had shifted from the CH₄ oxidizing bacteria to AOB. Hence, the result of lower CH₄ consumption in February than April suggests that a shift towards CH₄ production rather than consumption in the (NH₄)₂SO₄ fertilizer treatment is plausible. This also indicates that (NH₄)₂SO₄ treatment should lead to higher N₂O production however there are many other factors to consider.

An increased concentration of N₂O compared to atmosphere was detected, although the N₂O fluxes seem very low compared to what have been reported by others. For example, Ruser et al. (2005) recorded a rate of approximately 1 g m⁻²h⁻¹ in soil with 90% WFPS. Even though emissions were low some trends in relation to soil treatment and sampling occasion were observed. The fluxes tended to be higher in February 2009 than April 2008 across all treatments. This is rather perplexing since the soil was frozen in February and the soil temperature had been below zero for weeks before measurements were conducted. One would expect higher emissions when the soil starts to thaw since it has been shown in earlier studies

that freeze and thaw cycles increases N₂O emissions (Dusenbury et al. 2008). Maybe the temperature data used for the analysis was not sufficient. It showed that the soil was frozen at 5 cm depth but there could have been freeze and thaw cycles going on locally or at shallower depths. The highest overall N₂O emissions were from plots fertilized with manure, which might be explained by the fact that the manure treated plots had rather high pH and a low C:N ratio. Huang et al. (2004) has stated that N₂O production is negatively correlated with the C:N ratio. The difference in C:N ratio between the four treatments were small and they all have low C:N ratio so other factors such as dissolved organic carbon (DOC) could potentially be important. Cuhel et al (2010) reported that low pH increased the denitrification end product-ratio N₂O/(N₂O+N₂). Others have reported that denitrification is reduced by low pH (Baggs et al 2010), meaning that N₂O emissions could decrease with decreasing pH even if the N₂O/(N₂O+N₂) ratio would increase. Nitrification has been reported to have both increased and reduced activity at low pH and the microbial community is thought to be the differing factor. However, denitrification is thought to become the dominant N₂O production process from low pH.

Since (NH₄)₂SO₄ treatment N₂O emissions rates from April 2008 seem implausible and are even below background level and (NH₄)₂SO₄ N₂O emission rates from February 2009 were highest of all treatments, but with high standard deviation, it is hard to tell which trend is closest to reality. Some errors might have occurred during sampling such as problems with the pump or leaking gas flux chambers. Earlier studies have shown that CH₄ and N₂O emissions fluctuate both on a daily and a yearly basis. Hence, this study could not be considered as more than a pilot study since there were only samples from two occasions and “hot moments” were likely not captured. Flux chambers are considered good for measuring gas fluxes from soil in field experiments but it would be better to fix them and measure continuously over the season with automated chambers. Not only for better security against leakage but also to retrieve more reliable data. Liu et al (2011) used an automatic measuring apparatus which allowed them to receive eight samples per day with simultaneous temperature measurements and the method was used for two years before the data was analyzed.

CONCLUSIONS

It is difficult to conclude anything from the results since there are no statistical differences. More studies must be made to assess the question of how to mitigate high emissions since it is a complex matter. Analysis of the important factors for CH₄ and N₂O emissions and when these factors occur is far from being understood. It is of great importance that the relationships between soil type, temperature, nutrients and water content will be investigated in order to mitigate GHG emissions from agricultural lands.

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APPENDIX

Concentration vs. time figures from April 2008, to demonstrate this part of the work progress, with detected levels of CH₄ and N₂O from chromatography. Samples are displayed in chronological order from chamber application.

