



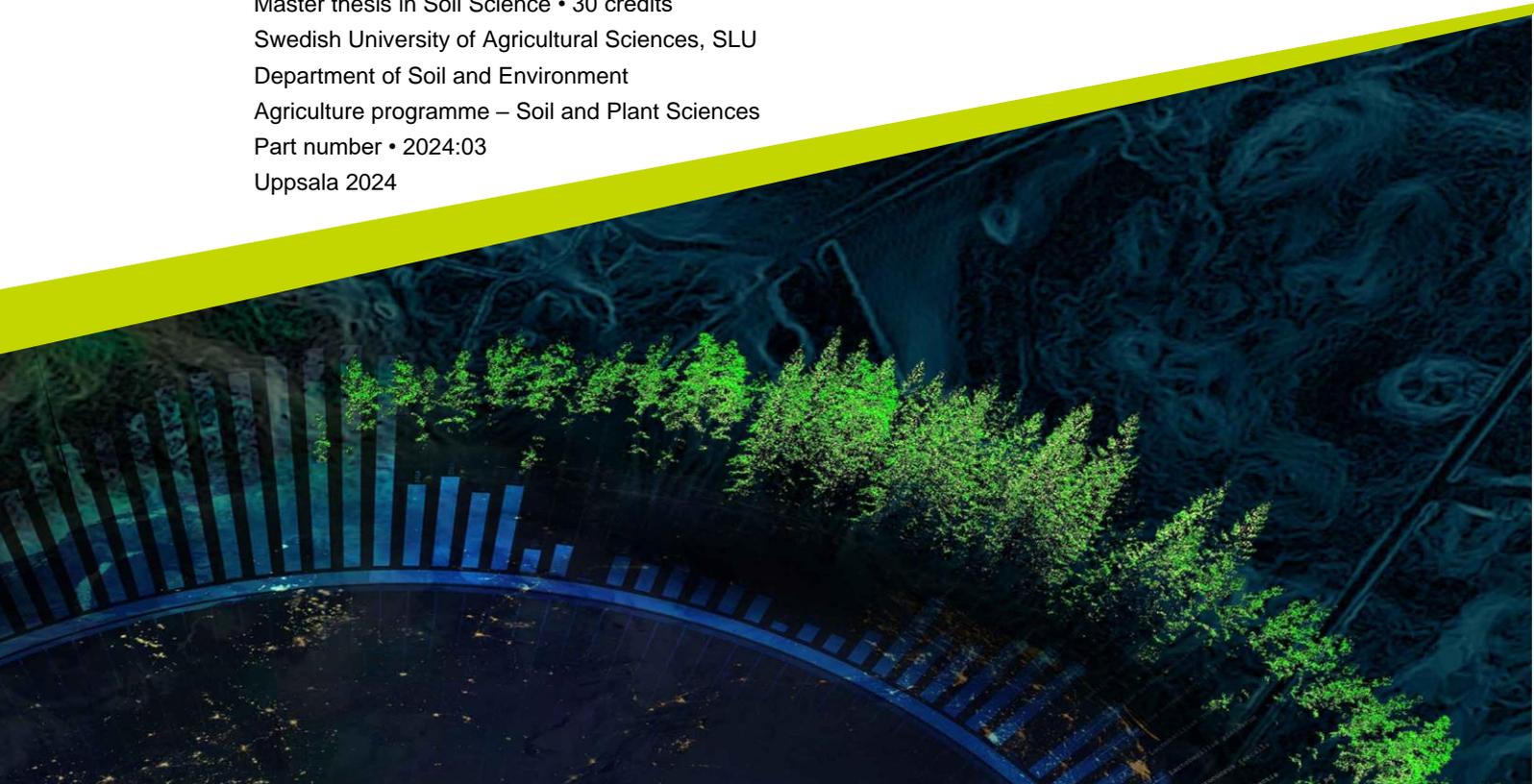
# Greenhouse gas emissions from peat soil thawing in spring

A comparison between fertilized and unfertilized soil

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Fanny Otterlin Karlsson

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Swedish University of Agricultural Sciences, SLU  
Department of Soil and Environment  
Agriculture programme – Soil and Plant Sciences  
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# Greenhouse gas emissions from peat soil thawing in spring. A comparison between fertilized and unfertilized soil.

*Växthusgasutsläpp från torvjord som tinar på våren. En jämförelse mellan gödslad och ogödslad jord.*

Fanny Otterlin Karlsson

**Supervisor:** Örjan Berglund, SLU, Department of Soil and Environment  
**Assistant supervisor:** Sabine Jordan, SLU, Department of Soil and Environment  
**Examiner:** Eveline Krab, SLU, Department of Soil and Environment

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**Swedish University of Agricultural Sciences**  
Faculty of Natural Resources and Agricultural Sciences  
Department of Soil and Environment



## Abstract

Peat soils drained for agriculture and forestry contribute to a significant amount of greenhouse gas emissions. Nitrous oxide is a greenhouse gas with high warming potential and agriculture in general accounts for about 70 % of nitrous oxide emissions. Much of the nitrous oxide emissions from soils occur during short periods of high emission peaks when conditions are favourable. For some soils, one of the most important events regarding nitrous oxide is spring thaw emissions, which is when most of the gas is released. Winter events, such as the spring thaw, are likely to change if the winter becomes warmer in the future, which in turn could affect the emissions. The fertilization rate might also affect the emission rate as substrate availability can affect the denitrifying organisms. Carbon dioxide contributes to the largest climate-warming potential from cultivated organic soils, so its emission trends are also interesting to study in freezing and thawing events.

This study aimed to investigate the impact of autumn fertilization on carbon dioxide and nitrous oxide emissions in the spring, and further to see if certain soil properties could be connected to higher emissions. Measurements of the two treatments (fertilized and unfertilized) were performed in a field experiment outside of Uppsala, combined with a laboratory study with soil samples from the same site. Several freezing and thawing cycles were performed on soil samples in the laboratory.

The results of the field measurement showed a large increase in emissions of both gases in late spring. There was no significant difference between the treatments for any of the gases, albeit the unfertilized samples showed a tendency of a higher average nitrous oxide emission level compared to the fertilized ones. In the laboratory experiment, the fertilized samples had significantly higher nitrous oxide emissions compared to the unfertilized samples in the first freezing and thawing cycle. There was no significant difference in the other cycles or between treatments of carbon dioxide emissions. Soil temperature in both field and laboratory experiments had a positive correlation with gas emissions, indicating that increasing soil temperature leads to higher greenhouse gas emissions. Soil water content did not correlate with the emissions, but volumetric water content was high in the soil samples, which indicates that the water content was within optimal range for denitrification.

This study does not provide an unequivocal result on whether fertilization increases or decreases nitrous oxide emissions. There is uncertainty about the conflicting results between treatments from the field and laboratory measurement, but nitrate leaching may be a reason for the lower nitrous oxide emissions from the field, due to late autumn fertilization. A warmer climate may result in more freezing and thawing cycles in the future, several cycles were not visible in the field measurement, but by using a higher frequency measurement method could it be studied more closely in the future.

*Keywords:* agricultural soil, carbon dioxide, freeze-thaw cycles, nitrous oxide, soil temperature, water content



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## Abbreviations

CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon dioxide
FTC	Freeze-thaw cycle
GHG	Greenhouse gas
GWP	Global warming potential
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium
NO <sub>3</sub> <sup>-</sup>	Nitrate
N <sub>2</sub>	Dinitrogen
N <sub>2</sub> O	Nitrous oxide
SOC	Soil organic content
VWC	Volumetric water content
WFPS	Water-filled pore space

# 1. Introduction

Peat soils cover about 2 – 3 % of the ice-free surface of the earth (Mokma 2005). Peat is formed when carbon inputs exceed carbon outputs (Page & Baird 2016), meaning plant degradation is inhibited and instead peat is accumulated. The soil is found in all climate zones but is most common in the Northern Hemisphere in areas with boreal and temperate climates (Mokma 2005; Xu et al. 2018). In these locations, annual precipitation will typically exceed annual evapotranspiration, resulting in a surplus of water. Water availability is important when organic soils are formed because accumulation is favoured by saturated conditions (Mokma 2005).

Peat is an important carbon storage; about 1/3 of the Earth's carbon is stored in peat soils (Joosten & Clarke 2002). The thickness of the peat and the high organic matter content of the soil account for its storage capacity. An average peat soil in northern Europe is approximately 1–2 m (Grønlund et al. 2006). However, when peat soils are drained, they are transformed from long-term carbon sinks to carbon sources (Leifeld & Menichetti 2018). The cause of this is the oxidation and decomposition of organic material, resulting in the emissions of the greenhouse gases (GHG) carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). Change in land use in peat soils may thus have a significant influence on future climate.

Nitrous oxide is one of the main greenhouse gases with a 300 times higher global warming potential than CO<sub>2</sub> (Myhre et al. 2013). Drained peat soils contribute to a considerable amount of anthropogenic GHG emissions, and agriculture is responsible for up to 70 % of the global emissions from the human activity of N<sub>2</sub>O. Previous studies have shown that N<sub>2</sub>O accounts for 5 – 75 % of total emissions (Maljanen et al. 2004; Grønlund et al. 2006). The lower number is on cultivated soil, and the higher is on compacted soil without vegetation. Overuse of nitrogen fertilizers on agricultural soils is considered a particular contributor to the high emissions.

Winter flows have been found to contribute to a considerable part of the annual fluxes of GHG. Especially N<sub>2</sub>O has been observed to have high peaks during thawing in spring. Previous studies on different soils have proven fluctuations to differ and it is still unclear how the thawing event is affected by fertilization. When working to reduce emissions from peat soils, it is vital to understand the factors affecting gas fluxes in order to optimize mitigation practices.

The high greenhouse gas emissions from cultivated peat soils have received increasing interest in recent decades. Many studies have tried to understand the high emissions in order to mitigate them. Nevertheless, several uncertainties remain. These include the factors affecting the amount and projections of future annual emissions. The factors that affect the amount of greenhouse gases in spring (e.g. the length of freeze and thaw cycles) are also still largely unknown.

This study aims to measure GHG emissions during thawing of organic soil in spring. Through a series of field and laboratory measurements, fertilized and unfertilized soil is compared to see if there is any difference in the magnitude of emissions of CO<sub>2</sub> and N<sub>2</sub>O. The results will be compared with multiple soil properties to determine if emissions can be correlated with soil properties. Possible future scenarios due to the changing winter climate are discussed.

The aim of this thesis is to contribute to our understanding of which factors that affects GHG emissions, and in what ways we may optimize mitigation efforts. This is done by comparing two treatments, one fertilized and one unfertilized in freeze and thaw related emissions.

The hypotheses of the experimental study from the information of the literature study include:

- A pulse of N<sub>2</sub>O and CO<sub>2</sub> occurs in spring when the soil is thawing.
- Soils fertilized with N fertilizers show higher N<sub>2</sub>O emissions than unfertilized samples.
- Multiple FTC will affect the emission rate of N<sub>2</sub>O and CO<sub>2</sub> emissions.
- Certain characteristics of the soil, such as lower pH and higher temperature, may predict higher emissions.

## 2. Literature review

### 2.1 Organic soils

In Sweden, organic soils are divided into peat and gyttja types. Peat is usually formed and accumulated upon gyttja. Berglund (2008) concludes that gyttja could be comparable to mineral soils rich in mull when looking at gas fluxes. Gyttja's organic matter is relatively stable, which is why peat is more interesting to study than gyttja when looking at gas fluxes (Berglund 2008).

#### 2.1.1 Formation of organic soils

Organic soils consist of organic material that has accumulated over time and a soil is classified as organic if the organic matter content is  $> 30\%$ . The characteristics of organic soils differ from mineral soils, with contrasting hydraulic and thermal properties (Lawrence & Slater 2008). Another contrasting characteristic is the high porosity of natural peat soils, which results in high hydraulic conductivity. Decomposition is the process when organic material breaks down and carbon dioxide is released and at natural state is the decomposition slow due to high water content (Barreto & Lindo 2020). After drainage, a higher decomposition rate is initiated which results in a decrease in conductivity after draining (Mokma 2005). Peat soil characteristics vary in different environments, depending on parent material, vegetation and acidity (Mokma 2005). In addition, a variety of degradation stages may result in a heterogeneous vertical soil profile.

Topography is also important as it determines how water will accumulate. A historical way of dividing organic soils is by their hydrological source into bog and fen peat (Joosten & Clarke 2002). Organic soils located in a depression where water comes into contact with groundwater are called fen peat, while bog peat receives water only from precipitation (Joosten & Clarke 2002). Fens are usually more nutrient-rich and have a higher pH, which is a result of the water coming from multiple sources. Another common way to classify organic soils is by the degree of humification, where the degradation phase is determined. A soil with a low degree of humification is in an earlier degradation phase with a higher proportion of cellulose. This soil type typically has a higher porosity and a lower

field capacity. Commonly, the degree of humification is variable in the soil profile, where the upper layer usually is of lower degree. pH in bogs is usually lower than in fens due to the water source. Some peat soils used for agriculture are limed to increase pH for better nutrient supply and thus better plant growth (Biasi et al. 2008).

### 2.1.2 Drainage for anthropogenic purposes

Sweden's history of farming on peat soils began in the mid-19<sup>th</sup> century when the population started to grow at an accelerating rate, causing an increasing need for food. The soils could produce a large harvest in some favourable years, but the costs and inputs were often high. Drainage is considered a requirement for successful farming and due to subsidence, it is a recurring event. As modern agriculture developed, giving higher yields on mineral soils, interest in farming on peat soils began to wane. Instead, there was a growing interest in using peat in various ways, like for fuel and animal bedding. (Berglund 2008)

As in Sweden, organic soils in the rest of the world have been drained for agriculture and forestry for centuries (Kreyling et al. 2021). About 10–15 % of the total organic soil area in the world has been drained (Joosten 2022). In Sweden, 5.6 % of the agricultural soil is peat soil (Berglund et al. 2009) and the trend is decreasing agricultural production on peat soils both in Sweden and the rest of Europe (Berglund 2008). An ongoing problem is that drained peat fields are no longer in production but still producing greenhouse gas emissions (Berglund et al. 2009). At drained conditions, the peat soil properties change. A large problem when water levels drops in drained peat soils is continuous subsidence (lowering of the surface), which is caused by a number of factors (Lee et al. 2017). The most important is the setting of soil when the support from water disappear and shrinkage of the soil over the groundwater table. Microbial respiration (oxidation) will release CO<sub>2</sub>, which also causes subsidence (Berglund 2008).

Other anthropogenic activities, such as mining and fuel combustion, also contribute to carbon emissions. Sweden with Finland, Ireland, Belarus and Russia, accounts for about 90 % of global energy peat production and use (Strack 2008). However, energy peat production in Sweden has declined in the last decades and now accounts for only a small share of energy production. Instead, horticultural peat production is increasing and is the largest use of peat extraction (SGU 2020). According to Naturvårdsverket (2021), ¼ of Sweden's GHG emissions are from drained organic soils, as much as the country's passenger car traffic.

### 2.1.3 Management methods

Soil management methods, such as crop choice, fertilization, tillage, and rewetting, may impact GHG production and emission. There are still uncertainties

about which strategies and management methods are most effective for reducing emissions from organic soils. Crops have differing abilities to take up CO<sub>2</sub> from the air which in turn affect the microbial activity in the soil beneath them, thus indirectly affecting GHG. There is no clear evidence that the choice of crop could reduce the emissions of CO<sub>2</sub> from soil (Norberg et al. 2016). However, not leaving the soil bare is important to reduce the N<sub>2</sub>O emission rate (Berglund 2011). The roots reduce the available NO<sub>3</sub><sup>-</sup> and water content, which reduces the risk of denitrification. Fertilizer use is a possible method to influence GHG emissions since it affects the concentration of nutrients in the soil, as input of nutrients provides increased resources for denitrification (Pan et al. 2022). Tillage is another method that possibly affects emission rate, where ploughing can increase emissions when increasing the mineralization rate (Bhattacharyya et al. 2022). But no-tillage has been reported to increase CO<sub>2</sub> and N<sub>2</sub>O emissions, which is an effect of more anaerobic conditions (Shakoor et al. 2021).

An approach that often comes back when discussing GHG emissions from peat soils is to rewet them (Page & Baird 2016). The idea is to stop the loss of carbon through emissions by rewetting the peatland. CO<sub>2</sub> emissions are reduced and other benefits include increased biodiversity and ecosystem function (Kreyling et al. 2021). Although methane increases with rewetting, peatland restoration is considered an important option for climate change mitigation. However, some studies have shown that restoration can be unpredictable and slow (Page & Baird 2016) and is not suited for all sites. The most effective way to prevent negative impacts on the climate seems to be to avoid draining peat soils from the beginning.

## 2.2 Greenhouse gas emissions and organic soils

Peatlands can be a sink or a source of GHGs in terrestrial ecosystems. The three main greenhouse gases are carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>). In their natural state, peat soils act as a sink for GHGs, but a source for CH<sub>4</sub>. When natural peat soils are drained and cultivated, decomposition of the accumulated organic material increases, where the degradation rate is correlated with the amount of emissions (Berglund & Berglund 2011). It turns the peat soil from a sink to a source of GHG emissions. Organic soils used for agricultural purposes often represent a smaller fraction of total arable land but contribute to a seemingly large amount of GHGs (Regina et al. 2015).

Carbon dioxide is the most ubiquity GHG emitted from cultivated organic soils (Myhre et al. 2013) and contributes to the largest climate-warming potential (Grønlund et al. 2006). Although nitrous oxide has about 300 times stronger global warming potential (GWP) for a 100 years period than CO<sub>2</sub> and 12 times stronger than CH<sub>4</sub> (Myhre et al. 2013), it is emitted at a lower rate. Studies on

cultivated peat soils has shown that CO<sub>2</sub> accounts for about 85 – 95 % of GWP, N<sub>2</sub>O for 5 – 15 % and CH<sub>4</sub> for < 1 % (Maljanen et al. 2004; Grønlund et al. 2006). In another study, Maljanen et al. (2004) found that N<sub>2</sub>O was responsible for a GWP of 57 – 75 % from bare soil, providing another range. Agriculture accounts for 70 % of anthropogenic N<sub>2</sub>O (Tian et al. 2020), making it one of the main sources of anthropogenic N<sub>2</sub>O emissions to the atmosphere (Risk et al. 2013). The emissions come from microbial activity and are present in almost all soils, but with fertilization, more nutrients become available to the microbes, thus increased fertilization increase N<sub>2</sub>O emissions.

Various factors control emissions from agricultural land, including soil characteristics, climate and vegetation (Taft et al. 2017). Often might the same factors regulate multiple emissions but in opposite ways (Yang et al. 2022). Agricultural management will affect these factors in different ways, so choosing of management method is important when trying to mitigate emissions.

### 2.2.1 CO<sub>2</sub> emissions

Peat soils consists of organic material, which contains a high amount of carbon. The carbon in the decomposing peat could produce CO<sub>2</sub>, which is made possible through aeration in the top layer. The emission is thus a result of photosynthetic uptake, combined with root respiration and respiration by soil organisms (Moore 1994). The net ecosystem CO<sub>2</sub> exchange is between respiration and CO<sub>2</sub> uptake by plants. Drainage affects soil oxidation but also physical and chemical soil properties causing soil subsidence. Kuzyakov and Gavrichkova (2010) state five main sources of CO<sub>2</sub> from soil: the microbial decomposition of 1) SOM, 2) dead plant remains, 3) rhizodeposits of living roots, 4) additional SOM and 5) root respiration. The contribution of the different sources varies depending on biotic and abiotic factors.

The main abiotic factors controlling emissions of CO<sub>2</sub> are substrate availability, soil temperature, water and oxygen availability (Strack 2008; Page & Baird 2016). The availability of substrates for microorganisms is important as it otherwise limits microbial activity, as they require certain nutrient to execute life functions, such as consumption of organic material, in which CO<sub>2</sub> is a residual product (Kuzyakov & Gavrichkova 2010). Norberg (2017) found that a higher organic matter content might result in higher emissions of CO<sub>2</sub>. More available carbon often results in a higher microbial activity (Wang et al. 2021). Varying studies have investigated which factor is the best predictor of the amount of emissions, with varying result. In an experiment by Taft et al. (2017), soil temperature was shown to be the best predictor for CO<sub>2</sub> emissions, followed by the mean daily air temperature, presumably due to their impact on soil respiration rate. The same study found that water depth was shown to have a negative association with CO<sub>2</sub> emissions (Taft et al. 2017), meaning that raising the water

table could decrease the CO<sub>2</sub> emissions from these soils (Strack 2008). However, contradicting results were found by Berglund and Berglund (2011) where higher CO<sub>2</sub> emissions were registered from peat soils with a water depth of 40 cm compared with a water depth of 80 cm. In terms of soil water content, it has been suggested that CO<sub>2</sub> emissions occur at different water content levels as long as the water is not limited (Ruser et al. 2006).

The annual emission of CO<sub>2</sub> follows a seasonal pattern, where it increases during the growing season due to higher temperatures combined with root and soil respiration. During the frozen period, root and soil respiration is usually low, resulting in a lower emission rate.

### 2.2.2 N<sub>2</sub>O emissions

Three biological processes from the nitrogen cycle contribute to the production of N<sub>2</sub>O in soil: nitrification, denitrification and nitrifier denitrification (Regina et al. 1996). The third process is sometimes considered together with nitrification. This process is less studied but seems more important on soils with low C and N content (Wrage et al. 2001). Nitrification is the process by which ammonium (NH<sub>4</sub><sup>+</sup>) or ammonia (NH<sub>3</sub>) oxidize to nitrate (NO<sub>3</sub><sup>-</sup>) (Figure 1). The process depends on aerobic conditions and is performed by a few different groups of microorganisms, collectively called nitrifiers (Ward 2008). N<sub>2</sub>O can emit as an intermediate step in nitrification.

Denitrification (reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>) occurs under anaerobic conditions by denitrifying microorganisms that require simple carbon compounds and NO<sub>3</sub><sup>-</sup> (Figure 1) (Priemé & Christensen 2001). Production of N<sub>2</sub>O is an intermediate step that, compared to nitrification and nitrifier denitrification, is obligate. Emissions are favoured by certain factors when the reduction of N<sub>2</sub> ceases (Risk et al. 2013). Three examples of such conditions are low pH (Hénault et al. 2019), oxygen availability (Knowles 1982) and high NO<sub>3</sub><sup>-</sup> concentration (Wrage et al. 2001). Denitrifying microorganisms use N<sub>2</sub>O as an electron acceptor to reduce to N<sub>2</sub>, which can occur when the concentration of NO<sub>3</sub><sup>-</sup> is low.

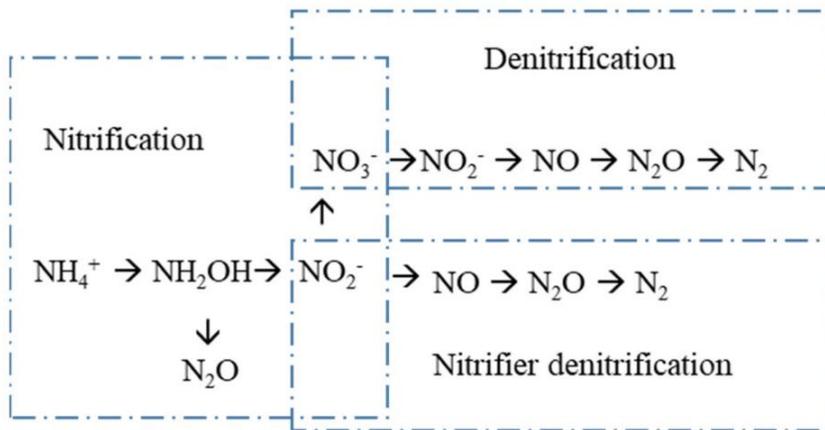


Figure 1. Main pathways for N in soils. From: Wang et al. (2021).

Bouwman et al. (2002b) divided the factors affecting N<sub>2</sub>O emissions into environmental, management and measurement (Table 1).

It is generally accepted that denitrification is the main source of N<sub>2</sub>O emissions in peat soils (Pihlatie et al. 2004), although nitrification also contributes. As denitrification dominates at anaerobic conditions and nitrification at aerobic conditions, soil water content has an important role; when the soil water content is low, nitrification dominates and vice versa (Pihlatie et al. 2004). Soil water can be presented as water-filled pore space (WFPS). When WFPS is above 60 %, denitrification is the dominant process and beyond 80 %, the production of N<sub>2</sub> favoured (Veldkamp et al. 1998). The percentage is from the average WFPS at field capacity (Davidson et al. 2000). Davidson et al. (2000) theorized on mineral soils that for a given water availability at 60 %, both processes would occur simultaneously, causing the highest peaks. However, this has been questioned when other studies have shown peaks at different water availability points. It has been suggested that the peaks also depend on whether other factors are limited, such as NO<sub>3</sub><sup>-</sup> concentration and temperature. It also depends on soil texture, as field capacity varies among soils.

On organic soil, Pärn et al. (2018) instead used volumetric water content (VWC) (WFPS multiplied with total porosity). They concluded that an intermediate VWC (50 – 80 %) promotes denitrification and contributes to a higher NO<sub>3</sub><sup>-</sup> concentration, thus also N<sub>2</sub>O production (Pärn et al. 2018). The C/N ratio of the topsoil can also be a predictor of annual N<sub>2</sub>O emissions; according to Klemetsson et al. (2005), a soil C/N below 20 gives an increased risk of nitrogen release to atmosphere. A higher ratio favours the fixation of NO<sub>3</sub><sup>-</sup>, thus reducing N<sub>2</sub>O emissions (Yang et al. 2022).

Soil pH also influences denitrification, as it affects various processes in the soil. In acidic soil where denitrification is the main source of N<sub>2</sub>O emissions, higher pH usually results in reduced N<sub>2</sub>O emissions (Yamulki et al. 1997). A

higher SOC content in the soil also affects the rate of N<sub>2</sub>O since it results in higher microbial activity (Weier et al. 1993).

Emissions of N<sub>2</sub>O have been influenced by anthropogenic effects, such as the use of nitrogen fertilizers (Ito et al. 2018). The usage has increased rapidly in recent decades due to the invention of Haber-Bosch and the pressure of a growing population. Often, fertilizers used in agricultural systems convert to NO<sub>3</sub><sup>-</sup>, which is mobile and easily lost through leachate with water (Ward 2008). As a result, nitrogen-use efficiency is quite low, leading to environmental impacts such as GHG emissions and eutrophication. According to Liu et al. (2010), only 55 % of the applied N is taken up by plants and the rest is lost to leaching (16 %), soil erosion (15 %) and gaseous emissions (14 %). The indirect emissions of N<sub>2</sub>O from the leaching are uncertain (Taft et al. 2017).

N<sub>2</sub>O emissions vary more throughout the year than CO<sub>2</sub> (Taft et al. 2017) and have a large spatial variation. Direct emissions of N<sub>2</sub>O often occur in small areas (hotspots) of microbial activity and after short periods after rainfall or when the soil thaws (Congreves et al. 2018).

*Table 1. Summary of the different groups of factors affecting the N<sub>2</sub>O emissions in soils. From: Wang et al. (2021).*

<b>Environmental Factors</b>	<b>Management Factors</b>	<b>Measurement Factors</b>
Microbial population	Fertilizer application	Length of measurement period
Soil available carbon	Tillage system	Types of measurements
Soil N concentration	Harvest and crop residues	
Soil water content	Irrigation	
Soil texture		
Soil temperature		
Soil pH and salinity		

## 2.3 Influence of winter flows on GHG emissions

### 2.3.1 Freeze and thaw cycle

The annual flux of GHG, particularly N<sub>2</sub>O, varies throughout the year and it has been found that a significant amount of emissions are produced outside of the growing season (Regina et al. 2004). A key event to these emissions is the soil thawing in spring. These emissions can be linked to the freeze-thaw cycles (FTC) occurring in the soil during autumn and spring in temperate climates. A freezing

and thawing event is defined as when the temperature drops below 0°C. Emissions from these short periods, often lasting only a few days (Priemé & Christensen 2001), can account for up to 70 % of the annual N<sub>2</sub>O loss in these climates (Röver et al. 1998). However, this number varies between studies depending on the chemical and physical properties of the soil (Regina et al. 2004). Henry (2007) also suggested that some inconsistencies may be due to methodological differences between studies.

There are likely two causes for the large release: 1) sudden physical release of N<sub>2</sub>O produced and accumulated under the barrier and 2) newly produced N<sub>2</sub>O when conditions become favourable for biological activity (Risk et al. 2013; Yang et al. 2022). Of these two processes, the latter is considered to contribute the most (Teepe et al. 2001). The new conditions result in increased amounts of nutrients that become available after freezing and microbial activity is stimulated (Yang et al. 2022). Badewa et al. (2022) divided the cycle into three phases: waterlogged, wet and dry. Their study concluded that N<sub>2</sub>O emissions were highest under wet conditions and lowest under waterlogged (Badewa et al. 2022).

In organic soils, the water content is still high at low temperatures because of the high organic matter and low thermal conductivity, making it possible for microbial survival in water films at low temperatures. Teepe et al. (2001) found that the average WFPS in the top layer (0 – 5 cm) was positively correlated with winter N<sub>2</sub>O emissions. Production of N<sub>2</sub>O can also occur in soil layers deeper in the profile, which is less affected by the low temperatures.

The temperature during freezing and thawing also seems to contribute to the amount of GHG emissions (Risk et al. 2013). In a laboratory study showed Koponen and Martikainen (2004) that lower freezing temperatures may increase the emission rate. Organic soil samples thawed from -15 °C produced twice as much CO<sub>2</sub> emissions as when thawed from -1.5 °C (Koponen & Martikainen 2004). Higher emissions at lower freezing temperatures may be due to aggregate decomposition and destruction of fine roots, leading to more available nutrients in the soil (Koponen & Martikainen 2004).

Since snow cover affects soil temperatures, its removal may also affect the emissions (Maljanen et al. 2007; Risk et al. 2013). Temperature fluctuations are more frequent when there is less snow cover, which can result in increased emissions in spring. It may be due to an increased number of substrates available for denitrification at higher temperatures (Regina et al. 2004). Peat soils usually have low thermal conductivity, giving a similar thermal insulation effect comparable to snow (Congreves et al. 2018). However, in the absence of snow, the albedo will be lower and the soil temperature higher (Marsh & Pomeroy 1996), which may give sites with favourable conditions for N<sub>2</sub>O emissions (Yates et al. 2006). More energy is required to freeze and thaw water in peat because of the low thermal conductivity.

During spring and autumn, the soil is often exposed to multiple freezing-thawing cycles. Depending on the frequency of the temperature fluctuations, the amount varies greatly. Studies have shown that the N<sub>2</sub>O emission rate is the highest under the first cycle (Schimel & Clein 1996; Koponen & Martikainen 2004). The reason could be that the high amount of substrates released when the soil thaws decrease with each cycle, resulting in a lower emission rate (Koponen & Martikainen 2004). However, emissions will be lower if thawing occurs in the middle of winter (Müller et al. 2003). A shorter freezing time is considered the reason (Teepe et al. 2001). An experiment from mineral soils concluded that the more FTC the soil has, the more peaks of N<sub>2</sub>O and thus higher N<sub>2</sub>O emissions (Abalos et al. 2016).

Regarding CO<sub>2</sub>, a large flux can occur after thawing, but over the year this plays a minor role (Matzner & Borken 2008). Since the amount of C available in organic soils is already high, so it will not have the same effect as it has for nitrifiers (Koponen & Martikainen 2004). The large emissions are instead in the growing season.

### 2.3.2 Dry and wet cycle

Another process that affects N<sub>2</sub>O production similarly to the freeze-thaw cycle is the dry-wet cycle (Kim et al. 2012). This cycle is considered to contribute less to the total amount of N<sub>2</sub>O emissions (Congreves et al. 2018). Under dry conditions, substrates will accumulate, as there is low biological activity to decompose it, and there is little to no loss through leachate. The flux of N<sub>2</sub>O increases when dry soil conditions gain access to water, increasing availability of nitrogen and carbon which increases microbial activity. Thus, it got a similar driver as the FTC. However, it has different characteristics in other parts of the process that can affect the amount of N<sub>2</sub>O emissions. During the drying-wetting cycle no ice or snow is present, so the gas diffusivity will not interfere when no gas is trapped under an impermeable layer. The dry-wet cycle seems important in dry arid climates, with annual cycles of drying and wetting (Priemé & Christensen 2001). It is unclear how the two cycles affect the response to the other and how this will change with climate change. This cycle can be seen as separate, but it also occurs simultaneously with the freeze and thaw cycle.

### 2.3.3 Fertilized and unfertilized soil

The substrate availability for the denitrifying organisms seems to be an important factor in determining the amount of N<sub>2</sub>O production (Nykänen et al. 1995; Risk et al. 2013). The reason is that N applied as fertilizer is immobilized to microbial biomass and becomes available again after thawing (Müller et al. 2002).

Therefore, the emission rate in some soils may rise when nitrogen fertilizer is applied (Müller et al. 2002).

However, reports have shown variable results of N<sub>2</sub>O emissions of FTC from fertilized and unfertilized organic soils. Some studies have found greater emissions from fertilized soil (e.g. Bouwman et al. 2002; Müller et al. 2002), while others have seen no difference (Regina et al. 2004; Rochette et al. 2010). Maljanen et al. (2004) even found that soils receiving fertilizer had a lower emission rate. The reason why the result differs much between studies is not known, but some factors could contribute to it.

An example of a contributing factor is the fertilizing type. According to Bouwman et al. (2002), nitrate-based (NO<sub>3</sub><sup>-</sup>) fertilizers have a low impact on the emission rate, while ammonium-based (NH<sub>4</sub><sup>+</sup>) fertilizers and animal manure have a higher impact. Müller et al. (2003) found the opposite result, with the highest emissions observed from soils fertilized with nitrate-based fertilizers. Theoretically, an excess of NO<sub>3</sub><sup>-</sup> should increase the N<sub>2</sub>O emission rate more than an excess of NH<sub>4</sub><sup>+</sup> since the latter must undergo nitrification instead of denitrification, assuming that denitrification is the main contributor. A theory from a study in China of mineral soils concluded that it may be the long-time use of excess fertilizer that acidifies the soil, leading to greater GHG emissions (Qu et al. 2014). It leads back to pH as a contributing factor to the amount of GHG.

A combination of different factors could also lead to an increased effect, like cultivation and fertilizing (Regina et al. 1996). Other reasons for different results between fertilization and N<sub>2</sub>O emissions may be due to vegetation; if there are no plants that can take up nitrogen, it is more available for denitrification and N<sub>2</sub>O production (Maljanen et al. 2004). The fertilization rate and weather conditions after fertilization may also be important. Precipitation after fertilization may be an important factor for the magnitude of emissions, by affecting soil moisture levels (Abalos et al. 2016). There is usually a peak of N<sub>2</sub>O emissions just after N fertilization application.

### 2.3.4 A changing climate

Warmer winters are predicted in areas at high latitudes, where peat soils most often are found, due to climate change. Over the 21<sup>st</sup> century, it is predicted that temperatures in the Northern Hemisphere might increase by 2 – 6 °C (SMHI 2022). In Sweden, the mean temperature increased by approximately 2 °C in the last 150 years, 1 °C more than the world's average (SMHI 2022). Uppsala had an annual average of 94 days of snow between 1951 and 2014 (Wern 2015). The number of days with snow has decreased significantly in southern and central Sweden in recent decades (SMHI 2021).

Winter processes like FTCs are affected when the climate is changing. The snowpack is an essential part since it affects the soil temperature. Milder winters

result in fewer days with snow cover and thus more fluctuations in temperature during winter. However, there are uncertainties about how the FTC might be affected by climate change. More alternation in temperature and precipitation is expected to contribute to changes. In more southern latitudes, like central Europe, frost might become less frequent during winter. This could result in less FTCs. Another difference is that more precipitation could fall as rain instead of as snow.

At northern latitudes, less snow cover can lead to colder soils. This would then affect FTCs differently. Mellander et al. (2007) have modelled, based on a forest area in Sweden and possible CO<sub>2</sub> emission scenarios, that the frequency of FTCs could increase by over 30 %. As field studies are complicated to subject to FTC experiments, it is difficult to predict how emissions would be affected.

*Table 2. Summary of the main factors affecting the GHG emissions in drained peat soils. Columns without data mean that the factor does not affect the emission rate, or that data are missing.*

<b>Increase of</b>	<b>Trend for CO<sub>2</sub> emissions</b>	<b>Trend for N<sub>2</sub>O emissions</b>
pH		Decrease <sup>1</sup>
Oxygen	Increase <sup>2</sup>	Decrease <sup>3</sup>
Nutrients		Increase <sup>4</sup>
Air temperature	Increase <sup>5</sup>	Increase <sup>6</sup>
Soil temperature	Increase <sup>5</sup>	Increase <sup>6</sup>
Water table position	Decrease <sup>7</sup>	Increase <sup>8</sup>
C/N		Decrease <sup>9</sup>
Freeze duration	Decrease <sup>10</sup>	
Deep frost		Increase <sup>11</sup>
FTC*		Increase <sup>12</sup>

\*Increase in the number of FTCs

<sup>1</sup> Yamulki et al. (1997)

<sup>2</sup> Moore (1994)

<sup>3</sup> Knowles (1982)

<sup>4</sup> Maljanen et al. (2004)

<sup>5</sup> Taft et al. (2017)

<sup>6</sup> Wang et al. (2021)

<sup>7</sup> Strack (2008)

<sup>8</sup> Pihlatie et al. (2004)

<sup>9</sup> Klemetsson et al. (2005)

<sup>10</sup> Teepe et al. (2001)

<sup>11</sup> Koponen & Martikainen (2004)

<sup>12</sup> Abalos et al. (2016)

### 3. Material and methods

#### 3.1 Field site and field measurement

The field site is located in Broddbo, approximately 10 km west of Björklinge, Uppsala at a soil with ongoing field trials. The plots were not included in any experiment and were grass-covered. It has been undisturbed for several years.

On 30<sup>th</sup> November 2022, eight lysimeters (height 20 cm, ø19 cm) were placed in the field in undisturbed soil. The lysimeters were hammered into the soil, to approximately 10 cm depth. Half of the samples were then fertilized (Figure 2). A fertilizer solution was prepared and applied at a rate of 50 kg N/ha. Deionized water was used with NPK fertilizer (N 11 kg, P 5 kg, K 18 kg per ha). When fertilizing, 1 dl of the solution was applied to each cylinder.

Field measurements of GHG emissions (CO<sub>2</sub>, N<sub>2</sub>O) were performed at the field a total of 9 times between 2<sup>nd</sup> February and 30<sup>th</sup> May.

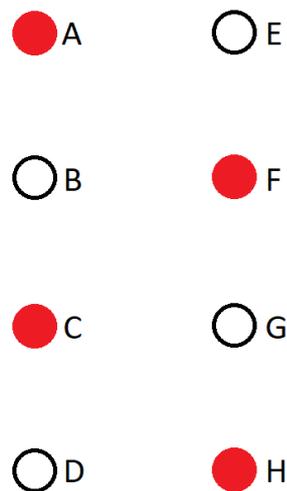


Figure 2. The lysimeters in the field. The fertilized samples are marked in red (Photo: Fanny Otterlin Karlsson).

## 3.2 Laboratory experiments

### 3.2.1 Laboratory emission measurements

The laboratory experiments were performed on soil samples collected from undisturbed soil at Broddbo in November 2022. A total of eight soil samples were taken for laboratory measurements. The plots were chosen randomly within the selected area. Lysimeters (height 20 cm,  $\varnothing$ 19 cm) were hammered completely into the soil and dug up, then the soil surface of the lysimeter was sealed using a lid. The samples were then transported to the laboratory where they were prepared by removing excess soil from the bottom of the lysimeter and placing it in plastic bags. A lid was then placed at the bottom of the lysimeter, and the samples were turned with the ground surface facing upwards. Half of the samples were fertilized with 1 dl and the rest received the same amount of deionized water. The same fertilizer was used for the laboratory experiment as for the field experiment. After preparation, all samples were placed in the freezer with lids at -18 °C for 13 weeks (Figure 4). The plastic bags containing the excess soil were placed in a refrigerator for storage until pH and loss of ignition (SOC) measurements were performed.

After freezing, the samples were placed at room temperature (21 °C). A hole was drilled in the lysimeters, and a thermometer was placed in each (Figure 4). On the first day, the hole was 5 cm down, due to impermeable compaction, and the rest of the measurements it was approximately 10 cm down. Every thermometer was set to the same average room temperature.

The laboratory measurement was performed in a fume hood (see 3.3 for measurement method). In the first cycle, samples were measured every day for two weeks (10 days) before being returned to the freezer for 10 days. In the second cycle (7 days), measurements were performed twice a day for the first three days of the cycle, and once a day the following four. The samples were measured for seven days. In the third cycle, the samples were frozen for three days and measurements were performed once a day in the last cycle (7 days) (Figure 3).

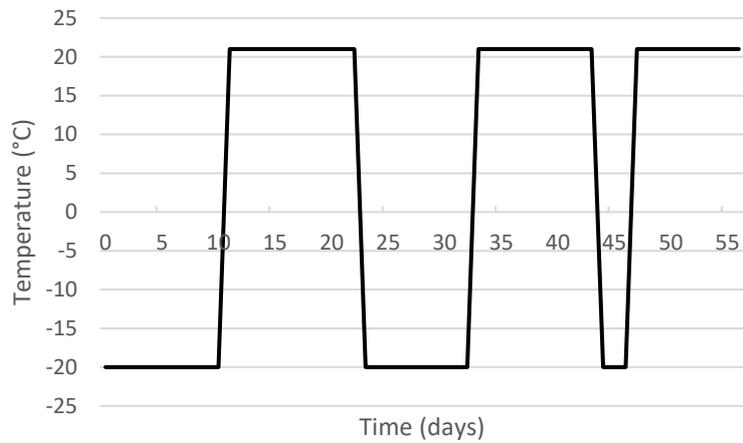


Figure 3. Temperature regimes for the experiment. The first freeze period is not visible in its entirety.

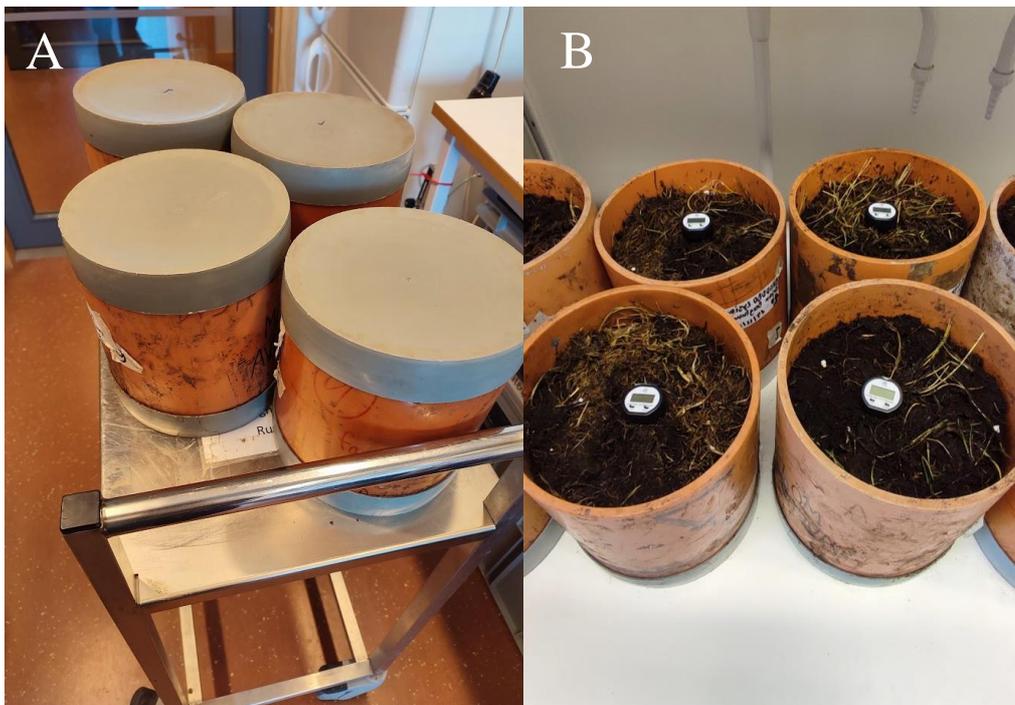


Figure 4. (A) Prepared samples with lids and (B) samples during thawing with thermometers. (Photos: Fanny Otterlin Karlsson).

### 3.2.2 Soil properties

The soil properties included in this experiment was pH, soil organic carbon (SOC) content, dry bulk density and water content.

For pH, loose soil from the excess soil was placed in plastic containers for air drying at 30 °C for three days. Each soil sample was then grinded and sieved

through a 2 mm screen. One part soil and five parts deionized water were mixed and shaken for five minutes. The samples were set to sediment for two hours before measuring pH. A second measurement was performed 24 hours after the first one and an average value was calculated from the two measurements.

The SOC content was measured as loss of ignition. Soil samples from the excess soil were dried in an oven at 105 °C for 24 hours. The samples were grinded and sieved through a 2 mm screen. They were then incinerated at 550 °C for three hours. The samples were then cooled in a desiccator and weighed.

The water content of the cylinders was determined by weighing the samples at each measurement. At the end of the experiment after the freezing and thawing cycles, the samples were air-dried for two weeks and then weighed. The water content was also determined by drying a small amount of each sample in an oven at 105 °C for 24 hours. The method that resulted in the highest water content, i.e., the method where the samples lost the highest amount of water, was used. Both gravimetric and volumetric water content was calculated, as well as the bulk density of the soil.

The water content in the field was measured using a WET sensor (Delta-T) when the soil was unfrozen.

Previous measurements of the C/N-ratio from the same plots without treatment have been between 13.91 – 14.1 (Mattsson 2018; Nordgren 2021). It is within range for decomposed peat soil. A new measurement of the C/N-ratio was not included in this work due to a shortage of resources. However, since previous samples are measured on the same soil, these are assumably values for these soil samples too.

### 3.3 Emission measurements

Measurements of fluxes by CO<sub>2</sub> and N<sub>2</sub>O were made with a closed chamber technique. This technique only measures soil respiration CO<sub>2</sub>. All eight lysimeters were measured using a Gaset GT5000 Terra portable gas analyser. A manual opaque chamber (height 18 cm, ø 18cm) was attached to the lysimeter during the measurement (Figure 5). The measurements took 5 minutes with a sampling rate of 5 seconds. Between each measurement, the value of CO<sub>2</sub> in the air was measured. This was done to get an accurate difference from the values in the closed chamber. A background value of N<sub>2</sub> was measured by flowing the Gaset with pure N<sub>2</sub> in the laboratory before measuring. The air temperature was noted with a temperature sensor during all measurements. The soil temperature in the field was measured using a WET sensor (Delta-T) when the soil was unfrozen (Figure 5). It measured the soil temperature at a depth of about 5 cm. A weather station on the field, which measures the temperature at 15 and 45 cm depth, was used for soil temperature during the frozen period.



Figure 5. (A) Gas emission measurement with Gaset and (B) soil temperature with WET sensor. (Photos: Fanny Otterlin Karlsson).

### 3.4 Calculations

The equation to calculate the emissions was made according to Equation 1 for each gas. It was calculated from the average increase in gas concentration in the chamber using the chamber's volume and area. The gas flux  $F$  was estimated in  $\text{mg m}^{-2} \text{h}^{-1}$  for  $\text{CO}_2$  and  $\mu\text{g m}^{-2} \text{h}^{-1}$  for  $\text{N}_2\text{O}$ .

Equation 1.

$$F = \frac{\left(\frac{\Delta c}{\Delta t} * \frac{V}{A} * \rho * M\right)}{R * T}$$

Where:

$\frac{\Delta c}{\Delta t}$  is the average change in gas concentration during the measured time (ppm/h)

$V$  is the volume of the chamber ( $\text{m}^3$ )

$A$  is the area of the chamber ( $\text{m}^2$ )

$\rho$  is the atmospheric pressure ( $101325 \text{ N m}^{-2}$ )

$M$  is the molecular mass for the gases ( $M_{\text{CO}_2}$ :  $44.01 \text{ g mol}^{-1}$ ,  $M_{\text{N}_2\text{O}}$ :  $44.01 \text{ g mol}^{-1}$ )

$R$  is the ideal gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  is the air temperature (K)

The gaseous volume was calculated by an estimation of four internal heights of the lysimeters for each soil sample.

Analyses of repeated measures were carried out in accordance with the guidelines set forth by Littell and colleagues in 2006, utilizing the Mixed model in JMP PRO 16.0 (Littel 1996). This was made for both the laboratory and field measurements separately. The average value from the treatments has been used, with standard errors for all measurements.

## 4. Results

### 4.1 Weather conditions during winter 22/23

The first snow of the season came on 21<sup>st</sup> November and melted after three days, about a week before the soil samples were collected and lysimeters were placed. One weather station in Björklinge had snow 80 days during the winter season between November and mid-April (SMHI 2023a). The last snow from that weather station melted on 12<sup>th</sup> April. The weather station at the field that shows the soil temperature only had minor differences during the winter season between January and mid-April. The mean temperature for the period was 0 °C at 15 cm depth and 1.4 °C at 45 cm depth.

Both January and February were mild this year compared to the reference period (1991-2020), while March and April was colder than usual (Table 3) (SMHI 2023b). The precipitation was higher in January and March compared to the reference period, while it was lower in the other three months (Table 3).

*Table 3. Mean air temperature and total precipitation in Uppsala in winter and spring 2023 compared to the reference period 1991-2020. From: SMHI (2023b)*

<b>Month</b>	<b>Mean temperature 2023 °C</b>	<b>Normal mean temperature °C</b>	<b>Precipitation 2023 (mm)</b>	<b>Normal precipitation (mm)</b>
January	0.2	-2.0	66	39
February	-0.2	-2.0	24	32
March	-0.7	1.0	69	29
April	5.1	6.0	17	32
May	12.1	11.1	31	39

### 4.2 Field measurements

The first measurement in early February showed negligible emissions of all gases. Therefore, it was decided to wait for further measurements until the soil started to thaw. A measurement was performed in late March after a period of warmer

weather. The result showed slightly higher CO<sub>2</sub> emissions but no difference in N<sub>2</sub>O emissions. Shortly after, a new period of cold weather with snow began and lasted for about two weeks. The next measurement was carried out in mid-April, three weeks after the second. It showed negligible emissions of N<sub>2</sub>O from both the fertilized and unfertilized samples. Hereafter, field measurements were performed weekly until the end of May.

Figure 6 shows the result of the fertilized and unfertilized samples in CO<sub>2</sub> emissions from the field measurement. Each point is the mean value of the four samples in both treatments. Standard errors have been calculated for the four samples within each treatment. There is no significant difference between the fertilized and unfertilized samples. The measurement varied greatly within the treatments; this is especially true for the measurements in May. For example, on 15<sup>th</sup> May, the lowest and highest emissions was 680 and 2793 mg CO<sub>2</sub>/m<sup>2</sup>/h respectively. The lowest emission is from an unfertilized sample and the highest from a fertilized sample.

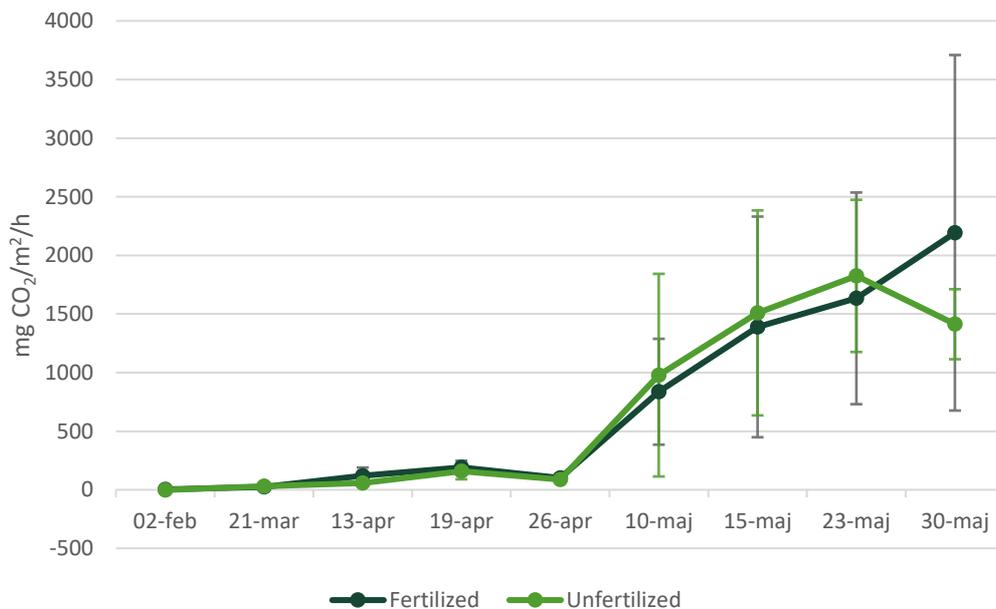


Figure 6. CO<sub>2</sub> emissions from the lysimeters measured in the field. Each point is an average of the four measurements within the treatments and the standard errors are based on these.

The statistics for the measurements of CO<sub>2</sub> is displayed in Figure 7 and 8. Temperature and water content are used from the weather station in the first three measurements due to frozen soil. Figure 7 shows an actual by predicted plot, where actual values are the measured values compared against predicted values based on a model. If the points are close to the diagonal line, the predicted values are close to the measured and the model explains real conditions well (JMP Statistical Discovery 2023a). This can be seen with a goodness-to-fit value, where a high value indicates a good fit to the model. The goodness-to-fit test used was

Shapiro-Wilk, where a p-value above 0.05 means that the null hypothesis that the residuals are normally distributed is not rejected (JMP Statistical Discovery 2023b). The value for CO<sub>2</sub> measurements is Prob<W 0.01, which means that the data is not normally distributed. In Figure 8 is the residual quantile plot, which shows that the data is still reasonably well distributed (Personal communication with statistician Claudia von Brömssen, October 2023).

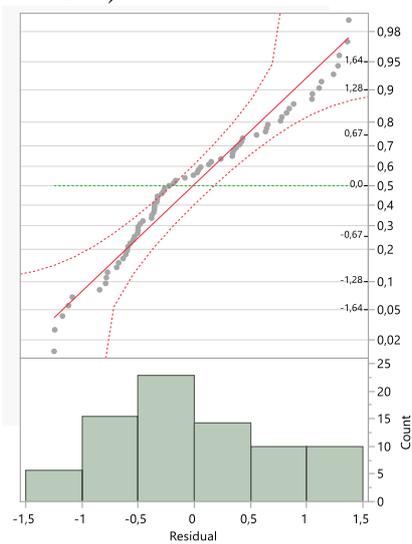
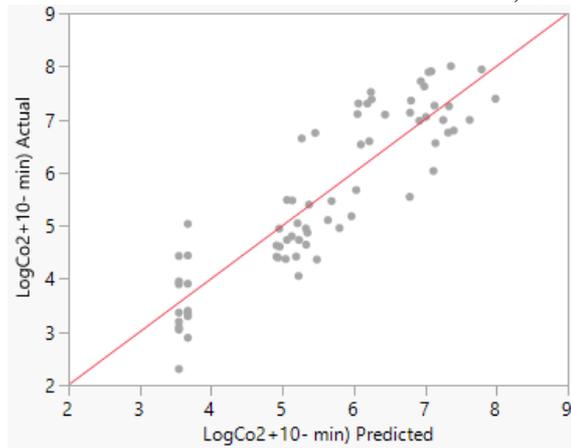


Figure 7. An actual by predicted plot of CO<sub>2</sub> from the field measurement. On the X axis is the actual values and on the Y axis the predicted. The X and Y-axis is transformed to log values from the measured values.

Figure 8. The residual quantile plot for CO<sub>2</sub> from the field measurements.

In Table 4 is a summary of the statistical analysis for the field measurement of CO<sub>2</sub>. The estimate is an assessment of the average value for the term based on the measured values. With the standard error and 95 % lower/upper is it possible to see the variation within the measurement. By looking at the t Ratio and Prob>|t| is it possible to see if the result is significant. The result shows that there is a significant correlation to soil temperature and intercept, but not to treatment or water content.

Table 4. The fixed effects parameter estimates model for the field measurement of CO<sub>2</sub>.

Term	Estimate	Std Error	t Ratio	Prob> t	95% Lower	95% Upper
Intercept	3,65	0,39	9,28	<,0001*	2,87	4,44
Soil temperature	0,22	0,02	10,8	<,0001*	0,18	0,26
Method [Fertilized]	0,06	0,10	0,61	0,55	-0,15	0,28
WET (%)	0,00	0,01	-0,14	0,89	-0,02	0,01

In Figure 9, the N<sub>2</sub>O emissions are plotted for the fertilized and unfertilized samples during the measuring time from the field measurement. The unfertilized showed a tendency of a higher emission rate, but there is no significant difference

between the fertilized and unfertilized samples. Like CO<sub>2</sub>, the emissions of N<sub>2</sub>O vary greatly within each measurement occasion, especially in May. This is true for both the fertilized and unfertilized samples, but the standard error was higher for the unfertilized samples. On 15<sup>th</sup> May, the lowest and highest emissions were measured at 236 and 3187 μg N<sub>2</sub>O/m<sup>2</sup>/h respectively. The highest emission rate is from an unfertilized sample and the lowest in a fertilized sample.

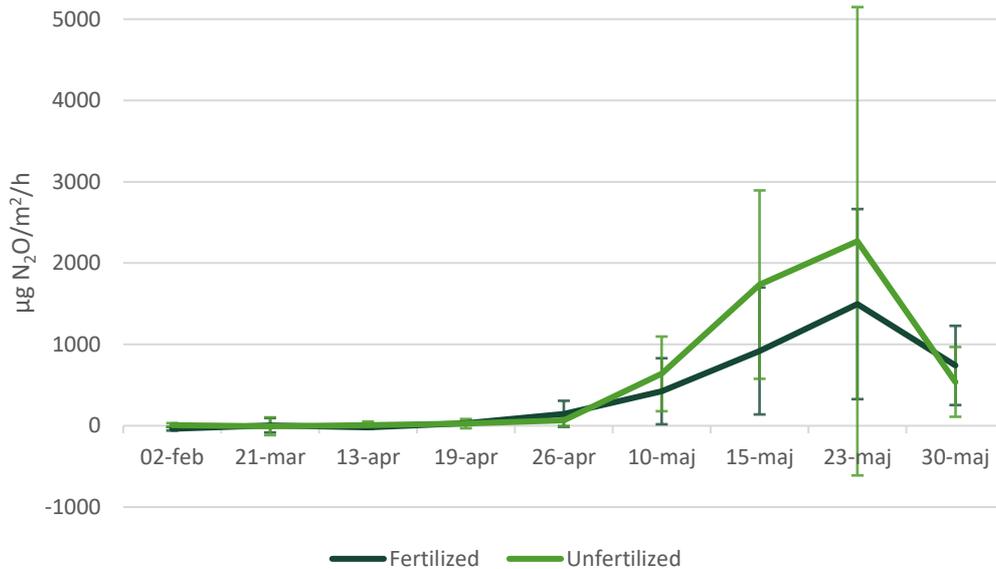


Figure 9. N<sub>2</sub>O emissions from the lysimeters measured in the field. Each point is an average of the four measurements within the treatments and the standard errors are based on these.

The statistics for the measurements of N<sub>2</sub>O is shown in Figure 10 and 11. Temperature and water content are used from the weather station in the first three measurements due to frozen soil. Four outliers were removed from the measurements. Figure 10 shows an actual by predicted plot, from the field measurement the residuals of N<sub>2</sub>O is Prob<W 0.057, which means that the data is normally distributed. This can also be seen in Figure 11 which shows the residual quantile plot, it is not completely normally distributed but still reasonably well distributed (Personal communication with statistician Claudia von Brömssen, October 2023).

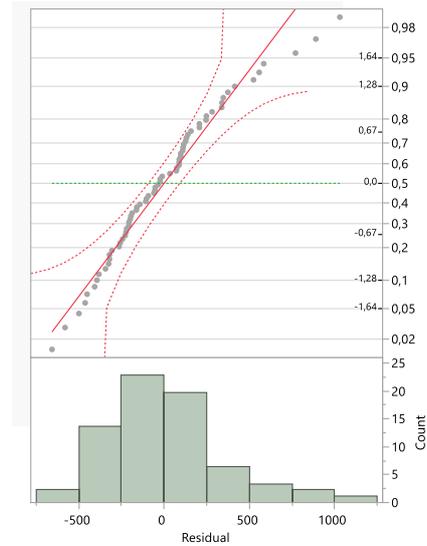
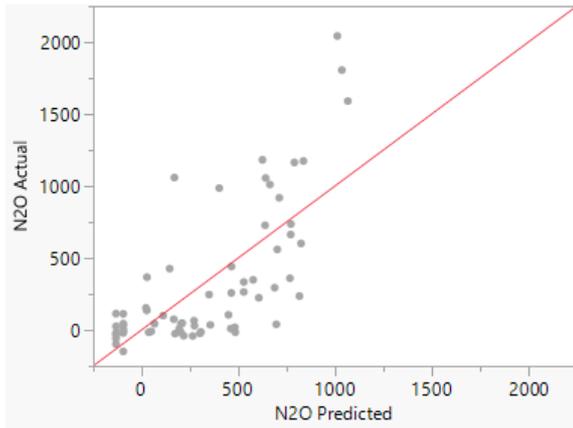


Figure 10. An actual by predicted plot of N<sub>2</sub>O from the field measurement. On the X-axis is the actual values and, on the Y-axis, the predicted. The X and Y-axis is transformed to log values from the measured values

Figure 11. The residual quantile plot for N<sub>2</sub>O from the field measurements.

Table 5 shows a summary of the statistical analysis for the field measurements of N<sub>2</sub>O. The result shows that there is a significant correlation between N<sub>2</sub>O emissions to soil temperature and water content, but not to treatment.

Table 5. The fixed effects parameter estimates model for the field measurement of N<sub>2</sub>O.

Term	Estimate	Std Error	t Ratio	Prob> t	95% Lower	95% Upper
Intercept	192	191	1,00	0,32	-191	575
Soil temperature	70,2	9,77	7,19	<,0001*	50,7	89,8
Method [Fertilized]	-18,6	41,7	-0,45	0,65	-102	64,6
WET (%)	-8,04	3,97	-2,03	0,0469*	-15,9	-0,11

Figure 12 shows the correlation between N<sub>2</sub>O to soil water content (soil moisture) and temperature. The R<sup>2</sup> value for water content and N<sub>2</sub>O emission is 0.601, which is moderately strong, and for soil temperature 0.938, which indicates a strong correlation.

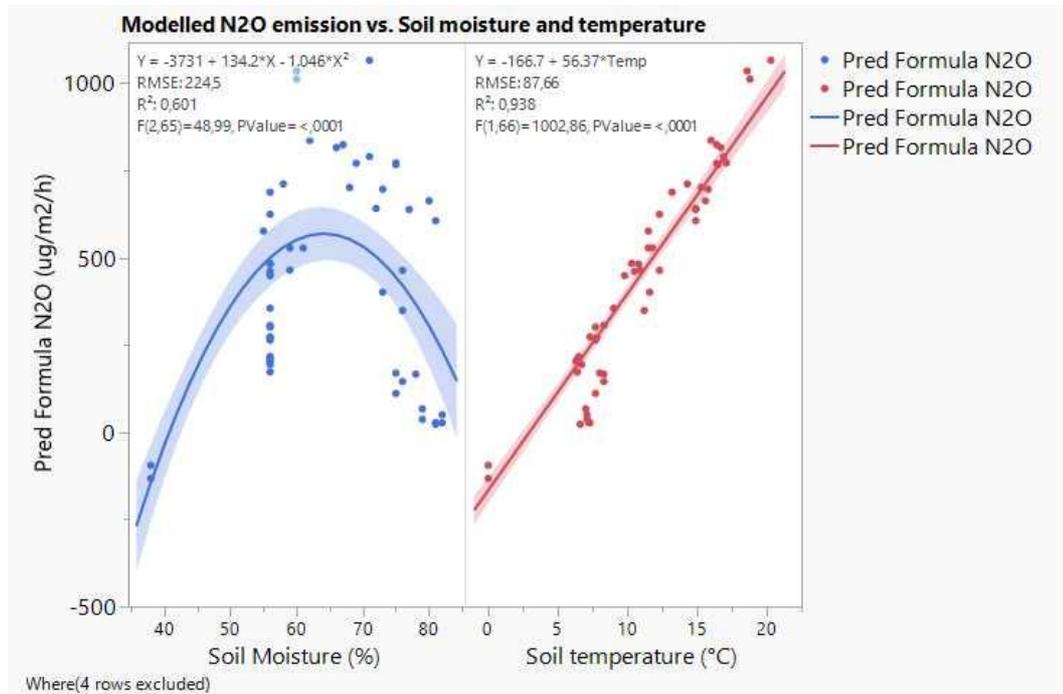


Figure 12. Regression lines with N<sub>2</sub>O emissions against soil moisture (%) and temperature (°C). The marked area in blue and red represent 95% confidence limits of the regression lines.

There is a small difference between the fertilized and unfertilized samples for both gases. The average value of CO<sub>2</sub> between the treatments had a small variation (Figure 13). For N<sub>2</sub>O, the average value for the unfertilized samples is slightly higher than for the fertilized samples (Figure 14). There is no significant difference between the range of the two treatments, which means that the differences observed between fertilized and unfertilized treatments are likely to be due to chance rather than true treatment effect.

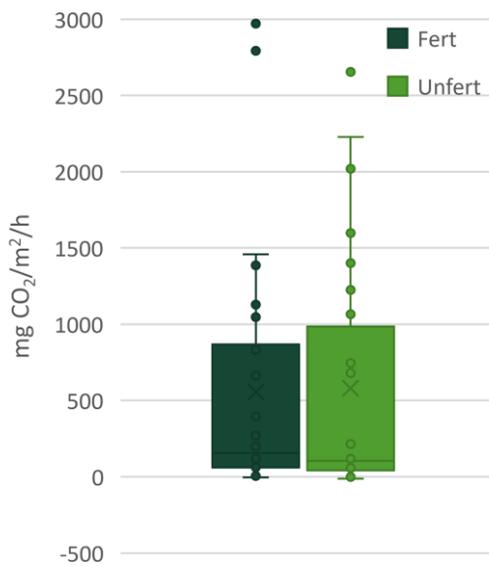


Figure 13. Box plot analysis of the CO<sub>2</sub> emissions during the field measurement

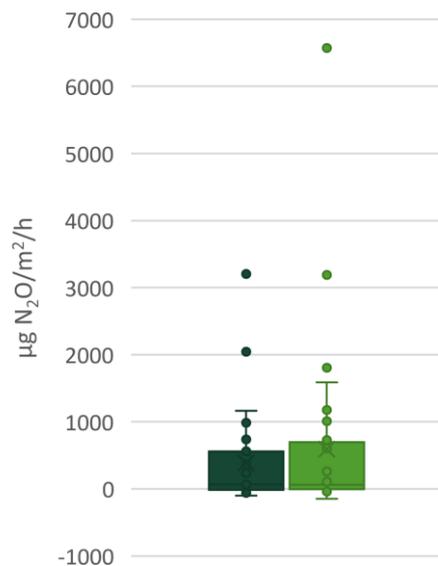


Figure 14. Box plot analysis of the N<sub>2</sub>O emissions during the field measurement

## 4.3 Laboratory experiments

### 4.3.1 Laboratory emission measurements

For CO<sub>2</sub>, emissions increased rapidly during the first three days after thawing. After reaching a peak, emissions decrease slowly in the following days. This pattern can be seen in all cycles, albeit the pulse is lower in the following cycles (Figure 15). There is a slight difference between the fertilized and unfertilized samples, especially in the first and third cycles. In the second cycle, the emissions are very similar. There is no significant difference between treatments in any of the cycles, which means that the differences observed between fertilized and unfertilized treatments are likely to be due to chance rather than true treatment effect.

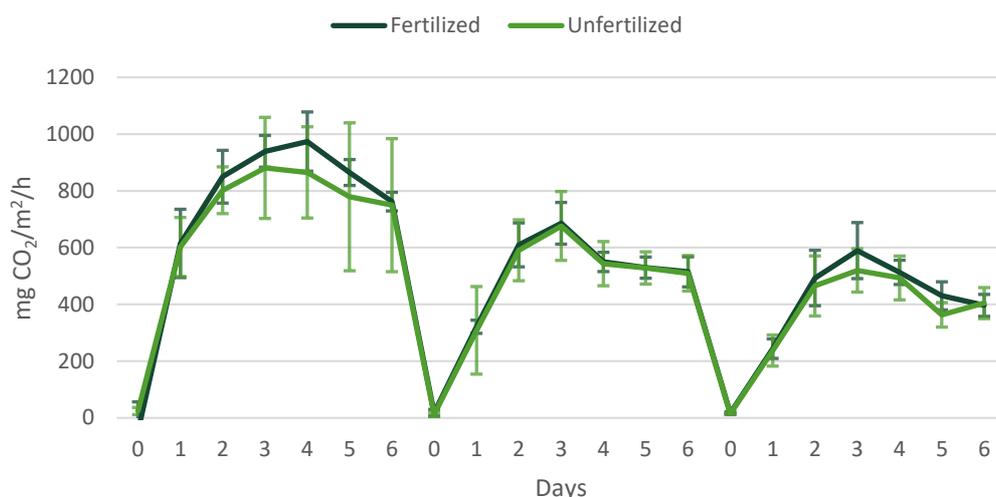


Figure 15. CO<sub>2</sub> emissions with standard errors for each measurement from the three FTC. The measurement performed directly after the samples were removed from the freezer is marked as day 0.

Figure 16 shows an actual by predicted plot for each cycle of measured CO<sub>2</sub> in the laboratory experiment. Two outliers were removed from the second measurement. The goodness-to-fit value of the residuals was above 0.05 for every measurement (Prob<W=0.95, 0.22, 0.21), indicating that the data is normally distributed.

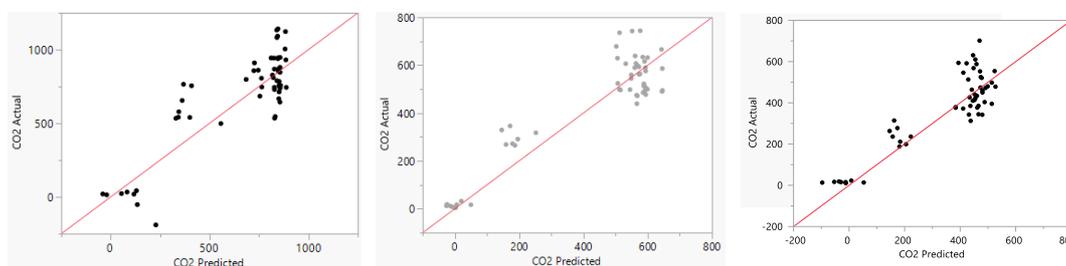


Figure 16. Actual by predicted plots for the first to third FTC of CO<sub>2</sub> emissions from the laboratory experiment. On the X-axis is the actual values and, on the Y-axis, the predicted. The X and Y-axis is transformed to log values from the measured values.

Table 6 shows a summary of the statistical analysis for the field measurements of N<sub>2</sub>O. The result shows that there is a significant correlation between CO<sub>2</sub> emissions to soil temperature in every cycle, but not to treatment or water content.

Table 6. The fixed effects parameter estimates model for the laboratory measurement of CO<sub>2</sub> emissions for the three FTCs.

Term	Estimate	Std Error	t Ratio	Prob> t	95% Lower	95% Upper
<b>1st cycle</b>						
Intercept	-48,5	710	-0,07	0,95	-1610	1513
Treatment [Fertilized]	5,19	36,6	0,14	0,89	-77,1	87,4
Soil temperature	25,4	2,38	10,7	<,0001*	20,6	30,2

Term	Estimate	Std Error	t Ratio	Prob> t	95% Lower	95% Upper
Volumetric water content	523	958	0,55	0,59	-1588	2634
<b>2nd cycle</b>						
Intercept	-260	381	-0,68	0,52	-1154	634
Treatment [Fertilized]	5,83	23,7	0,25	0,81	-52,4	64,0
Soil temperature	20,1	1,14	17,6	<,0001*	17,8	22,4
Volumetric water content	627	546	1,15	0,29	-658	1913
<b>3rd cycle</b>						
Intercept	-217	349	-0,62	0,55	-1017	582
Treatment [Fertilized]	8,81	22,0	0,40	0,70	-44,5	62,1
Soil temperature	14,6	0,83	17,7	<,0001*	12,9	16,3
Volumetric water content	602	537	1,12	0,29	-633	1838

Figure 17 shows the correlation between CO<sub>2</sub> and soil temperature. The R<sup>2</sup> value for soil temperature and CO<sub>2</sub> emissions are between 0.98 – 0.99 for the three FTCs, which indicates a strong correlation.

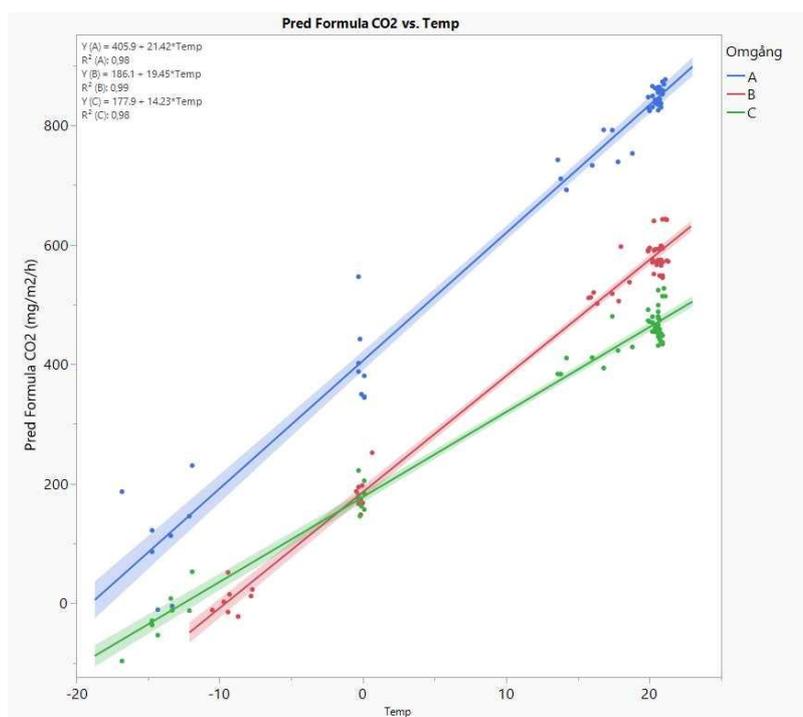


Figure 17. Regression lines from the three FTCs with CO<sub>2</sub> emissions against soil temperature (°C). The marked areas represent 95% confidence limits of the regression lines.

In the first FTC, there is a high pulse of N<sub>2</sub>O after two days in all soil samples. The peak is higher for the fertilized samples, it is a significant difference. After the high emissions, the emission level decreases considerably. In the second cycle, N<sub>2</sub>O emissions showed a tendency of following a similar pattern (Figure 18). However, the pulse seems lower for the fertilized samples and higher for the

unfertilized ones compared to the first cycle. There is no significant difference between the treatments in this cycle. The last cycle creates the lowest peak and has the smallest difference between the fertilized and unfertilized samples with no significant difference.

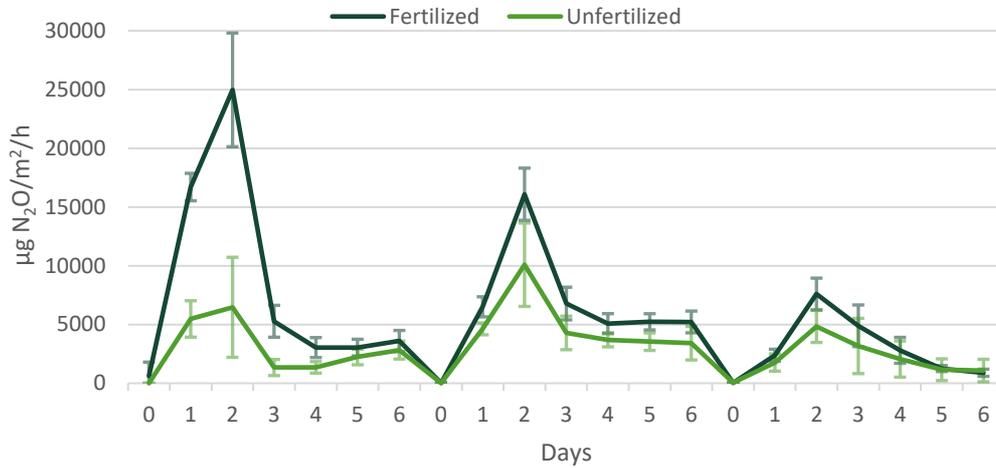


Figure 18. N<sub>2</sub>O emissions with standard errors for each measurement from the three FTC. The measurement performed directly after the samples were removed from the freezer is marked as day 0.

Figure 19 shows an actual by predicted plot for each cycle of measured N<sub>2</sub>O in the laboratory experiment. One outlier was removed from the first and second cycle respectively. The goodness-to-fit value was below 0.05 in the first and second measurement (Prob<W=0.003, 0.004), with residuals that were not normally distributed. The third measurement had a Prob<W value of 0.66, indicating normally distributed data.

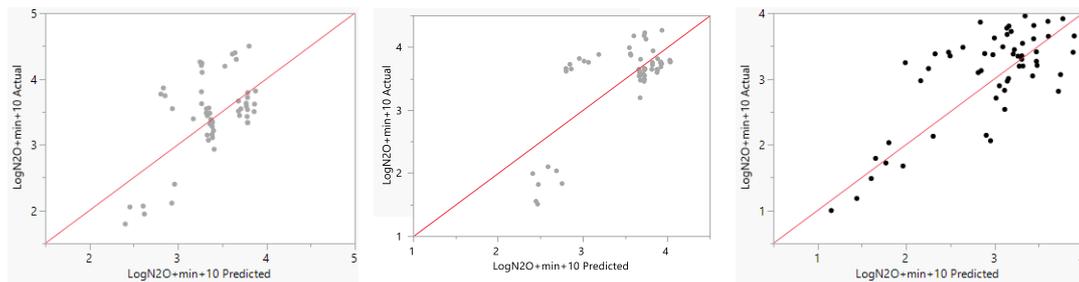


Figure 19. Actual by predicted plots for the first to third FTC of N<sub>2</sub>O emissions from the laboratory experiment. On the X-axis is the actual values and, on the Y-axis, the predicted. The X and Y-axis is transformed to log values from the measured values.

Table 7 shows a summary of the statistical analysis for the field measurements of N<sub>2</sub>O. The result shows that there is a significant correlation between N<sub>2</sub>O

emissions to soil temperature in every cycle and to water content in the third cycle. There is a positive correlation to treatment in the first cycle.

Table 7. The fixed effects parameter estimates model for the laboratory measurement of N<sub>2</sub>O emissions for the three FTCs.

Term	Estimate	Std Error	t Ratio	Prob> t	95% Lower	95% Upper
<b>1<sup>st</sup> cycle</b>						
Intercept	2,01	1,67	1,20	0,24	-1,48	5,50
Treatment [Fertilized]	0,21	0,08	2,52	0,0207*	0,03	0,38
Soil temperature	0,03	0,00	4,05	0,0002*	0,01	0,04
Volumetric water content	1,38	2,25	0,61	0,54	-3,29	6,06
<b>2<sup>nd</sup> cycle</b>						
Intercept	1,98	1,06	1,87	0,06	-0,14	4,11
Treatment [Fertilized]	0,10	0,06	1,63	0,11	-0,02	0,23
Soil temperature	0,04	0,00	7,25	<,0001*	0,03	0,05
Volumetric water content	1,36	1,50	0,91	0,37	-1,65	4,38
<b>3<sup>rd</sup> cycle</b>						
Intercept	-2,21	1,69	-1,30	0,22	-5,92	1,50
Treatment [Fertilized]	0,06	0,10	0,59	0,57	-0,16	0,29
Soil temperature	0,05	0,00	8,62	<,0001*	0,03	0,06
Volumetric water content	7,00	2,60	2,69	0,0205*	1,29	12,7

The temperature in the soil samples increased quickly and was stable after three days at room temperature in all cycles (Figure 20).

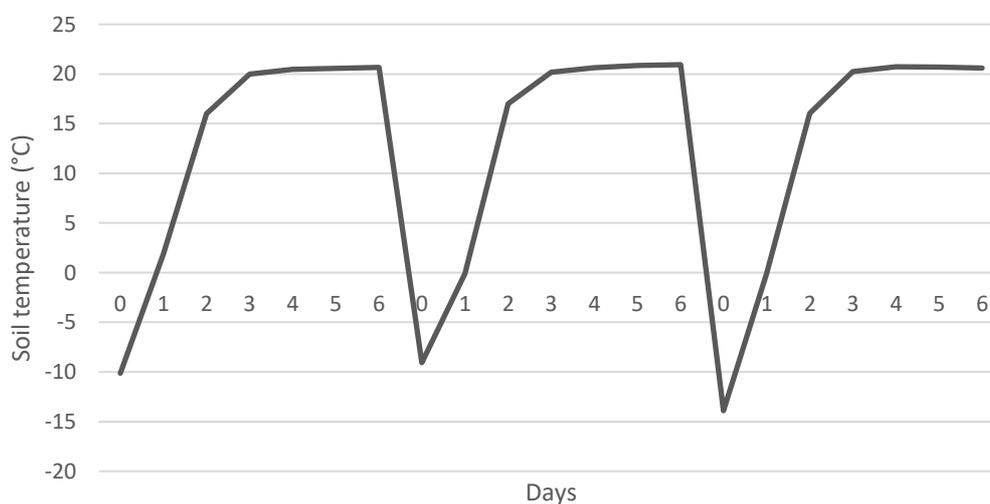


Figure 20. The mean value of the soil temperature from all soil samples. The measurement performed directly after the samples were removed from the freezer is marked as day 0. The first measurement in each cycle is made at 5 cm depth and the rest at 10 cm depth.

### 4.3.2 Soil properties

There were small differences in pH between the samples (Figure 21). pH in all samples increased in the second measurement, 24 hours after the first, from an average value of 5.6 to a value of 5.9. The average pH for the soil used for the fertilized and unfertilized soils did not differ (5.8).

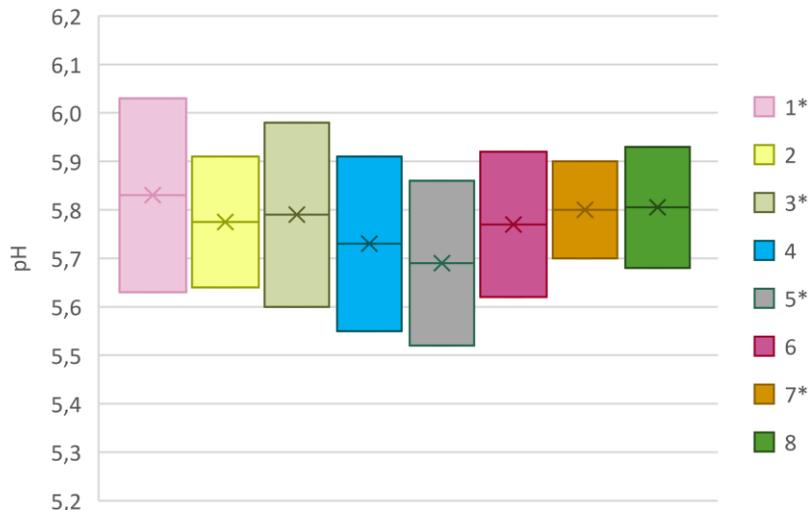


Figure 21. pH from all soil samples. Fertilized samples are marked with (\*).

Loss of ignition was high, indicating a high organic carbon content, and differed very little between the samples (Table 8). The bulk density varied between an average of 0,37 g/cm<sup>3</sup> in the first cycle to 0,34 g/cm<sup>3</sup> in the last cycle. There is no difference between the average value of the two treatments. The gravimetric water content in the eight samples was determined through oven drying after the laboratory measurements. The result from the volumetric water content shows varying result between all the samples (Table 8). There is no difference in the average value of the water content between fertilized (69 %) and unfertilized (70 %) samples. There was only one significant positive correlation between water content and gas emissions from the laboratory experiment, which was in the last cycle of N<sub>2</sub>O emissions.

Table 8. Calculation of loss of ignition, water content and bulk density. Bulk density and water content are calculated as an average of the three FTCs. Fertilized samples are marked with (\*).

	Loss of ignition (%)	Gravimetric water content (%)	Volumetric water content (%)	Bulk density (g/cm <sup>3</sup> )
1.*	87	206	76	0,37
2.	87	221	72	0,32
3.*	86	205	70	0,34
4.	86	201	69	0,34

5.*	87	189	62	0,33
6.	87	197	72	0,37
7.*	86	195	69	0,36
8.	86	179	67	0,37

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## 5. Discussion

The aim with this thesis is to compare two treatments in freeze and thaw related emissions to increase the understanding in which factors that affect GHG emissions. In this section is the results from the field measurement and laboratory experiment discussed, with suggestions on further work on the subject.

### 5.1 Field measurements

The results of the field measurements show that there was no significant difference between the fertilized and unfertilized samples for either CO<sub>2</sub> or N<sub>2</sub>O emissions. There was a strong increase in emissions in the spring for both gases and the results indicate that there was a decrease in emissions for N<sub>2</sub>O after the thawing. However, the standard error was high.

Starting by looking at CO<sub>2</sub> emissions, there were small differences during the measurements until May, then the increase was high. There is no significant difference between the treatments. Compared to the average for the period February to April, the fertilized samples had about 20 times higher emission levels during the peak, while the unfertilized had about 30 times higher, the numbers are with high uncertainty and the tendency is that the treatments show a similar result. In the last measurement, there was a decrease in emission levels for the unfertilized samples, while the fertilized ones continued to increase. Since the measurement did not continue, is it difficult to conclude if the emission decreased or kept at the same emission rate. The result of the N<sub>2</sub>O emissions from the field measurement also shows a high increase from the same time in May. In comparison to the average for the period February to April, the fertilized samples had about 60 times higher emission levels during the peak, while the unfertilized had about 110 times higher, but the numbers are with high uncertainty. Compared to CO<sub>2</sub>, emissions in both treatments decreased in the last measurement, indicating that the peak was reached during the measurement period.

For both gases, there is a large difference in emission rate between the samples within the treatments in the measurements in May, which can be seen with the high standard errors. It increases the uncertainty for the pulse and the difference between the treatments. There was no statistically significant difference between the treatments for any of the gases. However, the unfertilized samples show a

higher emission rate than the fertilized ones for both gases. This contradicts the literature and the result of the laboratory measurements. It is found by other reports (Regina et al. 2004), although it is more usual to see a higher emission rate in fertilized samples (Bouwman et al. 2002; Müller et al. 2002). The reason could be that the highest pulse did not appear during the short measurement time (5 min), but earlier or later. According to the literature review, the emission pulse is brief and often lasts only hours to a few days (Schimel & Clein 1996; Koponen & Martikainen 2004), which can also be seen in the laboratory experiment (Figure 13). For all cycles, the pulse appeared within two days after the samples were removed from the freezer. However, in the laboratory experiment, the fertilized samples always had higher emissions than the unfertilized ones. Another explanation could be high rainfall after application in the autumn, which caused the fertilizer to leak out.

Spring was later this year than normal and both March and April were colder than the reference period (1991-2020). For both CO<sub>2</sub> and N<sub>2</sub>O in the field experiment, the soil temperature correlates with the emission rate. However, the peak does not occur directly after the upper soil is unfrozen and the soil temperature at 15 cm had been increasing steadily for about a month before the high flush. It would have been beneficial to have a measurement at 5 cm depth from the weather station to see a clearer correlation between temperature and emission levels.

The measurement technique used to measure emissions in the field is a low-frequency method, and the risk of missing peaks is high. A high-frequency measurement method with automatic sampling could have been more beneficial for this type of measurement. If the pulse only lasts a few days, comparing the emission rate between days would be easy. It could also be possible to see if multiple cycles of freezing and thawing occur in the field. However, this greatly increases the cost of projects and was not possible in this work. With a low number of measurements, it is also difficult to calculate the amount of N<sub>2</sub>O emissions during the period. In addition, to see how spring emissions account for the total annual emissions, it would be necessary to measure the annual for at least one year.

One problem with using lysimeters in the field measurement is that they may not represent the actual field conditions. In visual observation, the soil appeared more frozen in the lysimeters than in the field. Three of the lysimeters accumulated water early in the winter season. These conditions were not visible in the rest of the field. The water in the lysimeters froze during the winter, resulting in a frozen layer of over 10 cm. As the soil thawed, an excess of water was found in these lysimeters. However, by the third field visit in mid-April, the excess water was gone. The lysimeters containing the excess water did not show any different emission results compared to the other lysimeters.

## 5.2 Laboratory measurement

The result from the laboratory measurement shows that there was a significant difference between the fertilized and unfertilized samples for N<sub>2</sub>O emissions in the first cycle, but not in the other cycles or for CO<sub>2</sub> emissions. Although not significant, the fertilized samples show higher N<sub>2</sub>O emissions in all cycles compared to the unfertilized ones. This is in line with other reports on the subject (Bouwman et al. 2002; Müller et al. 2002).

The effect of multiple cycles can be seen in the laboratory experiment, with the second and third cycles resulting in lower pulses than the first. If more cycles were performed, the emission peak would probably continue to decrease, due to less available material in the samples (Abalos et al. 2016). An exception is the average value of the unfertilized samples, which indicates an increase in the second cycle. However, there is a high uncertainty and the difference in N<sub>2</sub>O emissions is small for the unfertilized samples in comparison with the fertilized ones.

The emissions of both CO<sub>2</sub> and N<sub>2</sub>O increase rapidly as the soil thaws, but the pattern after the peak is different for the two gases. CO<sub>2</sub> decreases slowly after reaching a peak and N<sub>2</sub>O decreases drastically. This pattern is supported by Koponen and Martikainen (2004). They suggest that the production of N<sub>2</sub>O benefits more than CO<sub>2</sub> by the freezing and thawing process, as denitrifiers increase their activity more than soil respiration does with the additional nutrient supply (Koponen & Martikainen 2004).

There were extreme temperature differences during the laboratory experiment, from -18°C to thawing at +21°C. Koponen and Martikainen (2004) conclude that lower freezing temperatures lead to higher emissions. They suggest that the reason is that more aggregates, cells and roots are breaking up, increasing nutrient supply (Koponen & Martikainen 2004). In addition to the unrealistic temperatures, there is also a lack of precipitation during the experiment. There was no snowmelt and the amount of water added in the experiment was not related to the actual amount that usually falls on the site. Under field conditions, such a large part of the soil profile would not be exposed to multiple freezing and thawing.

A problem that arises in both the field and laboratory experiments is the difficulty in representing real field conditions, which is most evident in the laboratory experiment. In addition to the unrealistic climate conditions in the laboratory, the lysimeter contains only the topsoil layer of about 20 cm and the lid at the bottom prevents leaching. This makes the result from the field more reliable than the result from the laboratory experiment.

The result from this study showed that in the laboratory experiment, there is no significant difference between fertilized and unfertilized soil in CO<sub>2</sub> emissions. For N<sub>2</sub>O emissions, there is significantly higher for the fertilized treatment in the

first cycle. In the field experiment, there is no significant difference between the treatments. A suggestion from this may be that fertilized peat soils do not have higher emissions in spring than unfertilized soils. However, there are multiple sources of error in the work, with the largest being the few samples investigated and late fertilizing. The late fertilizing might have resulted in leachate since  $\text{NO}_3^-$  is very mobile in the soil (Ward 2008). The result from this study should be put in a larger context before drawing any final conclusions and recommendations.

In conclusion, several interesting patterns are visible in the laboratory experiment, where the fertilized samples showed a significantly higher emission rate than the unfertilized ones in the first cycle. However, it does not reflect the real climate conditions.

### 5.3 Soil properties

One of the aims of the work was to investigate whether it was possible to see if soil properties can be linked to GHG emissions. The soil properties examined in the laboratory experiment were pH, SOC, water content, dry bulk density and soil temperature. In the field, the soil temperature and water content were examined. It is also for these two properties that a statistical analysis has been carried out. The other properties were compared between each other and the average emissions of the samples in the laboratory experiment.

For pH, the value varied very little between the samples. This is not surprising as all lysimeters were taken close to each other and have not been subjected to any soil disruption for a long time. pH is low in the samples (5.8), like in many organic soils. Hénault et al. (2019) suggest that soils with a pH lower than 6.4 have a low capacity to reduce  $\text{N}_2\text{O}$  in soils and raising the pH with, for example, liming could be an option to reduce emissions. However, it would require more investigation whether it would be appropriate in other agronomic and economic terms. As for pH, SOC content and bulk density in the samples varied very little.

The water content is one of the most important factors controlling denitrification. However, there was no correlation between water content and  $\text{N}_2\text{O}$  emissions in either the laboratory experiment or the field measurement. The reason may be that the water content is within range for optimum emissions (Pärn et al. 2018), and that water is not the limiting factor (Ruser et al. 2006). Since the volumetric water content (VWC) in the laboratory experiment is within the suggested range (60 – 80%) (Veldkamp et al. 1998), is it unlikely that the main source would be nitrification instead of denitrification.

There is a positive correlation that is statistically significant between the emissions of both gases and soil temperature, both in the laboratory experiment and in the field measurement. Taft et al. (2017) found that soil temperature was

the most successful trait in predicting the amount of CO<sub>2</sub> emissions, which this study also shows among the properties examined.

All soil samples are taken from the same location, which means that soil properties do not differ significantly between samples. This makes it possible to compare the soil treatments effectively. However, it also means that it is not possible to compare contrasting soil properties in different locations, such as pH and SOC. To see a clear link between soil properties and emissions, one possibility would be to expand the sampling sites. A conclusion is that the soil in general does have many characteristics that tend to lead to increased emissions during spring thaw. This is a low pH, low C/N, and high SOC. Some correlation to the soil temperature could be seen in both the laboratory and field study. However, no further correlation could be drawn between soil properties and the emission rates of CO<sub>2</sub> and N<sub>2</sub>O in this study.

## 5.4 Freezing and thawing cycles in peat soils in the future

The conclusion from previous studies is that warmer winters can affect the pattern of freezing and thawing in spring. However, to what extent and how it might affect greenhouse gas emissions is still unclear. Several sources report the importance of the snow depth for the magnitude of the emissions. It would be interesting to look closer into that relationship.

There are several difficulties in investigating the impact of snow cover on emissions. In the laboratory, it is difficult to recreate real field conditions. In field experiments, an accessible way would be to examine the same soil and remove the snow cover during the winter. However, it is very time-consuming to do a whole winter season and would not be possible in this work. There are several other ways to investigate less snow cover that require more resources. For example, buried heated cables (Peterjohn et al. 1994) and heaters that melt snow from above (Nijs et al. 1996).

It is also possible to model N<sub>2</sub>O emissions related to FTCs. This is considered a challenge since many different factors contribute (Yadav & Wang 2021). Another challenge with experiments of FTCs is to compare results from other experiments. Often, the soil characteristics differ and the experimental methods are performed differently.

## 5.5 Improvements and further research

Several improvements could be made to this experiment. For the field measurement, a higher measurement frequency would be beneficial to catch the

highest emission peak. For the laboratory measurement, preparation could have been made to have an equal number of freezing and thawing days since the freezing duration is a factor that can contribute to the emission rate. This is mostly the last freezing cycle that was much shorter than the others due to lack of time. The measurement frequency could have been increased during the peak days. This was done in the second FTC, where measurements were performed twice a day. Since the peaks occurred very quickly in the laboratory measurement, this would be beneficial in order not to miss peaks in the peak itself. Another improvement would be to imitate real climate conditions at the field location. This could have been done by letting them thaw in a fridge. It would have been possible to examine the influence of the number of FTCs by having more cycles for some soil samples and comparing them with samples with fewer cycles. However, more soil samples would be required as the number of samples in each treatment would be very small in this experiment.

It would have been interesting to make a larger comparison between soil properties and agricultural practices. This could be done by comparing different sites of drained peat soils. Another aspect is the use of different vegetation on agricultural land. It would be interesting to compare emissions from bare soil with grass cover and crops. It has been found that grass-covered sites have produced higher N<sub>2</sub>O emissions compared to arable land (Priemé & Christensen 2001). This can be interesting in the work with drained peat soils in the future.

## 6. Conclusion

- A peak of both N<sub>2</sub>O and CO<sub>2</sub> was visible after thaw in May in the field measurement.
- A peak of both N<sub>2</sub>O and CO<sub>2</sub> was visible after thaw in the laboratory experiment.
- No statistically significant difference between treatments was found in the field measurement. The fertilized samples showed significantly higher N<sub>2</sub>O emissions in the first cycle of the laboratory experiment.
- The trend of decreasing peaks through multiple cycles was visible in the laboratory experiment, where the pulse decreases with each cycle.
- There was a correlation between soil temperature and gas emissions, both in laboratory and field, indicating temperature to be the main driving factor.
- There was no correlation found between soil water and gas emissions, neither in the field nor laboratory.
- The soil had characteristics that could increase the likelihood of high emissions.

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## Popular science summary

In recent decades, peat soils drained for agriculture and forestry have received increasing interest from both scientists and the public. The main reason is that natural peat soils often store carbon, while drained peat soils have high greenhouse gas emissions of especially CO<sub>2</sub> and N<sub>2</sub>O.

During the year, there are both periods of low and high emissions. Winter is a time with low emissions when the soil is often frozen for a long period. Previous reports have shown that when the soil thaws in the spring, there are large emissions of both CO<sub>2</sub> and especially N<sub>2</sub>O. The reason for this large emission and why it seems to vary a lot between soils has been widely discussed and it is still not fully understood. There are also different opinions on whether emissions are affected by nitrogen fertilization and if soil properties can affect the result.

This study aimed to investigate the impact of fertilization on CO<sub>2</sub> and N<sub>2</sub>O emissions in the spring during thawing and to see if certain soil properties could be connected to higher emissions. The emissions of two treatments (fertilized and unfertilized) were compared and performed in a field and laboratory experiment. The result of the field measurement showed a large increase in emissions of both gases in late spring, but there was no significant difference between the treatments. In the laboratory experiment, the fertilized samples had significantly higher N<sub>2</sub>O emissions in the first cycles, while there was no difference between treatments for CO<sub>2</sub> emissions. A possible reason for the contradicting result between the field and laboratory experiment could be nitrate leaching in the field due to late fertilization. The soil properties could not be directly correlated to the emissions.

An important part of working with peat soils is to determine how the soil will be managed in the future. Warmer winter temperatures are already affecting the winter season in northern parts of the world, where peat soils are often found. It is still unclear how the emissions that occur when the soil thaws are affected if the winter season changes. One of the reasons is that there are many difficulties in conducting realistic experiments in the laboratory. Another reason is that the properties of organic soils differ greatly, and it can be difficult to draw conclusions from the results of only a few experiments.

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