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MAARIT LIIMATAINEN

**FACTORS CONTROLLING NITROUS OXIDE EMISSIONS FROM
DRAINED PEAT SOILS – EFFECTS OF WOOD ASH FERTILIZATION**

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*Factors controlling nitrous
oxide emissions from
drained peat soils – effects
of wood ash fertilization*

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ABSTRACT

When peatlands are drained, the emissions of nitrous oxide (N_2O), a potent greenhouse gas, may increase significantly, especially in nutrient rich peatlands. The estimation of N_2O budgets from such peatlands faces substantial challenges due to the high variation in N_2O emission rates. For example, fertilization of forests may affect N_2O fluxes and nowadays, peatland forests are being increasingly fertilized with wood ash which is formed as a byproduct when biomass is burned for energy production. However, the effects of wood ash on greenhouse gas fluxes, especially on N_2O , are still far from clear.

The aim of this work was to study what factors, in addition to a low carbon to nitrogen (C/N) ratio (less than 25), account for the high variation in N_2O emissions in drained northern peatlands with different land-use options. There were together 11 study sites in Finland, Sweden and Iceland representing five different land-use types (forested and cultivated peatlands, afforested or abandoned formerly cultivated peatlands, as well as drained peatland that was not used for any purpose). The factors determining the variation in N_2O emission rates were studied in different laboratory experiments and data was available also for the annual N_2O emissions. The second main aim was to study the effects of wood ash fertilization on soil properties and N_2O emissions in boreal peatland forests with the focus on granulated wood ash. This is currently the most common ash form applied in the fertilization of peatland forests although it has been less extensively studied than the formerly used loose ash. The effects of granulated wood ash on N_2O emissions were studied in three peatland forests in Finland for two years. Laboratory studies were also conducted to reveal the mechanisms behind the changes in the N_2O production when peat is treated with granulated ash.

There was extensive variation within the land-use types in the N_2O emissions. The results show that also in peat soils with an optimum C/N ratio for N_2O emissions, the availability of mineral

N is an important factor to regulate N₂O production in nitrification and denitrification processes. It was found that the availability of P could also regulate the production and emission of N₂O. In addition, there was evidence that Cu availability is associated with the N₂O production in peat soils. Management intensity was linked to the N₂O emissions, with cultivated peatlands showing the highest emissions. However, within one single land-use group, there was variation (high/low) in the N₂O emission rates.

Nitrous oxide fluxes were not affected by granulated wood ash fertilization in the field experiments in the studied peatland forests. However, the results of the laboratory experiments indicated that granulated wood ash possesses the potential to decrease N₂O production. It is likely that rapidly leaching ions (salts) reduce N₂O production by inhibiting nitrification, which is the main process producing N₂O in our study.

Universal Decimal Classification: 502.3, 504.7, 546.172.5, 631.41, 631.432, 631.445.1, 631.831

CAB Thesaurus: greenhouse gases; nitrous oxide; peat soils; peatlands; boreal forests; soil properties; soil management; cultivation; variation; drainage; fertilization; wood ash; granules; carbon-nitrogen ratio; nitrogen; phosphorus; copper; Finland; Sweden; Iceland

TIIVISTELMÄ

Kun soita ojitetaan, dityppioksidin (N_2O), voimakkaan kasvihuonekaasun, päästöt saattavat nousta merkittävästi, etenkin ravinteikkailla turvemaidella. Ojitetuilla turvemaidella N_2O -päästöjen suuruuden arviointi on erittäin haasteellista, koska N_2O -päästöt vaihtelevat suuresti. Esimerkiksi metsien lannoitus saattaa vaikuttaa N_2O -päästöihin ja nykyään metsiä lannoitetaan enenevässä määrin puuntuhkalla, jota muodostuu sivutuotteena, kun energiantuotannossa poltetaan biomassaa. Puuntuhkan vaikutuksista kasvihuonekaasupäästöihin, etenkin N_2O :in, tiedetään kuitenkin vielä varsin vähän.

Työn tavoitteena oli tutkia, mitkä tekijät alhaisen (alle 25) hiili/typpi-suhteen (C/N) lisäksi selittävät eri maankäyttömuodossa olevien pohjoisten ojitettujen turvemaiden N_2O -päästöjen suurta vaihtelua. Tutkimuksessa oli mukana yhteensä 11 koealuetta Suomesta, Ruotsista ja Islannista, jotka edustivat viittä eri maankäyttömuotoa (suo- ja suopeltoja, metsitettyjä tai hylättyjä suopeltoja sekä ojitettu suo, jota ei oltu hyödynnetty ojituksen jälkeen mihinkään). Dityppioksidipäästöihin vaikuttavia tekijöitä tutkittiin erilaisin laboratorionkokein verraten tuloksia saatavilla oleviin koealueiden vuosittaisiin N_2O -päästöihin. Tämän tutkimuksen toisena tavoitteena oli tutkia miten puuntuhkalannoitus, erityisesti rakeistettu puuntuhkalannoitus, vaikuttaa maaperän ominaisuuksiin ja edelleen N_2O -päästöihin borealisessa turvemetsässä. Rakeistettu puuntuhka on tällä hetkellä yleisimmin käytetty tuhkamuoito lannoituksessa, mutta sen vaikutuksia on tutkittu paljon vähemmän kuin aiemmin paljon käytetyn hienotuhkan vaikutuksia. Rakeistetun puuntuhkan vaikutuksia N_2O -päästöihin tutkittiin kahden vuoden ajan kolmessa suometsässä Suomessa. Lisäksi tehtiin laboratorionkokeita, joissa tutkittiin millä mekanismilla raetuhka vaikuttaa turpeen N_2O -tuottoon.

Eri maankäyttömuotojen välillä oli suurta vaihtelua N_2O -päästöissä. Tulokset osoittavat, että myös turvemaidella, joilla C/N-suhde on optimivälillä korkeiden N_2O -päästöjen esiintyvyyden

suhteen, mineraalisen tyyppien saatavuudella on suuri merkitys N₂O-tuoton ohjailussa nitrifikaatio- ja denitrifikaatioprosessien kautta. Fosforin saatavuus vaikutti myös säätelevän N₂O-päästöä ja tuottoa. Lisäksi oli viitteitä siitä, että kuparin saatavuus on yhteydessä N₂O-tuottoon turvemaidella. Turvemaan käsittely-intensiteetillä on yhteys N₂O-päästöihin, sillä suopelloilla oli suurimmat N₂O-päästöt. Toisaalta myös yksittäisten maankäyttömuotojen sisällä oli suurta vaihtelua alhaisista korkeisiin N₂O-päästöihin.

Rakeistettu puuntuhka ei vaikuttanut N₂O-päästöihin kenttäkokeissa tutkituissa turvemetsissä. Laboratoriokokeiden perusteella raetuhkalla on kuitenkin suuri potentiaali alentaa N₂O-tuottoa. Tämä johtui luultavasti nopeasti liukenevista ioneista (suoloista), jotka pienentävät N₂O tuottoa inhiboimalla nitrifikaatioprosessia, joka oli pääasiallinen N₂O:a muodostava reitti tutkimuksissamme.

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Yleinen suomalainen asiasanasto: kasvihuonekaasut; dityppioksidi; eloperäiset maat; turvemaidet; suometsät; boreaalinen vyöhyke; vaihtelu; metsänkäsittely; ojitus; lannoitus; puuntuhka; rakeistus; hiili; typpi; fosfori; kupari; Suomi; Ruotsi; Islanti

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Kuopio, November 2016

Maarit Liimatainen

LIST OF ABBREVIATIONS

at%	atomic percent
C ₂ H ₂	acetylene
CH ₄	methane
C/N	carbon to nitrogen ratio
CO ₂	carbon dioxide
DOC	dissolved organic carbon
EA	elemental analyzer
EC	electrical conductivity
GC	gas chromatograph
GHG	greenhouse gas
GWP	global warming potential
IC	ion chromatograph
IRMS	isotope ratio mass spectrometer
KCl	potassium chloride
K ₂ SO ₄	potassium sulfate
N ₂ O	nitrous oxide
NO ₂ ⁻	nitrite
NO ₃ ⁻	nitrate
NH ₃	ammonia
NH ₄ ⁺	ammonium
OM	organic matter
SIR	substrate induced respiration
SO ₄ ²⁻	sulfate
TOC	total organic carbon analyzer
TP	total porosity

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to by the Roman numerals I–IV.

- I** Liimatainen M, Martikainen PJ, Voigt C and Maljanen M. Factors behind the variation in nitrous oxide emissions from managed northern peat soils with low C/N ratio. *Manuscript*.
- II** Maljanen M, Liimatainen M, Hytönen J and Martikainen PJ. The effect of granulated wood ash fertilization on soil properties and greenhouse gas (GHG) emissions in boreal peatland forests. *Boreal Environment Research* 19: 295-309, 2014.
- III** Liimatainen M, Martikainen PJ and Maljanen M. Why granulated wood ash decreases N₂O production in boreal acidic peat soil? *Soil Biology & Biochemistry* 79: 140-148, 2014.
- IV** Maljanen M, Liimatainen M and Sigurdsson B. Effect of volcanic ash on GHG production rates and soil properties in a drained peat soil compared to wood ash. *Icelandic Agricultural Sciences* 28: 25-28, 2015.

The above publications have been included at the end of this thesis with their copyright holders' permission.

AUTHOR'S CONTRIBUTION

- I** The author, Maarit Liimatainen, designed the study together with Marja Maljanen and Pertti J Martikainen. She had the main responsibility of the laboratory work, data processing and statistical analyses. The author wrote the first version of the manuscript.
- II** The author contributed to the design of the study and was partly responsible for both field and laboratory measurements. She contributed to the writing process with the other co-authors.
- III** The author, Maarit Liimatainen, designed the study together with Marja Maljanen and Pertti J Martikainen. She had the main responsibility for the laboratory work, data processing and statistical analyses. The author wrote the first version of the manuscript.
- IV** The author contributed to the design of the study and had the main responsibility for the laboratory work. She contributed to the writing process with the other co-authors.

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1 Introduction

In natural peatlands, the ground water table is close to the soil surface; in these wet and anoxic conditions, the processes decomposing organic matter work slowly. The three most important greenhouse gases are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Natural peatlands are usually a sink for CO₂ because the uptake of carbon as CO₂ through photosynthesis is higher than the loss via respiration and leaching (Gorham 1991). A water-logged environment with a limited oxygen supply creates favorable conditions for anaerobic CH₄ production and natural peatlands are globally important sources for CH₄ (Roulet et al. 1992, Schlesinger 1997). In addition to carbon (C), also nitrogen (N) is accumulated in the peat. There is a low production of N₂O in natural peatlands because nitrate (NO₃⁻) production (nitrification) is limited by the lack of oxygen and low N mineralization (Martikainen et al. 1993). Natural peatlands can even act as a minor sink for atmospheric N₂O (e.g. Regina et al. 1996, Chapuis-Lardy et al. 2007, Lohila et al. 2010).

Natural peatlands have to be drained before they can be used for forestry and agriculture. After the Second World War, more than half of the Finnish original peatland area (10.4 million ha) has been drained for forestry and about 1% for agriculture (statistics for the year 2000, Turunen 2008). Nowadays in Finland, as much as 24% of the total tree stand volume is growing on peatland forests (Päivänen 2008), and peat soils comprise 3.8 % of the total agricultural area (Myllys & Sinkkonen 2004). Peat extraction for energy production is the third most important land-use option for peatlands, 0.6% of peatland area is drained for peat extraction (Turunen 2008). There are currently 50 000 ha of peat extraction sites where peat extraction has ceased and annually 2000-3000 ha of peat extraction sites are abandoned with extraction having ceased (Silvan & Hytönen 2016). These areas can be abandoned, afforested or used for agriculture.

When a natural peatland is drained, there is a major alteration in the exchange of greenhouse gases (GHG). When the water table is lowered, there is an increase in oxygen availability in peat. This accelerates the decomposition of organic matter and mineralization, releasing especially CO₂ but also ammonium (NH₄⁺) for nitrification producing NO₃⁻ and nitrite (NO₂⁻) which are the key compounds for the N₂O production via denitrification (the microbial process with the greatest potential for N₂O production). Aerobic conditions and increased organic matter decomposition can convert a drained peatland from a CO₂ sink into a source of CO₂ (Schlesinger 1997). The elevated aerobic conditions mean that drained peatlands can act as a sink for CH₄ because increased oxygen availability limits CH₄ production but favors CH₄ oxidation in peat (Martikainen et al. 1995, Nykänen et al. 1998). Drainage of the natural peatlands can significantly increase N₂O emissions, but this depends on the fertility of the peatlands. A lowering of the water table enhances N₂O emissions more from the minerotrophic (nutrient rich) than from the ombrotrophic (nutrient poor) peatlands (Martikainen et al. 1993; 1995). In general, N₂O emissions are highest from agricultural peatlands but substantial emissions have also been measured from peatland forests (e.g. Martikainen et al. 1993, Regina et al. 1996, Maljanen et al. 2010a). Land-use, including drainage, is thus the most important factor affecting the GHG budget of peatlands.

It is known that drained organic soils have a high capacity to produce N₂O when the soil carbon to nitrogen (C/N) ratio is below 25 (Klemetsson et al. 2005, Maljanen et al. 2006a; 2010b; 2012). However, there is extensive variation in the N₂O emissions from those organic soils with C/N ratios below this threshold value (Maljanen et al. 2010b, Ojanen et al. 2010, Leppelt et al. 2014) indicating that the C/N ratio does not fully explain the N₂O emissions.

Fertilization of peatland forests affects the GHG fluxes. The use of biomass in energy production has increased, resulting in the extensive production of ash in power plants. Wood ash contains many other nutrients except N (e.g. Steenari & Lundqvist 1997, Steenari et al. 1999, Sarenbo & Claesson 2004,

Nieminen et al. 2005). Peat usually contains enough N but lacks other nutrients required for optimum plant growth such as potassium (K), boron (B) and phosphorus (P) (Hytönen 2003, Moilanen et al. 2005). Therefore, wood ash is a suitable fertilizer for peatland forests. Previously, peatland forests were fertilized with loose ash but nowadays this is conducted mainly with stabilized ash products which are easier to transport and spread. Nonetheless, granulation changes the physical and chemical characteristics of ash (Steenari & Lundqvist 1997, Steenari et al. 1999). Nutrients are released slowly from the ash granules and cause only a minor increase in soil pH (Steenari et al. 1999, Holmberg & Claesson 2001, Nieminen et al. 2005). Until now, the effects of wood ash on soil processes have been studied mainly with loose ash (as reviewed by Huotari et al. 2015). In particular, the effects of granulated wood ash on the emissions and production of GHGs in soil have been poorly studied. So far, the effects of loose ash (Maljanen et al. 2006a; 2006b, Moilanen et al. 2012) and self-hardened and crushed wood ash (Ernfors et al. 2010, Klemetsson et al. 2010, Rütting et al. 2014) on GHGs have been examined but there are no reports investigating the effects of granulated wood ash on GHGs. For example, more field and laboratory studies have been conducted with granulated wood ash on the dissolution properties of ash granules (Callesen et al. 2007, Mellbo et al. 2008), the solubility of cadmium (Cd) (Kapanen et al. (2005), C and N mineralization (Rosenberg et al. 2010) and effects on soil properties and soil fauna (Nieminen et al. 2012), but no studies have evaluated N₂O production.

Currently wood ash is the only commercial fertilizer available for peatland forests. Earlier, the Yara company produced a PK-fertilizer for peatland forests. Because the use of biomass in energy production is increasing, the amount of ash produced as a by-product is also increasing simultaneously. Nowadays, companies in Finland producing ash have to pay a waste tax if they dump ash in a landfill which encourages them to seek alternative ways for after-use of ash. In the future, it seems likely that the use of granulated wood ash as a fertilizer in peatland forests will increase.

The first aim of this study was to examine if there are biological, physical or chemical factors in the characteristics of peat which would explain the variation in N₂O emissions from drained peat soils within the optimum C/N range for high N₂O emissions. We selected 11 drained boreal peatland sites with a peat C/N ratio within the optimum range for N₂O emission. Several environmental factors and biogeochemical processes believed to be associated with the N₂O production were studied in an attempt to determine other factors, in addition to the C/N ratio, which could account for the variation in N₂O emission rates. The second aim was to study how granulated wood ash affects the N₂O emissions in boreal peatland forests. As discussed above, the use of granulated wood ash in peatland forest fertilization is increasing but its effects on GHGs, especially on N₂O, have been poorly studied. The hypothesis was that changes in pH and salts derived from added ash would affect N₂O production and emissions.

2 Literature review

2.1 Nitrous oxide in the atmosphere: sources and sinks

Concentrations of all GHGs have increased more or less linearly since preindustrial times (IPCC 2014, **Fig 1.**). Recent GHG concentrations of CO₂, CH₄ and N₂O are 399.5 ppm, 1834 ppb and 328 ppb, respectively (Blasing 2016). Compared to the period before industrialization, the corresponding concentrations are now 40%, 150% and 20% higher (IPCC 2013). Different GHGs can be compared by using the global warming potential (GWP) approach. The GWP of CO₂ is set to 1 and other GHGs are compared to CO₂. The amount of heat that is trapped by a GHG is expressed in mass units. When estimated in mass units, CH₄ and N₂O are more effective as GHGs than CO₂. Thus, the GWPs for CH₄ and N₂O are 28 and 265 at a 100-year time horizon, respectively (IPCC 2014). The lifetimes of these gases in the atmosphere are also different. The exact lifetime for CO₂ is unknown but the lifetime for CH₄ is 12 years and even longer for N₂O, 121 years (IPCC 2014). However, although CH₄ and N₂O are more potent GHGs than CO₂, their concentrations in the atmosphere are much lower than that of CO₂ which makes it the most important GHG. If one estimates the total anthropogenic GHGs, then one can calculate that 76% is attributable to CO₂, 16% originates from CH₄ and 6% from N₂O in 2010. The concentration of CO₂ is increasing by approximately 2 ppm annually. Methane had almost reached a steady state but now its concentration in the atmosphere is increasing again (**Fig 1.**). The N₂O concentration has increased annually by about 0.73 ppb during last three decades (IPCC 2014). In addition to having a high GWP, N₂O is harmful in the troposphere because it participates in chemical reactions destroying ozone and it is the most important ozone depleting gas (Ravishankara et al. 2009, IPCC 2013).

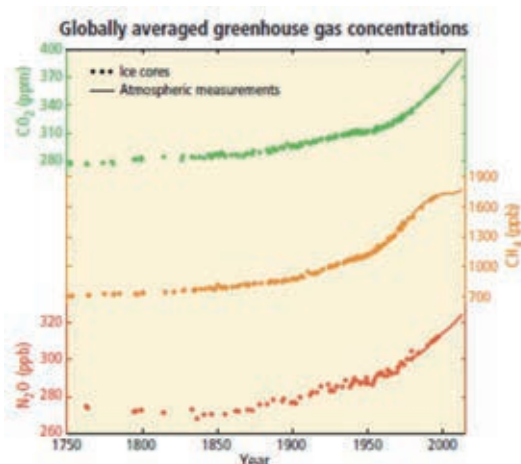


Fig 1. Trends in atmospheric concentrations of CO₂ (green dots), CH₄ (orange dots) and N₂O (red dots) since 1750 (Figure taken from: IPCC 2014, *Climate Change – Synthesis Report*).

A large proportion (30-45 %) of the total global N₂O emissions originate from anthropogenic sources with the rest being natural emissions (Fowler et al. 2009, IPCC 2013). Agriculture is the most important anthropogenic source but also biomass burning, energy production and industry contribute to the N₂O emissions (**Table 1.**). Microbial processes occurring in terrestrial and aquatic ecosystems are responsible for most of the natural sources. The estimated natural emissions from soils is 6.6 and that from oceans 3.8 Tg N₂O-N y⁻¹ (Fowler et al. 2009). The most important sinks for N₂O (**Table 1.**) are chemical reactions which take place in the stratosphere. Soils can be also a sink for N₂O (Chapuis-Lardy et al. 2007) but the soil microbial N₂O sink is less important in the total N₂O sink (Fowler et al. 2009).

In comparison to the situation with CO₂ and CH₄, attempts to mitigate N₂O emissions are challenging because agriculture is the main source for anthropogenic N₂O emissions (IPCC 2014) with more than 80% of the N₂O emissions originating from farming and cultivation (Davidson 2012). The increase in the N₂O emissions which occurred about one hundred years ago has been linked to the beginning of N fertilization practices in agriculture (IPCC 2014). The key to making it possible to produce N

fertilizers from atmospheric nitrogen (N₂) was the invention of the Haber-Bosch process, which led to the wide-scale use of N fertilizers. As the Earth's population has grown, the use of fertilizers has increased rapidly during recent decades. In this way, humans have added a huge amount of extra N fixed industrially, into the natural N cycle (Vitousek et al. 1997a; 1997b, Canfield et al. 2010). The increase in the use of fertilizers has been rapid. It has been estimated that in the most recent 40-year period (1960-2000), the use of N fertilizers increased by 800% (Canfield et al. 2010). One of the greatest problems in fertilization is its low efficiency. A remarkable proportion of the fertilizer N is not taken up by the target plants and thus the efficiency can be as low as 40%. Most N fertilizers contain ammonia and NO₃⁻. Nitrate can be lost via leaching and microbial denitrification. The ammonium in the fertilizer is nitrified (to nitrite) and then further converted into NO₃⁻. Some ammonia, especially from fertilizer urea and manure, can be directly volatilized into the atmosphere (Canfield et al. 2010).

Table 1. Sources and sinks of N₂O (adapted and modified from Fowler et al. 2009).

		Tg N₂O-N y⁻¹
Natural sources		
	Oceans	3.8
	Atmosphere	0.6
	Soils	6.6
Anthropogenic sources		
	Agriculture	2.8
	Biomass burning	0.7
	Energy & industry	0.7
	Others	2.5
	Total sources	17.7
Sinks		
	Stratosphere	12.5
	Soils	1.5-3
	Total sinks	14

If they are to be used for food production, peatlands have to be drained, which increases GHG emissions. Therefore, it is an important but demanding challenge to mitigate the negative climatic impacts of cultivation of peat soils. Mitigation should not decrease significantly the crop productivity and financial outcomes otherwise farmers will not adopt mitigation strategies unless their loss of income is compensated (Schaller et al. 2011, Regina et al. 2015). It has proven to be difficult to reduce N₂O emissions from cultivated peat soils because climate policies and recommendations do not deal sufficiently with this problem, and they may often be in conflict with national regulations or strategies (Regina et al. 2016).

2.2 Nitrous oxide production and affecting factors

It is challenging to estimate N₂O emissions and to extrapolate the results in order to construct accurate N₂O budgets because there is extensive variation in the N₂O emissions. In fact, this variation can be high within a small scale (van den Heuvel et al. 2009) and therefore, terms like “hot spots” or “hot moments” are often used to describe variations in the N₂O emissions (e.g. Groffman et al. 2009, van den Heuvel et al. 2009, Giles et al. 2012).

Many environmental parameters affect microbial N₂O production. The two most important microbial processes in the production of N₂O are nitrification and denitrification.



Nitrification is an aerobic process whereas denitrification is an anaerobic process (De Boer & Kowalchuk 2001) although there is evidence that denitrification can take place also in the presence of oxygen (e.g. Baggs 2011). In nitrification, ammonia oxidizing bacteria (AOB) convert ammonia (NH₃) into nitrite (NO₂⁻) through hydroxylamine (NH₂OH) (Baggs & Philippot 2010). It

has to be noted that it is NH_3 , not NH_4^+ , which AOBs use as their substrate (Kowalchuk & Stephen 2001). The ratio of NH_3 to NH_4^+ depends on pH, with the latter form predominating at low pH (see later more). In the second step, nitrite-oxidizing bacteria (NOB) convert NO_2^- to NO_3^- . The enzyme ammonia mono-oxygenase catalyzes the reaction from NH_3 to NH_2OH and during this step of nitrification, N_2O emissions may occur (Baggs & Philippot 2010). It is known that in addition to AOBs, also some archaea (AOA) are able to oxidize ammonia (Prosser & Nicol 2012) and numerically, AOA have been shown to predominate over AOB in some soils (Leininger et al. 2006). However, it is still a topic of research how much AOA contribute to nitrification activity (Leininger et al. 2006, Baggs & Philippot 2010, Prosser & Nicol 2012) although there is convincing evidence that AOA dominate over AOBs in terms of ammonia oxidation in acidic soils where pH is less than 5.5 (Prosser & Nicol 2012). In the denitrification process, NO_3^- is reduced to N_2 via NO_2^- , nitric oxide (NO) and N_2O (Knowles 1982, Zumft 1997). From the intermediate products, NO and N_2O are gases which can be emitted (Conrad 1996). Each step is catalyzed by a specific enzyme: nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase (Zumft 1997). Denitrifiers are a very heterogeneous group. Most of them are heterotrophic bacteria belonging to over 50 genera (Knowles 1982, Baggs & Philippot 2010).

Nitrification and denitrification processes may occur simultaneously in the soil because even an aerated soil contains both aerobic and anaerobic microenvironments. Nitrate produced in the upper aerobic soil profile can also be leached into the deeper oxygen-depleted soil layers where it can be denitrified. There are several important environmental variables associated with nitrification and denitrification i.e. availability of mineral N, moisture (oxygen), availability of organic substrates, pH and temperature (Bremner 1997, Wrage et al. 2001, Baggs & Philippot 2010, Bakken et al. 2012, Giles et al. 2012, Butterbach-Bahl et al. 2013) as discussed in more detail below.

The total gaseous emissions including N_2O , NO and N_2 are usually lower in acidic soils compared to soils with neutral or more alkaline conditions (Šimek & Cooper 2002). The effect of pH can be also indirect because in acidic conditions there is less available organic C and mineral N (Šimek & Cooper 2002). Under acidic conditions, the ratio of $\text{N}_2\text{O}/\text{N}_2$ in denitrification is higher than in more neutral conditions (Knowles 1982, Čuhel et al. 2010, Bakken et al. 2012, Giles et al. 2012) because the enzyme mediating the last step in the denitrification process i.e. nitrous oxide reductase which reduces N_2O to N_2 , is sensitive to low pH. Under acidic conditions, the denitrification process does not proceed to the end stage and the final product is N_2O instead of N_2 (Šimek & Cooper 2002). Changes in pH can affect the structure of soil microbial communities as was observed in the study of Baggs et al. (2010). When they increased the pH from 4.5 to 7, ammonia oxidation started to predominate instead of denitrification. However, not all nitrifiers are sensitive to low pH. Some nitrifiers have adapted to acidic conditions (De Boer & Kowalchuk 2001) including also AOA (Stahl & de la Torre 2012) which can compete for ammonia in environments with an acidic pH and a low availability of substrates (He et al. 2012, Hermann et al. 2012). It has been found that decreasing pH can increase N_2O emissions e.g. in acidic boreal forest soil (Martikainen 1985a) and in forested river areas (riparian) (van den Heuvel et al. 2011). In boreal peatland forests, this has been postulated to be linked with higher fungal dominance in acidic locations (Rütting et al. 2013) because some fungal species can produce N_2O (Baggs & Philippot 2010, Butterbach-Bahl et al. 2013). On the other hand, regardless of the pH conditions, there are soils that have a minor capacity to undergo nitrification. With respect to the ammonia oxidizing nitrifiers, pH conditions play an important role because soil pH determines whether it is NH_4^+ or ammonia (NH_3) which will predominate (De Boer & Kowalchuk 2001). Under acidic conditions, NH_4^+ dominates over NH_3 in contrast to alkaline conditions where NH_3 is the predominant form. Thus, in acidic conditions, ammonia oxidizers can suffer from a lack of substrate (NH_3 , see above).

Moisture conditions affect greatly microbial processes in soil because soil oxygen status largely depends on the soil water content. The optimum water filled pore space (WFPS) for denitrification is approximately 70% (Bateman & Baggs 2005). Values of WFPS higher than 80% favor N_2 production during denitrification, i.e. N_2O is reduced efficiently to N_2 (Butterbach-Bahl et al. 2013). On the other hand, in the study of Schindlbacher et al. (2004), maximum N_2O emissions for sandy and loamy forests soils were measured at WFPS% between 80 and 95 and Pihlatie et al. (2004) reported that maximum N_2O emissions in the studied soils (peat, clay, loamy sand) were detected at WFPS 100%. It has to be noted that in soil, denitrification largely depends on NO_3^- availability. If soil receives external NO_3^- (fertilization, deposition, leaching) then denitrification can occur in water-logged conditions. However, mostly internal NO_3^- production, i.e. nitrification, is needed for the NO_3^- supply. Therefore, conditions where the soil is waterlogged are usually not optimum for denitrification (Schlesinger 1997).

For nitrification, the optimal WFPS range is between 35 and 60% (Bateman & Baggs 2005). In the study of Bateman & Baggs (2005), 80% of N_2O was produced by nitrification in a silty loam soil when WFPS was 60%. Pihlatie et al. (2004) also noted that 70-80% of N_2O production originated from nitrification in peat, loamy sand and clay soils at the same WFPS of 60%. At 100% WFPS, denitrification was the main production pathway for N_2O in peat soil whereas in loamy sand soil, nitrification was still dominating, even in the wettest conditions. Therefore, it seems that the source of N_2O depends also on the site and soil type, not only on the value of WFPS (Butterbach-Bahl et al. 2013).

Nitrous oxide emissions are affected by temperature, directly and indirectly (Bremner 1997). With increasing temperature, denitrification and N_2O production increase as do microbial processes in general (e.g. Schaufler et al. 2010). Soil freezing and thawing cycles have a significant impact on N_2O emissions since the highest N_2O emissions are usually measured during freezing and thawing events (e.g. Koponen et al. 2006). The amount of N_2O emitted during thawing depends on the severity of the frost and

soil moisture. Low freezing temperatures and high soil moisture favor N₂O emission (Koponen & Martikainen 2004). The N₂O bursts during thawing, especially in springtime, can be high and these short ‘hot moments’ can account for a large part of the annual N₂O emissions (Maljanen et al. 2004). These high peaks of N₂O emissions can also depend on abundance of vegetation. In bare soil, plants will not be utilizing N and there can be high peaks of N₂O during freezing (Maljanen et al. 2004). Nitrous oxide is produced all year-round, emphasizing the need for annual measurements (Maljanen et al. 2003a; 2010a, Regina et al. 2004, Groffman et al. 2006a). It has been demonstrated that N₂O can be produced at temperatures as low as -6 °C (Koponen et al. 2004). It has been proposed that when soil freezes, it destroys soil aggregates and microbes, which increases the concentrations of nutrients. Those microbes that are still active in the soil benefit from the liberated nutrients (Skogland et al. 1988). It has been also suggested that there can be microbial activity in the water film on surfaces of soil aggregates, because these can stay unfrozen even at temperatures as low as -20 °C (Rivkina et al. 2000). The decline in plant N uptake during wintertime increases microbial N transformation and N accumulation. This could favor N₂O production and explain the high wintertime N₂O fluxes (Groffman et al. 2006a and references therein). Temperature can also exert indirect effects e.g. via oxygen consumption in soil respiration. Respiration is enhanced as the temperature increases, causing higher oxygen consumption and ultimately oxygen deficiency in soil. An elevation in temperature can also increase the availability of organic substrates to the denitrifying microbes. The availability of organic C affects denitrification because most denitrifiers need organic C as an electron donor (they are heterotrophic microbes) in the reduction of NO₃⁻ (Bremner 1997). Especially when soil is anaerobic and there is enough NO₃⁻, it is the availability of organic C that is often the limiting factor (Bremner 1997). Plant roots release organic exudates and therefore denitrification is more active in the rhizosphere (Bremner 1997, Baggs & Philippot 2010).

2.3 Drainage of boreal peatlands

Approximately 30 % of the land area in Finland (30.5 million ha in total) are classified as peatlands, most of these are located in northern and western parts of the country (Turunen 2008). In 1950, over 80 % of the peatlands were in a natural state, but 50 years later, over 50 % had been drained for forestry and agriculture (**Table 2.**) (Turunen 2008). From the total area of cultivated soils in Finland, 300 000 ha (13.6 %) are organic soils where the organic matter content is over 20 % (Myllys & Sinkkonen 2004). From that, 85 000 ha (3.8 %) are drained peat soils where the organic matter content is more than 40 %. The others (214 000 ha, 9.7 %) are mull soils, where the organic matter content ranges from 20 to 40 % (Myllys & Sinkkonen 2004). In the past, peatlands were taken for agricultural use because they were easier to change to agricultural land than forests with a mineral soil. It has been estimated that approximately 700 000 ha of peatland area has been used for cultivation during the entire time when people have lived in Finland (Turunen 2008).

Table 2. Use of peatlands in Finland in 2000 (modified from Turunen 2008).

Land-use	%
Natural peatlands	38.4 (4 mil ha)
Forestry	54.9 (5.7 mil ha)
Agriculture	0.8 (85 000 ha)
Peat extraction	0.6 (63 000 ha)
Water reservoirs	0.6 (60 000 ha)
Under roads	0.3 (35 000 ha)
Unknown	4.4

When peatland is drained, the ground water table falls and the amount of oxygen increases in the top peat. The elevated oxygen availability enhances C and N mineralization (organic matter decomposition). The decreasing amount of water in peat leads to a compaction of the peat. Due to compaction (and decomposition) of the peat, the depth of the ditches decreases with time and the water table level increases (Regina et al. 2015). This requires

deepening of the ditches or reinstallation of ditch pipes deeper into the peat to maintain the hydrology of the site suitable for cultivation. This induces more degradation and further subsidence of the peat (Kasimir-Klemedtsson et al. 1997). Thus, with time, the organic matter content decreases, and especially in cultivated peatlands, the mineral soil below the peat starts to mix with peat when the soil is ploughed (Myllys 2008). As a consequence, soils classified as peat, fall into the category of mull when their organic matter content declines to less than 40%.

In Finland, peatlands are considered to be suitable for forestry if there is enough N in the peat that can be turned into an available form after drainage (Laiho 2008). Most of the drained areas have been oligotrophic pine mires, in fact, it is estimated that the vast majority (80 %) of these have been drained nowadays (Turunen 2008). Drainage of nutrient poor peatlands is not so common since it is believed to achieve only a weak tree growth after they have been drained. For this reason, approximately 80% of nutrient poor peatlands are still undrained (Turunen 2008). In the southern part of Finland, it is more feasible to drain nutrient poorer peatlands for forestry than would be commercially viable in the northern parts of Finland (Laiho 2008).

2.4 Nitrous oxide emissions in drained peatlands

As mentioned above, the highest increase in N₂O emissions after drainage occurs in the nutrient rich peatlands (Martikainen et al. 1993). Peat characteristics and the nutrient level are associated with the dominating vegetation type and vice versa. Peatlands with *Carex* peat are nutrient rich whereas peatlands with *Sphagnum* peat are nutrient poor (Myllys 2008). Nitrous oxide emissions are usually highest in cultivated peatlands as a result of ploughing and fertilization and lowest in peat extraction sites with old recalcitrant peat on the surface (Regina et al. 1996, Kasimir-Klemedtsson et al. 1997, Maljanen et al. 2010b). Especially in cultivated and forested peatlands, there are both high and low N₂O emissions. However, it is not only the nutrient

level of the site that determines N₂O emissions, there are also other factors which influence this process.

Cultivated peatlands differ in many ways from peatland forests. During active cultivation, fertilization is given regularly and liming is applied to increase soil pH. Cultivated peat soils are also managed actively e.g. by ploughing, sowing and irrigation which increases their N₂O emissions (Maljanen et al. 2007, Kasimir-Klemedtsson et al. 2009). As discussed above, decomposition and compaction of cultivated peat leads to mixing of peat with mineral soils (tilling and ploughing) (Myllys 2008). Sometimes mineral soil is mixed intentionally with the peat to improve the characteristics of the soil so it will be more suitable for cultivation purposes (Maljanen et al. 2004; 2012) but nowadays this is rarely done (Myllys 2008). Mixing mineral soil with peat changes the quality of the peat and can increase N₂O emissions (Maljanen et al. 2004; 2012). Nonetheless, it is known that the type of management practices and the crop being cultivated affect the N₂O emissions (e.g. Regina et al. 2004, Weslien et al. 2012). In particular, high N₂O emissions can be measured from bare soils because there are no plants to compete with microbes for N (Maljanen et al. 2004). When cultivation is ended, the area is usually afforested or abandoned. Even though active cultivation management has ended, the emissions of N₂O may not decline. Emissions from afforested cultivated peatlands and abandoned cultivated peatlands can remain high for several reasons, e.g. increased amounts of nutrients, changes in the physical characteristics of the peat and increase in soil pH (Maljanen et al. 2007; 2011, Mäkiranta et al. 2007, Ojanen et al. 2010).

Emissions of N₂O in peatland forests are usually lower than in cultivated peatlands. However, some peatland forests display high emissions even without fertilization (Maljanen et al. 2010b). Drained peatlands are usually acidic, especially peatland forests, and their high N₂O emissions are believed to be linked to the low pH of the soil (e.g. Weslien et al. 2009, Rütting et al. 2013). Low pH has an inhibitory effect on N₂O reduction in denitrification and favors N₂O emission. An environment with a low pH can also

support N₂O producing fungi (Rütting et al. 2013). Furthermore, tree species can modify the N₂O emissions. N₂O emissions have been reported to be higher in deciduous than in coniferous peatland forest (von Arnold et al. 2005).

2.5 Fertilization of peatland forests with wood ash

The use of biomass in energy production is increasing in Finland because the aim is to increase energy production based on national energy sources and to avoid the consumption of fossil fuels. Nonetheless, the increase in biomass burning in power stations increases the production of ash. In Finland, wood and peat are often combusted for energy production. Therefore, the ash produced is mainly wood ash, peat ash or their mixture. About 600 000 Mg of wood, peat or wood and peat ash are formed as a byproduct of biomass combustion in Finland every year (Emilsson 2006, Väätäinen et al. 2011, Huotari et al. 2015). Nowadays, ash is classified as a waste and if it has to be transported to a landfill, a tax has to be paid which is based on the weight of the ash. This has proved to be a good incentive to develop other after-use options to avoid landfill dumping. Almost half of the ash produced is now used e.g. in ground work and road construction and to a lesser extent as fertilizer (Väätäinen et al. 2011). However, part of the ash is still transported to landfills.

When trees are harvested, a large amount of nutrients is removed from the forest depending on the harvesting intensity. Harvesting also increases leaching of nutrients (Laiho & Laine 1995). Granulated wood ash contains an abundance of many different nutrients such as Ca, K, P, Mg and Mn but no N (Steenari & Lindqvist 1997, Steenari et al. 1999); this is because N evaporates during the burning process. When ash produced in biomass burning is used as a fertilizer, the nutrients are returned back to the forests (Ingerslev et al. 2001). In peatlands, mineral soil lies under the peat layers and weathering does not bring

nutrients to the upper soil for vegetation. However, peat contains N, with the amount and quality depending on the peat type. *Carex* peat contains higher amount of N than *Sphagnum* peat. Thus, although many peatlands have enough N, there may be a deficiency of other nutrients, especially P and K and sometimes also boron (Hytönen 2003, Hånell & Magnusson 2005, Moilanen et al. 2010; 2013, Huotari et al. 2015). Mineral soils usually lack available N and in forests on mineral soils sites (upland forests), supplementation with wood or peat ash alone exerts no significant effect on tree stand growth (Saarsalmi & Mälkönen 2001, Jacobson 2003, Moilanen et al. 2013). Ash fertilization is beneficial in upland forests if acidification is a problem or if the nutrient balance needs to be corrected (Saarsalmi & Mälkönen 2001). In mineral and upland forests as well as in nutrient poor peatlands, wood or peat ash fertilization needs to be complemented with N supplementation if one wishes to increase tree growth (Saarsalmi et al. 2006, Helmisaari et al. 2009, Mandre et al. 2010). Recommendations for the ash dose are different for upland and peatland forests, 2.5-3 t ha⁻¹ and 4-5 t ha⁻¹, respectively (Moilanen et al. 2013). It has been claimed that if one wishes to acquire the greatest benefit, ash fertilization should be applied in nutrient-rich peatlands. Peatlands with the poorest nutrient status, e.g. sites having different *Cladonia* species and *Sphagnum fuscum*, are not suitable for forestry even after fertilization (Päivänen & Hånell 2012).

2.5.1 Characteristics of wood ash

Ash produced in power plants is in a loose form and it can be used as a fertilizer as such. However, without stabilization, loose ash suffers from many disadvantages (Emilsson 2006, Väättäinen et al. 2011). The loose ash has a small particle size and nutrients are liberated immediately after fertilization causing a salt (ion) shock to the vegetation (Steenari & Lundqvist 1997, Steenari et al. 1999, Pitman 2006). A dusty material, such as loose ash, is difficult to transport and spread in the forests (Väättäinen et al. 2011). As a consequence, ash is nowadays stabilized either by granulation or

subjected to a self-hardening process followed by crushing of the hardened ash (Steenari & Lindqvist 1997, Huotari et al. 2015). One option for ash stabilization is compaction into ash pellets (Hytönen 1999, Emilsson 2006). These are produced by pressing wet ash through a cylinder using different kinds of cylinder compaction methods (Emilsson 2006). Loose ash can be spread with a tractor but another option, especially in forests, is to use a helicopter for spreading the ash although this requires a spread area of at least 30-40 hectares if it is to be commercially feasible (Väättäinen et al. 2001).

The quality of ash produced reflects the material that has been burned and therefore, wood ash and peat ash exhibit some differences (Steenari & Lindqvist 1997, Steenari et al. 1999). Peat ash usually contains high amounts of P, but has a lower amount of other elements e.g. K and B than wood ash (Hytönen 2003, Piirainen et al. 2013). If peat ash is used as a fertilizer in cut-away peatlands to establish a tree stand, it is recommended to use biotite (a material containing K) together with peat ash (Huotari et al. 2011).

Heavy metals can be a problem associated with the utilization of ash and there are strict regulations defining how much heavy metals can be present in the ash. In particular, high concentrations of Cd may be a problem when applying ash fertilization (Perkiömäki & Fritze 2005, Emilsson 2006). There is legislation controlling the nutrient contents of ashes that can be used in fertilization in Finland. There are variable requirements for the P, K and Ca contents depending on whether ash is used in forest fertilization or for some other purposes. Obviously, in food production, the threshold limits are tighter than in forest fertilization. For example, the threshold value for Cd in ash is 25 mg kg⁻¹ in forest fertilization but ten times lower (2.5 mg kg⁻¹) for other purposes such as crop production and horticulture (Ministry of Agriculture and Forestry in Finland, decree 24/11). Often threshold limits allow ash to be used only in forest fertilization.

Wood ash contains a high amount of Ca; in loose ash it is mainly in the form of calcium oxide (CaO) and portlandite

(Ca(OH)₂) both of which dissolve rapidly (Steenari & Lindqvist 1997, Steenari et al. 1999) increasing soil pH when loose ash is applied (e.g. Weber et al. 1985, Bååth & Arnebrant 1994, Steenari et al. 1999, Saarsalmi et al. 2001, Nieminen et al. 2005). The stabilization process changes the chemical characteristics of wood ash, reducing the nutrient release rate and decelerating leaching which prolongs the fertilization effect (Steenari & Lindqvist 1997, Steenari et al. 1999). In the granulation process, water is used to moisten the ash. In the presence of water, CaO is converted to Ca(OH)₂ which is further transformed in the presence of CO₂ into calcium carbonate (CaCO₃) and therefore in granulated ash, Ca is less soluble than in its loose counterpart (Steenari et al. 1999). There are reports that the application of stabilized ash does not increase soil pH (Rosenberg et al. 2010, Nieminen et al. 2012) or the increase in pH is only minor (Ernfors et al. 2010).

Wood ash fertilization especially increases the amounts of Ca, K, Mg, B and Al in soil (e.g. Ludwig et al. 2002, Park et al. 2005, Ring et al. 2006, Helmisaari et al. 2009, Norström et al. 2012, Saarsalmi et al. 2001; 2012). For example, Na and K are present in ash as chlorides and sulfates and these are leached rather quickly from the ash granules (Nieminen et al. 2005). The stabilization process does not change significantly the leaching rate of these cations (Steenari et al. 1999). Ash granules have high pH values, over 10, and in these highly alkaline conditions, many elements, such as P, are insoluble or dissolve only slowly (Steenari & Lindqvist 1997, Steenari et al. 1999). Thus, granulated wood ash has lower solubility than self-hardened and crushed wood ash or loose ash (Nieminen et al. 2005) whereas in the study of Ring et al. (2006) pelleted ash exerted no statistically significant effects on soil chemistry compared to crushed wood ash.

2.5.2 Effects of wood ash on tree stand and vegetation

Ash fertilization enhances tree biomass production, but the extent depends on the nutrient status, (especially on N availability), as well as on properties associated with the site i.e. is the drainage system working properly (e.g. Moilanen et al. 2013,

Omil et al. 2013). Single ash treatment has a long lasting effect (20-50 years) on tree growth (Moilanen et al. 2002, Perkiömäki & Fritze 2005). Good results in tree biomass production are achieved, especially in sites where N availability has not been the factor limiting the growth but instead the trees are severely deficient in P and K (Moilanen et al. 2013). When planting tree seedlings (Pärn et al. 2009, Mandre et al. 2010) or establishing vegetation including trees on cut-away peatlands (Huotari et al. 2007; 2008; 2011), wood ash fertilization effectively supports plant growth.

Another problem associated with loose wood ash is that moss cover often decreases, especially with high doses (Ozolinčius et al. 2007, Pärn et al. 2009). On the other hand, in the study of Jacobson & Gustafsson (2001), bryophytes suffered badly immediately after the fertilization when using self-hardened and crushed wood ash but this phenomenon was not seen with pelleted wood ash. In addition, regardless of the ash form, ash fertilization decreased the coverage of *Cladina* lichens and dwarf shrubs (Jacobson & Gustafsson 2001). On the other hand, it has been shown that in drained peatland having mainly mosses and low shrubs, wood ash increases the amount of herbs and grasses usually growing in upland forests (Moilanen et al. 2002). When turning cut-away peatlands into forests and fertilizing them with wood ash, this form of fertilization seems to favor the growth of mosses that usually thrive in areas influenced recently by fire (Huotari et al. 2007). Although ash fertilization evokes changes in understory vegetation, elements from ash have not been found to accumulate in berries or mushrooms (e.g. Levula et al. 2000, Perkiömäki et al. 2003, Moilanen et al. 2006).

Ash fertilization has its greatest impact on the soil surface but due to leaching, its effects extend also deeper into the soil. Therefore, ash fertilization can affect plant roots. Granulated wood ash was reported to increase (Majdi et al. 2008) or to exert no effect on total root biomass (Püttsepp et al. 2006). In addition, there are studies where fine root biomass has either increased (Püttsepp et al. 2006) or decreased (Helmisaari et al. 2009). Wood ash may increase fine root density and growth as well as the root

length (Genenger et al. 2003). On the other hand, root diameter may decrease (Genenger et al. 2003) and the fine roots may spread deeper into the soil after ash fertilization (Helmisaari et al. 2009). However, all of these studies relating to the effects of ash fertilization on roots were conducted in spruce forests with mineral soils, not in peat soils.

2.5.3 Effects of wood ash on soil microbes

Ash contains nutrients promoting the metabolic activity of soil microbes (Weber et al. 1985, Omil et al. 2013) and ash fertilization has been shown to cause changes in soil microbial communities (Schutter & Fuhrmann 2001, Perkiömäki & Fritze 2002, Gömöryová et al. 2016). Both the ash dose and its form determine whether ash is beneficial or harmful for microbes (Bååth et al. 1995, Perkiömäki & Fritze 2002, Perucci et al. 2008). Generally, loose ash exerts greater effects on soil microbes than stabilized ash (Perkiömäki & Fritze 2002) mainly because the nutrients leach much more rapidly from loose ash and there is a notable increase in pH. For this reason, bacteria can benefit from the increase in pH (Rousk et al. 2009) and e.g. loose ash has been found to increase the soil respiration rate (Bååth & Arnebrant 1994, Sarangi et al. 2001, Zimmermann & Frey 2002, Saarsalmi et al. 2010; 2014), accelerate C turnover (Omil et al. 2013) and to increase the microbial biomass C (Zimmermann & Frey 2002). Although granulated wood ash does not change soil pH as much as loose ash, it does increase CO₂ production in N rich in contrast to N poor sites (Rosenberg et al. 2010). In the study of Perkiömäki & Fritze (2002), fungi and gram-positive bacteria were favored more than other microbial groups by loose ash fertilization. Wood ash fertilization has also been claimed to change the community of archaea in the humus layer of a mineral forest (Yrjälä et al. 2004). On the other hand, various microorganisms have different tolerance levels towards wood ash e.g. depending on their pH requirements (Mahmood 2003, Jokinen et al. 2006).

2.5.4 Effect of wood ash on N dynamics in the soil

The effects of ash fertilization on N dynamics tend to be variable. Ash fertilization can affect both nitrification and denitrification. Loose ash fertilization can stimulate nitrification in acidic soils (Martikainen 1984, Schutter & Fuhrmann 1999, Maljanen et al. 2006b). In the study of Odlare & Pell (2009), the denitrification rate was reduced due to loose wood ash fertilization whereas ammonium oxidation was either decreased or increased. There is a report that the application of coal loose ash increased the number of denitrifiers by 200-fold in soil (Schutter & Fuhrmann, 1999).

Wood ash increases mineralization and N availability in acidic forest soils (Weber et al. 1985) and also in mineral soil if ash is supplied together with N (Saarsalmi et al. 2012). On the other hand, there are also studies where net N mineralization has decreased in some soils (Omil et al. 2013) or there has not been any significant change (Saarsalmi et al. 2014). In a nutrient poor peatland forest, crushed wood ash fertilization has reduced net ammonification and net N mineralization whereas in a nutrient rich peatland forest, this type of ash had no effects (Björk et al. 2010). In an N rich forest growing on mineral soil, granulated wood ash increased net N mineralization, but not in N poor forest (Rosenberg et al. 2010). In a cut-away peatland wood ash fertilization has reduced the NH_4^+ and NO_3^- concentrations in soil (Huotari et al. 2011). It seems that the characteristics of the site determine the impacts of ash on N dynamics. Clearly, there is a need to study in greater detail the effects of granulated wood ash on N dynamics, especially in peatland forests.

2.5.5 Effects of ash fertilization on GHGs with the focus on N_2O emissions

Loose ash increases CO_2 emissions significantly, even decades after ash fertilization (Moilanen et al. 2002; 2012, Maljanen et al. 2006a). In field experiments, loose wood ash was reported to exert no effects on the N_2O emissions in mineral or peat soils (Maljanen

et al. 2006a; 2006b) but ash fertilization has increased the CH₄ oxidation (Maljanen et al. 2006a; 2006b).

Little is known about how stabilized wood ash influences GHG fluxes, especially on N₂O fluxes. The few studies investigating this topic have shown no effect (Ernfors et al. 2010) or a minor decrease in the N₂O emissions (Klemedtsson et al. 2010, Rütting et al. 2014). Crushed wood ash fertilization has been reported to increase CH₄ uptake in a site (Klemedtsson et al. 2010) for at least 4-5 years with an ash dose of 6.6 t ha⁻¹ (Rütting et al. 2014). Within two years after fertilization, crushed wood ash decreased CO₂ emissions compared to control and decreased N₂O emissions by 34-50% depending on the year and ash dose. In the study of Rütting et al. (2014), ash fertilization decreased N₂O emissions 5 years after fertilization but its effects on N₂O were not constant within this 5 year after fertilization. During the first two years after fertilization, the decrease in N₂O emissions seemed to be due to the increase in soil pH (Klemedtsson et al. 2010). In later years, at the same site, the pH value was the same in control and ash treatment and thus decrease in N₂O emissions had to be attributable to some factor(s) other than pH (Rütting et al. 2014). The effects of wood ash fertilization on N₂O emissions have varied in different studies from a decrease in emissions to no signs of an effect. Therefore, more research is needed e.g. investigations into the effects of different ash forms, the weather conditions and site-specific properties.

3 Aims of the study

The main objectives of this work were:

- 1) to attempt to explain the variation in the N₂O emissions in drained peatlands having optimum soil C/N ratio for N₂O production (I)
- 2) to examine the effects of ash on peat properties and N₂O emissions with focus on granulated wood ash applied in peatland forests (II, III, IV)

4 Materials and methods

4.1 Study sites

In article I, the study sites were chosen so that the C/N ratios would lie within the optimum range of 15 to 25 for high N₂O emissions. Drained peatland sites with available year-round N₂O emission data were chosen for the study. Overall, there were 11 study sites from Finland, Sweden and Iceland representing five different land-use types. There were two forest sites (SF, JF) in Finland and three cultivated sites; two in Finland (SC, KC) and one in Iceland (IC). There were also two abandoned, formerly cultivated sites in Finland (AB, BB) and three afforested, formerly cultivated sites; two in Finland (LA, RA) and one in Sweden (GA). Additionally, there was one site in Iceland (ID) that was drained but not used for any other purpose. The second letter of the site code refers to the land-use type:

- peatland forests (F)
- cultivated peatlands (C)
- afforested formerly cultivated peatlands (A)
- abandoned formerly cultivated peatlands (B)
- peatland that had been drained but not used for forestry or agriculture (D).

In forest sites (SF, JF; **Fig. 2**), we measured N₂O emissions (II) but for the other sites, annual N₂O emission data was used (**Table 3.**). In the Icelandic sites IC and ID, the N₂O flux data was based on measurements taken during the growing season (May-August) and thus the annual N₂O flux is only an estimate. All sites are described in detail in article I. The NF site was excluded from article I due to its high C/N ratio.

In article II, there were three study sites located in the western part of Finland and two of them were the same sites as examined in article (I). Site SF was fertilized with granulated wood ash (5000 kg ash ha⁻¹) in May 2010, and sites JF and NF in 2003. From

the sites, SF was the most fertile, NF the most nutrient poor and the site JF had a fertility between SF and NF. From these three sites, NF had a poorly working drainage system.

Table 3. Drained peatland study sites in three countries (FIN = Finland, ICE = Iceland, SWE = Sweden) where field measurements were conducted or where soil samples for laboratory experiments were collected for all 4 articles (I-IV). The table shows also the land-use type for each site. Soil samples were collected from all sites but field experiments were done only in forests sites (SF, JF, NF). The annual N₂O fluxes shown in the table are published in following articles: ^aMaljanen et al. (2014), ^bMaljanen et al. (2009), ^cMaljanen et al. (2010a), ^dRegina et al. (2004), ^eMaljanen et al. (2012), ^fKlemetsson et al. (2010). We measured the soil C/N ratio (± standard deviation) for each study site and result is an average from 0-10 cm and 10-20 cm soil layers. Site NF was excluded from the article I due to higher C/N ratio.

Site	Country	Land-use	N ₂ O flux (g N m ⁻² y ⁻¹)	C/N (0-20 cm)	Articles
SF	FIN	Forest	1,43 ± 0,59 ^a	22 ± 0,7	I-IV **
JF	FIN	Forest	0,07 ± 0,03 ^a	18 ± 1,3	I-II **
SC	FIN	Cultivated field	2,38 ± 1,49 ^b	17 ± 0,4	I **
IC	ICE	Cultivated field	0,03 ± ^c	16 ± 0,9	I
KC	FIN	Cultivated field	0,73 ± 0,12 ^d	22 ± 0,2	I **
LA	FIN	Afforested former field	2,14 ± 0,60 ^e	18 ± 0,6	I **
RA	FIN	Afforested former field	0,07 ± 0,07 ^e	25 ± 2,4	I **
GA	SWE	Afforested former field	0,26 ± 0,08 ^f	26 ± 1,5	I **
ID	ICE	Drained*	0,04 ± ^c	15 ± 0,8	I
AB	FIN	Abandoned former field	0,41 ± 0,17 ^e	21 ± 2,0	I **
BB	FIN	Abandoned former field	1,42 ± 0,68 ^e	26 ± 1,2	I **
NF	FIN	Forest	0,02 ± 0,01 ^a	82 ± 4,6	II **

* Drained but not used for agriculture or forestry

** Water table (WT) level known, in article I the WT ranged from -25 cm to 1m among sites on average and in site NF the WT was -16 cm.

The mechanism behind granulated wood ash affecting N₂O production was studied more closely (III). The results from article (II) indicated that granulated wood ash possessed the potential to decrease N₂O production and this phenomenon was studied with several laboratory experiments (III). In the laboratory studies, we used soil from the SF site where we also measured the highest N₂O emissions among the three peatland forest sites.

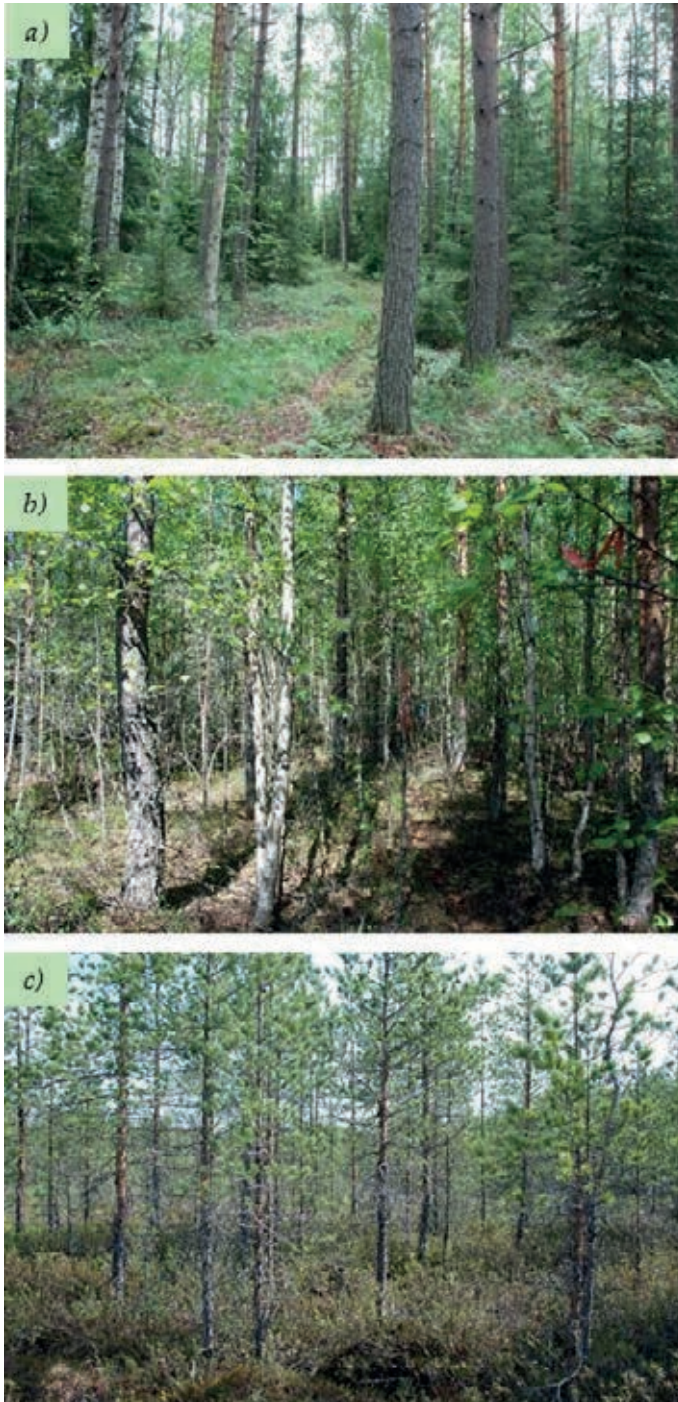


Figure 2. Peatland forest sites SF (fig. a), JF (fig. b) and NF (fig. c) where ash fertilization experiments and gas measurements in situ were conducted.

The results showed that the volcanic ash deposition could affect peat properties and N₂O emissions in Icelandic soils (I). Therefore, the effects of volcanic ash on GHG production were studied more closely with soil sampled from the SF site and results were compared with granulated wood ash (IV).

All study sites where field experiments were done or where soil samples were collected are listed in **Table 3** and described in more detail in the articles I-IV.

4.2 Methods

4.2.1 Physical, chemical and microbial methods (articles I-IV)

Laboratory experiments were done with fresh soil samples with the exception of the soil samples from Sweden (site GA) which were frozen after sampling. Gravimetric water content (GWC), pH_{H₂O}, electrical conductivity (EC), NO₃⁻, NO₂⁻, NH₄⁺ and dissolved organic carbon (DOC) concentrations were determined immediately from all soil samples after they arrived in the laboratory. In addition, organic matter content (OM%), particle density and water holding capacity (WHC) were measured. The N₂O production was studied in soil incubation experiments in the laboratory in aerobic conditions at +15°C (5 replicates). Field moist soil samples were used except for the Icelandic soils (IC and ID) which were rather dry compared to the other soils. Their WHC was adjusted to 60% for the N₂O production studies. In all of the incubation experiments investigating the N₂O production, it was decided to utilize field moist soil samples because in all study sites in article I the upper soil profile had been oxic. Field moist soil samples reflect the actual oxic conditions in the field and therefore we did not manipulate the soil moisture. The aim was not to study the potential N₂O production under anaerobic conditions. The production rate of N₂O was measured twice: at the beginning of the experiment (0 wk) and at 2 weeks after the start of the experiment (2 wk) to determine whether there had been any changes in the N₂O production with time. In this thesis,

the terms “N₂O emission” or “N₂O flux” refer to field measurements and the term “production” to incubation experiments conducted in the laboratory. After incubation, soil pH, EC and concentrations of NO₃⁻ and NH₄⁺ were measured again. The aim was to measure NO₃⁻ and NH₄⁺ concentrations at the beginning and at the end of the experiment to see if there had been NO₃⁻ or NH₄⁺ available during the entire incubation experiment i.e. allowing both nitrification and denitrification to take place.

Gross N mineralization and gross nitrification were assessed with the ¹⁵N pool dilution technique (Kirkham & Bartholomew 1954; 1955) in 6 replicates. Soils were pre-incubated for one week at +15°C. Samples for evaluating gross N mineralization were labeled with (¹⁵NNH₄)₂SO₄ (98 at%) and samples for gross nitrification with K¹⁵NNO₃ (60 at%). The sampling times during the incubation were 4 h and 24 h. The concentrations of NH₄⁺ and NO₃⁻ were analyzed from the KCl and H₂O extracts in a spectrophotometer and with ion chromatograph, respectively. Extracts of NH₄⁺ and NO₃⁻ were transferred from the liquid to gas phase by trapping them in filter papers inside Teflon traps using the microdiffusion technique for the determination of ¹⁵N atom % (at %) (Brooks et al. 1989). The filter papers were dried in an H₂SO₄ atmosphere inside a desiccator, placed in tin cups and analyzed for ¹⁵N at% with an elemental analyzer (EA).

Microbial biomass of soil was determined with the substrate induced respiration (SIR) method. Moisture was adjusted to WHC 60 % and SIR was conducted in 5 replicates. The optimum amount of substrate (glucose) was determined for each soil separately. The maximum soil respiration was measured during an incubation lasting from 2h to 2 h 45 min with 4 gas samples being taken during this period. The gas samples were analyzed immediately for CO₂ with GC and the CO₂ production rate was calculated from the linear increase in the concentration in the headspace. The microbial biomass C was calculated using the formula from Anderson and Domsch (1978).

Gross N mineralization, gross nitrification, soil microbial biomass C and particle density analyzes were conducted for the

10-20 cm soil layer and other analyzes for both 0-10 cm and 10-20 cm soil layers. All analyzes are described in more detail in article I.

4.2.2 Field studies (article II)

Site SF was fertilized with granulated wood ash in 2010, and sites JF and NF in 2003 using an ash dose of 5000 kg ha⁻¹ (Table 4.) The applied amount of ash is a standard dose in peatland forest fertilization in Finland. Field experiments started in sites SF and JF in May 2010 and in site NF in May 2011. The experiments ended in September 2012.

Table 4. The composition of elements in the granulated wood ash that was used to fertilize the SF site in May 2010. Ash was from the Ecolan company in Viitasaari. The ash used for the sites JF and NF sites contained P 15, K 38, Ca 167, Mg 27 and B 0.32 g kg⁻¹.

Element	g kg ⁻¹
Al	36
B	0,25
Ca	170
Cd	0,01
Cr	0,08
Cu	0,11
Fe	27
K	26
Mg	17
Mn	6,4
Na	9,6
Ni	0,04
P	10
Pb	0,13
S	19
Zn	1,8

The effects of granulated wood ash on N₂O fluxes were measured with static chamber technique (**Fig. 3.**) using 60x60x30 cm aluminum collars which were installed permanently into the peat with the same size of chambers inserted into the collars during the measurements. During the 35 min measuring time, a total of 4 gas samples of 30 ml were taken with syringes. Gas samples were injected from the syringes into 12 ml gas vials within 24h and analyzed later with GC for their N₂O and CH₄

concentrations. The results were calculated from the linear increase or decrease during the measuring period. The static chamber method was used when the snow cover was less than 10 cm. If there was more than 10 cm of snow, GHG emissions were measured from snow with the gas gradient method described by Maljanen et al. (2003b).



Figure 3. Static chamber measurement to analyze N₂O flux.

In the soil gas concentration measurements, silicone tubes were installed at depths of 5 and 20 cm, and in sites SF and JF also at 40 cm depth, in the peat to collect soil pore space gas samples for N₂O and CH₄ concentrations analysis. The water table (WT) level was followed from the perforated tubes installed in the soil. Peat temperature was measured manually during the sampling and also constantly with data loggers installed in the soil. Soil samples were taken from depths of 0-10 and 10-20 cm three times during the growing season. In the laboratory, pH_{H₂O}, EC and concentrations of NO₃⁻, NO₂⁻, NH₄⁺, chloride (Cl⁻), sulfate (SO₄²⁻) and DOC were analyzed from the samples to study the effects of wood ash fertilization on soil properties. At the end of the field experiments, soil samples were collected once from the depth of 0-40 cm to repeat the analyses.

When examining the effect of ash on organic matter decomposition, cellulose and tea bag decomposition experiments were made. Birch cellulose pieces or tea bags were buried in the peat for three months and decomposition rates were calculated

based on the weight loss. The standardized method called the Tea Bag Index (Keuskamp et al. 2013) was used with two different types of tea (rooibos and green tea). Root samples were collected from control and from ash fertilized plots (0-10 and 10-20 cm) at the end of the experiment to determine whether the ash fertilization had affected the root biomass.

To follow the effect of ash fertilization on tree stand growth, stem volume growth was measured in 2007 and 2012 at site JF and 2010 and 2012 at the NF site which had been fertilized in 2003 but not at site SF which was fertilized in 2010. A vegetation survey was conducted in all sites to determine how ash fertilization had influenced the ground vegetation in either the short-term or over the long-term.

All experiments and analyses have been described in detail in the article (II).

4.2.3 Process studies in the laboratory (articles II-IV)

As a follow-up to the field studies (II), we performed several laboratory incubation experiments to examine in detail the effects of wood ash. The laboratory experiments were conducted using soil samples from the SF site showing the highest N₂O emissions *in situ*. All incubation experiments were undertaken with field moist soil samples. In the laboratory, we studied how ash fertilization affected N₂O production in a temperature range of -6.4 to +12.5° during a 10-week soil incubation experiment. The second experiment examined the effects of different ash doses (0, 2500, 5000 and 10000 kg ash ha⁻¹) on the N₂O production. These experiments (II) indicated that granulated wood ash displayed a potential to decrease N₂O production. Therefore, the aim of article III was to study in more detail the mechanism behind this inhibition. All laboratory experiments done in article III are listed in **Table 5**. In the first experiment (Exp. 1 in **Table 5**.), the two main processes capable of producing N₂O, i.e. nitrification and denitrification, were studied by adding low (0.003 %) and high amount (2.5 %) of C₂H₂. With the low C₂H₂ addition, nitrification

is inhibited whereas with high levels of C_2H_2 , not only nitrification but also the last phase of denitrification (i.e. the reduction of N_2O to N_2) are inhibited (Klemedtsson et al. 1988).

The second experiment was divided into four parts (**Table 5**). In the first part (Exp. 2A), the effects of ions (“salts”) leaching from ash on the N_2O production were studied. We used two salts (K_2SO_4 and $(NH_4)_2SO_4$) and wood ash in granulated (AG) or in loose ash (AF) form. In this study, the granulated wood ash was powdered so that the ash was in a fine particle form. The amount of salts needed to achieve a similar increase in EC as with the ash addition had been tested beforehand. The second part of the experiment (Exp. 2B) tested the effects of soil pH on the N_2O production. We adjusted pH to 4 or 6 using $CaCO_3$ with and without ash addition. In third part of the experiment (Exp. 2C), we examined the combination of salts and pH but used only K_2SO_4 at pH 6. We also tested the possibility that the effects on N_2O would depend on the chemical used to adjust soil pH. Therefore, the incubation experiment was conducted by increasing soil pH to 6 with three different chemicals ($CaCO_3$, Na_2CO_3 , $NaOH$).

Table 5. A summary of laboratory experiments conducted in article (III). All the experiments are incubation studies with different kinds of set-up and treatments using field moist soil samples. In the ash form, AG refers to granulated wood ash and AF to loose ash. In our study, loose ash was powdered by ourselves from granulated wood ash. The pH manipulation describes which reagent was used to increase soil pH as well as the target pH value.

Exp.	Soil samples		Ash form	Salt additions	pH manipulation	C_2H_2 %	Oxygen
	0-10 cm	10-20 cm					
1	no	yes	AG	-	-	0.003 and 2.5	aerobic
2 a	no	yes	AG+AF	K_2SO_4 and $(NH_4)_2SO_4$	-	2.5	aerobic
b	no	yes	AG	-	$CaCO_3$ (pH4 and 6)	2.5	aerobic
c	no	yes	AG	K_2SO_4	$CaCO_3$ (pH6)	2.5	aerobic
d	no	yes	-	-	$CaCO_3$, $NaOH$ and Na_2CO_3 (pH6)	2.5	aerobic
3	yes	yes	AG*	-	-	2.5	aerobic
4	no	yes	AG	-	-	2.5	aerobic and anaerobic

* fertilization done in the field, not in the laboratory

The motivation behind the third experiment (Exp. 3, **Table 5.**) was the study of Maljanen et al. (2014, II) where ash fertilization had no effect on N₂O emissions in the field. For that purpose, soil samples were collected from the control (no fertilization) and from the ash-fertilized plots and incubated in the laboratory. Fertilization in the field had been done two years before the soil samples were taken.

The last experiment (Exp. 4, **Table 5.**) evaluated how aerobic or anaerobic conditions could affect N₂O production with and without ash addition.

The final article (IV) compared the effects of granulated wood ash and volcanic ash on N₂O production rate. The same amounts (corresponding to 5000 kg ha⁻¹) of granulated wood ash or volcanic ash were used in this experiment. Incubation was conducted similarly as described earlier. Acetylene inhibition with 2.5% of C₂H₂ was applied.

4.2.4 Statistical analyses

Statistical analyses except for the principle component analysis (PCA) were made with IBM SPSS Statistics software. The normal distribution of the data was tested with Kolmogorov-Smirnov and Shapiro-Wilk tests and homogeneity of variances with Levene's test. Differences between treatments when data was normally distributed were evaluated with one-way ANOVA. If homogeneity of variances was obtained, differences between treatments were examined with Tukey's HSD post hoc test and in cases when homogeneity of variances was not obtained, Tamhane's post hoc test was used. When a normal distribution of data was not fulfilled, differences between treatments were determined with non-parametric Kruskal-Wallis test for several independent samples. The effects of C₂H₂ were assessed with paired samples t-test if the data was normally distributed and with the non-parametric Wilcoxon signed-rank test if the data was not normally distributed (II-IV). Correlations between N₂O fluxes and other variables (I-II) were tested with Pearson's bivariate correlation test if the data was normally distributed and

with the non-parametric Spearman rank-order correlation test if the normal distribution of the data was not fulfilled. Statistical significances in correlations are shown with ** when $p < 0.01$ and * when $p < 0.05$. The PCA was applied in article (I) with R version 3.2.2 (R Core Team, 2015). The WT was not included in the PCA because data was not available for all sites.

5 Results

5.1 Factors behind variation in the N₂O emissions from managed northern peat soils with low C/N ratio (article I)

The variation in N₂O emission rates was studied in drained peatlands under different land-uses. The aim was to study which other factors, in addition to the C/N ratio, could explain this high variation of N₂O emissions. The N₂O production and soil microbial biomass were highest in the SC and AB soils. Lowest N₂O production and the smallest microbial biomass C were detected in the RA soil which also exhibited one of the lowest N₂O emissions (**Table 3.**). The N₂O production and soil microbial biomass were strongly linked to each other (0.745**). Gross N mineralization rate was highest in the LA and IC sites and lowest in the RA and SC soils. The gross nitrification rate was highest in the LA and SF sites and lowest in Icelandic IC and ID sites and in the RA soil.

Flux and production of N₂O were strongly dependent on soil N dynamics. In the surface layer, the N₂O production correlated especially with NH₄⁺ concentrations before (0.715*) and after (0.665*) incubation experiment and gross N mineralization with initial NO₃⁻ concentration (0.755**). The NO₃⁻ concentration (0.761**) and gross nitrification (0.818**) in 10-20 cm layer correlated with the N₂O emissions.

In PCA, component 1 in both soil layers represents the chemical status of the soils. There were several elements as well as pH which displayed the high loadings. In the surface soil layer, N₂O flux had highest loadings in component 3 and in the deeper soil layer in component 2. Land-use types, with the exception of cultivated soils, were located rather closely to each other in the PCA figure. Cultivated soils (SC, IC and KC) were scattered more widely, especially when using data from the 10-20 cm soil depth.

According to the PCA, parameters of WFPS, humification, C/N, P, Ca and Cu, were associated with the N₂O emission and production. The link between N₂O emission and P concentration was supported by their statistically significant correlation (0.709*), i.e. those soils with the highest N₂O emissions and production had also the highest P content in the soil. With respect to the Cu content, the trend was the same, i.e. the soil with the highest N₂O production and emissions exhibited the highest Cu content. The connection with the C/N, and N₂O emission and production, reflects the impact of mineral N availability on the processes behind the N₂O production.

5.2 Field experiments with granulated wood ash fertilization (article II)

5.2.1 Soil properties, ground vegetation and tree growth

The effects of granulated wood ash on GHGs and soil properties were studied by conducting field and laboratory experiments. Ash fertilization had no effect on soil pH (SF) or increased it only slightly (0.3 pH units, JF and NF). The EC was similar both in control and ash-fertilized plots in all sites. Ash fertilization increased the concentration of sulfate (SO₄²⁻) in the SF and JF soils.

Soil samples were taken several times during the growing season from a depth of 0-20 cm except in September 2012 when the field experiments ended, and soil samples were taken from depths of 0-40 cm. The results from that sampling are presented in **Table 6**. The average values of the growing seasons 2011 and 2012 for a depth of 0-20 cm are shown in Maljanen et al. (2014). **Table 6** shows the change in the basic soil parameters in the soil profile. In the SF and JF sites, soil pH increased in the deeper soil layer compared to the soil surface layers whereas in the NF site, pH was lower deeper in the soil. EC was highest in the soil layer of 10-20 cm both in control and in ash-fertilized plot in the SF site but in the JF site EC was highest in the 0-10 cm layer of both in

control and ash-treated soils. The concentration of NO_3^- increased with depth, especially in the SF site. Concentrations of NH_4^+ were higher in the deeper soil layers in the control plots both in the SF and JF sites whereas this was not seen in the ash-fertilized plots (Table 6.). In the NF site, there were low concentrations of NO_3^- and NH_4^+ only in the soil layer of 30-40 cm and only in the ash-fertilized plot. Sulfate concentrations were higher in the ash-fertilized plots in all sites and in all soil layers. The DOC concentration in the NF and JF sites was slightly higher in the ash treated than in the control soil. In the SF site, the DOC concentration was similar in the various soil layers both in the control and ash-treated soil.

Table 6. The degree of humification (*H*) determined using von Post (1922) scale, bulk density ($g_{dw} cm^{-3}$) of the peat and mean values (\pm SD, $n=3$) of soil pH, EC ($\mu S cm^{-1}$) and concentrations of nitrate (NO_3^- -N), ammonium (NH_4^+ -N), sulfate (SO_4^{2-}) and dissolved organic carbon (DOC) from control (C) and ash-fertilized (A) study plots at the depth of 0-40 cm. DOC concentrations are in $mg C g_{dw}^{-1}$ and others in $\mu g g_{dw}^{-1}$. Soil samples for these analyses were taken in September 2012 when the field experiments ended.

Site	Depth	<i>H</i>	BD	pH _{H2O}	EC	NO_3^- -N	NH_4^+ -N	SO_4^{2-}	DOC	
SF	C	0-10	7-8	0,19	3,84 \pm 0,03	67 \pm 2	5,4 \pm 0,2	2,9 \pm 0,3	20 \pm 4	0,64 \pm 0,08
		10-20	8	0,21	3,61 \pm 0,02	88 \pm 7	14 \pm 0,1	1,3 \pm 0,3	37 \pm 3	0,62 \pm 0,06
		20-30	8-9		3,75 \pm 0,02	85 \pm 2	40 \pm 1,4	0,8 \pm 0,1	46 \pm 7	0,66 \pm 0,03
	A	30-40	8-9		4,12 \pm 0,01	65 \pm 23	31 \pm 0,6	22 \pm 2,1	49 \pm 4	0,58 \pm 0,11
		0-10		0,17	4,02 \pm 0,03	59 \pm 1	2,7 \pm 0,01	2,2 \pm 0,2	32 \pm 5	0,58 \pm 0,05
		10-20		0,20	3,67 \pm 0,01	82 \pm 6	7,2 \pm 0,4	1,0 \pm 0,2	44 \pm 5	0,49 \pm 0,08
		20-30			3,74 \pm 0,02	71 \pm 15	30 \pm 0,9	0,5 \pm 0,3	49 \pm 2	0,68 \pm 0,09
		30-40			4,04 \pm 0,01	65 \pm 14	38 \pm 0,1	1,6 \pm 0,1	53 \pm 7	0,57 \pm 0,01
		JF	C	0-10	6-7	0,16	3,87 \pm 0,03	56 \pm 2	0,1 \pm 0,1	2,5 \pm 0,1
10-20	7-8			0,18	4,11 \pm 0,02	32 \pm 1	2,2 \pm 0,1	2,0 \pm 0,2	28 \pm 3	0,51 \pm 0,11
20-30	4-5				4,62 \pm 0,01	33 \pm 22	6,5 \pm 0,8	22 \pm 0,5	15 \pm 1	0,36 \pm 0,02
30-40	4-5				4,81 \pm 0,01	22 \pm 1	3,8 \pm 0,3	47 \pm 2,7	21 \pm 1	0,32 \pm 0,01
A	0-10			0,17	4,71 \pm 0,12	50 \pm 3	0 \pm 0	0 \pm 0	134 \pm 5	0,45 \pm 0,03
	10-20			0,18	4,44 \pm 0,01	37 \pm 15	2,4 \pm 0,2	0 \pm 0	76 \pm 10	0,35 \pm 0,04
	20-30				4,73 \pm 0,01	25 \pm 3	5,3 \pm 0,1	0,5 \pm 0,3	46 \pm 7	0,35 \pm 0,04
	30-40				4,93 \pm 0,01	26 \pm 1	3,8 \pm 0,3	0,5 \pm 0,6	67 \pm 8	0,30 \pm 0,01
	NF		C	0-10	1-2	0,05	4,23 \pm 0,02	25 \pm 5	0 \pm 0	0 \pm 0
10-20		2		0,05	4,03 \pm 0,01	28 \pm 5	0 \pm 0	0 \pm 0	38 \pm 11	0,78 \pm 0,11
20-30		2-3			4,10 \pm 0,01	32 \pm 6	0 \pm 0	0 \pm 0	15 \pm 2	0,72 \pm 0,04
30-40		2-3			4,02 \pm 0,06	39 \pm 2	0 \pm 0	0 \pm 0	18 \pm 2	0,90 \pm 0,08
A		0-10		0,06	4,52 \pm 0,06	25 \pm 7	0 \pm 0	0 \pm 0	16 \pm 3	1,14 \pm 0,19
		10-20		0,05	4,14 \pm 0,02	28 \pm 7	0 \pm 0	0 \pm 0	45 \pm 8	0,90 \pm 0,02
		20-30			4,09 \pm 0,04	37 \pm 3	0 \pm 0	0 \pm 0	43 \pm 3	0,74 \pm 0,05
		30-40			4,02 \pm 0,07	40 \pm 4	0,1 \pm 0,2	0,8 \pm 0,2	64 \pm 58	0,99 \pm 0,12

Ground vegetation had been changed by the ash fertilization in the SF site. The location of the collars was chosen on control and ash-fertilized plots such that the pairs would have similar

vegetation (**Fig. 4**). Two years after the fertilization, vegetation had flourished in the ash-fertilized plots; coverage of grasses and herbs had increased (short-term effects). Thus, in the ash-fertilized plot, plant coverage was $82 \pm 8 \%$ whereas it was less in the control plot, $57 \pm 15 \%$. When the effects were assessed 10 years after the ash-treatment they differed from those seen two years after the treatment. In the JF site, the mean coverage of grasses and herbs was higher in the control plots than in the ash-fertilized plots and the ash-fertilized plots had less mosses. In the NF site, there was no difference in vegetation between the control and ash plots. Ash fertilization had increased tree stand growth in the JF and NF sites. Tree growth was not measured in the SF as the duration of the monitoring was too short after ash fertilization to have exerted any meaningful impact.



Figure 4. Effects of granulated wood ash fertilization on ground vegetation. Collars in control and in ash-fertilized plots were chosen at the beginning of the field experiments when installing the collars in pairs having similar vegetation. In the figure a) and b) are one pair and c) and d) other pair. These photos were taken two years after the ash fertilization and in figures b) and c) can be seen how fertilization has increased the total coverage of the plants and changed the composition of the plant community into a more fertile type compared to control collars a) and d).

In the SF site, there was no change in the decomposition rate after ash fertilization. However, in the JF site, the cellulose decomposition rate was higher in the ash fertilized plots in the surface soil but there was no change in the tea-bag decomposition rate. In the NF site, cellulose decomposition was faster in the ash-fertilized plot than in the control plot in the deeper soil layer.

In the NF site ash, fertilization increased the mean total root biomass when considering both soil layers together. The highest increase took place in the surface layer. In the SF site, the root biomass was higher in the surface layer in the ash-fertilized plot than in control plot but when an average was calculated for both layers, there was no significant difference. Ash fertilization did not change root biomass in the JF site.

5.2.2 GHG fluxes and gas concentrations in the soil

Granulated wood ash fertilization had no effect on N₂O or CH₄ emissions *in situ* in any of the sites. The effects were similar regardless of the fertility of the forest site. However, granulated wood ash increased soil respiration in the JF and NF sites. In the JF site, respiration was 250 ± 110 mg CO₂ m⁻² h⁻¹ in the control and 320 ± 130 mg CO₂ m⁻² h⁻¹ in the ash-fertilized plot. In the NF site, respiration was 120 ± 50 mg CO₂ m⁻² h⁻¹ in the control but almost doubled in the ash treatment (220 ± 90 mg CO₂ m⁻² h⁻¹). Soil respiration was not measured in the SF site.

The nitrous oxide concentrations in soil were highest in the SF site and lowest in the NF site. In the NF site, the N₂O concentrations in soil were below the atmospheric (ambient) N₂O level. In the SF and JF sites, N₂O concentrations in the soil increased by more than 10-fold with depth in both treatments. In the ash-fertilized plots, N₂O concentrations were higher than in the control plots in the depth of 20 and 40 cm in the SF site and in the depths of 5 and 20 cm in the JF site.

In the SF site, CH₄ concentrations (from 1.9 to 3.0 ppm) were close to the ambient level (1.8 ppm) at all depths and similar in the ash treatment and control sites. In the JF site, CH₄ concentrations increased with depth from ambient concentrations (5 cm depth) to 17 ppm CH₄ (40 cm depth). Compared to the SF and JF sites, CH₄ concentrations in the soil of the NF sites were extremely high, from 1280 to 104000 ppm (~ 10 %). At the depth of 20 cm, all sites displayed higher CH₄ concentrations in the ash-fertilized plots than in the control plots.

5.3 Laboratory experiments to study the effects of granulated wood ash (articles II-IV)

5.3.1 Temperature and ash dose (II)

Article II had its focus in field studies, but there were also two laboratory experiments. We tested how granulated wood ash fertilization (corresponding to 5000 kg ha⁻¹) would affect N₂O production rates at different temperatures (from -6.4 to 12.5 °C). Ash fertilization decreased N₂O production by 70-80 % when the temperature was above 0°C whereas when the temperature was below zero, there was no difference in the N₂O production rates. Acetylene addition of 2.5 % decreased N₂O production by 80-90 % but not below 0°C degrees. The NO₃⁻ concentrations were similar at all temperatures, but NH₄⁺ concentrations increased more in the ash treatment at temperatures above 0°C; than in the control. The DOC concentrations were higher in the control and increased as the temperature rose. In the control, there was a decrease in pH with increasing temperature. The EC was much higher in the ash treatment than in the control.

The effects of ash on the N₂O production were tested using ash doses corresponding to 2500, 5000 and 10000 kg ha⁻¹. The production of N₂O decreased with increasing ash dose but with the smallest dose there was no statistically significant effect. Soil pH was similar between different ash doses but EC increased with as the ash dose was elevated.

All results from field studies are in article II, (Maljanen et al. 2014).

5.3.2 Ash form, pH, salts and comparison of laboratory and *in situ* ash treatments (III)

Laboratory experiments were conducted in article III to examine in greater detail the decrease in the N₂O production by granulated wood ash. This reduction was observed already in the laboratory experiments described in article II.

The first experiment focused on the contribution of nitrification and denitrification to N₂O production. We applied low (0.003 %) and high (2.5 %) concentrations of C₂H₂ and it was

noted that ash addition decreased the N₂O production. The higher concentration of C₂H₂ was more efficacious at inhibiting the N₂O production. There was an accumulation of NH₄⁺ in all treatments during the incubation, especially in the samples treated with ash.

In the first part of the second experiment (Exp. 2A), the “salt effect” caused by ion compounds leaching from ash granules was studied. Salt additions decreased N₂O production similarly in both granulated wood ash (WA) and loose ash (AF). AF increased soil pH by almost 3 units in contrast to WA which lightly reduced the value of soil pH. Nitrate concentrations were similar in the control soil and the AF treatment, but AG and salts decreased NO₃⁻ concentrations in soil.

In the second part of this experiment (Exp. 2B), we studied how changes in pH with or without ash additions affected N₂O production. Ash treatment alone increased pH by 0.4 units. In all treatments with ash, the NO₃⁻ concentrations were reduced. Concentrations of NH₄⁺ increased in all other treatments except for AGpH6 where NH₄⁺ concentration were similar to the control. The N₂O production was highest in the control and in the pH6 treatment and smallest in the ash treatments. The addition of C₂H₂ decreased N₂O production in samples without ash addition (C, pH4, pH6).

In the third part of the experiment (Exp. 2C), we studied the combinations of salt and pH. In the first sampling, the highest N₂O production was in treatments where pH was increased to 6 (pH6, K₂SO₄pH6 and AGpH6). In next sampling, which was conducted one week after starting the incubation, N₂O production was highest in the control. During the incubation period (2 weeks), N₂O production was always lowest in the K₂SO₄ and ash treatments. Addition of C₂H₂ (2.5%) decreased N₂O production especially in the control but also in the K₂SO₄pH6 and AGpH6 treatments. Nitrate concentrations decreased during the incubation in the K₂SO₄ and pH6 treatments whereas in the other treatments, NO₃⁻ concentrations were similar to control. The concentrations of NH₄⁺ increased in all treatments.

In the fourth part of the experiment 2 (Exp. 2D), we tested if CaCO_3 , which is used to increase pH, would affect N_2O production as such. Nitrous oxide production in peat was measured after addition of CaCO_3 , NaOH or Na_2CO_3 in the soil. The CaCO_3 caused the greatest decrease in the N_2O production, but this treatment caused also the greatest elevation of pH after the incubation compared to the other treatments which weakens the interpretation of the results.

The aim of the third experiment (Exp. 3) was to study if *in situ* ash fertilization would decrease N_2O production in laboratory studies. The N_2O production in the ash-fertilized soil was lower than in the control soil, especially in the 0-10 cm soil layer. In the surface layer, the N_2O production was higher than in the deeper soil layer.

In the fourth experiment (Exp. 4), we studied N_2O production in anaerobic conditions with or without ash additions. The N_2O production was similar between the control soil and ash treated soil. When C_2H_2 was added, N_2O production decreased in both treatments, though in the surface soil more than in the deeper soil. The NH_4^+ concentrations increased in all treatments during the incubation. The NO_3^- concentrations were higher in the control soil than in the ash-treated soil.

The results are explained in more detail in article III.

5.3.3 Differences between wood ash and volcanic ash (IV)

The total amount of measured elements (e.g. B, K, Cd, Cu) was generally lower in volcanic ash (VA) than in wood ash (WA) (IV, **Table 1**). However, the concentrations of iron and nickel were similar in both ashes. The VA did not increase the EC of the soil compared to granulated WA. The VA was alkaline ($\text{pH}_{\text{H}_2\text{O}}$ 7.8) similarly as WA ($\text{pH}_{\text{H}_2\text{O}}$ 8.8) and it increased soil pH values slightly, as did WA (IV, **Table 2**). The calcium content in VA was $\text{Ca } 4 \text{ mg mg}_{\text{dw}}^{-1}$ whereas WA contained $180 \text{ mg Ca mg}_{\text{dw}}^{-1}$. Despite the fine texture of VA, it did not increase soil pH similarly to the loose ash as detected in article III. The VA decreased but WA increased the NH_4^+ concentrations. WA decreased NO_3^- concentrations but with VA there was no change in NO_3^- .

Results

Chloride and sulfate concentrations increased in the WA treatment but not in the VA treatment. Volcanic ash had no effects on the production of N₂O. All results are shown in article IV.

6 Discussion

6.1 Variation of N₂O emissions in drained peatlands

One of the key parameters affecting N₂O emissions is the water table level (e.g. Martikainen et al. 1993, Nykänen et al. 1998) because decreasing WT level increases N₂O emissions. On the other hand, if WT is low enough, N₂O production can be limited (Maljanen et al. 2012). Thus, an increase in the level of WT has been postulated to be one way to lower N₂O emissions from drained peatlands (e.g. Berglund et al. 2011, Maljanen et al. 2012, Regina et al. 2015). When the WT level is increased closer to the peat surface, mineralization of peat decreases and emissions of N₂O as well as CO₂ are reduced (Regina et al. 2015). On the other hand, increasing WT may turn soil from a CH₄ sink into a source (Maljanen et al. 2012). Although adjusting the WT to an optimum level is an effective way to mitigate GHGs, it needs to be carried out by taking into consideration the cultivation practices. For example, the study of Regina et al. (2015) suggested that for grass production, the optimum WT level with which to mitigate GHGs but still allowing an optimal growth of grass would be 30 cm below the soil surface. In our studies, we used field moist soil samples since we wanted to keep the natural moisture level for each of the soils without drying or wetting the soils. The water content in drained peat soil is not the only factor affecting N₂O emissions, this was evident also in the soils studied here.

It has been noted that high N₂O emissions require a certain optimum soil C/N ratio, i.e. less than 25-30 (Klemedtsson et al. 2005, Maljanen et al. 2010b, Leppelt et al. 2014). The highest N₂O emissions have been detected in nutrient rich peatlands (Martikainen et al. 1993, Regina et al. 1996, Ojanen et al. 2010) and N₂O emissions are usually highest from cultivated peat soils (Martikainen et al. 1993, Regina et al. 1996, Maljanen et al. 2010b, Leppelt et al. 2014). This was also seen in our studies (I). The sites

showing the highest N₂O emissions were found to include either actively cultivated sites or sites cultivated in the past but now abandoned. As a result of cultivation history, the soil pH is usually increased due to liming and there is an increase in the amount of nutrients resulting from the fertilization practices favoring N₂O emissions. However, there was extensive variation in the emissions within a land-use type. In the present context, peatland forests represent land-use with the lowest management intensity. One of the two studied peatland forests exhibited one of the lowest N₂O emission of all of the land-use types studied whereas the other displayed a rather high N₂O emission.

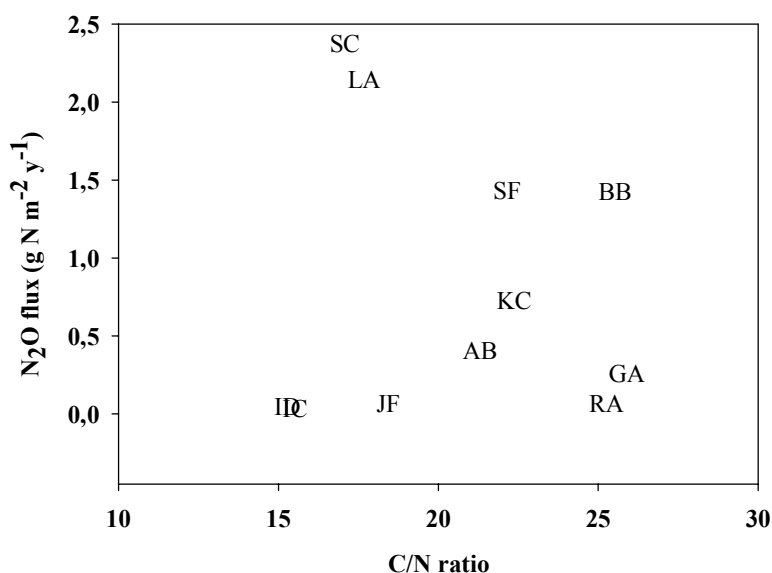


Fig. 5. A relationship between C/N ratio and N₂O flux in drained peatland study sites.

When considering N₂O emissions from drained peatlands in general (including peatland forests together with other land-use options such as agriculture), it seems that the soil C/N ratio predicts rather well the potential for high N₂O emissions (Maljanen et al. 2010b, Leppelt et al. 2014). However, the C/N ratio as such often does not reveal whether the N₂O emission is high or low as can be seen in **Fig. 5** where C/N ratios of the study sites in article I are plotted against N₂O fluxes measured in the

field. The figure shows that with C/N ratios less than 30, fluxes can be either high or low. This phenomenon was described also by Maljanen et al. (2010b), Ojanen et al. (2010) and Leppelt et al. (2014). Also, in the study by Tiemeyer et al. (2016) the correlation between C/N ratios and N₂O emissions was not that clear as shown by Klemedtsson et al. (2005). In other words, there have to be factors regulating the N₂O emissions which are not tightly linked to the C/N ratio.

It is known that P generally limits tree growth on drained peatlands and there is evidence that also microbes in peat can suffer from P deficiency (see article I and references there). Our results suggest that the availability of P could regulate N₂O production in peat soils, in agreement with the results of Regina et al. (1996). The sites here displaying the highest N₂O emissions had also the highest content of P in the peat (I). These sites are presently under cultivation or they have been used in the past for cultivation. Their soil nutrient status has been improved with regular fertilization and this is reflected in the high soil P content. As mentioned above, P has been linked to microbial respiration in peat. However, it is not known how the key microbes in N₂O production, nitrifiers and denitrifiers, are affected by P availability in peat. The effect of P on these microbes could be indirect via an increase in the N availability, resulting from the increase in decomposition processes (see Fig. 6/I). We did not study experimentally how the addition of P would influence N₂O production. However, we conducted both laboratory and field experiments where granulated wood ash was added to soil (see later). Wood ash contains P but the laboratory experiments conducted did not reveal any positive effect of ash on N₂O production, in fact if anything, ash decreased the N₂O production (II-IV).

The results obtained with the granulated wood ash are interesting because it had a minor effect on soil pH when applied in the field (no change in pH or increase of 0.3 unit, II) whereas when applied in the laboratory experiments, it could cause also some reduction in the pH (0.1 to 0.4 units) (III). This change in pH may have affected the overall denitrification/nitrification balance

and changed the N_2O/N_2 ratio for denitrification (Richardson et al. 2009). In this respect, the effects from nutrients and pH cannot be differentiated. An important finding was that also loose ash which increases soil pH by as many as 3 units, decreased the N_2O production (III). The conclusion is that it is the ions derived from ash which are responsible for inhibiting the N_2O production, not the change in soil pH. The inhibition would be expected to be higher in the laboratory experiments where the ash is well mixed with soil in comparison with the situation in the field, where ash is applied on top of the soil's surface. The mechanisms for these inhibition are discussed later in the chapter 6.2.

The results of the present study suggest that in addition to P, also Cu could be linked to the N_2O production/emission in peat soils. As discussed in article I, Cu is needed by the key enzymes of both ammonia oxidizing and denitrifying microbes. As mentioned above, our results suggest that ammonium oxidation is important in N_2O production. It may well be that a low availability of Cu limits ammonium oxidation and the subsequent N_2O production in non-fertilized peat soils. According to the published results, the importance of N_2O production associated “directly” with nitrification varies in peat soils (Regina et al. 1996; 1998, Andert et al. 2011). In the study of Regina et al. (1998), nitrification associated with N_2O production was most important in the soil surface (0-5 cm) layer, not deeper in the peat horizon. Here, Cu was linked to N_2O production /emission especially in the uppermost (0-10 cm) soil layer (I/Table S4).

The geographical origin of the sites had an impact on the N_2O emissions. Most of the study sites are located in the boreal region, although in Iceland, the surrounding ocean affects the climate and winter is relatively mild with respect to latitude. Nonetheless, the fertile Icelandic site even though cultivated, had low N_2O emissions (I). The volcanic ash deposition history of the site could influence its soil chemistry and processes involved in the production of N_2O . We anticipated that volcanic ash would change GHG production rates. However, addition of volcanic ash

to peatland forest soil (SF) exerted no effect on N₂O, CO₂ or CH₄ production (IV).

6.2 Mechanisms behind the effects of granulated wood ash

There are several reviews (Demeyer et al. 2001, Aronsson & Ekelund 2004, Perkiömäki & Fritze 2005, Pitman 2006, Augusto et al. 2008, Huotari et al. 2015) examining the effects of wood ash fertilization on different aspects of the environment including soil chemistry, vegetation, microbes and soil fauna etc. However, there are rather few studies on GHGs, especially on N₂O production and emissions. As far as we are aware, this is the first time when the effects of granulated wood ash have been studied on GHGs both in the laboratory and in the field.

In this study, granulated wood ash had no inhibitory effect on N₂O dynamics based on *in situ* studies covering both emissions and N₂O concentrations in the peat profile. The laboratory experiments revealed that N₂O production can be inhibited by wood ash. The field results do not reflect the actual N₂O production because N₂O emissions and concentrations are affected by both production and consumption of N₂O.

Despite the stabilization process, certain ions leach easily from ash granules (Steenari & Lindqvist 1997, Nieminen et al. 2005), e.g. sulfates are highly soluble compounds (Augusto et al. 2008). In our experiments, granulated ash and sulfate containing salts (K₂SO₄ or (NH₄)₂SO₄) decreased N₂O production. These treatments were tested several times with field moist soil sampled at different time points (month/year), and the outcome was always the same, i.e. a significant decrease in the N₂O production (III) irrespective of the different moisture levels. Of course, the results expressed here do not reflect the possible differences in N₂O production and mechanisms in the case of frequent water-logging leading to anaerobic conditions in peat. We conducted the laboratory experiments with soil samples taken from a peatland forest (I, SF site) where we had evidence from inhibitor experiments that N₂O was being produced mainly through

nitrification (II-III). The basis of the C_2H_2 inhibition method is that high concentration of acetylene (2.5% in our studies) inhibits ammonium oxidizers as well as N_2O reductase in denitrification (Klemetsson et al. 1988) whereas a low concentration (we used 0.003%) inhibits ammonium oxidizing bacteria and archaea but exerts no effect on denitrifiers (De Boer & Kowalchuk 2001). If the NO_3^- content in soil is low in the beginning of the experiment, the use of nitrification inhibitors causes an underestimation of the N_2O production via denitrification (Groffman et al. 2006b). Another problem with C_2H_2 is the fact that in the presence of oxygen, nitric oxide (NO) can be oxidized to nitrogen dioxide (NO_2) lowering the denitrification rates (Bollmann & Conrad 1997). In the ash experiments, the use of the C_2H_2 inhibition technique was justified because the SF site is fertile with a high NO_3^- pool. The use of the C_2H_2 technique is discussed more in article III. In addition, in the ash incubation experiments, we measured NO_3^- and NH_4^+ concentrations after the end of the incubation; NO_3^- concentrations tended to be decreased and NH_4^+ concentrations increased indicating that nitrification had been suppressed.

Soil pH is one of the most important factors impacting on N_2O production (e.g. Wrage et al. 2001, Šimek & Cooper 2002, Mørkved et al. 2007, Cuhel et al. 2010, Bakken et al. 2012). Granulated wood ash had no effect on pH in the field experiments (II). In the laboratory experiments, loose ash increased soil pH 3 units compared to control (III), but granulated wood ash decreased or increased soil pH only slightly, up to 0.4 units (II-IV). This is explained by the granulation process which stabilizes the ash (Steenari & Lindqvist 1997; 1999). The small changes in pH in granulated wood ash treatments likely did not affect the N_2O production. In our incubation experiments, N_2O production increased when soil pH was increased from 3 to 6 with $CaCO_3$ only (Exp. 2B and 2C, III). When pH was increased to 6 with $CaCO_3$ together with ash, N_2O production decreased significantly compared to control, indicating that the ash had exerted an inhibitory effect on N_2O production. This was supported by the fact that both granulated wood ash and loose

ash decreased N₂O production similarly (Exp. 2A, III). Addition of salts decreased N₂O production similarly as ash application confirming that N₂O production had been inhibited by ions leaching from the ash granules.

Salts are known to inhibit nitrification in acidic forest soils (Martikainen 1985b, Cheng et al. 2013) and our study confirmed this. The inhibitory effect of salts on N₂O production was supported by the experiment where we tested different ash doses; the N₂O production decreased with increasing ash doses (II). Both field (II) and laboratory studies (II-IV) support the conclusion that the decrease in the N₂O production is not a result of any change in pH. In the field and laboratory studies, the changes in soil pH with granulated ash were minor compared to the changes caused by loose ash which increased the pH by as much as 3 units (Huotari et al. 2015). We observed a similar increase in pH when applying loose ash in the laboratory (III). In our experiments, there was a similar decrease in N₂O production with both granulated wood ash and with loose wood (III) ash, suggesting that the readily soluble salts inhibit N₂O production in peat, but not by changing the soil pH. As far as we are aware, there are no previous laboratory studies investigating the effect of granulated wood ash on N₂O production in drained peat soil. In the study of Maljanen et al. (2006b), addition of loose ash had no effects on N₂O production but the experiment was conducted with mineral soil slurries.

In the laboratory experiments, the addition of loose wood ash increased CO₂ production e.g. as shown earlier by Saarsalmi et al. (2012) whereas granulated wood ash had no effect on CO₂ production (data not shown). Ash fertilization has long lasting effects on CO₂ production because in the study by Saarsalmi et al. (2012) fertilization had been conducted 30 years ago before starting the experiments but nonetheless CO₂ production was enhanced under laboratory experiments. The increase in CO₂ production by loose ash in our studies was associated with an increase in peat decomposition and mineralization, mainly resulting from the increase in soil pH. Increased DOC concentrations have also been postulated as one explanation for

the increase in CO₂ production (Saarsalmi et al. 2012). However, higher DOC concentrations can also be at least partly due to the increased pH caused by the addition of loose ash.

6.3 Climatic effect of wood ash fertilization

From a climatic perspective, drained peatlands are a risk due to the increase in peat decomposition (CO₂ loss) and N₂O emissions. Nonetheless, in fertile peatland, tree stand growth can compensate for the C loss and N₂O emissions and the site can act as a GHG sink (as shown by the GWP approach) (Ojanen et al. 2013). Wood ash fertilization enhances the growth and C sequestration in tree stands (e.g. Moilanen et al. 2012; 2013, Rütting et al. 2014, Huotari et al. 2015) as was seen also in our study sites. In the study of Moilanen et al. (2012), ash fertilization increased C sequestration of tree stands by about ten times in comparison to control. The essential question with respect to the atmosphere is how the CO₂ and N₂O emissions are affected by ash. Klemedtsson et al. (2010) claimed that crushed wood ash fertilization decreased the total GHG emissions during the first two years after fertilization. However, there are also studies not confirming this decreasing trend (Maljanen et al. 2006a, 2006b, Ernfors et al. 2010, Rütting et al. 2014) nor was it observed in our study. There are rather few studies on stabilized ash fertilization where all three GHG's (CO₂, CH₄, N₂O) have been measured *in situ*. As far as we are aware, this is the first study where the effects of granulated wood ash on fluxes of N₂O and CH₄ as well as soil respiration have been studied *in situ* in drained peatland forests.

Wood ash fertilization has been proposed to represent an option to mitigate N₂O and CH₄ emissions in fertile drained peatlands (Gundersen et al. 2012). In the study of Gundersen et al. (2012), this mitigation proposal was based on a study where crushed wood ash decreased both N₂O and CH₄ emissions. In our study sites, granulated wood ash had no effects on N₂O or CH₄ emissions *in situ*. However, in laboratory experiments, granulated wood ash decreased significantly N₂O production.

Discussion

The results suggest that wood ash has the potential to decrease N₂O emissions but more studies will be needed to clarify the mechanism behind how wood ash fertilization can alter N₂O emission in various peatland forests.

7 *Summary and conclusions*

One aim of this study was to examine if there are biological, chemical and/or physical characteristics of peat that would explain the variation in the N₂O emissions from drained peat soils which have an optimum C/N ratio but various land-use and management histories. In addition, the effects of wood ash on N₂O emissions in drained peatland forests were evaluated focusing on granulated wood ash.

The main findings are:

- I Within the optimum C/N ratio (less than 25) for the N₂O emissions, the emissions are still associated by the availability of mineral N linked to the land-use type and management intensity of the site. However, even within a single land use type, there can be extensive variation in the N₂O emissions. We found some evidence that the availabilities of both P and Cu are important in the regulation of N₂O production and emission in peat soils.
- II Granulated wood ash fertilization has no effect on soil pH and N₂O emissions in drained peatland forests regardless of the fertility of the site. However, based on the laboratory studies, granulated wood ash possesses potential to decrease N₂O production in drained peatland forest soil. This was not seen in the field, most likely due leaching of the nutrients and utilization of nutrients by vegetation.
- III Soluble ions rapidly leaching from the ash granules likely inhibit N₂O production. Nitrification was the most important process in N₂O production in the studied acidic peatland forest soil.

- IV Volcanic ash and granulated wood ash differ in their chemical composition and effects on production of GHGs. Volcanic ash seems to exert no effect on the N₂O production rate.

References

- Anderson JPE, Domsch KH, 1978. A physiological method for the quantitative measurement of microbial biomass in soils. *Soil Biol Biochem* 10: 215-221.
- Andert J, Wessén E, Börjesson G, Hallin S, 2011. Temporal changes in abundance and composition of ammonia-oxidizing bacterial and archaeal communities in a drained peat soil in relation to N₂O emissions. *JSS* 11: 1399-1407.
- Aronsson KA, Ekelund NGA, 2004. Biological effects of wood ash application to forest and aquatic ecosystems. *J Environ Qual* 33: 1595-1605.
- Augusto L, Bakker MR, Meredieu C, 2008. Wood ash application to temperate forest ecosystems – potential benefits and drawbacks. *Plant Soil* 306: 181-198.
- Baggs E, Philippot L, 2010. Microbial terrestrial pathways to nitrous oxide. pp 4-35. In: *Nitrous oxide and climate change*. Smith K (ed.). Earthscan. Routledge. Taylor & Francis. UK. USA.
- Baggs EM, Smales CL, Bateman EJ, 2010. Changing pH shifts the microbial source as the magnitude of N₂O emission from soil. *Biol Fertil Soils* 46: 793-805.
- Baggs L, 2011. Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction. *Curr Opin Environ Sustain* 3: 321-327.
- Bakken LR, Bergaust L, Liu B, Frostegård Å, 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N₂O emissions from soils. *Phil Trans R Soc B* 367: 1226-1234.
- Bateman EJ, Baggs EM, 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biol Fertil Soils* 41: 379-388.
- Berglund Ö, Berglund K, 2011. Influence of water table level and soil properties on emissions of greenhouse gases from cultivated peat soil. *Soil Biol Biochem* 43: 923-931.

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- Björk RG, Ernfors M, Sikström U, Nilsson MB, Andersson MX, Rütting T, Klemetsson L, 2010. Contrasting effects of wood ash application on microbial community structure, biomass and processes in drained forested peatlands. *FEMS Microbiol Ecol* 73: 550-562.
- Blasing TJ, 2016. Recent greenhouse gas concentrations. US Department of Energy, Carbon Dioxide Information Analysis Center (CDIAC). Oak Ridge National Laboratory. Available in: http://cdiac.ornl.gov/pns/current_ghg.html (5.10.2016).
- Bollmann A, Conrad R, 1997. Acetylene blockage technique leads to underestimation of denitrification rates in oxic soils due to scavenging of intermediate nitric oxide. *Soil Biol Biochem* 29: 1067-1077.
- Bremner JM, 1997. Sources of nitrous oxide in soils. *Nutri Cycl Agroecosyst* 49: 7-16.
- Brooks PD, Stark JM, McIner BB, Preston T, 1989. Diffusion method to prepare soil extracts for automated nitrogen-15 analysis. *Soil Sci Soc Am J* 53: 1707-1711.
- Burke RA, Zepp RG, Tarr MA, Miller WL, Stocks BJ, 1997. Effect of fire on soil –atmosphere exchange of methane and and carbon dioxide in Canadian boreal forest sites. *J Geophys Res* 102: 29289-29300.
- Butterbach-Bahl K, Baggs EM, Dannenmann M, Kiese R, Zechmeister-Bolterstern S, 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Phil Trans R Soc B* 368: 20130122.
- Bååth E, Arnebrant K, 1994. Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. *Soil Biol Biochem* 26: 995-1001.
- Bååth E, Frostegård Å, Pennanen T, Fritze H, 1995. Microbial community structure and pH response in relation to soil organic matter quality in wood-ash fertilized, clear-cut or burned coniferous forest soils. *Soil Biol Biochem* 27: 229-240.
- Canfield DE, Glazer AN, Falkowski PG, 2010. The evolution and future of Earth's nitrogen cycle. *Science* 330: 192-196.
- Chapuis-Lardy L, Wrage N, Metay A, Chotte J-L, Bernoux M, 2007. Soils, a sink for N₂O? A review. *Glob Chang Biol* 13: 1-17.
- Cheng Y, Wang J, Mary B, Zhang J-b, Cai Z-c, Chang SX, 2013. Soil pH has contrasting effects on gross and net nitrogen mineralizations in

References

- adjacent forest and grassland soil in central Alberta, Canada. *Soil Biol Biochem* 57: 848-857.
- Conrad R, 1996. Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O, and NO). *Microbiol Rev* 60: 609-640.
- Cuhel J, Simek M, Laughlin J, Bru D, Chèneby D, Watson CJ, Philippot L, 2010. Insights into the effect of soil pH on N₂O and N₂ emissions and denitrifier community size and activity. *Appl Environ Microbiol* 76:6: 1870-1878.
- Davidson EA, 2012. Representative concentration pathways and mitigation scenarios for nitrous oxide. *Environ Res Lett* 7: 024005.
- De Boer W, Kowalchuk GA, 2001. Nitrification in acid soils: microorganisms and mechanisms. *Soil Biol Biochem* 33: 853-866.
- Demeyer A, Voundi Nkana JC, Verloo MG, 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresour Technol* 77: 287-295.
- Emilsson S, 2006. International Handbook: from Extraction of Forest fuels to ash recycling. Skogsstyrelsen, Swedish Forest Agency. http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=Recash_International_Handbook_Final2006_EN.pdf, (30.09.2016). ISBN 91-9755555-1-7. 42pp.
- Ernfors M, Sikström U, Nilsson M, Klemedtsson L, 2010. Effects of wood ash fertilization on forest floor greenhouse gas emissions and tree growth in nutrient poor drained peatland forests. *Sci Total Environ* 408: 4580-4590.
- Fowler D, Pilegaard K, Sutton MA, Ambus P, Raivonen M, Duyzer J, Simpson D, Fagerli H, Fuzzi S, Schjoerring JK, Granier C, Neftel A, Isaksen ISA, Laj P, Maione M, Monks PS, Burkhardt J, Daemmgen U, Neiryneck J, Personne E, Wichink-Kruit R, Butterbach-Bahl K, Flechard C, Tuovinen JP, Coyle M, Gerosa G, Loubet B, Altimir N, Gruenhage L, Ammann C, Cieslik S, Paoletti E, Mikkelsen TN, Ro-Poulsen H, Cellier P, Capen JN, Horvath L, Loreto F, Niinemets Ü, Palmer PI, Rinne J, Misztal P, Nemitz E, Nilsson D, Pryor S, Gallagher MW, Vesala T, Skiba U, Brüggemann N, Zechmeister-Boltenstern S, Williams J, O'Dowd C, Facchini MC, de Leeuw G, Flossman A, Chaumerliac N, Erisman JW, 2009. Atmospheric

- composition change: Ecosystems-atmosphere interactions. *Atmos Environ* 43: 5193-5267.
- Genenger M, Zimmermann S, Frossard E, Brunner I, 2003. The effects of fertilizer or wood ash on nitrate reductase activity in Norway spruce fine roots. *For Ecol Manage* 175: 413-423.
- Giles M, Morley N, Baggs EM, Daniell TJ, 2012. Soil nitrate reducing processes – drivers, mechanisms for spatial variation, and significance for nitrous oxide production. *Front Microbiol* 3: 407.
- Gorham E, 1991. Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecol Appl* 1: 182-195.
- Groffman PM, Hardy JP, Driscoll CT, Fahey TJ, 2006a. Snow depth, soil freezing, and fluxes of carbon dioxide, nitrous oxide and methane in a northern hardwood forest. *Glob Chang Biol* 12: 1748-1760.
- Groffman PM, Altabet MA, Böhlke JK, Butterbach-Bahl K, David MB, Firestone MK, Giblin AE, Kana TM, Nielsen LP, Voytek MA, 2006b. Methods for measuring denitrification: diverse approach to a difficult problem. *Ecological Applications* 16: 2091-212.
- Groffman PM, Butterbach-Bahl K, Fulweiler RW, Gold AJ, Morse JL, Stander EK, Tague C, Tonitto C, Vidon P, 2009. Challenges to incorporating spatially and temporally explicit phenomena (hot spots and hot moments) in denitrification models. *Biogeochemistry* 93: 49-77.
- Gundersen P, Christianse JR, Alberti G, Brüggemann N, Castaldi S, Gasche R, Kitzler B, Klemetsson L, Lobo-do-Vale R, Moldan F, Rütting T, Schleppi P, Weslien P, Zechmeister-Boltenstern S, 2012. The response of methane and nitrous oxide fluxes to forest change in Europe. *Biogeosciences* 9: 3999-4012.
- Gömöryová E, Pichler V, Tóthová S, Gömöry D, 2016. Changes of chemical and biological properties of distinct forest floor layers after wood ash application in a Norway spruce stand. *Forests* 7: 108.
- He J-Z, Hu H-W, Zhang L-M, 2012. Current insights into the autotrophic thaumarchaeal ammonia oxidation in acidic soils. *Soil Biol Biochem* 55: 146-154.
- Helmisaari H-S, Saarsalmi A, Kukkola M, 2009. Effects of wood ash and nitrogen fertilization on fine root biomass and soil and foliage nutrients in a Norway spruce stand in Finland. *Plant Soil* 314: 121-132.

References

- Hermann M, Hädrich A, Küsel K, 2012. Predominance of thaumarchaeal ammonia oxidizer abundance and transcriptional activity in an acidic fen. *Environ Microbiol* 14: 3013-3025.
- Holmberg SL, Claesson T, 2001. Mineralogy of granulated wood ash from a heating plant in Kalmar, Sweden. *Environ Geol* 40: 820-828.
- Huotari N, Tillman-Sutela E, Kauppi A, Kubin E, 2007. Fertilization ensures rapid formation of ground vegetation on cut-away peatlands. *Can J For Res* 37: 874-883.
- Huotari N, Tillman-Sutela E, Pasanen J, Kubin E, 2008. Ash-fertilization improves germination and early establishment of birch (*Betula pubescens Ehrh.*) seedlings on a cut-away peatland. *For Ecol Manage* 255: 2870-2875.
- Huotari N, Tillman-Sutela E, Kubin E, 2011. Ground vegetation has a major role in element dynamics in an ash-fertilized cut-away peatland. *For Ecol Manage* 261: 2081-2088.
- Huotari N, Tillman-Sutela E, Moilanen M, Laiho R, 2015. Recycling of ash – For the good of the environment? *For Ecol Manage* 348: 226-240.
- Hytönen J, 1999. Tuhkapellettien hajoaminen maastossa (in Finnish). *Metsätieteen aikakauskirja* 3: 533-538.
- Hytönen J, 2003. Effects of wood, peat and coal ash fertilization on Scots pine foliar nutrient concentrations and growth on afforested former agricultural peat soils. *Silva Fenn* 37: 219-234.
- Hånell B, Magnusson T, 2005. An evaluation of land suitability for forest fertilization with biofuel ash on organic soils in Sweden. *For Ecol Manage* 209: 43-55.
- Ingerslev M, Mälkönen E, Nilsen P, Nohrstedt H-Ö, Óskarsson H, Raulund-Rasmussen K, 2001. Main findings and future challenges in forest nutritional research and management in the Nordic countries. *Scand J For Res* 16: 488-501.
- IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM (eds.)]. Cambridge University Press, Cambridge, UK and New York, NY, USA, 1535 pp.

- IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri RK and Meyer LA (eds.)]. IPCC, Geneva, Switzerland, 151 pp.
- Jacobson S, Gustafsson L, 2001. Effects on ground vegetation of the application of wood ash to a Swedish Scots pine stand. *Basic Appl Ecol* 2: 233-241.
- Jacobson S, 2003. Addition of stabilized wood ashes to Swedish coniferous stands on mineral soils – effects on stem growth and needle nutrient concentrations. *Silva Fenn* 37: 437-450.
- Jokinen HK, Kiikkilä O, Fritze H, 2006. Exploring the mechanisms behind elevated microbial activity after wood ash application. *Soil Biol Biochem* 38: 2285-2291.
- Kasimir-Klemedtsson Å, Klemedtsson L, Berglund K, Martikainen P, Silvola J, Oenema O, 1997. Greenhouse gas emissions from farmed organic soils: a review. *Soil Use Manage* 13: 245-250.
- Kasimir-Klemedtsson Å, Weslien P, Klemedtsson L, 2009. Methane and nitrous oxide fluxes from a farmed Swedish histosol. *Eur J Soil Sci* 60: 321-331.
- Keuskamp J, Dingemans B, Lehtinen T, Sarneel J, Hefting M, 2013. Tea Bag Index: a novel approach to collect uniform decomposition data across ecosystems. *Methods Ecol Evol* 4: 1070–1075.
- Kirkham D Bartholomew WV, 1954. Equations for following nutrient transformations in soil, utilizing tracer data. *Soil Sci Soc Am J* 18: 33-34.
- Kirkham D, Bartholomew WV, 1955. Equations for following nutrient transformations in soil, utilizing tracer data: II. *Soil Sci Soc Am J* 19: 189-192.
- Klemedtsson L, Svensson BH, Rosswall T, 1988. A method of selective inhibition to distinguish between nitrification and denitrification as sources of nitrous oxide in soil. *Biol Fertil Soils* 6: 112-119.
- Klemedtsson L, Von Arnold K, Weslien P, Gundersen P, 2005. Soil CN ratio as a scalar parameter to predict nitrous oxide emissions. *Glob Chang Biol* 11: 1142-1147.
- Klemedtsson L, Ernfors M, Björk RG, Weslien P, Rütting T, Crill P, Sikström U, 2010. Reduction of greenhouse gas emissions by wood

References

- ash application to a *Picea abies* (L.) Karst. forest on a drained organic soil. *Eur J Soil Sci* 61: 734-744.
- Knowles R, 1982. Denitrification. *Microbiol Rev* 46: 43-70.
- Koponen HT, Martikainen PJ, 2004. Soil water content and freezing temperature affect freeze-thaw related N₂O production in organic soil. *Nutr Cyc Agroecosys* 69: 213-219.
- Koponen HT, Flöjt L, Martikainen PJ, 2004. Nitrous oxide emissions from agricultural soils at low temperatures: a laboratory microcosm study. *Soil Biol Biochem* 36: 757-766.
- Koponen HT, Jaakkola T, Keinänen-Toivola MM, Kaipainen S, Tuomainen J, Servomaa K, Martikainen PJ, 2006. Microbial communities, biomass, and activities in soil as affected by freeze thaw cycles. *Soil Biol Biochem* 38: 1861-1871.
- Kowalchuk GA, Stephen JR, 2001. Ammonia-oxidizing bacteria: a model for molecular microbial ecology. *Annu Rev Microbiol* 55: 485-529.
- Laiho R, Laine J, 1995. Changes in mineral element concentrations in peat soils drained for forestry in Finland. *Scand J For Res* 10: 218-224.
- Laiho R, 2008. Suoekosysteemistä metsäekosysteemiksi. pp 152-157. In: Suomi – Suonmaa, soiden ja turpeen tutkimus sekä kestävä käyttö (in Finnish). Korhonen R, Korpela L, Sarkkola S (eds.). Finnish Peatland Society. Maahenki Oy. Art Print Oy. Finland. 288 pp.
- Leininger S, Urich T, Schloter M, Schwark L, Qi J, Nicol GW, Prosser JL, Schuster SC, Schleper C, 2006. Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature* 442: 806-809.
- Leppelt T, Dechow R, Gebbert S, Freibauer A, Lohila A, Augustin J, Drösler M, Fiedler S, Glatzel S, Höper H, Järveoja J, Lærke PE, Maljanen M, Mander Ü, Mäkiranta P, Minkkinen K, Ojanen P, Regina K, Strömberg M, 2014. Nitrous oxide emission budgets and land-use-driven hotspots for organic soils in Europe. *Biogeosciences* 11: 6595-6612.
- Levula T, Saarsalmi A, Rantavaara A, 2000. Effects of ash fertilization and prescribed burning on macronutrient, heavy metal, sulphur and ¹³⁷Cs concentrations in lingonberries (*Vaccinium vitis-idaea*). *For Ecol Manage* 126: 269-279.

Liimatainen M: Factors controlling nitrous oxide emissions from drained peat soils – effects of wood ash fertilization

- Lohila A, Aurela M, Hatakka J, Pihlatie M, Minkkinen K, Penttilä T, Laurila T, 2010. Responses of N₂O fluxes to temperature, water table and N deposition in a northern boreal fen. *Eur J Soil Sci* 61: 651-661.
- Ludwig B, Rumpf S, Mindrup M, Meiwes K-J, Khanna PK, 2002. Effects of lime and wood ash on soil-solution chemistry, soil chemistry and nutritional status of a pine stand in northern Germany. *Scand J For Res* 17: 225-237.
- Mahmood S, 2003. Colonisation of spruce roots by two interacting ectomycorrhizal fungi in wood ash amended substrates. *FEMS Microbiol Lett* 221: 81-87.
- Majdi H, Truus L, Johansson U, Nylund J-E, Wallander H, 2008. Effects of slash retention and wood ash addition on fine root biomass and production and fungal mycelium in a Norway spruce stand in SW Sweden. *For Ecol Manage* 255: 2109-2117.
- Maljanen M, Liikanen A, Silvola J, Martikainen PJ, 2003a. Nitrous oxide emissions from boreal organic soil under different land-use. *Soil Biol Biochem* 35: 1-12.
- Maljanen M, Liikanen A, Silvola J, Martikainen PJ, 2003b. Measuring N₂O emissions from organic soils by closed chamber or soil/snow N₂O gradient methods. *Eur J Soil Sci* 54: 625-631.
- Maljanen M, Komulainen V-M, Hytönen J, Martikainen PJ, Laine J, 2004. Carbon dioxide, nitrous oxide and methane dynamics in boreal organic agricultural soils with different soil characteristics. *Soil Biol Biochem* 36: 1801-1808.
- Maljanen M, Nykänen H, Moilanen M, Martikainen PJ, 2006a. Greenhouse gas fluxes of coniferous forest floors as affected by wood ash addition. *Forest Ecol Manage* 237: 143-149.
- Maljanen M, Jokinen H, Saari A, Strömmer R, Martikainen PJ, 2006b. Methane and nitrous oxide fluxes, and carbon dioxide production in boreal forest soil fertilized with wood ash and nitrogen. *Soil Use Manage* 22: 151-157.
- Maljanen M, Hytönen J, Mäkiranta P, Alm J, Minkkinen K, Laine J, Martikainen PJ, 2007. Greenhouse gas emissions from cultivated and abandoned organic croplands in Finland. *Bor Environ Res* 12: 133-140.
- Maljanen M, Virkajärvi P, Hytönen J, Öquist M, Sparrman T, Martikainen PJ, 2009. Nitrous oxide production in boreal soils with

References

- variable organic matter content at low temperature – snow manipulation experiment. *Biogeosciences* 6: 2461-2473.
- Maljanen M, Hytönen J, Martikainen PJ, 2010a. Cold-season nitrous oxide dynamics in a drained boreal peatland differ depending on land-use practice. *Can J For Res* 40: 565-572.
- Maljanen M, Sigurdsson BD, Guðmundsson J, Óskarsson H, Huttunen JT, Martikainen PJ, 2010b. Greenhouse gas balances of managed peatlands in the Nordic countries - present knowledge and gaps. *Biogeosciences* 7: 2711-2738.
- Maljanen M, Shurpali N, Hytönen J, Mäkiranta P, Aro L, Potila H, Laine J, Li C, Martikainen PJ, 2012. Afforestation does not necessarily reduce nitrous oxide emissions from managed boreal peat soils. *Biogeochemistry* 108: 199-218.
- Mandre M, Pärn H, Klõšeiko J, Ingerselv M, Stupak I, Kört M, Paasrand K, 2010. Use of biofuel ashes for fertilization of *Betula pendula* seedlings on nutrient poor peat soil. *Biomass Bioenerg* 34: 1384–1392.
- Martikainen PJ, 1984. Nitrification in two coniferous forest soils after different fertilization treatments. *Soil Biol Biochem* 16: 577-582.
- Martikainen PJ, 1985a. Nitrous oxide emission associated with autotrophic ammonium oxidation in acid coniferous forest soil. *Appl Environ Microbiol* 50: 1519-1525.
- Martikainen PJ, 1985b. Nitrification in forest soil of different pH as affected by urea, ammonium sulphate and potassium sulphate. *Soil Biol Biochem* 17: 363-367.
- Martikainen PJ, Nykänen H, Crill P, Silvola J, 1993. Effect of a lowered water table on nitrous oxide fluxes from northern peatlands. *Nature* 366: 51-53.
- Martikainen PJ, Nykänen H, Alm J, Silvola J, 1995. Change in fluxes of carbon dioxide, methane and nitrous oxide due to forest drainage of mire sites of different trophy. *Plant Soil* 168-169: 571-577.
- Moilanen M, Silfverberg K, Hokkanen TJ, 2002. Effects of wood-ash on the tree growth, vegetation and substrate quality of a drained mire: a case study. *For Ecol Manage* 171: 321-338.
- Moilanen M, Silfverberg K, Hökkä H, Issakainen J, 2005. Wood ash as a fertilizer on a drained mires – growth and foliar nutrients of Scots pine. *Can J For Res* 35: 2734-2742.

Liimatainen M: Factors controlling nitrous oxide emissions from drained peat soils – effects of wood ash fertilization

- Moilanen M, Fritze H, Nieminen M, Piirainen S, Issakainen J, Piispanen J, 2006. Does wood ash application increase heavy metal accumulation in forest berries and mushrooms? *For Ecol Manage* 226: 153-160.
- Moilanen M, Saarinen M, Silfverberg K, 2010. Foliar nitrogen, phosphorus and potassium concentrations of Scots pine in drained mires in Finland. *Silva Fenn* 44: 583-601.
- Moilanen M, Hytönen J, Leppälä M, 2012. Application of wood ash accelerates soil respiration and tree growth on drained peatland. *Eur J Soil Sci* 63: 467-475.
- Moilanen M, Saarsalmi A, Kukkola M, Issakainen J, 2013. Effects of stabilized wood ash on nutrient status and growth of Scots pine – Comparison between uplands and peatlands. *For Ecol Manage* 295: 136-144.
- Myllys M, Sinkkonen M, 2004. Viljeltyjen turve- ja multamaiden pinta-ala ja alueellinen jakauma Suomessa. Summary: The area and distribution of cultivated peat soils in Finland. *Suo* 55: 53–60.
- Myllys M, 2008. Soiden maatalouskäyttö tänään. 138-143 pp. In: Suomi – Suonmaa, soiden ja turpeen tutkimus sekä kestävä käyttö (in Finnish). Korhonen R, Korpela L, Sarkkola S (eds.). Finnish Peatland Society. Maahenki Oy. Art Print Oy. Finland. 288 pp.
- Mäkiranta P, Hytönen J, Aro L, Maljanen M, Pihlatie M, Potila H, Shurpali NJ, Laine J, Lohila A, Martikainen PJ, Minkkinen K, 2007. Soil greenhouse gas emissions from afforested organic soil croplands and cutaway peatlands. *Bor Environ Res* 12: 159-175.
- Nieminen M, Piirainen S, Moilanen M, 2005. Release of mineral nutrients and heavy metals from wood and peat ash fertilizers: field studies in Finnish forest soils. *Scand J For Res* 20: 146-153.
- Nieminen JK, Räisänen M, Haimi J, 2012. Spot mounding and granulated wood ash increase inorganic N availability and alter key component of the soil food web in clear-cut Norway spruce forests. *For Ecol Manage* 263: 24-30.
- Norström SH, Bylund D, Vestin JLK, Lundström US, 2012. Initial effects of wood ash application to soil and soil solution chemistry in a small, boreal catchment. *Geoderma* 187-188: 85-93.
- Nykänen H, Alm J, Silvola J, Tolonen K, Martikainen PJ, 1998. Methane fluxes on boreal peatlands of different fertility and the effect of long-

References

- term experimental lowering of the water table on flux rates. *Glob Biogeochem Cycles* 12: 53-69.
- Odlare M, Pell M, 2009. Effect of wood fly ash and compost on nitrification and denitrification in agricultural soil. *Appl Energ* 86: 74-80.
- Ojanen P, Minkkinen K, Alm J, Penttilä T, 2010. Soil-atmosphere CO₂, CH₄, and N₂O fluxes in boreal forestry-drained peatlands. *For Ecol Manage* 260: 411-421.
- Ojanen P, Minkkinen K, Penttilä T, 2013. The current greenhouse gas impact of forestry-drained boreal peatlands. *For Ecol Manage* 289: 201-208.
- Omil B, Piñeiro V, Merino A, 2013. Soil and tree responses to the application of wood ash containing charcoal in two soils with contrasting properties. *For Ecol Manage* 295: 199-212.
- Ozolinčius R, Buožytė R, Varnagirytė-Kabašinskiėnė I, 2007. Wood ash and nitrogen influence on ground vegetation cover and chemical composition. *Biomass Bioenerg* 31: 710-716.
- Park BB, Yanai RD, Sahn JM, Lee DK, Abrahamson LP, 2005. Wood ash effects on plant and soil in a willow bioenergy plantation. *Biomass Bioenerg* 28: 355-365.
- Perkiömäki J, Fritze H, 2002. Short and long-term effects of wood ash on the boreal forest humus microbial community. *Soil Biol Biochem* 34: 1343-1353.
- Perkiömäki J, Kiiikkilä O, Moilanen M, Issakainen J, Tervahauta A, Fritze H, 2003. Cadmium-containing wood ash in a pine forest: effects on humus microflora and cadmium concentrations in mushrooms, berries, and needles. *Can J For Res* 33: 2443-2451.
- Perkiömäki J, Fritze H, 2005. Cadmium in upland forests after vitality fertilization with wood ash - a summary of soil microbiological studies into the potential risk of cadmium release. *Biol Fertil Soils* 41: 75-84.
- Perucci P, Monaci E, Onofri A, Vischetti C, Casucci C, 2008. Changes in physico-chemical and biochemical parameters of soil following addition of wood ash: a field experiment. *Europ J Agronomy* 28: 155-161.
- Pihlatie M, Syväsalo E, Simojoki A, Esala M, Regina K, 2004. Contribution of nitrification and denitrification to N₂O production in

- peat, clay and loamy sand soils under different soil moisture conditions. *Nutr Cycl Agroecosys* 70: 135-141.
- Piirainen S, Domisch T, Moilanen M, Nieminen M, 2013. Long-term effects of ash fertilization on runoff water quality from drained peatland forests. *For Ecol Manage* 287: 53-66.
- Pitman RM, 2006. Wood ash use in forestry – a review of the environmental impacts. *Forestry* 79: 563-588.
- Prosser JI, Nicol GW, 2012. Archaeal and bacterial ammonia-oxidizers in soil: the quest for niche specialization and differentiation. *Trends Microbiol* 20: 523-531
- Püttsepp Ü, Lõhmus K, Persson HÅ, Ahlström K, 2006. Fine-root distribution and morphology in an acidic Norway spruce (*Picea abies* (L.) Karst.) stand in SW Sweden in relation to granulated wood ash application. *For Ecol Manage* 221: 291-298.
- Päivänen J, 2008. Soiden metsätaloudellinen käyttöönotto. 96-100 pp. In: Suomi – Suonmaa, soiden ja turpeen tutkimus sekä kestävä käyttö (in Finnish). Korhonen R, Korpela L, Sarkkola S (eds.). Finnish Peatland Society. Maahenki Oy. Art Print Oy. Finland. 288 pp.
- Päivänen J, Hännell B, 2012. Peatland ecology and forestry – a sound approach. University of Helsinki Department of Forest Sciences Publications 3: 1-267. ISBN 978-952-10-4531-8. Vammalan kirjapaino. Finland.
- Pärn H, Mandre M, Tilk M, 2009. changes in the growth of Silver Birch (*Betula pendula* Roth) and black alder (*Alnus glutinosa* (L.) Gaertn.) seedlings on peat soils fertilized with wood and peat ashes. *Balt For* 15: 168-176.
- Ravishankara AR, Daniel JS, Portmann RW, 2009. Ozone-depleting substance emitted in the 21st century. *Science* 326: 123-125.
- R Core Team, 2015. R: A language and environment for statistical computing. R Foundation for Statistical Computing.
- Regina K, Nykänen H, Silvola J, Martikainen PJ, 1996. Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity. *Biogeochemistry* 35: 401-418.
- Regina K, Silvola J, Martikainen PJ, 1998. Mechanisms of N₂O and NO production in the soil profile of a drained and forested peatland, as studied with acetylene, nitrapyrin and dimethyl ether. *Biol Fertil Soils* 27: 205-210.

References

- Regina K, Syväsalto E, Hannukkala A, Esala M, 2004. Fluxes of N₂O from farmed peat soils in Finland. *Eur J Soil Sci* 55: 591-599.
- Regina K, Sheehy J, Myllys M, 2015. Mitigating greenhouse gas fluxes from cultivated organic soils with raised water table level. *Mitig Adapt Strateg Glob Change* 20: 1529-1544.
- Regina K, Budiman A, Greve MH, Grønlund A, Kasimir Å, Lehtonen H, Petersen SO, Smith P, Wösten H, 2016. GHG mitigation of agricultural peatlands requires coherent policies. *Clim Policy* 16: 522-541.
- Ring E, Jacobson S, Nohrstedt H-Ö, 2006. Soil-solution chemistry in a coniferous stand after adding wood ash and nitrogen. *Can J For Res* 36: 153-163.
- Rivkina EM, Friedmann EI, McKay CP, Gilichinsky DA, 2000. Metabolic activity of permafrost bacteria below the freezing point. *Appl Environ Microbiol* 66: 3230-3233.
- Rosenberg O, Persson T, Högbom L, Jacobson S, 2010. Effects of wood-ash application on potential carbon and nitrogen mineralization at two forest sites with different tree species, climate and N status. *For Ecol Manage* 260: 511-518.
- Roulet N, Moore T, Bubier J, Lafleur P, 1992. Northern fens: methane flux and climatic change. *Tellus* 44B: 100-105.
- Rousk J, Brookes PC, Bååth E, 2009. Contrasting soil pH effects on fungal and bacterial growth suggest functional redundancy in carbon mineralization. *Appl Environ Microbiol* 75: 1589-1596.
- Rütting T, Huygens D, Boeckx P, Staelens J, Klemedtsson L, 2013. Increased fungal dominance in N₂O emission hotspots along a natural pH gradient in organic forest soil. *Biol Fertil Soils* 49: 715-721.
- Rütting T, Björk RG, Meyer A, Klemedtsson L, Sikström U, 2014. Reduced global warming potential after wood ash application in drained Northern peatland forests. *For Ecol Manage* 328: 159-166.
- Saarsalmi A, Mälkönen E, 2001. Forest fertilization research in Finland: a literature review. *Scand J For Res* 16: 514-535.
- Saarsalmi A, Mälkönen E, Piirainen S, 2001. Effects of wood ash fertilization on forest soil chemical properties. *Silva Fenn* 35: 355-368.
- Saarsalmi A, Kukkola M, Moilanen M, Arola M, 2006. Long-term effects of ash and N fertilization on stand growth, tree nutrient status and soil chemistry in a Scots pine stand. *For Ecol Manage* 235: 116-128.

- Saarsalmi A, Smolander A, Kukkola M, Arola M, 2010. Effect of wood ash and nitrogen fertilization on soil chemical properties, soil microbial processes, and stand growth in two coniferous stands in Finland. *Plant Soil* 331: 329-340.
- Saarsalmi A, Smolander A, Kukkola M, Moilanen M, Saramäki J, 2012. 30-year effects of wood ash and nitrogen fertilization on soil chemical properties, soil microbial processes and stand growth in a Scots pine stand. *For Ecol Manage* 278: 63-70.
- Saarsalmi A, Smolander A, Moilanen M, Kukkola M, 2014. Wood ash in boreal, low-productive pine stands on upland and peatland sites: Long-term effects on stand growth and soil properties. *For Ecol Manage* 327: 86-95.
- Saranghi PK, Mahakur D, Mishra PC, 2001. Soil biochemical activity and growth response of rice *Oryza sativa* in fly ash amended soil. *Bioresour Technol* 76: 199-205.
- Sarenbo SL & Claesson T, 2004. Limestone and dolomite powder as binders for wood ash agglomeration. *Bull Eng Geol Env* 63: 191-207.
- Schaller L, Kantelhardt J, Drösler M, 2011. Cultivating the climate: socio-economic prospects and consequences of climate-friendly peat land management in Germany. *Hydrobiologia* 674: 91-104.
- Schaufler G, Kitzler B, Schindlbacher A, Skiba U, Sutton MA, Zechmeister-Boltenstern S, 2010. Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. *Eur J Soil Sci* 61: 683-696.
- Schindlbacher A, Zechmeister-Boltenstern S, Butterbach-Bahl K, 2004. Effects of soil moisture and temperature on NO, NO₂ and N₂O emissions from European forest soils. *J Geophys Res* 109: D173302.
- Schlesinger WH, 1997. *Biogeochemistry - An analysis of global change*. 2nd ed. 588 pp. Academic Press. Elsevier. USA.
- Schutter ME, Fuhrmann JJ, 1999. Microbial responses to coal fly ash under field conditions. *J Environ Qual* 28: 648-652.
- Schutter ME, Fuhrmann JJ, 2001. Soil microbial community responses to fly ash amendments as revealed by analyses of whole soils and bacterial isolates. *Soil Biol Biochem* 33: 1947-1958.
- Silvan N, Hytönen J, 2016. Impact of ash-fertilization and soil preparation on soil respiration and vegetation colonization on cutaway peatlands. *AJCC* 5: 178-192.

References

- Šimek H, Cooper, JE 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Eur J Soil Sci* 53: 345-354.
- Skogland T, Lomeland S, Goksøyr J, 1988. Microbial response to freeze-thaw cycles in tundra and taiga soils. *Soil Biol Biochem* 20: 851-856.
- Stahl DA, de la Torre JR, 2012. Physiology and diversity of ammonia-oxidizing archaea. *Annu Rev Microbiol* 66: 83-101.
- Steenari B-M, Lindqvist O, 1997. Stabilization of biofuel ashes for recycling to forest soil. *Biomass Bioenerg* 13: 39-50.
- Steenari B-M, Karlsson LG, Lindqvist O, 1999. Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. *Biomass Bioenerg* 16: 119-136.
- Tiemeyer B, Albiac Borraz E, Augustin J, Bechtold M, Beetz S, Beyer C, Drösler M, Ebli M, Eickenscheidt T, Fiedler S, Förster C, Freibauer A, Giebels M, Glatzel S, Heinichen J, Hoffmann M, Höper H, Jurasinski G, Leiber-Sauheitl K, Peichl-Brak M, Roßkopf N, Sommer M, Zeitz J, 2016. High emissions of greenhouse gases from grasslands on peat and other organic soils. *Glob Chang Biol* 22: 4134-4149.
- Turunen J, 2008. Development of Finnish peatland area and carbon storage 1950-2000. *Bor Environ Res* 13: 319-334.
- van den Heuvel RN, Hefting MM, Tan NCG, Jetten MSM, Verhoeven JTA, 2009. N₂O emission hotspots at different spatial scales and governing factors for small scale hotspots. *Sci Total Environ* 407: 2325-2332.
- van den Heuvel RN, Bakker SE, Jetten MSM, Hefting MM, 2011. Decreased N₂O reduction by low soil pH causes high N₂O emissions in a riparian ecosystem. *Geobiology* 9: 294-300.
- Vitousek PM, Aber JD, Howarth RW, Likens, GE, Matson PA, Schindler DW, Schlesinger WH, Tilman DG, 1997a. Human alteration of the global nitrogen cycle: sources and consequences. *Ecol Appl* 7: 737-750.
- Vitousek PM, Mooney HA, Lubchenco J, Melillo JM, 1997b. Human domination of Earth's ecosystems. *Science* 277: 494-499.
- von Arnold K, Nilsson M, Hånell B, Weslien P, Klemedtsson L, 2005. Fluxes of CO₂, CH₄ and N₂O from drained organic soils in deciduous forests. *Soil Biol Biochem* 37: 1059-1071.

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- von Post L, 1922. Sveriges Geologiska Undersöknings torvinventering och några av dess hittills vunna resultat. Svenska Mosskulturföreningens Tidskrift 37: 1-27.
- Väätäinen K, Sirparanta E, Räisänen, M., Tahvanainen T, 2011. The costs and profitability of using granulated wood ash as a fertilizer in drained peatland forests. Biomass Bioenerg 35: 3335-3341.
- Weber A, Karsisto M, Leppänen R, Sundman V, Skujinš, 1985. Microbial activities in a histosol: effects of wood ash and NPK fertilizers. Soil Biol Biochem 17: 291-296.
- Weslien P, Kasimir Klemedtsson Å, Börjesson G, Klemedtsson L, 2009. Strong pH influence on N₂O and CH₄ fluxes from forested organic soils. Eur J Soil Sci 60: 311-320.
- Weslien P, Rütting T, Kasimir-klemedtsson Å, Klemedtsson L, 2012. Carrot cropping on organic soil is a hotspot for nitrous oxide emissions. Nutr Cycl Agroecosyst 94: 249-253.
- Wrage N, Welthof GL, van Beusichem ML, Oenema O, 2001. Role of nitrifier denitrification in the production of nitrous oxide. Soil Biol Biochem 33: 1723-1732.
- Yrjälä K, Katainen R, Jurgens G, Saarela U, Saano A, Romantschuk M, Fritze H, 2004. Wood ash fertilization alters the forest humus *Archaea* community. Soil Biol Biochem 36: 199-201.
- Zumft WG, 1997. Cell biology and molecular basis of denitrification. Microbiol Mol Biol Rev 61: 533-616.

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When peatlands are drained, emissions of nitrous oxide (N_2O) may increase significantly, but variation in emission rates is high. One of the key regulators of N_2O emissions is carbon to nitrogen (C/N) ratio. In this study was examined what other factors besides soil C/N ratio can explain the high variation. Furthermore, the effect of wood ash fertilization on N_2O emissions was studied with field and laboratory experiments to evaluate if ash fertilization can be used as a mitigation option for N_2O emissions in peatland forests.



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